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Supporting Information

Origin of ¹³C NMR chemical shifts elucidated based on molecular orbital theory: paramagnetic contributions from orbital-to-orbital transitions for the pre-α, α, β, α-X, β-X and *ipso*-X effects, along with effects from characteristic bonds and groups⁺

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Species	(symmetry)		$\sigma^{t}(C)$	$-\Delta\sigma^t(C)$ TMS	$\delta(C)_{obsd}$
TMS	$SiMe_4(T_d)$		182.99	0.00	0.0
methane	$CH_4(T_4)$		189 32	-6.33	-4.6
ethane	$(CH_2CH_2; D_{24})$		173 39	9.60	73
propape	$(H_2(H_2(H_2)))$		160.10	22.80	16.4
<i>n</i> poptane	$m C_{2} = (C_{2})$		140.10	42.05	24.8
<i>n</i> -pentane	$n - C_{51112}(C_{2v})$		140.94	42.03	20.5
<i>n</i> -neptane	(C_{1})		144.07	20.92 20.70	29.5
<i>n</i> -nonane	(C_{2v})		144.20	30.79	29.8
methylamine	$(CH_3NH_2: C_s)$		150.01	32.98	28.4
methanol	$(CH_3OH: C_s)$		127.49	55.50	50.2
fluoromethane	$(CH_3F: C_{3v})$		106.99	/6.00	/1.6
dimethylamine	$Me_2NH(C_s)$		141.04	41.95	38.2
trimethylamine	$Me_3N(C_{3v})$		133.29	49.70	47.6
acetonitrile	$MeCN(C_{3v})$		181.70	1.29	1.7
methyl isocyanide	$MeNC(C_{3v})$		156.37	26.62	26.8
nitromethane	$MeNO_2(C_s)$		117.50	65.49	62.5
acetaldehyde	$CH_3CHO(C_s)$		148.14	34.85	31.3
acetone	$CH_3COCH_3(C_{2v})$		151.13	31.86	30.9
acetic acid	$CH_3COOH(C_s)$		162.24	20.75	20.8
methyl acetate	CH_3COOCH_3 (C_s)		160.82	22.17	20.6
methanethiol	CH ₃ SH (Cs)		170.23	12.76	6.5
dimethyl sulfide	$CH_3SCH_3(C_{2v})$		159.29	23.70	19.3
DMSO	$CH_3S(O)CH_3(C_s)$		136.64	46.35	41.0
methane sulfonic acid	$CH_3SO_3H(C_1)$		139.67	43.32	39.6
chloromethane	$CH_3Cl(C_{3v})$		150.42	32.57	25.6
dimethyl ether	$CH_3OCH_3(C_{2v})$		119.08	63.91	60.9
methyl ethyl ether	$MeOEt(C_s)$		120.39	62.60	57.6
methyl iso-propyl ether	$MeOPr-i(C_1)$		123.55	59 44	54.9
methyl tert-butyl ether	$MeOBu-t(C_1)$		120.00	52.25	494
ethylene	$CH_2 = CH_2 (D_{2k})$		52.08	130.91	123.3
trans-butadiene	$t_{\rm CH_2-CH_2}(D_{2n})$	C1	58.69	124 30	117 5
<i>irans-butachene</i>		C^{1}	34 30	1/8 60	137.8
cis butadiana	$c CH_2 - CHCH - CH_2 (C_2)$	C_{1}^{2}	58.85	1740.00	117.5
<i>cis-outadiene</i>	t - c H_2 - c H c H_2 (c $_2$)	C_{2}	34.12	124.14	117.5
nronulana	CH_{1} - $CHCH_{2}(C)$	C_{1}^{2}	34.12	140.07	137.0
рюруше	$CH_2 - CHCH_3 (C_s)$	C_{1}	57.20	145.79	140.2
		C2	01.05	121.50	113.7
		C 1	159.80	25.15	24.2
vinyl alcohol	$CH_2=CHOH(C_s)$	CI	26.57	156.42	149.0
		C2	89.96	93.03	88.0
methyl vinyl ether	$CH_2=CHOMe(C_s)$	CI	19.36	163.63	152.9
		C2	97.51	85.48	85.5
acrolein	$CH_2=CHCHO(C_s)$	C4	33.08	149.91	138.5
		Cl	37.88	145.11	138.0
methyl vinyl ketone	$CH_2=CHCOCH_3$ (C_s)	C4	33.38	149.61	137.5
		C1	48.01	134.98	129.0
<i>cis</i> -acrylic acid	c -CH ₂ =CHCOOH (C_s)	C4	47.71	135.28	128.1
		C1	40.18	142.81	133.2
trans-acrylic acid	t-CH2=CHCOOH (Cs)	C2	44.90	138.09	128.1
-		C1	43.00	139.99	133.2
nitroethylene	$CH_2=CHNO_2(C_s)$	C4	26.55	156.44	144.7
-	× /	C1	53.02	129.97	121.5
isocyanoethylene	$CH_2=CHNC(C_s)$	C1	55.11	127.88	121.0
5 5	~ /	C4	56.04	126.95	119.3
<i>N</i> , <i>N</i> -dimethylethenamine	(C_1)	C13	166.61	16.38	12.8
		C10	124.24	58.75	53.6
		C1	138.89	44.10	44.6

Table S1. The $\sigma^t(C; S)$, and $-\Delta \sigma^t(C; S)$ and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under B3LYP/BSS-A.

Species	(symmetry)		$\sigma^t(C)$	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4(T_d)$		186.63	0.00	0.0
methane	$CH_4(T_d)$		192.76	-6.13	-4.6
ethane	$(CH_3CH_3; D_{3d})$		177.83	8.80	7.3
propane	$CH_3CH_2CH_3(C_{2y})$		165.50	21.13	16.4
<i>n</i> -pentane	$n-C_5H_{12}(C_{2y})$		145.62	41.01	34.8
<i>n</i> -heptane	$n-C_7H_{16}(C_{2y})$		148.90	37.73	29.5
<i>n</i> -nonane	(C_{2y})		149.00	37.63	29.8
methylamine	$(CH_3NH_2; C_s)$		154.83	31.80	28.4
methanol	$(CH_3OH: C_3)$		131.95	54.67	50.2
fluoromethane	$(CH_3F^*C_{3y})$		110.87	75 76	71.6
dimethylamine	$Me_2NH(C_s)$		145.61	41.02	38.2
trimethylamine	$Me_{2}N(C_{3y})$		137.49	49 14	47.6
acetonitrile	$MeCN(C_{3y})$		186.01	0.62	17.0
methyl isocyanide	$MeNC (C_{3v})$		160.01	26.08	26.8
nitromethane	$MeNO_2(C_2)$		121 34	65 29	62.5
acetaldebyde	$CH_2CHO(C_1)$		151 71	34.91	31.3
acetone	$CH_2COCH_2(C_{2n})$		154 35	32.28	30.9
acetic acid	$CH_2COOH(C_2)$		165.68	20.95	20.8
methyl acetate	$CH_{3}COOCH_{2}(C)$		164.24	20.25	20.8
methanethiol	$CH_3COOCH_3(C_8)$		176 13	10.50	20.0
dimethyl sulfide	$CH_3SII(Cs)$		164.74	21.80	10.3
DMSO	$CH_3SCH_3(C_{2v})$ $CH_3S(O)CH_2(C_1)$		1/6.86	21.07	17.5
methane sulfonic acid	$CH_3S(O)CH_3(C_s)$ $CH_2SO_2H(C_1)$		140.00	30/18	30.6
chloromethane	$CH_3O_3H(C_1)$		156 74	20.40	25.6
dimethyl ether	$CH_{3}CI(C_{3v})$		123.74	63 10	23.0 60.0
methyl ethyl ether	$M_{0}OEt(C)$		123.44	61.82	57.6
methyl iso propyl other	$M_{0}OPr i(C_{s})$		124.01	01.02 48.51	54.0
methyl tert butyl ether	$M_{e}OBu t(C)$		135.12	40.31 51 31	J4.9 10 1
athylono	$CH_{2} = CH_{2} (D_{2})$		53.52	122.26	47.4
trans but diono	$t C H_2 - C H_2 (D_{2h})$	C1	55.20	135.50	123.3
trans-butadiene	l-CII ₂ -CIICII-CII ₂ (C _{2h})	C_{1}	25.87	120.32	117.5
ais butadiana	$a CU_{a} - CUCU - CU_{a} (C_{a})$	C_{1}^{2}	55.67 63.10	130.70	137.0
<i>cis</i> -butadiene	\mathcal{E} -CH2=CHCH=CH2 (C2)	C_{1}	27.01	123.43	117.5
propulana	$CU_{2} - CUCU_{2}(C)$	C_{1}^{2}	37.91	140.72	137.0
propyrene	CH_2 -CHCH3 (C_8)	C_{1}	50.90	147.04	140.2
		C2	164.24	22.30	24.2
vinul alashal	CH_{2} $-CHOH(C)$	C1	104.24	22.39	140.0
villyi alcolloi	CH_2 -CHOH (Cs)	C_{1}	20.47	136.10	149.0 88.0
mothyl yinyl othor	$CH_{2}-CHOM_{2}(C)$	C_{1}^{2}	20.00	95.20	152.0
meuryr vinyr euler	CH_2 -CHOIVIE (C_8)	C_{1}	20.90	87.54	85.5
acrolain	$CU_{2} - CUCUO(C)$	C_{L}	99.00 34.68	07.3 4 151.04	03.3
acrolem	CH_2 -CHCHO (Cs)	C_{1}	34.00 20.99	131.94	130.3
mother winey botons	$CU_{-}CUCOCU_{+}(C)$	C_1	39.88	140.73	138.0
methyl vinyl ketone	$CH_2 = CHCOCH_3(C_s)$	C4 C1	54.90 40.45	131./3	137.3
sis complia coid	$-CU_{C}CU_{C}OOU_{C}$		49.45	13/.18	129.0
cis-acrylic acid	C-CH2=CHCOOH (Cs)	C4	49.77	130.80	128.1
	(CIL CUCOOU(C)		41.19	145.45	133.2
trans-acrylic acid	t-CH ₂ =CHCOOH (C _s)	C_{1}	40.89	139.74	128.1
	CU_{1} $CUNO_{1}(C)$		44.00	142.57	133.2
nitroetnylene	$CH_2 = CHNO_2(C_s)$	C4	29.43	157.20	144.7
· · · · · · · · · · · · · · · · · · ·			53.94	132.09	121.5
isocyanoethylene	$CH2=CHNC(C_s)$		57.65	128.98	121.0
N N dim other lath	(C_{i})	C4	30.11 170.66	150.52	119.3
iv,iv-aimethylethenamine	(C1)	C13	1/0.60	13.90	12.8
		C10	129.33	57.30	55.6
		C I	136.45	50.18	44.6

Table S2. The $\sigma^t(C; S)$, and $-\Delta \sigma^t(C; S)$ and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under CAM-B3LYP/BSS-A.

Species	(symmetry)		$\sigma^t(C)$	$-\!\Delta\sigma^t\!(C)_{\text{TMS}}$	$\delta(C)_{obsd}$
TMS	$SiMe_4(T_d)$		181.82	0.00	0.0
methane	$CH_4(T_d)$		189.44	-7.62	-4.6
ethane	$(CH_3CH_3; D_{3d})$		172.53	9.29	7.3
propane	$CH_3CH_2CH_3(C_{2y})$		158.68	23.14	16.4
<i>n</i> -pentane	$n-C_5H_{12}(C_{2y})$		138 77	43.05	34.8
<i>n</i> -heptane	$n - C_7 H_{16} (C_{2v})$		142 18	39.64	29.5
<i>n</i> -nonane	(C_{2y})		142.10	39.51	29.8
methylamine	$(CH_3NH_2; C_3)$		148.22	33.60	29.0
methanol	$(CH_2OH; C_2)$		125.11	56 71	50.2
fluoromethane	$(CH_2F^*C_{2n})$		104.13	77 69	71.6
dimethylamine	$Me_{2}NH(C_{2})$		138 76	43.06	38.2
trimethylamine	$Me_2N(C_{2v})$		130.70	50.99	47.6
acetonitrile	$MeCN(C_{2v})$		180.03	1 38	17
methyl isocyanide	$MeNC(C_{2n})$		155 55	26.27	26.8
nitromethane	$MeNO_{2}(C)$		116 56	65.26	20.8 62.5
acataldabyda	$CH_{2}CH_{2}(C_{s})$		146 41	35.42	21.2
	$CH_{3}CHO(U_{s})$		140.41	31.00	20.0
acetione	$CH_{3}COCH_{3}(C_{2v})$		149.04	10.80	20.9
methyl acetate	$CH_{3}COOP(C_{s})$		160.50	19.09	20.8
methor athic	$CH_3COUCH_3(C_s)$		160.39	21.25	20.0
dimentional culfide	$CH_{3}SH(CS)$		109.38	12.43	0.3
DMSO	$CH_3SCH_3(C_{2v})$		157.08	24.14	19.5
	$CH_3S(U)CH_3(C_s)$		137.40	44.30	41.0
methane suffonic acid	$CH_3SU_3H(C_1)$		140.54	41.28	39.6
chloromethane	$CH_3CI(C_{3v})$		150.09	31./3	25.6
dimethyl ether	$CH_3OCH_3 (C_{2v})$		115.95	65.88	60.9
methyl ethyl ether	$MODEt (C_s)$		11/.41	64.42	57.6
methyl iso-propyl ether	MeOPr- i (C ₁)		131.84	49.99	54.9
methyl tert-butyl ether	$MeOBu-t(C_s)$		128.48	53.34	49.4
ethylene	$CH_2 = CH_2 (D_{2h})$	C 1	51.43	130.39	123.3
trans-butadiene	t -CH ₂ =CHCH=CH ₂ (C_{2h})	CI	57.93	123.89	117.5
		C2	34.20	147.62	137.8
cis-butadiene	c -CH ₂ =CHCH=CH ₂ (C_2)	CI	61.90	119.92	117.5
		C2	36.78	145.04	137.8
propylene	$CH_2 = CHCH_3 (C_s)$	Cl	37.45	144.38	140.2
		C2	60.96	120.86	115.7
			158.11	23.72	24.2
vinyl alcohol	$CH_2=CHOH(C_s)$	C1	27.11	154.71	149.0
		C2	90.87	90.95	88.0
methyl vinyl ether	CH_2 =CHOMe (C_s)	C1	20.37	161.45	152.9
		C2	97.94	83.88	85.5
acrolein	$CH_2 = CHCHO(C_s)$	C4	33.28	148.54	138.5
		C1	35.72	146.10	138.0
methyl vinyl ketone	$CH_2 = CHCOCH_3 (C_s)$	C4	33.88	147.94	137.5
		C1	47.31	134.51	129.0
<i>cis</i> -acrylic acid	c -CH ₂ =CHCOOH (C_s)	C4	47.08	134.75	128.1
		C1	40.20	141.62	133.2
trans-acrylic acid	<i>t</i> -CH ₂ =CHCOOH (<i>C</i> _s)	C2	44.42	137.41	128.1
		C1	43.15	138.68	133.2
nitroethylene	$CH_2=CHNO_2(C_s)$	C4	25.98	155.84	144.7
-		C1	53.63	128.19	121.5
isocyanoethylene	$CH_2=CHNC(C_s)$	C1	55.06	126.76	121.0
		C4	56.19	125.63	119.3
<i>N</i> , <i>N</i> -dimethylethenamine	(C_1)	C13	165.89	15.93	12.8
-		C10	121.55	60.27	53.6
		C1	129.74	52.08	44.6

Table S3. The $\sigma^t(C; S)$, and $-\Delta \sigma^t(C; S)$ and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under PBE/BSS-A.

Species	(symmetry)		$\sigma^t(C)$	$-\!\Delta\sigma^t(C)_{\text{TMS}}$	$\delta(C)_{obsd}$
TMS	$SiMe_4(T_d)$		187.78	0.00	0.0
methane	$CH_4(T_d)$		193.26	-5.48	-4.6
ethane	$(CH_3CH_3; D_{3d})$		178.68	9.10	7.3
propane	$CH_3CH_2CH_3(C_{2v})$		166.69	21.10	16.4
<i>n</i> -pentane	$n-C_5H_{12}(C_{2y})$		147.39	40.39	34.8
<i>n</i> -heptane	$n-C_7H_{16}(C_{2y})$		150.50	37.29	29.5
<i>n</i> -nonane	(C_{2v})		150.62	37.16	29.8
methylamine	$(CH_3NH_2; C_s)$		155.86	31.92	28.4
methanol	$(CH_3OH; C_s)$		133.95	53.83	50.2
fluoromethane	$(CH_3E; C_{3v})$		114.00	73.78	71.6
dimethylamine	$Me_2NH(C_s)$		146.71	41.07	38.2
trimethylamine	$Me_{3}N(C_{3y})$		138 75	49.03	47.6
acetonitrile	$MeCN(C_{3y})$		186.23	1 55	17
methyl isocyanide	$MeNC(C_{3v})$		161.84	25.94	26.8
nitromethane	$MeNO_2(C_s)$		124 54	63.24	62.5
acetaldehyde	$CH_2CHO(C_2)$		153 37	34 41	31.3
acetone	$CH_3COCH_3(C_{2y})$		156.00	31.78	30.9
acetic acid	$CH_{2}COOH(C_{2})$		167.36	20.43	20.8
methyl acetate	$CH_2COOCH_2(C_1)$		166.08	21.70	20.6
methanethiol	$CH_2SH(C_s)$		176 75	11.03	6.5
dimethyl sulfide	$CH_2SCH_2(C_{2n})$		165.67	22.12	19.3
DMSO	$CH_2S(\Omega)CH_2(C_2)$		1/8 1/	39.64	41.0
methane sulfonic acid	$CH_2SO_2H(C_1)$		1/0.03	37.85	39.6
chloromethane	$CH_2Cl(C_{2u})$		158.04	29.74	25.6
dimethyl ether	$CH_2OCH_2(C_{2\pi})$		125.04	62 57	60.9
methyl ethyl ether	$M_{eOEt}(C_{e})$		125.22	61 29	57.6
methyl iso-propyl ether	MeOPr- $i(C_1)$		139.95	47.83	54.9
methyl tert-butyl ether	$MeOBu_t(C)$		137.04	50.74	J4.J 10 1
ethylene	$CH_2 - CH_2 (D_2)$		56 1/	131.64	123.3
trans-butadiene	t_{12} – CH_{2} (D_{2n})	C1	62 52	125.26	125.5
<i>irans-butachene</i>		C^{1}	30.78	1/8 01	137.8
cis-butadiene	$c_{-}CH_{2}-CHCH_{-}CH_{2}(C_{2})$	C_{1}^{2}	65.66	122 12	117.5
ers outdetene	$c cm_2$ -emem-em ₂ (c_2)	C^2	41.93	145.85	137.8
propylene	$CH_2 - CHCH_2(C_2)$	C_1	42.82	143.05	140.2
propyrene		C^{1}	65 35	122 43	115 7
		C2	164.87	22.43	24.2
vinyl alcohol	$CH_2 - CHOH(C_2)$	C1	32.02	154.86	1/0 0
villy aconor		C^{1}	94.61	03 17	88.0
methyl yinyl ether	$CH_2 - CHOMe(C_2)$	C_1^2	25.01	161.86	152.9
methyr vinyr ether		C^{1}	101 73	86.05	85.5
acrolein	$CH_2 - CHCHO(C_2)$	C^{2}	38.89	1/8 89	138.5
actorem		C_{τ}	<i>A</i> 1 29	146.50	138.0
methyl vinyl ketone	$CH_2 - CHCOCH_2(C_2)$	C_{1}	30.00	140.30	137.5
methyl vinyl ketone		C_{+}	51.57	136.70	120.0
cis acrulic acid	$CH_{2}-CHCOOH(C)$	C_{1}	52.03	134.85	129.0
ets-activité actu		C_{1}	J2.93 13 71	134.03	120.1
trans perulie peid	$t CH_2 - CHCOOH(C)$	C_{2}	43.74 50.15	137.63	133.2
trans-activite actu		C_{1}^{2}	J0.13 46.03	137.03	120.1
nitroethylene	$CH_{2}-CHNO_{2}(C)$	C_{1}	33 20	154 40	133.2
Introethylene	CH_2 - $CHNO_2$ (Cs)	C_{1}	56.65	134.49	144.7
isocyanoethylene	$CH_{2}-CHNC(C)$	C_1	50.05	127.70	121.5
1500 yanoeniy tene	CH2-CHINC (Cs)	C_{1}	57.77 60.21	127.17	121.0
N N dimethylathanamina	(C_1)	C^{+}	172.06	127.34	117.5
		C13	172.00	56.82	12.0 53.6
		C_{10}	130.90	50.02 50.11	55.0 11.6
			1.0/.0/	50.11	44.0

Table S4. The $\sigma^t(C; S)$, and $-\Delta \sigma^t(C; S)$ and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under PBE0/BSS-A.

<u> </u>			t(O)	1 t(0)	S(G)
Species	(symmetry)		$\sigma'(C)$	$-\Delta\sigma'(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4(T_d)$		192.27	0.00	0.0
methane	$CH_4(T_d)$		196.42	-4.15	-4.6
ethane	$(CH_3CH_3; D_{3d})$		184.00	8.27	7.3
propane	$CH_3CH_2CH_3(C_{2y})$		173.58	18.69	16.4
<i>n</i> -pentane	$n-C_5H_{12}(C_{2y})$		154.78	37.49	34.8
<i>n</i> -heptane	$n-C_7H_{16}(C_{2y})$		157.44	34.83	29.5
<i>n</i> -nonane	(C_{2y})		157 55	34 72	29.8
methylamine	$(CH_3NH_2; C_s)$		161.80	30.47	28.4
methanol	$(CH_3OH: C_s)$		138.67	53.60	50.2
fluoromethane	$(CH_3F^*C_{3y})$		116.47	75.80	71.6
dimethylamine	$Me_2NH(C_s)$		152.83	39.44	38.2
trimethylamine	$Me_{2}N(C_{3v})$		144 55	47 72	47.6
acetonitrile	$MeCN(C_{2y})$		190.21	2.06	17
methyl isocyanide	$MeNC(C_{2v})$		165.45	2.00	26.8
nitromethane	$MeNO_2(C_1)$		127.05	65 22	20.0 62.5
acetaldebyde	$CH_{2}CHO(C)$		157.38	3/ 80	31.3
acetone	$CH_2COCH_2(C_2)$		150.23	33.04	30.0
acetic acid	$CH_{3}COCH_{3}(C_{2v})$		139.23	22.04	20.9
methyl acetate	$CH_{3}COOCH_{2}(C)$		160.20	22.01	20.8
methonothiol	$CH_3COOCH_3(C_5)$		102.04	23.23	20.0
dimothyl sulfide	$CH_3SII(CS)$ $CH_3SCH_2(C_2)$		103.01	10.20	10.3
DMSO	$CH_3SCH_3(C_{2v})$ $CH_2S(O)CH_2(C_1)$		175.07	19.20	19.5
DMSO methana sulfenia agid	$CH_{3}S(U)CH_{3}(C_{s})$		152.66	33.00	41.0
abloromethene	$CH_3SU_3H(C_1)$		155.00	30.01 26.82	39.0 25.6
dimothyl other	$CH_3CI(C_{3v})$		103.44	20.05	23.0
uniferry enter	$M_{2}OEt(C)$		121.20	02.14	00.9 57.6
methyl euryl ether	$M_{2}OP_{\pi} \neq (C_{s})$		131.30	00.97	54.0
methyl iso-propyl ether	$M_{2}OP_{1} + (C_{1})$		145.79	40.40	54.9 40.4
inethyl tert-butyl ether	$\frac{MeODu-l(C_s)}{CU}$		141.41	30.80	49.4
ethylene turus buts diene	$CH_2 = CH_2 (D_{2h})$	C^{1}	50.05	130.24	123.3
trans-butadiene	l-CH ₂ =CHCH=CH ₂ (C _{2h})		02.34	129.75	117.3
-i- lauto di an a		C_{1}	40.82	131.43	137.8
cis-butaulelle	C-CH ₂ -CHCH-CH ₂ (C ₂)	C_{1}	42.02	127.34	117.5
	CU CUCU (C)	C_{1}	42.02	130.23	137.8
ргоругене	$CH_2 = CHCH_3(C_s)$		45.05	140.02	140.2
		C2	03.14	127.15	24.2
		C 1	1/0.45	21.82	24.2
vinyi alconol	$CH_2 = CHOH(C_s)$		33.03	159.24	149.0
we athen 1 and we all a the sec	CU $CUOM_{2}(C)$	C_2	94.03	98.24	88.0
methyl vinyl ether	$CH_2 = CHOMe(C_s)$		25.45	166.82	152.9
1- ¹		C_{2}	101.05	90.62	85.5
acrolein	$CH_2 = CHCHO(C_s)$	C4	39.45	152.82	138.5
		CI	43.01	149.26	138.0
methyl vinyl ketone	$CH_2 = CHCOCH_3 (C_s)$	C4	39.28	152.99	137.5
		CI	52.20	140.07	129.0
cis-acrylic acid	c -CH ₂ =CHCOOH (C_s)	C4	53.42	138.85	128.1
		CI	43.80	148.47	133.2
trans-acrylic acid	t -CH ₂ =CHCOOH (C_s)	C2	50.78	141.49	128.1
•1 1		CI	46.95	145.32	133.2
nitroethylene	$CH_2 = CHNO_2(C_s)$	C4	34.08	158.19	144.7
• .a a		CI	56.75	135.52	121.5
isocyanoethylene	$CH_2=CHNC(C_s)$	CI	60.27	132.00	121.0
		C4	58.97	133.30	119.3
/v,/v-dimethylethenamine	(C ₁)	CI3	176.94	15.33	12.8
		C10	137.82	54.45	53.6
		C1	143.56	48.71	44.6

Table S5. The $\sigma^t(C; S)$, and $-\Delta \sigma^t(C; S)$ and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under LC- ω PBE/BSS-A.

Species	(symmetry)		$\sigma^t(C)$	$-\Delta\sigma^t(C)$ TMS	$\delta(C)_{obsd}$
TMS	$SiMe_4(T_d)$		188.17	0.00	0.0
methane	$CH_4(T_d)$		192.93	-4.76	-4.6
ethane	$(CH_3CH_3: D_{3d})$		178.91	9.26	7.3
propane	$CH_3CH_2CH_3$ (C_{2y})		167.63	20.54	16.4
<i>n</i> -pentane	$n-C_5H_{12}(C_{2y})$		148.34	39.83	34.8
<i>n</i> -heptane	$n-C_7H_{16}(C_{2y})$		151.40	36.77	29.5
<i>n</i> -nonane	(C_{2y})		151.39	36.78	29.8
methylamine	$(CH_3NH_2; C_s)$		156.46	31 71	28.4
methanol	$(CH_3OH: C_3)$		134 57	53 60	50.2
fluoromethane	$(CH_3F^*C_{3y})$		114 22	73.95	71.6
dimethylamine	$Me_2NH(C_s)$		147 30	40.87	38.2
trimethylamine	$\frac{Me_2N(C_3)}{Me_3N(C_3)}$		139.09	49.08	47.6
acetonitrile	$MeCN(C_{3v})$		186.29	1.88	17
methyl isocyanide	$MeNC(C_{2v})$		161.30	26.87	26.8
nitromethane	$MeNO_2(C_2)$		123 55	64.63	62.5
acetaldebyde	$CH_2CHO(C_1)$		153 58	34 59	31.3
acetone	$CH_2COCH_2(C_{2n})$		155.50	32.69	30.9
acetic acid	$CH_2COOH(C_2)$		166 70	21.07	20.8
methyl acetate	$CH_{3}COOCH_{2}(C)$		165.37	21.47	20.8
methanethiol	$CH_3COOCH_3(C_8)$		177 23	10.04	20.0
dimethyl sulfide	$CH_3SII(CS)$ $CH_2SCH_2(C_2)$		166.46	10.94 21.71	10.3
DMSO	$CH_3SCH_3(C_{2v})$ $CH_2S(O)CH_2(C_1)$		148 52	21.71	19.5
methane sulfonic acid	$CH_3S(O)CH_3(C_s)$ $CH_3SO_2H(C_1)$		140.32	39.00	30.6
abloromathana	$CH_3O_3\Pi(C_1)$		149.11	39.07	39.0 25.6
dimothyl other	$CH_{3}CI(C_{3v})$		125.04	50.39	23.0
mothyl othyl othor	$M_{2}OEt(C)$		123.94	61.07	00.9 57.6
methyl iso propyl other	MeODEr (C_s)		127.11	48.22	54.0
methyl tort butyl othor	$M_{0}OP_{u} t(C)$		137.00	40.32	J4.9 40.4
athylana	$CH_{2} = CH_{2} (D_{2})$		137.20 56.10	122.07	47.4
trans but diono	$t C \mathbf{U}_2 - C \mathbf{U}_2 (D_{2h})$	C1	50.10 65.24	132.07	123.3
<i>trans</i> -butadiene	l-CII ₂ -CIICII-CII ₂ (C _{2h})	C_{1}	20.04	122.03	117.5
ais butadiana	$a CU_{a} - CUCU - CU_{a} (C_{a})$	C_{1}	57.7 4 65.66	140.24	137.0
<i>cis</i> -butadiene	c- c II ₂ - c II ₂ - c II ₂ (c ₂)	C^{1}	41.60	122.52	117.5
propulana	$CU_{2} - CUCU_{2}(C)$	C_{1}	41.09	140.40	137.0
propyrene	CH_2 -CHCH3 (C_s)	C^{1}	42.00	143.49	140.2
		C2	165 74	122.03	24.2
vinul alashal	CH_{2} – $CHOH(C)$	C1	22.61	22. 4 3 155 56	24.2
villyl alcollol	CH_2 -CHOH (Cs)	C^{1}	52.01	04.10	149.0
mothyl yinyl othor	$CU_{2}-CUOM_{2}(C)$	C_{1}	94.07 25.18	162 00	152.0
mentyl vinyl emer	$CH2-CHOIVIE(C_s)$	C^{1}	23.10	86 70	85.5
acrolain	$CU_{2}-CUCUO(C)$	C_{1}^{2}	101.47	140.75	05.5
acroiem	$CH2=CHCHO (C_s)$	C_{1}	30.43 43.00	149.75	130.5
mathyl yinyl katona	$CH_{2}-CHCOCH_{2}(C)$	C_1	45.00	143.17	130.0
methyl vinyl ketone	$CH_2 = CHCOCH_3(C_s)$	C_{1}	50.40 50.19	149.70	137.3
aig comulia agid	$\circ CU_{-}CUCOOU(C)$	C_1	52.10	133.99	129.0
cis-activite actu	C-CH2=CHCOOH (Cs)	C_{1}	52.52 44.41	133.03	120.1
turna comulio coid	$4 CU_{\rm CU} - CUCOOU(C)$	C1	44.41	145.70	135.2
trans-activite actu	l-CH2=CHCOOH (Cs)	C_{1}	49.01	130.57	120.1
nitroothylana	$CH_{2}-CHNO_{2}(C)$	C_1	47.04	140.33	135.2
Introetinyiene	$CH_2 = CHNO_2(C_s)$	C4 C1	52.59	133.70	144.7
isooyonoothylana	$CH_{2}-CHNC(C)$	C^1	51.52 60.56	130.03	121.3 121.0
isocyanoemytene	CH_2 -CHINC (Cs)	C_{1}	50.02	127.01	121.0 110.2
N N dimothylathanamina	(C_{i})	C^{12}	37.03 171.00	127.14	117.5
	(CI)	C13	1/1.90	10.20 56.09	12.0
		C_{10}	131.17	50.90 50.06	55.0 11 6
		N . I	1.10.17	11111	++.U

Table S6. The $\sigma^t(C; S)$, and $-\Delta \sigma^t(C; S)$ and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under $\omega B97X$ -D/BSS-A.

Species (symmetry) $\sigma'(C)$ $-\Delta\sigma'(C)$ has a $\delta(C)$ shout TMS SiMea (Ta) 197.32 0.00 0.0 methane CH4 (Ta) 201.35 4.02 4.6 ethane (CH4CH2, Day) 188.18 9.14 7.3 propane CH-CH-CH1 (Ca) 156.45 40.87 34.8 n-pentane n-C-H1 (Ca) 159.43 37.89 29.8 methylamine (CH3)H1; Co) 142.66 54.66 50.2 fluoromethane (CH3)H1; Co) 142.66 54.66 50.2 fluoromethane (CH4CCC) 135.04 62.29 62.5 acetonizthe MeNC (Co) 135.04 62.29 62.5 acetonizthe MeNC (Co) 135.04 62.29 62.5 acetoa CH4/COH (Ca) 157.60 32.23 30.9 acetic aid CH4/COH (Ca) 176.02 21.30 20.8 methyl acetate CH4/COCH (Ca) 177.53 32.60 20.6 dimethyl						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Species	(symmetry)		$\sigma^t(C)$	$-\!\Delta\sigma^t\!(C)_{TMS}$	$\delta(C)_{obsd}$
	TMS	$SiMe_4(T_d)$		197.32	0.00	0.0
ethane (CH ₂ CH ₂ (D_{3})) 188.18 9.14 7.3 propane (CH ₂ CH ₂ (D_{3})) 176.73 20.59 16.4 <i>n</i> -pentane <i>n</i> -C ₃ H ₁₂ (C_{23}) 156.45 40.87 34.8 <i>n</i> -heptane <i>n</i> -C ₃ H ₁₂ (C_{23}) 159.43 37.89 29.8 methylamine (CH ₃ NH ₂ : C_{3}) 164.24 33.08 28.4 methylamine (CH ₃ NH ₂ : C_{3}) 164.24 33.08 28.4 methylamine (CH ₄ SH ₂ : C_{3}) 164.24 33.08 28.4 (imethylamine Me ₂ NH (C_{3}) 122.79 74.54 71.6 dimethylamine Me ₂ NH (C_{3}) 145.86 51.46 47.6 acetonitrile MeCN (C_{3}) 193.63 3.69 1.7 methyl isocyanide MeNC (C_{3}) 185.11 42.21 38.2 trimethylamine Me ₂ NH (C_{3}) 168.67 28.66 26.8 nitromethane MeNC (C_{3}) 163.05 34.27 31.3 aceton acetonitrile MeNC (C_{3}) 165.09 32.23 30.9 acetic acid CH ₃ COCH ₃ (C_{23}) 165.09 32.23 30.9 acetic acid CH ₃ COCH ₃ (C_{23}) 165.09 32.23 30.9 acetic acid CH ₃ COCH ₃ (C_{23}) 177.73 22.60 20.6 methyl acetate CH ₃ COCH ₃ (C_{3}) 175.30 22.02 19.3 DMSO CH ₃ SOCH ₃ (C_{3}) 175.76 39.63 41.0 methanethiol CH ₃ SOH (C_{3}) 175.76 39.63 41.0 methanethiol CH ₃ SOH (C_{3}) 137.16 60.16 60.9 methyl subjleter MeOB ₁₄ (C_{3}) 137.16 60.16 60.9 methyl tethyl tether MeOB ₁₄ (C_{3}) 137.16 60.16 60.9 methyl tethyl tether MeOB ₁₄ (C_{3}) 137.16 60.16 60.9 methyl tethyl tether MeOB ₁₄ (C_{3}) 137.16 60.16 60.9 methyl tethyl tether MeOB ₁₄ (C_{3}) 137.16 60.16 60.9 methyl tethyl tether MeOB ₁₄ (C_{3}) 137.16 79.16 57.6 imethyl tethyl tether MeOB ₁₄ (C_{3}) 137.16 79.16 57.6 imethyl tethyl tether MeOB ₁₄ (C_{3}) 137.16 79.16 57.6 imethyl tethyl tether MeOB ₁₄ (C_{3}) 137.17 127.16 117.5 <i>c</i> 24.62 131.37.9 149.2 <i>c</i> 24.82 150.50 137.8 <i>c</i> 24.7 134.86 123.3 itrans-butadiene <i>c</i> CH ₂ =CHCH=CH ₂ (C_{20}) C1 70.17 127.16 117.5 <i>c</i> 24.82 10.50 137.8 <i>c</i> 24.90 (C ₄) 24.84.99 137.8 methyl vinyl tether CH ₂ =CHCH(C_{3}) C1 70.17 127.16 117.5 <i>c</i> 24.82 10.50 137.8 <i>c</i> 24.90 (C ₄) 24.41 144.91 137.5 <i>c</i> 24	methane	$CH_4(T_d)$		201.35	-4.02	-4.6
$\begin{array}{llllllllllllllllllllllllllllllllllll$	ethane	$(CH_3CH_3: D_{3d})$		188.18	9.14	7.3
$\begin{array}{llllllllllllllllllllllllllllllllllll$	propane	$CH_3CH_2CH_3$ (C_{2v})		176.73	20.59	16.4
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<i>n</i> -pentane	$n-C_5H_{12}(C_{2y})$		156.45	40.87	34.8
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<i>n</i> -heptane	$n-C_7H_{16}(C_{2y})$		159.47	37.86	29.5
methylamine (CH ₃ NH ₂ : C ₃) 164.24 33.08 28.4 methanol (CH ₃ OH; C ₃) 142.66 50.2 fluoromethane (CH ₃ OH; C ₃) 122.79 74.54 71.6 dimethylamine Me ₂ NH (C ₃) 122.79 74.54 71.6 38.2 trimethylamine Me ₂ NH (C ₃) 145.86 51.46 47.6 actonitrile Me(C (C ₃) 193.63 3.69 1.7 methyl isocyanide Me(N (C ₃) 163.05 34.27 31.3 acctonic acid CH ₃ COCH ₃ (C ₂) 165.09 32.23 30.9 acctia acid CH ₃ COCH ₃ (C ₂) 176.02 21.00 20.8 methyl acctate CH ₃ COCH ₃ (C ₂) 175.30 22.02 19.3 DMSO CH ₃ SOH (C ₃) 157.69 39.63 41.0 methyl sulfide CH ₃ SOH (C ₃) 157.69 39.63 41.0 methyl sulfide CH ₃ SOH (C ₃) 157.69 39.63 41.0 41.0 41.0 41.67 49.65 54.9 methyl sulfide CH ₃ SO	<i>n</i> -nonane	(C_{2y})		159.43	37.89	29.8
$ \begin{array}{c c} \mbox{Hore} & (CH3CH1:C_5) & 142.66 & 54.66 & 50.2 \\ \mbox{funct} & (CH3CH1:C_5) & 142.66 & 54.66 & 50.2 \\ \mbox{funct} & (CH3CH1:C_5) & 122.79 & 74.54 & 71.6 \\ \mbox{dimethylamine} & (CH3CH1:C_5) & 122.79 & 74.54 & 71.6 \\ \mbox{dimethylamine} & (CH3CH1:C_5) & 142.66 & 54.66 & 50.2 \\ \mbox{trimethylamine} & (CH3CH1:C_5) & 142.66 & 54.66 & 50.2 \\ \mbox{actentifile} & MeCN(C_5) & 145.86 & 51.46 & 47.6 \\ \mbox{actentifile} & MeCN(C_5) & 145.86 & 51.46 & 47.6 \\ \mbox{actentifile} & MeCN(C_5) & 168.67 & 28.66 & 26.8 \\ \mbox{nitromethane} & MeNO_2(C_3) & 165.09 & 32.23 & 30.9 \\ \mbox{acctaldehyde} & CH3CHO(C_5) & 165.09 & 32.23 & 30.9 \\ \mbox{acctaldehyde} & CH3CHO(C_5) & 176.00 & 21.30 & 20.8 \\ \mbox{methyl} acetate & CH3COOCH_3(C_4) & 174.73 & 22.60 & 20.6 \\ \mbox{methyl} acetate & CH3COOCH_3(C_6) & 177.50 & 39.66 & 41.0 \\ \mbox{methane} & CH3CH3(C_5) & 157.69 & 39.66 & 41.0 \\ \mbox{methane} & CH3CH(C_5) & 157.69 & 39.66 & 41.0 \\ \mbox{methane} & CH3CH3(C_5) & 157.69 & 39.66 & 41.0 \\ \mbox{methane} & CH3CH3(C_5) & 137.16 & 60.16 & 60.9 \\ \mbox{methyl} abcle ther & MeOBr-i(C_1) & 147.67 & 49.65 & 54.9 \\ \mbox{methyl} ther & CH_3CH3(C_5) & 137.16 & 60.16 & 60.9 \\ \mbox{methyl} ther & MeOBr-i(C_5) & 147.28 & 50.04 & 49.4 \\ \mbox{ethyl} entryl ther & MeOBr-i(C_1) & 147.67 & 49.65 & 54.9 \\ \mbox{methyl} ther & CH_2-CHCH=CH2(C_{2n}) & C1 & 69.27 & 128.05 & 117.5 \\ \mbox{c} C2 & 46.82 & 150.50 & 137.8 \\ \mbox{c} c1 & 45.61 & 151.71 & 49.0 \\ \mbox{c} C2 & 79.57 & 117.75 & 115.7 \\ \mbox{c} C2 & 46.82 & 150.50 & 137.8 \\ \mbox{c} c1 & 61.36 & 135.96 & 138.0 \\ \mbox{methyl} ther & CH_2-CHCH0(C_5) & C1 & 37.79 & 159.53 & 152.9 \\ \mbox{c} c1 & 62.64 & 134.49 & 133.5 \\ \mbox{methyl} thyl ketone & CH_2-CHCOH(C_5) & C1 & 37.79 & 159.53 & 152.9 \\ \mbox{c} c1 & 61.36 & 135.07 & 138.10 \\ \mbox{methyl} thyl ketone & CH_2-CHCOH(C_5) & C1 & 37.79 & 159.53 & 152.9 \\ \mbox{c} c1 & 61.36 & 133.64 & 133.2 \\ \mbox{c} c1 & 61.36 & 133.64 & 133.2 \\ \mbox{c} c1 & 62.90 & 133.42 & 128.1 \\ \mbox{c} c1 & 62.90 & 133.42 & 128.1 \\ \mbox{c} $	methylamine	$(CH_3NH_2; C_3)$		164 24	33.08	29.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	methanol	$(CH_2OH; C_2)$		142.66	54.66	50.2
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	fluoromethane	$(CH_2F^*C_{2n})$		122.00	74 54	71.6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	dimethylamine	$Me_{2}NH(C_{2})$		155 11	12 21	38.2
$\begin{array}{cccc} \text{Intromethylamine} & \text{MCN}(C_{3v}) & \text{IP3.63} & 3.69 & 1.7 \\ \text{methyl isocyanide} & \text{MCN}(C_{3v}) & \text{IP3.63} & 3.69 & 1.7 \\ \text{methyl isocyanide} & \text{MCN}(C_{3v}) & \text{IP3.63} & 3.69 & 1.7 \\ \text{methyl isocyanide} & \text{MCN}(C_{3v}) & \text{IP3.63} & 3.69 & 1.7 \\ \text{methyl isocyanide} & \text{MCN}(C_{3v}) & \text{IP3.63} & 3.427 & 31.3 \\ \text{acctina acid} & \text{CH}_3\text{COOH}(C_s) & \text{IP3.61} & 32.23 & 30.9 \\ \text{acctic} acid & \text{CH}_3\text{COOH}(C_s) & \text{IP3.61} & 21.30 & 20.8 \\ \text{methyl acetate} & \text{CH}_3\text{COOH}(C_s) & \text{IP3.73} & 22.60 & 20.6 \\ \text{methanethiol} & \text{CH}_3\text{SCH}_3(C_{2v}) & \text{IP3.53} & 22.00 & 19.3 \\ \text{Methanethiol} & \text{CH}_3\text{SCH}_3(C_{2v}) & \text{IP3.53} & 22.00 & 19.3 \\ \text{DMSO} & \text{CH}_3\text{SCH}_3(C_{2v}) & \text{IP3.53} & 22.00 & 19.3 \\ \text{DMSO} & \text{CH}_3\text{SCH}_3(C_{2v}) & \text{IP3.53} & 22.02 & 19.3 \\ \text{DMSO} & \text{CH}_3\text{SCH}_3(C_{2v}) & \text{IP3.53} & 22.02 & 19.3 \\ \text{DMSO} & \text{CH}_3\text{SCH}_3(C_{2v}) & \text{IP3.53} & 22.02 & 19.3 \\ \text{DMSO} & \text{CH}_3\text{SCH}_3(C_{2v}) & \text{IP3.53} & 22.02 & 19.3 \\ \text{DMSO} & \text{CH}_3\text{CH}_3(C_{3v}) & \text{IP3.75} & 39.6 \\ \text{chloromethane} & \text{CH}_3\text{CI}(C_{3v}) & \text{IP3.76} & 39.63 & 41.0 \\ \text{methyl ether} & \text{MeOPt-i}(C_{3}) & \text{IP3.76} & 59.16 & 57.6 \\ \text{methyl ether} & \text{MeOPt-i}(C_{2v}) & \text{IP3.16} & 57.6 \\ \text{methyl ether} & \text{MeOPt-i}(C_{3}) & \text{IP3.78} & 59.16 & 57.6 \\ \text{methyl ether} & \text{MeOPt-i}(C_{3}) & \text{IP3.78} & 17.5 & 59.16 & 57.6 \\ \text{methyl ether} & \text{MeOPt-i}(C_{3}) & \text{IP3.78} & 17.5 & 15.7 \\ \text{Trans-butadiene} & t-\text{CH}_2\text{-CHCH}=\text{CH}_2(\text{C}_{2v}) & \text{C1} & 70.17 & 127.16 & 117.5 \\ \text{C2} & 46.82 & 150.50 & 137.8 \\ \text{cis-butadiene} & t-\text{CH}_2\text{-CHCH}=\text{CH}_2(\text{C}_{2v}) & \text{C1} & 45.61 & 151.71 & 149.0 \\ \text{C2} & 19.33 & 137.99 & 140.2 \\ \text{C2} & 79.57 & 117.75 & 115.7 \\ & 174.74 & 22.59 & 24.2 \\ \\ \text{viryl alcohol} & \text{CH}_2\text{-CHCH}(C_{3}) & \text{C1} & 45.61 & 151.71 & 149.0 \\ \text{C2} & 19.33 & 137.99 & 140.2 \\ \text{C2} & 19.53 & 135.29 \\ & \text{C1} & 63.68 & 133.56 & 133.0 \\ \\ \text{methyl vinyl ether} & \text{CH}_2\text{-CHCH}(C_{3}) & \text{C4} & 52.41 & 144.91 & 137.5 \\ \text{c1} & 63.68 & 133.56 & 133.64 & 133.2$	trimethylamine	$Me_2N(C_{2n})$		1/5 86	51 /6	17.6
accontinue MeCr (C_{3y}) 153.03 1.05 1.17 mitromethane MeNO ₂ (C_{3y}) 168.67 28.66 26.8 nitromethane MeNO ₂ (C_{3y}) 163.05 34.27 31.3 acetaldehyde CH ₃ COCH ₃ (C_{2y}) 165.09 32.23 30.9 acetic acid CH ₃ COOH ₃ (C_{3y}) 176.02 21.30 20.8 methyl acetate CH ₃ COOCH ₃ (C_{3y}) 175.30 22.02 19.3 DMSO CH ₃ SCH ₃ (C_{2y}) 175.30 22.02 19.3 DMSO CH ₃ SO(DCH ₃ (C_{3}) 175.76 39.63 41.0 methyl solfide CH ₃ SO(DCH ₃ (C_{3}) 157.67 37.75 39.6 chloromethane CH ₄ COCH ₄ (C_{2y}) 137.16 60.16 60.9 methyl iso-propyl ether MeOPr-7 (C_{1}) 147.67 49.65 54.9 methyl iso-propyl ether MeOPr-7 (C_{1}) 147.28 50.04 49.4 thyl ethylene CH ₂ =CHCH=CH ₂ (C_{2}) C1 69.27 128.05	acetonitrile	$M_{0}CN(C_{2})$		103 63	3 60	47.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	mothyl isocyanida	$M_{0}NC(C_{2})$		168.67	28.66	26.8
$ \begin{array}{cccc} \text{number of } C(z) & 133.04 & 02.29 & 02.3 \\ \text{acctaldehyde} & CH_3CO(CH_3(C_2)) & 165.05 & 34.27 & 31.3 \\ \text{acctacid} & CH_3CO(H_3(C_2)) & 165.09 & 32.23 & 30.9 \\ \text{acctic acid} & CH_3CO(H_3(C_2)) & 176.02 & 21.30 & 20.8 \\ \text{methyl acctate} & CH_3CO(H_3(C_3)) & 174.73 & 22.60 & 20.6 \\ \text{methyl acctate} & CH_3CO(H_3(C_3)) & 177.30 & 22.02 & 19.3 \\ \text{DMSO} & CH_3S(H_3(C_2)) & 177.30 & 22.02 & 19.3 \\ \text{DMSO} & CH_3S(O)(H_3(C_3)) & 159.57 & 37.75 & 39.6 \\ \text{chloromethae} & CH_3C(L(C_3)) & 168.74 & 28.59 & 25.6 \\ \text{dimethyl ether} & CH_3OCH_3(C_2) & 137.16 & 60.16 & 60.9 \\ \text{methyl ether} & CH_3OCH_3(C_2) & 137.16 & 60.16 & 60.9 \\ \text{methyl ether} & MeOEr(C_3) & 147.28 & 50.04 & 49.4 \\ \text{ethyl ether} & MeOBu-r(C_3) & 147.28 & 50.04 & 49.4 \\ \text{ethylene} & CH_2=CH(2) & 147.28 & 50.04 & 49.4 \\ \text{ethylene} & CH_2=CH(2) & C1 & 69.27 & 128.05 & 117.5 \\ \text{c2} & 46.82 & 150.50 & 137.8 \\ \text{cis-butadiene} & c-CH_2=CHCH=CH_2(C_2) & C1 & 70.17 & 127.16 & 117.5 \\ \text{c2} & 46.82 & 150.50 & 137.8 \\ \text{cis-butadiene} & CH_2=CHCH(-CH_2(C_2) & C1 & 70.17 & 127.16 & 117.5 \\ \text{c2} & 46.83 & 148.79 & 137.8 \\ \text{propylene} & CH_2=CHCH(C_3) & C1 & 45.61 & 151.71 & 149.0 \\ \text{c2} & 177.50 & 89.82 & 88.0 \\ \text{methyl vinyl ether} & CH_2=CHOH (C_3) & C1 & 45.61 & 151.71 & 149.0 \\ \text{c2} & 114.20 & 83.12 & 85.5 \\ \text{acrolein} & CH_2=CHCHO (C_4) & C4 & 51.86 & 145.47 & 138.5 \\ \text{c1} & 50.90 & 133.64 & 133.2 \\ \text{c2} & 133.90 & 133.64 & 133.2 \\ \text{c1} & 63.69 & 128.42 & 129.0 \\ \text{c1} & 63.69 & 128.42 & 129.0 \\ \text{c1} & 63.69 & 128.42 & 129.0 \\ \text{c1} & 63.69 & 133.64 & 133.2 \\ \text{c1} & 63.60 & 133.64 & 133.2 \\ \text{c1} & 63.69 &$	nitromethane	$MeNO_{2}(C)$		125.04	28.00	20.8
acetane CH3CHO(C3) 165.09 34.27 31.3 acetica acid CH3COOH3(C2) 165.09 32.23 30.9 acetica acid CH3COOH4(C2) 176.02 21.30 20.8 methyl acetate CH3COOH3(C3) 174.73 22.60 20.6 methyl acetate CH3COOH4(C2) 175.30 22.02 19.3 methanethiol CH3SCO(H3(C2)) 175.769 39.63 41.0 methane sulfonic acid CH3CO(H3(C2)) 137.16 60.16 60.9 methyl teher CH3CO(H3(C2)) 137.16 60.16 60.9 methyl teher MeOEt (C3) 138.17 59.16 57.6 methyl teher MeOEt (C4) 147.67 49.65 54.9 methyl teher MeOBu+7 (C1) 147.67 49.65 54.9 methyl teher MeOBu+7 (C2) 147.67 138.17 10.16 61.75.6 methyl teher MeOBu+7 (C3) 147.67 49.45 49.4 4thylene 174.73 22.60 137.8 trans-butadiene c-C42=CHCH=CH2 (C2) C1 70.17		$CU_{CUO}(C_s)$		155.04	02.29	02.3
acetic acidCH3COCH3 (C_{2v})165.0952.2330.9acetic acidCH3COCH3 (C_{3})176.0221.3020.8methyl acetateCH3COOH (C_{3})174.7322.6020.6methanethiolCH3SCH3 (C_{3v})177.53022.0219.3DMSOCH3SO3H (C_{1})157.6939.6341.0methane sulfonic acidCH3SO3H (C_{1})159.5737.7539.6chloromethaneCH3CO(C_{3v})168.7428.5925.6dimethyl etherMeOEt (C_{3v})137.1660.1660.9methyl etherMeOEt_4 (C_{3v})137.1660.1667.6methyl iso-propyl etherMeOBr- <i>i</i> (C_{1})147.2850.0449.4ethyleneCH2=CH2 (D_{2h})62.47134.86123.3 <i>trans</i> -butadiene <i>t</i> -CH2=CHCH=CH2 (C_{2})C169.27128.05117.5 <i>cis</i> -butadiene <i>c</i> -CH2=CHCH=CH2 (C_{2})C170.17127.16117.5 <i>trans</i> -butadiene <i>c</i> -CH2=CHCH=CH2 (C_{2})C170.17127.16117.5 <i>trans</i> -butadiene <i>c</i> -CH2=CHCH=CH2 (C_{2})C159.83137.99140.2 <i>cis</i> -butadiene <i>c</i> -CH2=CHCH=CH2 (C_{2})C159.53152.9 <i>cis</i> -butadiene <i>c</i> -CH2=CHCH=CH2 (C_{3})C159.53152.9 <i>cis</i> -butadiene <i>c</i> -CH2=CHCH=CH2 (C_{3})C137.79159.53152.9 <i>cis</i> -cheinCH2=CHCHO (C_{3} C137.79159.53152.9<	acetandenyue	$CH_{3}CHO(C_{s})$		165.03	24.27	20.0
acente acid CH3COOFH (C_3) 176.02 21.50 20.8 methyl acetate CH3COOCH (C_3) 174.73 22.60 20.6 methyl acetate CH3COOCH (C_3) 174.73 22.60 20.6 methyl sulfide CH3CH3 (C_8) 187.17 10.15 6.5 dimethyl sulfide CH3COA(C_8) 175.30 20.02 19.3 DMSO CH3SCOA(C_8) 175.69 39.63 41.0 methane sulfonic acid CH3SO3H (C_1) 159.57 37.75 39.6 chloromethane CH3COCH3(C_8) 138.17 59.16 57.6 methyl ether MeOEt (C_4) 138.17 59.16 57.6 methyl iso-propyl ether MeOBt-r1 (C_5) 147.68 123.3 177.5 irrars-butadiene r-CH2=CHCH=CH2 (C_2n) C1 69.27 128.05 117.5 c:s-butadiene c-CH2=CHCH=CH2 (C_2n) C1 70.17 127.16 117.5 c:s-butadiene c-CH2=CHCH=CH2 (C_2) C1 70.17 127.16 117.5 vinyl alcohol CH2=CHOH (C_6) C1 37.79 140		$CH_3COCH_3(C_{2v})$		103.09	52.25 21.20	30.9 20.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	acetic acid	$CH_3COOH(C_s)$		170.02	21.50	20.8
$\begin{array}{llllllllllllllllllllllllllllllllllll$	methyl acetate	$CH_3COOCH_3 (C_s)$		1/4./3	22.00	20.0
andmentyl sulfideCH3SCH3 (C_{2v})175.3022.0219.3DMSOCH3S(O)CH3(C_s)157.6939.6341.0methane sulfonic acidCH3S(O)CH (C_s)157.6939.6341.0chloromethaneCH3Cl(C_{3v})188.7428.5925.6dimethyl etherCH3CCH3 (C_{2v})137.1660.1660.9methyl ethyl etherMeOEt (C_s)138.1759.1657.6methyl iso-propyl etherMeOPr-i (C_1)147.6749.6554.9methyl tert-butyl etherMeOBu-i (C_s)147.2850.0449.4ethyleneCH2=CH2 (D_{2h})62.47134.86123.3trans-butadienet-CH2=CHCH=CH2 (C_{2h})C169.27128.05117.5cis-butadienet-CH2=CHCH=CH2 (C_2)C170.17127.16117.5propyleneCH2=CHCH3 (C_s)C159.53137.99140.2cis-butadienec-CH2=CHCHG (C_s)C145.61151.71149.0cis-butadienec-CH2=CHCHG (C_s)C145.61151.71149.0cis-butadieneCH2=CHCH3 (C_s)C145.61151.71149.0cis-butadieneCH2=CHCHG (C_s)C145.61151.71149.0cis-acrylic acidCH2=CHOMe (C_s)C145.61151.71149.0cis-acrylic acidc-CH2=CHCOOH (C_s)C452.41144.91137.5cis-acrylic acidc-CH2=CHCOOH (C_s)C452.41144.91137	methanethiol	$CH_3SH(CS)$		18/.1/	10.15	0.5
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	dimethyl sulfide	$CH_3SCH_3(C_{2v})$		1/5.30	22.02	19.3
methane sultonic acidCH ₃ O(H159.57 37.75 39.6 chloromethaneCH ₃ Cl (C_{3v})168.7428.5925.6dimethyl etherCH ₃ O(H ₃ (C_{2v})137.1660.1660.9methyl iso-propyl etherMeOEt (C_{3})138.1759.1657.6methyl iso-propyl etherMeOBu-t (C_{1})147.2850.0449.4ethyleneCH ₂ =CH2 (D_{2h})62.47134.86123.3trans-butadienet-CH ₂ =CHCH=CH ₂ (C_{2h})C169.27128.05117.5cz46.85148.79137.817.817.8cis-butadienec-CH ₂ =CHCH=CH ₂ (C_{2})C170.17127.16117.5cz48.53148.79137.8140.222.924.2vinyl alcoholCH ₂ =CHOH (C_{s})C137.79140.222.9vinyl alcoholCH ₂ =CHOH (C_{s})C137.79159.53152.9cz114.2083.1285.588.088.088.0methyl vinyl etherCH ₂ =CHCOH (C_{s})C452.41144.91137.5cis-acrylic acidc-CH ₂ =CHCOOH (C_{s})C452.41144.91137.5cis-acrylic acidc-CH ₂ =CHCOOH (C_{s})C466.26131.07128.1cis-acrylic acidc-CH ₂ =CHCOOH (C_{s})C165.20133.42128.1cis-acrylic acidc-CH ₂ =CHCOOH (C_{s})C165.20133.42128.1nitroethyleneCH ₂ =CHNO ₂ (DMSO	$CH_3S(O)CH_3(C_s)$		157.69	39.63	41.0
chloromethane CH ₃ Cl (C_{3v}) 168.74 28.59 25.6 dimethyl ether CH ₃ OCH ₃ (C_{2v}) 137.16 60.16 60.9 methyl ether MeOEt (C_{3}) 147.67 49.65 54.9 methyl iso-propyl ether MeOBt- <i>i</i> (C_{1}) 147.67 49.65 54.9 methyl terl-butyl ether MeOBt- <i>i</i> (C_{2}) 147.67 49.65 54.9 methyl terl-butyl ether MeOBt- <i>i</i> (C_{2}) 147.67 49.65 117.5 <i>c</i> 2 46.82 150.50 137.8 <i>c</i> 2 46.82 150.50 137.8 <i>c</i> 3 <i>s</i> -butadiene <i>t</i> -CH ₂ =CHCH=CH ₂ (C_{2h}) C1 69.27 128.05 117.5 <i>c</i> 2 46.82 150.50 137.8 <i>c</i> 3 <i>s</i> -butadiene <i>c</i> -CH ₂ =CHCH=CH ₂ (C_{2}) C1 59.33 137.99 140.2 <i>c</i> 2 79.57 117.75 115.7 <i>c</i> 2 48.53 148.79 137.8 propylene CH ₂ =CHCH ₃ (C_{8}) C1 59.33 137.99 140.2 <i>c</i> 2 79.57 117.75 115.7 <i>c</i> 2 107.50 89.82 88.0 methyl vinyl ether CH ₂ =CHOH (C_{8}) C1 45.61 151.71 149.0 C2 107.50 89.82 88.0 methyl vinyl ether CH ₂ =CHCHO (C_{8}) C1 37.79 159.53 152.9 <i>c</i> 1 61.36 135.96 138.0 methyl vinyl ketone CH ₂ =CHCHO (C_{8}) C4 51.86 145.47 138.5 <i>c</i> 1 61.36 135.96 138.0 methyl vinyl ketone CH ₂ =CHCOOH (C_{8}) C4 51.86 145.47 138.5 <i>c</i> 1 61.36 135.96 138.0 methyl vinyl ketone CH ₂ =CHCOOH (C_{8}) C4 66.26 131.07 128.1 <i>c</i> 1 63.68 133.64 133.2 <i>trans</i> -acrylic acid <i>c</i> -CH ₂ =CHCOOH (C_{8}) C4 46.86 150.47 144.71 <i>c</i> 1 65.20 132.12 133.2 <i>trans</i> -acrylic acid <i>t</i> -CH ₂ =CHCOOH (C_{8}) C4 46.86 150.47 144.7 <i>c</i> 1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.60 121.5 <i>isocyanoethylene</i> CH ₂ =CHNC (C_{8}) C1 76.72 120.	methane sulfonic acid	$CH_3SO_3H(C_1)$		159.57	37.75	39.6
dimethyl ether $CH_3OCH_3 (C_{2v})$ 137.1660.1660.9methyl ethyl etherMeOEt (C_8)138.1759.1657.6methyl iso-propyl etherMeOPr-i (C1)147.6749.6554.9methyl iso-propyl etherMeOBu-t (C_8)147.2850.0449.4ethyleneCH_2=CH2 (D_{2h})62.47134.86123.3trans-butadienet-CH2=CHCH=CH2 (C_2)C169.27128.05117.5c246.82150.50137.8137.8propyleneCH2=CHCH=CH2 (C_2)C170.17127.16117.5propyleneCH2=CHCH3 (C_8)C159.33137.99140.2c279.57117.75115.7115.7vinyl alcoholCH2=CHOH (C_8)C137.79159.53152.9acroleinCH2=CHCOMe (C_8)C137.79159.53152.9acroleinCH2=CHCOOH (C_8)C161.36135.96138.0methyl vinyl ketoneCH2=CHCOOH (C_8)C452.41144.91137.5cis-acrylic acidc-CH2=CHCOOH (C_8)C462.6131.07128.1cis-acrylic acidt-CH2=CHCOOH (C_8)C163.68133.64133.2trans-acrylic acidt-CH2=CHCOOH (C_8)C446.86150.47144.7cis-acrylic acidt-CH2=CHCOOH (C_8)C176.72120.60121.5isocyanoethyleneCH2=CHNO2 (C_8)C446.86150.47144.7c1 </td <td>chloromethane</td> <td>$CH_3Cl(C_{3v})$</td> <td></td> <td>168.74</td> <td>28.59</td> <td>25.6</td>	chloromethane	$CH_3Cl(C_{3v})$		168.74	28.59	25.6
methyl ethyl etherMeOEt (C_s)138.1759.1657.6methyl iso-propyl etherMeOPr-i (C_1)147.6749.6554.9methyl tert-butyl etherMeOBu-r (C_s)147.2850.0449.4ethylene $CH_2=CH_2 (D_{2h})$ 62.47134.86123.3trans-butadiene $t-CH_2=CHCH=CH_2 (C_{2h})$ C169.27128.05117.5cis-butadiene $c-CH_2=CHCH=CH_2 (C_2)$ C170.17127.16117.5propylene $CH_2=CHCH=CH_2 (C_2)$ C170.17127.16117.5propylene $CH_2=CHCH_3 (C_s)$ C145.61151.71149.0c279.57117.75115.7115.7115.7propylene $CH_2=CHOH (C_s)$ C145.61151.71149.0c2107.5089.8288.088.088.1285.5acrolein $CH_2=CHOMe (C_s)$ C451.86145.47138.5c161.36135.96138.0137.99140.2cis-acrylic acid $c-CH_2=CHCOOH (C_s)$ C451.86145.47138.5c163.68133.64133.2148.9137.5cis-acrylic acid $t-CH_2=CHCOOH (C_s)$ C466.26131.07128.1c165.20132.12133.2133.2133.2133.2ntroethylene $CH_2=CHNO_2 (C_s)$ C446.86150.47144.7cis-acrylic acid $t-CH_2=CHCOOH (C_s)$ C175.91121.41121.0	dimethyl ether	$CH_3OCH_3 (C_{2v})$		137.16	60.16	60.9
methyl iso-propyl ether methyl tert-butyl etherMeOPr-i (C_i)147.6749.6554.9methyl tert-butyl etherMeOBu-t (C_s)147.2850.0449.4ethyleneCH2=CH2 (D2s)62.47134.86123.3trans-butadienet-CH2=CHCH=CH2 (C2s)C169.27128.05117.5c246.82150.50137.8cis-butadienec-CH2=CHCH=CH2 (C2)C170.17127.16117.5propyleneCH2=CHCH3 (Cs)C159.33137.99140.2c279.57117.75115.7174.7422.5924.2vinyl alcoholCH2=CHOH (Cs)C137.79159.53152.9methyl vinyl etherCH2=CHOMe (Cs)C137.79159.53152.9c2114.2083.1285.522.41144.91137.5c161.36135.96138.0C163.68136.4133.2methyl vinyl ketoneCH2=CHCOCH3 (Cs)C452.41144.91137.5cis-acrylic acidc-CH2=CHCOOH (Cs)C462.26131.07128.1cis-acrylic acidt-CH2=CHCOOH (Cs)C463.90133.42128.1trans-acrylic acidt-CH2=CHNO2 (Cs)C446.86150.47144.7isocyanoethyleneCH2=CHNC (Cs)C176.72120.60121.5isocyanoethyleneCH2=CHNC (Cs)C175.91121.41121.0C472.41124.92119.3144.6N,	methyl ethyl ether	MeOEt (C_s)		138.17	59.16	57.6
methyl tert-butyl ether ethyleneMeOBu- t (C ₅)147.2850.0449.4ethylene $CH_2=CH_2$ (D_{2h})62.47134.86123.3trans-butadiene t -CH ₂ =CHCH=CH ₂ (C_{2h})C169.27128.05117.5cis-butadiene c -CH ₂ =CHCH=CH ₂ (C_2)C170.17127.16117.5propyleneCH ₂ =CHCH=CH ₂ (C_3)C159.33137.99140.2C279.57117.75115.7propyleneCH ₂ =CHOH (C_8)C145.61151.71vinyl alcoholCH ₂ =CHOMe (C_8)C137.79159.53152.9methyl vinyl etherCH ₂ =CHCHO (C_8)C137.79159.53152.9cc114.2083.1285.588.0methyl vinyl ketoneCH ₂ =CHCOCH ₃ (C_8)C451.86145.47138.5methyl vinyl ketoneCH ₂ =CHCOOH (C_8)C451.86145.47138.5cis-acrylic acid c -CH ₂ =CHCOOH (C_8)C466.26131.07128.1trans-acrylic acid t -CH ₂ =CHCOOH (C_8)C466.26131.07128.1trans-acrylic acid t -CH ₂ =CHCOOH (C_8)C465.20132.12133.2nitroethyleneCH ₂ =CHNO ₂ (C_8)C475.91121.41121.0 C_1 64.86150.47144.7132.2132.2nitroethyleneCH ₂ =CHNO ₂ (C_8)C446.86150.47144.7isocyanoethyleneCH ₂ =CHNO ₂ (C_8) </td <td>methyl iso-propyl ether</td> <td>MeOPr-$i(C_1)$</td> <td></td> <td>147.67</td> <td>49.65</td> <td>54.9</td>	methyl iso-propyl ether	MeOPr- $i(C_1)$		147.67	49.65	54.9
ethylene $CH_2=CH_2(D_{2h})$ 62.47 134.86 123.3 trans-butadiene t -CH $_2=CHCH=CH_2(C_{2h})$ C1 69.27 128.05 117.5 cis-butadiene c -CH $_2=CHCH=CH_2(C_2)$ C1 70.17 127.16 117.5 propylene $CH_2=CHCH_3(C_s)$ C1 59.33 137.99 140.2 $C2$ 48.53 148.79 137.8 propylene $CH_2=CHCH_3(C_s)$ C1 59.33 137.99 140.2 $C2$ 79.57 117.75 115.7 vinyl alcohol $CH_2=CHOH(C_s)$ C1 45.61 151.71 149.0 methyl vinyl ether $CH_2=CHOMe(C_s)$ C1 37.79 159.53 152.9 acrolein $CH_2=CHCHO(C_s)$ C1 37.79 159.53 152.9 acrolein $CH_2=CHCHO(C_s)$ C4 51.86 145.47 138.5 methyl vinyl ketone $CH_2=CHCOCH_3(C_s)$ C4 52.41 144.91 137.5 $c1$ 63.68 133.64 133.2 $c1$ 63.68 133.64 133.2 $cis-acrylic acid$ t -CH $_2=CHCOOH(C_s)$ C2 63.90 133.42 128.1 $c1$ $c1$ $c2$ $c3.90$ 133.42 128.1 $c1$ $c2$ <td>methyl tert-butyl ether</td> <td>MeOBu-$t(C_s)$</td> <td></td> <td>147.28</td> <td>50.04</td> <td>49.4</td>	methyl tert-butyl ether	MeOBu- $t(C_s)$		147.28	50.04	49.4
trans-butadienet-CH2=CHCH=CH2 (C_{2h})C169.27128.05117.5cis-butadienec-CH2=CHCH=CH2 (C_2)C170.17127.16117.5propyleneCH2=CHCH3 (C_s)C159.33137.99140.2C279.57117.75115.7174.7422.5924.2vinyl alcoholCH2=CHOH (C_s)C145.61methyl vinyl etherCH2=CHOMe (C_s)C145.61c2117.515.7174.7422.5924.2vinyl alcoholCH2=CHOMe (C_s)C145.61methyl vinyl etherCH2=CHOMe (C_s)C161.36c2114.2083.1285.5acroleinCH2=CHCHO (C_s)C451.86methyl vinyl ketoneCH2=CHCOCH3 (C_s)C452.41cis-acrylic acidc-CH2=CHCOOH (C_s)C462.26cis-acrylic acidt-CH2=CHCOOH (C_s)C263.90cis-acrylic acidt-CH2=CHCOOH (C_s)C263.90nitroethyleneCH2=CHNO2 (C_s)C446.86c165.20132.12133.2nitroethyleneCH2=CHNC (C_s)C175.91c212.41124.92119.3N,N-dimethylethenamine(C1)C13181.0816.2512.8C10137.8259.51cisocyanoethyleneCH2=CHNC (C_s)C175.91cid137.8259.5153.6c1144.9452.3944.6	ethylene	$CH_2=CH_2(D_{2h})$		62.47	134.86	123.3
cis-butadiene $c-CH_2=CHCH=CH_2 (C_2)$ C_1 70.17 127.16 117.5 propylene $CH_2=CHCH_3 (C_s)$ C_1 79.33 137.99 140.2 C_2 79.57 117.75 115.7 $rate relation of the construction of the constructi$	trans-butadiene	t -CH ₂ =CHCH=CH ₂ (C_{2h})	C1	69.27	128.05	117.5
cis-butadiene $c-CH_2=CHCH=CH_2(C_2)$ C1 70.17 127.16 117.5 propyleneCH_2=CHCH3(C_3)C1 59.33 148.79 137.8 propyleneCH_2=CHCH3(C_3)C1 59.33 137.99 140.2 C2 79.57 117.75 115.7 vinyl alcoholCH_2=CHOH (C_s)C1 45.61 151.71 149.0 methyl vinyl etherCH_2=CHOMe (C_s)C1 37.79 159.53 152.9 acroleinCH2=CHCHO (C_s)C1 37.79 159.53 152.9 acroleinCH2=CHCHO (C_s)C1 61.36 135.96 138.0 methyl vinyl ketoneCH2=CHCOCH3 (C_s)C1 61.36 135.96 138.0 methyl vinyl ketoneCH2=CHCOOH (C_s)C4 66.26 131.07 128.1 cis -acrylic acid c -CH2=CHCOOH (C_s)C2 63.90 133.42 128.1 cis -acrylic acid t -CH2=CHCOOH (C_s)C2 63.90 133.42 128.1 cis ocyanoethyleneCH2=CHNO2 (C_s)C4 46.86 150.47 144.7 cis ocyanoethyleneCH2=CHNC (C_s)C1 75.91 121.41 121.0 cis C1 75.91 121.41 121.0 $C4$ 72.41 124.92 119.3 $nitroethylene$ CH2=CHNC (C_s)C1 75.91 121.41 121.0 $C4$ 72.41 124.92 119.3 $nitroethylene$ CH2=CHNC (C_s)C1 75.91 121.41 121.0			C2	46.82	150.50	137.8
propylene $CH_2=CHCH_3 (C_s)$ C_1 59.33 148.79 137.8 $C1$ 59.33 137.99 140.2 $C2$ 79.57 117.75 115.7 $Vinyl$ alcohol $CH_2=CHOH (C_s)$ $C1$ 45.61 151.71 $Vinyl$ alcohol $CH_2=CHOM (C_s)$ $C1$ 45.61 151.71 $Vinyl$ alcohol $CH_2=CHOM (C_s)$ $C1$ 37.79 159.53 152.9 $C2$ 107.50 89.82 88.0 methyl vinyl ether $CH_2=CHCHO (C_s)$ $C4$ 51.86 145.47 138.5 acrolein $CH_2=CHCOCH_3 (C_s)$ $C4$ 51.86 145.47 138.5 methyl vinyl ketone $CH_2=CHCOCH_3 (C_s)$ $C4$ 52.41 144.91 137.5 $C1$ 63.68 133.64 133.2 128.12 $C1$ 63.68 133.64 133.2 <i>trans</i> -acrylic acid t - $CH_2=CHCOOH (C_s)$ $C2$ 63.90 123.42 128.12 $C1$ 65.20 132.12 133.2 113.22 113.22 nitroethylene $CH_2=CHNO_2 (C_s)$ $C4$ 46.86 150.47 144.7 $C1$ 76.72 120.60 121.5 123.24 121.02 V_{A} V_{A} V_{A} 124.92 119.3 N_{A} -dimethylethenamine $C(1)$ $C13$ 181.08 16.25 12.8 $C1$ 144.94 152.39 144.6	cis-butadiene	c -CH ₂ =CHCH=CH ₂ (C_2)	C1	70.17	127.16	117.5
propylene $CH_2=CHCH_3(C_s)$ $C1$ 59.33 137.99 140.2 $C2$ 79.57 117.75 115.7 174.74 22.59 24.2 vinyl alcohol $CH_2=CHOH(C_s)$ $C1$ 45.61 151.71 149.0 methyl vinyl ether $CH_2=CHOMe(C_s)$ $C1$ 37.79 159.53 152.9 acrolein $CH_2=CHCHO(C_s)$ $C4$ 51.86 145.47 138.5 acrolein $CH_2=CHCHO(C_s)$ $C4$ 51.86 145.47 138.5 methyl vinyl ketone $CH_2=CHCOCH_3(C_s)$ $C4$ 51.86 145.47 138.5 $C1$ 61.36 135.96 138.0 $C1$ 68.90 128.42 129.0 <i>cis</i> -acrylic acid <i>c</i> -CH_2=CHCOOH (C_s) $C4$ 66.26 131.07 128.1 $C1$ 65.20 133.42 128.1 $C1$ 65.20 133.42 128.1 <i>nitroethylene</i> $CH_2=CHNO_2(C_s)$ $C4$ 46.86 150.47 144.7 <i>nitroethylene</i> $CH_2=CHNC(C_s)$ $C1$ 75.91 121.41 121.0 <i>N,N</i> -dimethylethenamine (C_1) $C13$ 181.08 16.25 12.8 $C10$ 137.82 59.51 53.6 $C10$ 137.82 59.51 53.6			C2	48.53	148.79	137.8
C2 79.57 117.75 115.7 vinyl alcoholCH2=CHOH (C_s)C1 45.61 151.71 149.0 C2 107.50 89.82 88.0 methyl vinyl etherCH2=CHOMe (C_s)C1 37.79 159.53 152.9 c2 114.20 83.12 85.5 acroleinCH2=CHCHO (C_s)C4 51.86 145.47 138.5 methyl vinyl ketoneCH2=CHCOCH3 (C_s)C4 52.41 144.91 137.5 cis-acrylic acid c -CH2=CHCOOH (C_s)C4 66.26 131.07 128.1 cis-acrylic acid t -CH2=CHCOOH (C_s)C2 63.90 133.42 128.1 nitroethyleneCH2=CHNO2 (C_s)C4 46.86 150.47 144.7 isocyanoethyleneCH2=CHNC (C_s)C1 75.91 121.41 121.0 A,N -dimethylethenamine(C1)C13 181.08 16.25 12.8 $C10$ 137.82 59.51 53.6 12.8	propylene	$CH_2 = CHCH_3 (C_s)$	C1	59.33	137.99	140.2
vinyl alcohol $CH_2=CHOH (C_s)$ $C1$ 45.61 151.71 149.0 methyl vinyl ether $CH_2=CHOMe (C_s)$ $C1$ 37.79 159.53 152.9 acrolein $CH_2=CHCMO (C_s)$ $C1$ 37.79 159.53 152.9 acrolein $CH_2=CHCHO (C_s)$ $C4$ 51.86 145.47 138.5 methyl vinyl ketone $CH_2=CHCOCH_3 (C_s)$ $C4$ 52.41 144.91 137.5 cis-acrylic acid c -CH $_2=CHCOOH (C_s)$ $C4$ 66.26 131.07 128.1 cis-acrylic acid t -CH $_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 cis-acrylic acid t -CH $_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 cis-acrylic acid t -CH $_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 cis-acrylic acid t -CH $_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 cis-acrylic acid t -CH $_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 cis-acrylic acid t -CH $_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 cis-acrylic acid t -CH $_2=CHNO_2 (C_s)$ $C4$ 46.86 150.47 144.7 cis-acrylic acid t -CH $_2=CHNC (C_s)$ $C1$ 75.91 121.41 121.0 $C1$ 76.72 120.60 121.5 121.5 123.6 124.92 119.3 N,N -dimethylethenamine (C_1) $C13$ 181.08 16.25 12.8 144.6 $C1$			C2	79.57	117.75	115.7
vinyl alcohol $CH_2=CHOH (C_s)$ $C1$ 45.61 151.71 149.0 methyl vinyl ether $CH_2=CHOMe (C_s)$ $C1$ 37.79 159.53 152.9 acrolein $CH_2=CHCHO (C_s)$ $C4$ 51.86 145.47 138.5 acrolein $CH_2=CHCHO (C_s)$ $C4$ 51.86 145.47 138.5 methyl vinyl ketone $CH_2=CHCOCH_3 (C_s)$ $C4$ 52.41 144.91 137.5 $C1$ 68.90 128.42 129.0 cis -acrylic acid c -CH2=CHCOOH (C_s) $C4$ 66.26 131.07 128.1 $C1$ 63.68 133.64 133.2 $C1$ 63.68 133.64 133.2 $trans$ -acrylic acid t -CH2=CHCOOH (C_s) $C2$ 63.90 133.42 128.1 $C1$ 65.20 132.12 133.2 1165.20 132.12 133.2 $riroethylene$ $CH_2=CHNO_2 (C_s)$ $C4$ 46.86 150.47 144.7 $cocyanoethylene$ $CH_2=CHNC (C_s)$ $C1$ 75.91 121.41 121.0 $C4$ 72.41 124.92 119.3 74.6 144.94 52.39 44.6				174.74	22.59	24.2
C2 107.50 89.82 88.0 methyl vinyl ether $CH_2=CHOMe(C_s)$ $C1$ 37.79 159.53 152.9 acrolein $CH_2=CHCHO(C_s)$ $C4$ 51.86 145.47 138.5 acrolein $CH_2=CHCOCH_3(C_s)$ $C4$ 51.86 145.47 138.5 methyl vinyl ketone $CH_2=CHCOCH_3(C_s)$ $C4$ 52.41 144.91 137.5 $C1$ 68.90 128.42 129.0 cis -acrylic acid c - $CH_2=CHCOOH(C_s)$ $C4$ 66.26 131.07 128.1 cis -acrylic acid t - $CH_2=CHCOOH(C_s)$ $C4$ 66.26 131.07 128.1 cis -acrylic acid t - $CH_2=CHCOOH(C_s)$ $C2$ 63.90 133.42 128.1 cis -acrylic acid t - $CH_2=CHCOOH(C_s)$ $C1$ 65.20 132.12 133.2 $rans$ -acrylic acid t - $CH_2=CHNO_2(C_s)$ $C4$ 46.86 150.47 144.7 cis ocyanoethylene $CH_2=CHNC(C_s)$ $C1$ 75.91 121.41 121.0 $c4$ 72.41 124.92 119.3 $C10$ 137.82 59.51 53.6 $cinristoreristoreristoreristoreristoreristoreristoreristoreC1ristoreristoreristoreristoreristoreristoreristoreristoreristoreristoreristoreristoreristoreristoreristoreristoreristoreristoreristore$	vinyl alcohol	$CH_2 = CHOH(C_s)$	C1	45.61	151.71	149.0
methyl vinyl ether $CH_2=CHOMe (C_s)$ $C1$ 37.79 159.53 152.9 acrolein $CH_2=CHCHO (C_s)$ $C4$ 51.86 145.47 138.5 methyl vinyl ketone $CH_2=CHCOCH_3 (C_s)$ $C4$ 52.41 144.91 137.5 $C1$ 61.36 135.96 138.0 methyl vinyl ketone $CH_2=CHCOCH_3 (C_s)$ $C4$ 52.41 144.91 137.5 $C1$ 68.90 128.42 129.0 cis -acrylic acid c -CH $_2=CHCOOH (C_s)$ $C4$ 66.26 131.07 128.1 $C1$ 63.68 133.64 133.2 $trans$ -acrylic acid t -CH $_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 $C1$ 65.20 132.12 133.2 nitroethylene $CH_2=CHNO_2 (C_s)$ $C4$ 46.86 150.47 144.7 $C1$ 76.72 120.60 121.5 isocyanoethylene $CH_2=CHNC (C_s)$ $C1$ 75.91 121.41 121.0 $C4$ 72.41 124.92 119.3 N,N -dimethylethenamine (C_1) $C13$ 181.08 16.25 12.8 $C10$ 137.82 59.51 53.6 $C1$ 144.94 52.39 44.6	-		C2	107.50	89.82	88.0
acrolein $CH_2=CHCHO (C_s)$ $C2$ 114.20 83.12 85.5 acrolein $CH_2=CHCHO (C_s)$ $C4$ 51.86 145.47 138.5 methyl vinyl ketone $CH_2=CHCOCH_3 (C_s)$ $C4$ 52.41 144.91 137.5 $C1$ 68.90 128.42 129.0 cis -acrylic acid c -CH2=CHCOOH (C_s) $C4$ 66.26 131.07 128.1 $crans$ -acrylic acid t -CH2=CHCOOH (C_s) $C4$ 66.26 131.07 128.1 $crans$ -acrylic acid t -CH2=CHCOOH (C_s) $C2$ 63.90 133.42 128.1 $crans$ -acrylic acid t -CH2=CHCOOH (C_s) $C2$ 63.90 133.42 128.1 $crans$ -acrylic acid t -CH2=CHCOOH (C_s) $C1$ 65.20 132.12 133.2 $riroethylene$ $CH_2=CHNO_2 (C_s)$ $C4$ 46.86 150.47 144.7 $crans-acrylic acidCH_2=CHNO_2 (C_s)C176.72120.60121.5riroethyleneCH_2=CHNC (C_s)C175.91121.41121.0crans-acrylic acidC1_2=CHNC (C_s)C175.91121.41121.0crans-acrylic acidC1_2=CHNC (C_s)C175.91121.41121.0crans-acrylic acidC1_2=CHNC (C_s)C175.91121.41121.0crans-acrylic acidC1_2=CHNC (C_s)C175.91121.41124.92119.3riroethyleneC1_2=CHNC (C_s)C1_3<$	methyl vinyl ether	$CH_2 = CHOMe(C_s)$	C1	37.79	159.53	152.9
acrolein $CH_2=CHCHO (C_s)$ $C4$ 51.86 145.47 138.5 methyl vinyl ketone $CH_2=CHCOCH_3 (C_s)$ $C4$ 52.41 144.91 137.5 cis-acrylic acid $c-CH_2=CHCOOH (C_s)$ $C4$ 66.26 131.07 128.1 c1 63.68 133.64 133.2 trans-acrylic acid $t-CH_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 c1 63.68 133.64 133.2 trans-acrylic acid $t-CH_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 c1 65.20 132.12 133.2 nitroethylene $CH_2=CHNO_2 (C_s)$ $C4$ 46.86 150.47 144.7 c1 76.72 120.60 121.5 isocyanoethylene $CH_2=CHNC (C_s)$ $C1$ 75.91 121.41 121.0 A,N -dimethylethenamine (C_1) $C13$ 181.08 16.25 12.8 $C10$ 137.82 59.51 53.6 $C1$ 144.94 52.39 44.6			C2	114.20	83.12	85.5
methyl vinyl ketone $CH_2=CHCOCH_3 (C_s)$ C_4 52.41 144.91 137.5 cis -acrylic acid c - $CH_2=CHCOOH (C_s)$ $C4$ 66.26 131.07 128.1 cis -acrylic acid t - $CH_2=CHCOOH (C_s)$ $C4$ 66.26 131.07 128.1 $c1$ 63.68 133.64 133.2 $trans$ -acrylic acid t - $CH_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 $c1$ 65.20 132.12 133.2 $c1$ 65.20 132.12 133.2 $c1$ 65.20 132.12 133.2 $c1$ $c67.72$ 120.60 121.5 $c1$ 76.72 120.60 121.5 $c2$ $c1$ 75.91 121.41 121.0 $c4$ 72.41 124.92 119.3 N,N -dimethylethenamine (C_1) $C13$ 181.08 16.25 12.8 $c10$ 137.82 59.51 53.6 $c1$ 144.94 52.39 44.6	acrolein	$CH_2=CHCHO(C_s)$	C4	51.86	145.47	138.5
methyl vinyl ketone $CH_2=CHCOCH_3 (C_s)$ $C4$ 52.41 144.91 137.5 cis -acrylic acid c - $CH_2=CHCOOH (C_s)$ $C4$ 66.26 131.07 128.1 cis -acrylic acid t - $CH_2=CHCOOH (C_s)$ $C4$ 66.26 131.07 128.1 $c1$ 63.68 133.64 133.2 $trans$ -acrylic acid t - $CH_2=CHCOOH (C_s)$ $C2$ 63.90 133.42 128.1 $c1$ 65.20 132.12 133.2 nitroethylene $CH_2=CHNO_2 (C_s)$ $C4$ 46.86 150.47 144.7 $c1$ 76.72 120.60 121.5 isocyanoethylene $CH_2=CHNC (C_s)$ $C1$ 75.91 121.41 121.0 $c4$ 72.41 124.92 119.3 N,N -dimethylethenamine (C_1) $C13$ 181.08 16.25 12.8 $c10$ 137.82 59.51 53.6 $c1$ 144.94 52.39 44.6			C1	61.36	135.96	138.0
cis -acrylic acid c -CH2=CHCOOH (C_s)C1 68.90 128.42 129.0 cis -acrylic acid c -CH2=CHCOOH (C_s)C4 66.26 131.07 128.1 $C1$ 63.68 133.64 133.2 $trans$ -acrylic acid t -CH2=CHCOOH (C_s)C2 63.90 133.42 128.1 cis -acrylic acid t -CH2=CHCOOH (C_s)C2 63.90 133.42 128.1 cis -acrylic acid t -CH2=CHCOOH (C_s)C2 63.90 133.42 128.1 cis -acrylic acid t -CH2=CHCOOH (C_s)C2 63.90 133.42 128.1 cis -acrylic acid t -CH2=CHNO2 (C_s)C4 46.86 150.47 144.7 cis -acrylic acid cis -CH2=CHNO2 (C_s) cis -CH 76.72 120.60 121.5 is -acrylic acid cis -CH2=CHNC (C_s) cis -CH2=CH2=CHNC (C_s) cis -CH2=CH2=CH2=CH2=CH2 cis -CH2=CH2=CH2=CH2=CH2=CH2=CH2=CH2=CH2=CH2=	methyl vinyl ketone	$CH_2 = CHCOCH_3 (C_s)$	C4	52.41	144.91	137.5
cis-acrylic acidc-CH2=CHCOOH (Cs)C466.26131.07128.1 $C1$ 63.68133.64133.2 $trans$ -acrylic acid t -CH2=CHCOOH (Cs)C263.90133.42128.1 $C1$ 65.20132.12133.2 $nitroethylene$ CH2=CHNO2 (Cs)C446.86150.47144.7 $C1$ 76.72120.60121.5 $isocyanoethylene$ CH2=CHNC (Cs)C175.91121.41121.0 $C4$ 72.41124.92119.3 N,N -dimethylethenamine(C1)C13181.0816.2512.8 $C10$ 137.8259.5153.6 $C1$ 144.9452.3944.6			C1	68.90	128.42	129.0
trans-acrylic acid t -CH2=CHCOOH (Cs)C163.68133.64133.2 $trans$ -acrylic acid t -CH2=CHCOOH (Cs)C263.90133.42128.1 $C1$ 65.20132.12133.2 $troethylene$ CH2=CHNO2 (Cs)C446.86150.47144.7 $C1$ 76.72120.60121.5 $troethylene$ CH2=CHNC (Cs)C175.91121.41121.0 $C4$ 72.41124.92119.3 N,N -dimethylethenamine(C1)C13181.0816.2512.8 $C10$ 137.8259.5153.6 $C1$ 144.9452.3944.6	<i>cis</i> -acrylic acid	c -CH ₂ =CHCOOH (C_s)	C4	66.26	131.07	128.1
trans-acrylic acidt-CH2=CHCOOH (C_s)C263.90133.42128.1nitroethyleneCH2=CHNO2 (C_s)C446.86150.47144.7c176.72120.60121.5isocyanoethyleneCH2=CHNC (C_s)C175.91121.41121.0 $C4$ 72.41124.92119.3 N,N -dimethylethenamine(C_1)C13181.0816.2512.8 $C10$ 137.8259.5153.6 $C1$ 144.9452.3944.6			C1	63.68	133.64	133.2
number dely ne dela $C C H2 = CHNO2 (C_s)$ $C L$ $C C L$ $C C L$ $C C L$ $C L L$	trans-acrylic acid	t -CH ₂ =CHCOOH (C_s)	C2	63.90	133.42	128.1
nitroethylene $CH_2=CHNO_2 (C_s)$ $C4$ 46.86 150.12 134.7 isocyanoethylene $CH_2=CHNC (C_s)$ $C1$ 76.72 120.60 121.5 N,N -dimethylethenamine (C_1) $C1$ 75.91 121.41 121.0 $C4$ 72.41 124.92 119.3 $C10$ 137.82 59.51 53.6 $C1$ 144.94 52.39 44.6	traits delyne dela		C1	65 20	132.12	133.2
Indocuty totle $CH_2=CHNC_2(C_3)$ C_1 10.00 150.17 111.7 isocyanoethylene $CH_2=CHNC_2(C_3)$ C_1 76.72 120.60 121.5 N,N -dimethylethenamine (C_1) C_1 75.91 121.41 121.0 C_4 72.41 124.92 119.3 C_10 137.82 59.51 53.6 C_1 144.94 52.39 44.6	nitroethylene	$CH_2 = CHNO_2(C_3)$	C4	46.86	150.47	144 7
isocyanoethylene $CH_2=CHNC(C_s)$ $C1$ 75.91 121.41 121.0 N,N -dimethylethenamine (C_1) $C1$ 75.91 121.41 121.0 $C4$ 72.41 124.92 119.3 $C13$ 181.08 16.25 12.8 $C10$ 137.82 59.51 53.6 $C1$ 144.94 52.39 44.6		\sim	$\tilde{C1}$	76 72	120.60	121.5
Notigeneous (C1)C1 121.41 121.61 N,N-dimethylethenamine(C1)C4 72.41 124.92 119.3 C13181.0816.25 12.8 C10137.82 59.51 53.6 C1144.94 52.39 44.6	isocyanoethylene	$CH_2 = CHNC(C_2)$	$\tilde{C1}$	75 91	121 41	121.0
N,N-dimethylethenamine (C_1) C_1 124.92 119.5 C13181.0816.2512.8C10137.8259.5153.6C1144.9452.3944.6	isseguiseurgiene	CH_2 -CHI (C (C s)	C4	72 41	121.41	1193
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N N-dimethylethenamine	(C_1)	C13	181 08	16.25	12.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(~1)	C10	137.82	59 51	53.6
			C1	144 94	52 39	44.6

Table S7. The $\sigma^t(C; S)$, and $-\Delta \sigma^t(C; S)$ and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under MP2/BSS-A.

Species	(symmetry)		$\sigma^t(C)$	$-\Delta \sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	$SiMe_4(T_d)$		183.45	0.00	0.0
methane	$CH_4(T_d)$		189.75	-6.29	-4.6
ethane	$(CH_3CH_3: D_{3d})$		173.69	9.76	7.3
propane	$CH_3CH_2CH_3(C_{2v})$		160.29	23.16	16.4
<i>n</i> -pentane	$n-C_5H_{12}(C_{2v})$		141.16	42.30	34.8
<i>n</i> -heptane	$n-C_7H_{16}(C_{2v})$		144.29	39.17	29.5
<i>n</i> -nonane	(C_{2v})		144.39	39.06	29.8
methylamine	$(CH_3NH_2: C_s)$		150.18	33.27	28.4
methanol	$(CH_3OH: C_s)$		127.30	56.15	50.2
fluoromethane	$(CH_3F: C_{3v})$		105.90	77.56	71.6
dimethylamine	$Me_2NH(C_s)$		141.30	42.16	38.2
trimethylamine	$Me_3N(C_{3v})$		133.54	49.91	47.6
acetonitrile	$MeCN(C_{3v})$		181.97	1.49	1.7
methyl isocyanide	MeNC (C_{3v})		155.96	27.50	26.8
nitromethane	$MeNO_2(C_s)$		115.52	67.93	62.5
acetaldehyde	$CH_3CHO(C_s)$		147.47	35.98	31.3
acetone	$CH_3COCH_3(C_{2v})$		150.11	33.34	30.9
acetic acid	$CH_3COOH(C_s)$		161.68	21.78	20.8
methyl acetate	$CH_3COOCH_3(C_s)$		160.34	23.12	20.6
methanethiol	CH ₃ SH (Cs)		170.38	13.08	6.5
dimethyl sulfide	$CH_3SCH_3(C_{2v})$		159.72	23.73	19.3
DMSO	$CH_3S(O)CH_3(C_s)$		138.63	44.82	41.0
methane sulfonic acid	$CH_3SO_3H(C_1)$		141.59	41.86	39.6
chloromethane	$CH_3Cl(C_{3v})$		149.76	33.69	25.6
dimethyl ether	$CH_3OCH_3(C_{2y})$		119.14	64.31	60.9
methyl ethyl ether	MeOEt (C_s)		120.49	62.97	57.6
methyl iso-propyl ether	MeOPr- $i(C_1)$		133.47	49.98	54.9
methyl tert-butyl ether	MeOBu- $t(C_s)$		130.67	52.79	49.4
ethylene	$CH_2 = CH_2(D_{2h})$		51.68	131.77	123.3
trans-butadiene	t -CH ₂ =CHCH=CH ₂ (C_{2h})	C1	58.32	125.14	117.5
		C2	34.14	149.31	137.8
cis-butadiene	c -CH ₂ =CHCH=CH ₂ (C_2)	C1	62.01	121.45	117.5
		C2	36.33	147.12	137.8
propylene	$CH_2 = CHCH_3 (C_s)$	C1	35.74	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
1 12		C2	62.44	121.01	115.7
			160.08	23.37	24.2
vinyl alcohol	$CH_2 = CHOH(C_s)$	C1	24.72	158.74	149.0
		C2	91.82	91.63	88.0
methyl vinyl ether	$CH_2 = CHOMe(C_s)$	C1	19.10	164.35	152.9
		C2	97.53	85.92	85.5
acrolein	$CH_2=CHCHO(C_s)$	C4	34.05	149.41	138.5
		C1	33.04	150.42	138.0
methyl vinyl ketone	$CH_2 = CHCOCH_3 (C_s)$	C4	34.44	149.02	137.5
		C1	43.47	139.99	129.0
<i>cis</i> -acrylic acid	c -CH ₂ =CHCOOH (C_s)	C4	48.02	135.43	128.1
		C1	38.25	145.20	133.2
trans-acrylic acid	t-CH ₂ =CHCOOH (C _s)	C2	45.88	137.57	128.1
		C1	39.93	143.52	133.2
nitroethylene	$CH_2=CHNO_2(C_s)$	C4	26.54	156.92	144.7
		C1	48.91	134.55	121.5
isocyanoethylene	$CH_2=CHNC(C_s)$	C1	52.33	131.13	121.0
		C4	55.91	127.55	119.3
<i>N</i> , <i>N</i> -dimethylethenamine	(C_1)	C13	166.68	16.77	12.8
		C10	124.47	58.99	53.6
		C1	132.41	51.05	44.6

Table S8. The $\sigma^t(C; S)$, and $-\Delta \sigma^t(C; S)$ and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method of B3LYP/BSS-A under the solvent effect of CHCl₃.

Species	(symmetry)		σ ^t (C)	$-\Delta\sigma^t(C)_{TMS}$	$\delta(C)_{obsd}$
TMS	SiMe ₄ (T_d)		183.49	0.00	0.0
methane	$CH_{4}(T_{d})$		190.37	-6.88	-4.6
ethane	$(CH_3CH_3; D_{3d})$		173.87	9.61	7.3
propane	$CH_3CH_2CH_3(C_{2y})$		160.72	22.77	16.4
<i>n</i> -pentane	$n-C_5H_{12}(C_{2y})$		141 79	41 70	34.8
<i>n</i> -heptane	$n - C_7 H_{16} (C_{2y})$		145.06	38.43	29.5
<i>n</i> -nonane	(C_{2y})		145.13	38.36	29.8
methylamine	$(CH_3NH_2; C_s)$		150.79	32.70	28.4
methanol	$(CH_3OH; C_s)$		128.75	54.74	50.2
fluoromethane	$(CH_3F; C_{3v})$		108.75	74.74	71.6
dimethylamine	$Me_2NH(C_s)$		142.13	41.36	38.2
trimethylamine	$Me_3N(C_{3v})$		134.60	48.89	47.6
acetonitrile	$MeCN(C_{3v})$		182.83	0.66	1.7
methyl isocyanide	MeNC (C_{3v})		158.13	25.36	26.8
nitromethane	$MeNO_2(C_s)$		119.19	64.29	62.5
acetaldehyde	$CH_3CHO(C_s)$		149.61	33.87	31.3
acetone	$CH_3COCH_3(C_{2v})$		152.45	31.04	30.9
acetic acid	$CH_3COOH(C_s)$		163.38	20.11	20.8
methyl acetate	CH_3COOCH_3 (C_s)		161.72	21.76	20.6
methanethiol	$CH_3SH(C_s)$		170.71	12.78	6.5
dimethyl sulfide	$CH_3SCH_3(C_{2v})$		160.07	23.42	19.3
DMSO	$CH_3S(O)CH_3(C_s)$		140.89	42.59	41.0
methane sulfonic acid	$CH_3SO_3H(C_1)$		142.75	40.74	39.6
chloromethane	$CH_3Cl(C_{3v})$		151.19	32.30	25.6
dimethyl ether	$CH_3OCH_3(C_{2v})$		120.43	63.06	60.9
methyl ethyl ether	MeOEt (C_s)		121.74	61.75	57.6
methyl iso-propyl ether	MeOPr- $i(C_1)$		135.03	48.46	54.9
methyl tert-butyl ether	MeOBu- $t(C_s)$		132.32	51.16	49.4
ethylene	$CH_2=CH_2(D_{2h})$		54.31	129.17	123.3
trans-butadiene	t -CH ₂ =CHCH=CH ₂ (C_{2h})	C1	61.16	122.32	117.5
		C2	36.46	147.03	137.8
<i>cis</i> -butadiene	c -CH ₂ =CHCH=CH ₂ (C_2)	C1	64.40	119.08	117.5
		C2	38.83	144.66	137.8
propylene	$CH_2 = CHCH_3 (C_s)$	Cl	39.27	144.22	140.2
		C2	63.78	119.70	115.7
		C3	160.66	22.83	24.2
vinyl alcohol	$CH_2 = CHOH(C_s)$	CI	28.52	154.97	149.0
4 1 * 1 4		C2	92.54	90.94	88.0
methyl vinyl ether	$CH_2 = CHOMe(C_s)$	CI	21.69	161.79	152.9
	CU_{1} $CUCUO(C)$	C_{2}	99.37	84.11	85.5
acrolein	$CH_2 = CHCHO(C_s)$	C4	35.80	147.09	138.5
mothyl yinyl latona	$CU_{-}CUCOCU_{+}(C)$	C_1	40.42	145.07	138.0
methyl vinyl ketone	$CH_2 = CHCOCH_3(C_s)$	C4 C1	50.01	14/.4/	137.3
aig appulia agid	CH_{2} CH_{2} CHCOOH (C)	C_{1}	JU.30 40.85	133.13	129.0
ets-activité actu	c-CII ₂ -CIICOOII (Cs)	C_{1}	49.03	133.04	120.1
trans perulic peid	$t CH_2 - CHCOOH(C)$	C_{2}	42.03	140.04	133.2
trans-activite actu		C_{1}^{2}	47.20	130.21	120.1
nitroethylene	$CH_2 - CHNO_2(C_2)$	C_{1}	28 53	154.95	133.2
Introetitylene	CH_2 = $CHNO_2$ (Cs)	C_{+}	20.33	134.95	121 5
isocyanoethylene	$CH_2 - CHNC(C_2)$	C^1	58 37	127.94	121.5
1500 yanooniy lene	C_{112} - C_{111} (C_{5})	C_{A}	50.52 57 / Q	126.00	1193
N N-dimethylethenamine	(C_1)	C13	167 52	15 97	12.5
	(~1)	C10	125.06	58 43	53.6
		C1	133.25	50.24	44.6

Table S9. The $\sigma^t(C; S)$, and $-\Delta \sigma^t(C; S)$ and $\delta(C)_{obsd}$ for various 40 species (54 plots), calculated with the GIAO-DFT method under B3LYP/def2TZVP.

Species ^b	$\Delta E^a/kJmol^{-1}$	$-\Delta\sigma^t(C1)_{TMS}$	$-\!\Delta\sigma^t(C2)_{TMS}$	$-\Delta\sigma^t(C3)_{TMS}$	$-\Delta\sigma^t(C4)_{TMS}$	$-\Delta\sigma^t(C5)_{TMS}$
tt	0.00	17.44	30.67	42.05	30.67	17.44
tg	3.69	15.05	28.70	39.53	26.74	17.53
gt	7.21	13.87	23.72	38.12	23.72	13.87
gga	6.75	13.53	22.17	34.86	22.17	13.53
ggb	14.25	17.04	31.57	36.40	29.53	19.91
$\delta(C_i)_{obsd}$		14.20	22.80	34.80	22.80	14.20

Table S10. The $-\Delta\sigma^{t}(C_{i}: i = 1-5)_{\text{calcd:TMS}}$ and $\delta(C_{i}: i = 1-5)_{\text{obsd:TMS}}$ for some conformers in *n*-Pentane, calculated with the GIAO-DFT method under B3LYP/BSS-A.^{*a*}

 ${}^{a}_{b} - \Delta \sigma^{t}(C)_{calcd:TMS} = -[\sigma^{t}(C: n\text{-pentane})_{calcd} - [\sigma^{t}(C: TMS)_{calcd}].$



Table S11. The $\sigma^m(C: S)$, $\Delta \sigma^m(C: S)$ and $\Delta \sigma^m(C: S)_e$ (m = d, p and t) for various species of **1–56** and **S1–S20**, along with the pre- α , α , β , γ , δ , α -X, β -X and *ipso*-X (*i*-X) effects and the effects from the characteristic bonds and groups,^{*a,b*} together with the Q(C) values.

Nos.	Species	sym	<i>Q</i> (C)	σ ^d (C)	σ ^p (C) ^c	σ ^t (C)	$\Delta \sigma^{t}(C)$	$\Delta \sigma^{d}(C)_{e}$	$^{d} \Delta \sigma^{p}(C)_{e}^{d}$	$\Delta \sigma^{t}(C)_{e}^{d}$	effect
1	C ^{4–}	O_{h}	-4.000	274.39	0.00	274.39	0.00	0.00	0.00	0.00	
2	HC ^{3−}	C∞v	-1.815	264.04	1807.41	2071.45	1797.06	-10.35	1807.41	1797.06	pre-α
3	H_2C^{2-}	C_{2v}	-2.156	261.96	137.46	399.42	125.03	-6.22	68.73	62.51	pre-α
4	H₃C⁻	C_{3v}	-1.400	249.53	-2.26	247.26	-27.13	-8.29	-0.75	-9.04	pre-α
5	CH ₄	T_{d}	-0.805	238.98	-49.66	189.32	-85.08	-8.85	-12.42	-21.27	pre-α
6	MeH₂C [−]	Cs	-1.000	250.87	-98.55	152.32	-122.08	1.34	-96.29	-94.95	α
7	EtH_2C^-	Cs	-0.915	248.89	-82.29	166.59	-107.80	-1.98	16.26	14.28	β
8	<i>i</i> -PrH₂C [−]	<i>C</i> ₁	-0.923	236.54	-94.11	142.43	-131.96	-7.16	2.22	-4.94	β
9	<i>t</i> -BuH₂C [−]	Cs	-0.985	236.18	-62.01	174.16	-100.23	-4.90	12.18	7.28	β
10	<i>n</i> -PrH₂C [−]	Cs	-0.990	260.85	-87.90	172.96	-101.44	11.97	-5.61	-5.61	γ
11	<i>n</i> -BuH₂C [−]	Cs	-0.938	262.85	-88.82	174.03	-100.37	1.99	-0.92	1.07	δ
12	MeCH₃	D_{3d}	-0.571	238.60	-65.21	173.39	-101.00	-0.38	-15.55	-15.92	α
13a	EtCH₃	C_{2v}	-0.568	232.81	-68.71	164.10	-110.30	-5.79	-3.51	-9.29	β
13b	Me_2CH_2	C_{2v}	-0.382	251.23	-91.12	160.10	-114.29	6.12	-20.73	-14.61	α
14a	<i>i</i> -PrCH₃	C_{3v}	-0.565	230.20	-73.87	156.33	-118.06	-4.20	-4.33	-8.53	β
14b	Me₃CH	C_{3v}	-0.232	267.54	-114.35	153.19	-121.21	9.52	-21.56	-12.04	α
15	<i>t</i> -BuCH₃	T_{d}	-0.563	229.82	-78.63	151.19	-123.20	-2.93	-4.47	-7.40	β
16a	<i>n</i> -PrCH₃	C_{2h}	-0.565	236.01	-70.67	165.34	-109.05	3.20	-1.96	1.24	γ
16b	EtMeCH ₂	C_{2h}	-0.377	244.34	-93.60	150.74	-123.66	-6.89	-2.48	-9.37	β
17a	<i>n</i> -BuCH₃	C_{2v}	-0.375	233.25	-67.69	165.55	-108.84	-2.77	2.98	0.21	δ
17b	<i>n</i> -PrMeCH ₂	C_{2v}	-0.564	252.13	-99.81	152.32	-122.08	7.79	-6.21	1.58	γ
18a	<i>i</i> -PrMeCH ₂	<i>C</i> ₁	-0.372	247.55	-102.18	145.37	-129.02	-1.84	-5.53	-7.37	β
18b	EtMe ₂ CH	<i>C</i> ₁	-0.225	265.39	-118.76	146.63	-127.77	-2.15	-4.41	-6.56	β
19	t-BuMeCH₂	Cs	-0.371	251.79	-112.21	139.58	-134.81	0.19	-7.03	-6.84	β
20	<i>n</i> -BuMeCH ₂	C_{2h}	-0.374	243.63	-101.29	142.33	-132.06	-8.50	-1.48	-9.98	δ
21	<i>i</i> -PrMe₂CH	C_{2h}	-0.219	259.35	-118.14	141.21	-133.18	-4.10	-1.89	-5.99	β
22	<i>t</i> -BuMe₂CH	Cs	-0.215	265.19	-127.39	137.80	-136.60	-0.78	-4.35	-5.13	β
23	<i>n</i> -PrMe₂CH	<i>C</i> ₁	-0.224	274.83	-128.33	146.50	-127.90	9.44	-9.57	-0.13	γ
24	<i>n</i> -BuMe₂CH	<i>C</i> ₁	-0.223	276.20	-128.65	147.55	-126.84	1.37	-0.31	1.06	δ
25	H ₃ C⁺	C_{3v}	0.362	240.45	-467.68	-227.23	-501.62	1.48	-418.02	-416.55	е
26	MeH_2C^+	Cs	-0.215	242.18	-219.86	22.32	-252.08	1.73	247.82	249.55	α
27	EtH_2C^+	Cs	-0.256	242.53	-140.46	102.07	-172.33	0.35	79.40	79.75	β
28	<i>i</i> -PrH₂C⁺	<i>C</i> ₁	-0.472	256.69	-139.73	116.96	-157.44	7.26	40.07	47.32	β
29	t-BuH₂C⁺	<i>C</i> ₁	-0.489	270.61	-149.75	120.85	-153.54	9.48	23.37	32.84	β
30	Me ₂ HC ⁺	<i>C</i> ₂	0.396	247.98	-400.37	-152.39	-426.79	3.76	33.66	37.42	α
31	EtMeHC ⁺	<i>C</i> ₁	0.366	256.56	-396.76	-140.20	-414.59	8.58	3.61	12.19	β
32	<i>i</i> -PrMeHC ⁺	<i>C</i> ₁	0.174	268.19	-284.57	-16.39	-290.78	10.10	57.90	68.00	β
33	<i>t</i> -BuMeHC⁺	<i>C</i> ₁	-0.327	293.49	-182.60	110.89	-163.50	15.17	72.59	87.76	β
34	Me₃C⁺	<i>C</i> ₁	0.536	242.28	-411.12	-168.84	-443.23	0.61	18.86	19.46	α
35	EtMe ₂ C ⁺	<i>C</i> ₁	0.540	242.21	-414.36	-172.15	-446.55	-0.07	-3.24	-3.31	β
36	<i>i</i> -PrMe ₂ C ⁺	<i>C</i> ₁	0.544	242.44	-404.51	-162.07	-436.46	0.08	3.30	3.39	β
37	t-BuMe₂C⁺	<i>C</i> ₁	0.537	242.76	-402.64	-159.88	-434.27	0.16	2.83	2.99	β

^{*a*}Calculated with the GIAO-DFT method under B3LYP/BSS-A. ^{*b*} $\Delta\sigma^m$ (C: S) = σ^m (C: S) – σ^m (C: C^{4–}) (*m* = d, p and t). ^{*c*} $\Delta\sigma^p$ (C) = σ^p (C), since σ^p (C: C^{4–}) = 0 ppm. ^{*d*} $\Delta\sigma^m$ (C: S) = (1/*n*)($\Delta\sigma^m$ (C: S) – $\Delta\sigma^m$ (C: S_e)), see text for *n*, S and S_e (*m* = d, p and t). ^{*e*}The effect beeing not defined. (Table S11 continues)

Nos.	Species	sym	Q(C)	σ ^d (C)	σ ^p (C) ^c	σ ^t (C)	$\Delta \sigma^{t}(C)$	$\Delta \sigma^{d}(C)_{e}^{a}$	$\Delta \sigma^{p}(C)_{e}^{d}$	$\Delta \sigma^{t}(C)_{e}{}^{d}$	effect
38	CH₃OH	Cs	-0.191	232.16	-104.67	127.49	-146.90	-6.82	-55.01	-61.82	α-Χ
39	CH₃SH	Cs	-0.692	243.86	-73.63	170.23	-104.16	4.88	-23.97	-19.09	α-Χ
40	CH₃SeH	Cs	-0.737	240.42	-66.34	174.08	-100.31	1.45	-16.68	-15.23	α-Χ
41	H₃CSSCH₃	<i>C</i> ₂	-0.709	241.38	-85.75	155.63	-118.77	2.40	-36.09	-33.69	α-Χ
42	CH₃F	C_{3v}	-0.066	232.99	-126.01	106.99	-167.41	-5.98	-76.35	-82.33	α-Χ
43	CH₃Cl	C _{3v}	-0.529	243.61	-93.19	150.42	-123.98	4.63	-43.53	-38.90	α-Χ
44	CH₃Br	C_{3v}	-0.601	241.70	-83.06	158.65	-115.75	2.73	-33.40	-30.67	α-Χ
45	CH₃I	C_{3v}	-0.719	236.32	-56.17	180.15	-94.24	-2.66	-6.51	-9.17	α-Χ
46	CH ₃ CO ₂ Me	Cs	-0.666	248.04	-87.22	160.82	-113.58	9.06	-37.56	-28.50	α-Χ
47	CH₃CN	C_{3v}	-0.677	220.25	-38.56	181.70	-92.70	-18.72	11.10	-7.62	α-Χ
48	CH_3NH_2	<i>C</i> ₁	-0.360	229.80	-79.79	150.01	-124.39	-9.18	-30.13	-39.31	α-Χ
49	CH_3NO_2	Cs	-0.410	231.58	-114.08	117.50	-156.90	-7.40	-64.42	-71.82	α-Χ
50a	CH_3CH_2OH	Cs	-0.016	225.96	-108.36	117.60	-156.80	-12.64	-43.15	-55.79	α-Χ
50b	CH_3CH_2OH		-0.587	245.33	-81.19	164.14	-110.26	6.73	-15.98	-9.25	β-Χ
S1a	CH_3CH_2SH	Cs	-0.484	250.44	-95.01	155.44	-118.96	11.84	-29.80	-17.96	α-Χ
S1b	CH_3CH_2SH		-0.583	236.08	-69.55	166.53	-107.86	-2.51	-4.34	-6.86	β-Χ
S2a	CH_3CH_2SeH	Cs	-0.521	243.61	-86.59	157.02	-117.37	5.01	-21.38	-16.37	α-Χ
S2b	CH_3CH_2SeH		-0.589	239.54	-72.79	166.75	-107.64	0.94	-7.58	-6.64	β-Χ
S3a	CH_3CH_2F	Cs	0.103	242.30	-77.83	164.47	-109.92	3.71	-12.63	-8.92	α-Χ
S3b	CH_3CH_2F		-0.610	228.26	-132.05	96.21	-178.19	-10.34	-66.85	-77.18	β-Χ
S4a	CH_3CH_2CI	Cs	-0.332	254.00	-121.40	132.61	-141.79	15.41	-56.19	-40.79	α-Χ
S4b	CH_3CH_2CI		-0.588	231.68	-70.51	161.17	-113.23	-6.92	-5.30	-12.22	β-Χ
S5a	CH_3CH_2Br	Cs	-0.392	247.97	-110.45	137.53	-136.87	9.38	-45.24	-35.87	α-Χ
S5b	CH_3CH_2Br		-0.592	235.52	-74.81	160.71	-113.68	-3.08	-9.60	-12.68	β-Χ
S6a	CH_3CH_2I	Cs	-0.491	244.82	-89.98	154.84	-119.56	6.22	-24.77	-18.55	α-Χ
S6b	CH ₃ CH ₂ I		-0.594	232.06	-72.45	159.60	-114.79	-6.54	-7.25	-13.79	β-Χ
S7a	$CH_3CH_2CO_2Me$	Cs	-0.475	278.88	-127.14	151.73	-122.66	40.28	-61.94	-21.66	α-Χ
S7b	$CH_3CH_2CO_2Me$		-0.569	223.20	-51.08	172.13	-102.27	-15.39	14.13	-1.26	β-Χ
S8a	CH_3CH_2CN	Cs	-0.484	235.78	-66.79	168.99	-105.40	-2.82	-1.58	-4.40	α-Χ
S8b	CH ₃ CH ₂ CN		-0.554	221.77	-52.62	169.15	-105.25	-16.83	12.59	-4.24	β-Χ
S9a	$CH_3CH_2NH_2$	Cs	-0.182	237.44	-99.33	138.11	-136.28	-1.16	-34.12	-35.28	α-Χ
S9b	$CH_3CH_2NH_2$		-0.586	236.72	-79.48	157.24	-117.15	-1.87	-14.27	-16.15	β-Χ
S10 a	$CH_3CH_2NO_2$	Cs	-0.222	239.28	-131.11	108.17	-166.22	0.68	-65.90	-65.22	α-Χ
S10b	$CH_3CH_2NO_2$		-0.597	238.65	-68.48	170.18	-104.22	0.06	-3.27	-3.22	β-Χ
51	H_2 C =C H_2	D_{2h}	-0.365	246.91	-194.83	52.08	-222.31	8.31	-129.62	-121.31	C_2H_4
52	H C ≡CH	D∞h	-0.225	255.62	-145.56	110.06	-164.34	17.03	-80.36	-63.33	C_2H_2

^{*a*}Calculated with the GIAO-DFT method under B3LYP/BSS-A. ^{*b*} $\Delta \sigma^m$ (C: S) = σ^m (C: S) – σ^m (C: C^{4–}) (*m* = d, p and t). ^{*c*} $\Delta \sigma^p$ (C) = σ^p (C), since σ^p (C: C^{4–}) = 0 ppm. ^{*d*} $\Delta \sigma^m$ (C: S) = (1/*n*)($\Delta \sigma^m$ (C: S) – $\Delta \sigma^m$ (C: S_e)), see text for *n*, S and S_e (*m* = d, p and t). (Table S11 continues)

Nos.	Species	sym	Q(C)	σ ^d (C)	σ ^p (C) ^c	σ ^t (C)	$\Delta \sigma^{t}(C)$	$\Delta \sigma^{d}(C)_{e}$	$^{d} \Delta \sigma^{p}(C)_{e}^{d}$	$\Delta \sigma^{t}(C)_{e}{}^{d}$	effect
53	C ₆ H ₆	D_{6h}	-0.106	239.66	-192.70	46.96	-227.43	1.06	-127.49	-126.43	C_6H_6
			-0.240	240.22	-193.26	46.96	-227.44	1.62	-128.06	-126.43	C_6H_6
54	C ₆ H₅OH (ipso)	Cs	0.449	258.53	-243.01	15.52	-258.88	18.86	-50.31	-31.45	i-X
S11	C ₆ H₅SH (ipso)	Cs	-0.155	157.15	-122.23	34.92	-239.47	-82.51	70.47	-12.04	i-X
S12	C ₆ H₅SeH (ipso)	C_1	-0.185	251.05	-219.65	31.40	-243.00	11.38	-26.95	-15.57	i-X
S13	C ₆ H₅F (ipso)	C_{2v}	0.542	274.86	-267.63	7.22	-267.17	35.19	-74.93	-39.74	i-X
S14	C ₆ H₅Cl (ipso)	C_{2v}	-0.038	213.33	-181.55	31.78	-242.62	-26.34	11.15	-15.19	i-X
S15	C ₆ H₅Br (ipso)	C_{2v}	-0.082	239.21	-206.95	32.25	-242.14	-0.46	-14.25	-14.71	i-X
S16	C ₆ H₅I (ipso)	C_{2v}	-0.181	211.11	-169.14	41.97	-232.42	-28.55	23.56	-4.99	i-X
S17	C ₆ H ₅ CO ₂ Me (ipso)	Cs	-0.043	200.85	-156.64	44.21	-230.18	-38.81	36.06	-2.75	i-X
S18	C ₆ H ₅ CN (ipso)	C_{2v}	-0.165	188.29	-127.29	61.00	-213.40	-51.37	65.41	14.04	i-X
S19	C ₆ H ₅ NH ₂ (ipso)	Cs	0.330	257.25	-231.43	25.81	-248.58	17.59	-38.73	-21.15	i-X
S20	C ₆ H ₅ NO ₂ (ipso)	C_{2v}	0.187	270.95	-246.35	24.59	-249.80	31.29	-53.65	-22.37	i-X
55	H ₂ C =O	C_{2v}	0.307	245.20	-263.64	-18.44	-292.83	13.05	-158.97	-145.93	C=O
56	H(HO) C =O	Cs	0.675	245.49	-228.53	16.97	-257.43	13.34	-123.86	-110.53	OC=O

^{*a*}Calculated with the GIAO-DFT method under B3LYP/BSS-A. ^{*b*} $\Delta \sigma^m$ (C: S) = σ^m (C: S) – σ^m (C: C^{4–}) (*m* = d, p and t). ^{*c*} $\Delta \sigma^p$ (C) = σ^p (C), since σ^p (C: C^{4–}) = 0 ppm. ^{*d*} $\Delta \sigma^m$ (C: S) = (1/*n*)($\Delta \sigma^m$ (C: S) – $\Delta \sigma^m$ (C: S_e)), see text for *n*, S and S_e (*m* = d, p and t).

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Nos	Species	σ^{d}	σ^{p}	$\sigma^{p_{i \to j} b}$	$\sigma^{p}_{i \rightarrow a}$	σ^{t}	$\Delta\sigma^{\mathrm{t}}(C^{4\text{-}})^d$	$\Delta \sigma^{t}$ (TMS) ^d	$\delta(C)_{obsd}{}^{e}$
1	C ⁴⁻	274.39	0.00			274.39	0.00		
S21	(C H ₃) ₄ Si (<i>T</i> _d)	248.95	65.96			182.99	-91.40	0.00	0.0
5	C H ₄ (<i>T</i> _d)	238.98	49.66	125.55	175.21	189.32	-85.07	-6.33	-4.6
12	C H ₃ CH ₃ (<i>D</i> _{3d})	238.60	65.21	121.88	187.09	173.39	-101.00	9.60	6.9
13	C H ₃ CH ₂ CH ₃ (<i>C</i> _{2v})	251.23	91.12	83.64	174.77	160.10	-114.29	22.89	16.4
17	<i>n</i> -C ₅ H ₁₂ (<i>C</i> _{2v})	236.68	95.74	124.40	220.14	140.94	-133.45	42.05	34.2
S22	<i>n-</i> C ₇ H ₁₆ (<i>C</i> _{2v})	251.38	107.31	88.74	196.05	144.07	-130.32	38.92	29.3
S23	<i>n</i> -nonane (C _{2v})	246.58	102.38	116.20	218.58	144.20	-130.19	38.79	29.8
S24	<i>n</i> -undecane (C _{2v})	257.19	112.95			144.24	-130.15	38.75	29.9
S25	<i>n</i> -tridecane (C _{2v})	249.18	104.87			144.31	-130.08	38.68	29.9
S26	<i>n</i> -pentadecane (C _{2v})	246.14	101.81			144.34	-130.05	38.65	29.9
48	CH_3NH_2 (C_s)	229.80	79.79	127.33	207.12	150.01	-124.38	32.98	28.4
38	C H ₃ OH (<i>C</i> _s)	232.16	104.67	109.59	214.26	127.49	-146.90	55.50	50.2
39	C H₃SH (<i>C</i> _s)	243.86	73.63	108.92	182.55	170.23	-104.16	12.76	6.5
S27	$\mathbf{C}H_3SCH_3$ (C_{2v})	243.04	83.75	109.94	193.69	159.29	-115.10	23.70	18.1
S28	C H ₃ S(O)CH ₃ (<i>C</i> _s)	247.68	111.05	83.30	194.34	136.64	-137.75	46.35	41.0
S29	C H ₃ SO ₂ CH ₃ (<i>C</i> _{2v})	245.01	107.45	95.39	202.85	137.56	-136.83	45.43	42.6
S30	$\mathbf{C}H_3SO_3H(C_1)$	246.80	107.13	85.97	193.10	139.67	-134.72	43.32	39.1
42	C H ₃ F (<i>C</i> _{3v})	232.99	126.01	97.78	223.78	106.99	-167.40	76.00	71.6
S31	$CH_2F_2(C_{2v})$	232.49	167.45	72.95	240.41	65.33	-209.06	117.66	109.0
S32	$\mathbf{C}HF_{3}(C_{3v})$	233.47	179.28	60.17	239.45	54.19	-220.20	128.80	116.0
S33	C F ₄ (<i>T</i> _d)	235.84	187.95	48.31	236.26	47.89	-226.50	135.10	122.3
S34	$(CH_3)_2 NH (C_s)$	233.02	91.99	120.41	212.40	141.04	-133.35	41.95	38.2
S35	(C H ₃) ₃ N (<i>C</i> _{3v})	235.94	102.65	114.79	217.44	133.29	-141.10	49.70	47.6
43	C H ₃ Cl (<i>C</i> _{3v})	243.61	93.19	98.87	192.06	150.42	-123.97	32.57	25.6
S36	$\mathbf{C}H_2Cl_2(C_{2v})$	253.17	142.22	67.87	210.09	110.95	-163.44	72.04	53.5
S37	\mathbf{C} HCl ₃ (C_{3v})	267.64	194.69	26.77	221.46	72.95	-201.44	110.04	77.2
S38	$\mathbf{C}Cl_4(T_d)$	283.05	248.49	14.05	234.44	34.56	-239.83	148.43	96.1
S39	$\mathbf{C}H_{3}Br(C_{3v})$	241.70	-83.06			158.65	-115.74	24.34	9.6
S40	$\mathbf{C}H_{2}Br_{2}(C_{2v})$	253.38	-136.40			116.98	-157.41	66.01	21.6
S41	CHBr ₃ (C_{3v})	266.11	-194.70			71.41	-202.98	111.58	11.0
S42	$\mathbf{C}Br_4(T_d)$	277.75	-254.74			23.01	-251.38	159.98	-29.7
46	\mathbf{C} H ₃ COOCH ₃ (C_s)	248.04	87.22	74.13	161.35	160.82	-113.57	22.17	20.6
S43	$\mathbf{C}\mathrm{H}_{3}\mathrm{OCH}_{3}\left(C_{2v}\right)$	234.85	115.77	105.27	221.04	119.08	-155.31	63.91	61.2
S44	\mathbf{C} H ₃ OEt (C_s)	235.22	114.82	105.92	220.74	120.39	-154.00	62.60	64.3
S45	C H ₃ OPr- <i>i</i> (<i>C</i> ₁)	236.44	112.90	108.23	221.13	123.55	-150.84	59.44	56.4
S46	$CH_3OBu-t(C_s)$	236.89	106.15	112.12	218.27	130.74	-143.65	52.25	50.1
47	$CH_3CN(C_{3v})$	220.25	38.56	166.16	204.72	181.70	-92.69	1.29	1.9
S47	$CH_3NC(C_{3v})$	233.20	76.83	120.88	171.36	156.37	-118.02	26.62	25.9
49	CH_3NO_2 (C_s)	231.58	114.08	107.14	221.22	117.50	-156.89	65.49	62.5
S48	$CH_3CHO(C_s)$	248.87	100.73	83.69	184.42	148.14	-126.25	34.85	30.9
S49	$CH_3COCH_3(C_{2v})$	242.82	91.69	90.74	182.43	151.13	-123.26	31.86	30.9
S50	C H ₃ COOH (<i>C</i> _s)	248.81	86.56	79.87	166.43	162.24	-112.15	20.75	20.8

Table S12. The σ^m (C: S) (m = d, p and t), $\sigma^{p}_{i \rightarrow j}$, $\sigma^{p}_{i \rightarrow j}$, $\Delta \sigma^{t}$ (C: S) and δ (C)_{obsd} for various species of **1–56** and **S21– S70**.^{*a*}

^{*a*}Calculated with the GIAO-DFT method under B3LYP/BSS-A. ^{*b*}Main contributions from the occupied-to-occupied orbital transitions on $\sigma^{p}(C)$. ^{*c*}Main contributions from the occupied-to-unoccupied orbital transitions on $\sigma^{p}(C)$. ^{*d*} $\Delta\sigma^{p}(C: S) = \sigma^{p}(C: S) - \sigma^{p}(C: C^{4-} \text{ or TMS})$. ^{*e*}Ovserved values.

(Table S12 continues)

Nos	Species	σ^{d}	σ^{p}	$\sigma^{p}_{i \rightarrow j}{}^{b}$	$\sigma^{p}_{i \rightarrow a}$	σ^{t}	$\Delta \sigma^{t}(C^{4-})^{d}$	$\Delta \sigma^{t}$ (TMS) ^d	$\delta(C)_{obsd}^{e}$
51	$CH_2=CH_2(D_{2h})$	246.91	194.83	69.30	264.12	52.08	-222.31	130.91	123.3
S51	c -CH ₂ =CHCH=CH ₂ (C_{2v})	249.95	201.24	80.13	281.37	48.70	-225.69	134.29	124.0
S52	t	-CH ₂ =CHCH	$H=CH_2(C_{2h})$	243.18	196.30	91.77	288.07	46.88	-227.51
	136.11	125.0							
S53a	$CH_2 = CHCH_3 (C_s)$	257.27	220.07	42.14	262.22	37.20	-237.19	145.79	133.9
S53b		233.71	172.08	110.86	282.94	61.63	-212.76	121.36	115.7
S54a		CH ₂ =C(CH	3)2 (C2v)	257.96	231.96	54.59	286.55	26.00	-248.39
	156.99	142.2							
S54b			230.39	163.89	138.33	302.22	66.50	-207.89	116.49
	109.8								
S55a	$CH_2 = CHCH_2CH_3$ (C_1)	253.85	224.16	43.93	268.09	29.69	-244.70	153.30	140.2
S55b		226.97	163.70	137.06	300.76	63.27	-211.12	119.72	113.5
S56a	$CH_2=CHCH(CH_3)_2(C_1)$	242.06	216.86	79.11	295.96	25.20	-249.19	157.79	146.0
S56b		226.45	159.59	138.69	298.28	66.86	-207.53	116.13	111.3
S57a	$CH_2=CHC(CH_3)_3$ (C_s)	252.36	232.00	41.11	273.11	20.35	-254.04	162.64	149.8
S57b		226.41	158.03	150.01	308.04	68.38	-206.01	114.61	109.0
S58 a	CH ₂ =CHOH (C _s)	244.16	-217.60	58.85	-276.45	26.57	-247.82	156.42	149.0
S58b		242.42	-152.46	88.19	-240.65	89.96	-184.43	93.03	88.0
S59a	$CH_2=CH(OMe)$ (C_s)	256.45	-237.09	24.22	-261.31	19.36	-255.03	163.63	152.9
S59b		240.60	-143.09	103.16	-246.25	97.51	-176.88	85.48	85.5
S60a	$CH_2=CH(OCOCH_3)$ (C_s)	276.98	-245.31			31.67	-242.72	151.32	141.4
S60b		218.39	-134.85			83.53	-190.86	99.46	97.5
S61a	$CH_2 = CHF(C_s)$	256.61	-240.72	11.05	-251.77	15.89	-258.50	167.10	147.7
S61b		240.84	-157.23	96.96	-254.19	83.61	-190.78	99.38	88.5
S62a	CH ₂ =CHCl (C _s)	256.35	-216.56	45.45	-262.01	39.78	-234.61	143.21	126.1
S62b		242.92	-182.88	83.68	-266.56	60.04	-214.35	122.95	117.4
S63a	$CH_2 = CHCHO(C_s)$	268.90	-235.82	9.94	-245.77	33.08	-241.31	149.91	138.5
S63b		232.74	-194.86	111.09	-305.96	37.88	-236.51	145.11	138.0
S64a	$CH_2 = CHCOCH_3 (C_s)$	260.78	-227.40	36.89	-264.30	33.38	-241.01	149.61	137.5
S64b		220.24	-172.23	147.25	-319.48	48.01	-226.38	134.98	129.0
S65a	<i>c</i> -CH ₂ =CHCOOH (<i>C</i> _s)	278.10	230.40	29.46	200.93	47.71	-226.68	135.28	128.1
S65b		226.69	186.51	132.80	319.31	40.18	-234.21	142.81	133.2
S66a	t-CH ₂ =CHCOOH (C _s)	263.04	218.14	29.41	247.55	44.90	-229.49	138.09	128.1
S66b		234.03	191.03	101.51	292.53	43.00	-231.39	139.99	133.2
S67a	$CH_2 = CHNO_2 (C_s)$	268.67	-242.12	-5.40	-236.73	26.55	-247.84	156.44	144.7
S67b		223.46	-170.43	121.43	-291.87	53.02	-221.37	129.97	121.5
S68a	CH ₂ =CHCN (C _s)	208.39	-142.42	176.84	-319.26	65.97	-208.42	117.02	107.8
S68b		251.42	-212.96	36.03	-248.99	38.46	-235.93	144.53	137.5
S69a	CH ₂ =CHNC (C _s)	262.73	-207.62	7.57	-215.19	55.11	-219.28	127.88	121.0
S69b		230.65	-174.61	118.10	-292.71	56.04	-218.35	126.95	119.3
S70a	N,N-Me ₂ EtN (C_1)	259.79	-229.47	31.16	-260.63	30.32	-244.07	152.67	144.5
S70b		230.90	-131.74	136.19	-267.93	99.16	-175.23	83.83	81.8

^{*a*}Calculated with the GIAO-DFT method under B3LYP/BSS-A. ^{*b*}Main contributions from the occupied-to-occupied orbital transitions on $\sigma^{p}(C)$. ^{*c*}Main contributions from the occupied-to-unoccupied orbital transitions on $\sigma^{p}(C)$. ^{*d*} $\Delta\sigma^{p}(C: S) = \sigma^{p}(C: S) - \sigma^{p}(C: C^{4-} \text{ or TMS})$. ^{*e*}Ovserved values.

MO (i in ψ_i)	$\sigma^{d}_{i}(C)$	$\sigma^{p_{i}}(C)$	$\sigma^{t_i}(C)$	
$CH_3NH_2(C_s)$				
1 (A'); 2 (A')	200.32	0.03	200.35	
3 (A')	6.57	-6.29	0.28	
4 (A')	22.01	4.47	26.48	
5 (A'')	2.62	-18.33	-15.70	
6 (A')	2.50	-46.12	-43.62	
7 (A')	2.37	-60.62	-58.25	
8 (A'')	-3.37	-61.13	-64.49	
9 (A')	-3.23	-19.13	-22.37	
Yocc to Yocc		127.33		
total	229.80	-79.79	150.01	
$CH_3NO_2(C_s)$				
1 (A')-4 (A')	200.29	0.03	200.32	
5 (A'); 6 (A'')	0.28	-2.00	-1.72	
7 (A'); 8 (A')	27.23	-2.54	24.69	
9 (A')	2.44	-13.41	-10.97	
10 (A')	1.87	-3.54	-1.67	
11 (A'')	0.89	-11.81	-10.92	
12 (A'')	-3.23	-81.05	-84.28	
13 (A')	-3.43	-77.33	-80.76	
14 (A'')	-0.02	-0.25	-0.28	
15 (A')	7.39	-12.65	-5.26	
16 (A'')	-2.13	-16.67	-18.80	
ψ_{occ} to ψ_{occ}		107.14		
total	231.58	-114.08	117.50	

Table S13. The $\sigma^{d}(C)$, $\sigma^{p}(C)$ and $\sigma^{t}(C)$ values of CH₃NH₂ and CH₃NO₂, given separately by each ψ_{i} .^{*a*}

^aCalculated with the GIAO method under B3LYP/BSS-A.

$i \rightarrow a^c$	$\sigma^{p}_{i \rightarrow a:xx}(C)$	$\sigma^{p}_{i \rightarrow a:yy}(C)$	$\sigma^{p}_{i \rightarrow a:zz}(C)$	$\sigma^{\mathbf{p}_{i\rightarrow a}}(\mathbf{C})$	
$CH_3NH_2(C_s)$					
7→26	0.00	0.00	-19.88	-6.63	
7→41	0.00	0.00	-18.80	-6.27	
8→23	-0.89	-31.43	0.00	-10.77	
8→26	-22.94	-0.26	0.00	-7.73	
8→40	-16.55	-1.82	0.00	-6.12	
$CH_3NO_2(C_s)$					
12→22	-19.21	-0.65	0.00	-6.62	
12→28	-28.68	-0.06	0.00	-9.58	
12→29	-2.96	-29.16	0.00	-10.71	
12→50	-8.52	-11.63	0.00	-6.72	
13→24	0.00	0.00	-18.14	-6.05	
13→28	0.00	0.00	-31.64	-10.55	
13→30	0.61	-20.27	0.00	-6.55	

Table S14. Main contributions from the $\psi_i \rightarrow \psi_a$ transitions on $\sigma^{p_i}_{i\rightarrow a:kk}$ (C: k = x, y and/or z) in CH₃NH₂ and CH₃NO₂.^{*a.b*}

^{*a*}Calculated with the GIAO method under B3LYP/BSS-A. ^{*b*}Magnitudes of $\sigma^{p}_{i \to a}(C)$ larger than 6 ppm are shown. ^{*c*}In $\psi_i \to \psi_a$.

MO (i in ψ_i)	$\sigma^{d}{}_{i}(C)$	$\sigma^{p_{i}}(C)$	$\sigma^{t_i}(C)$	
1 (A')	0.00	0.00	0.01	
2 (A')	200.29	0.00	200.29	
3 (A')-7 (A')	0.18	0.19	0.38	
8 (A')–12 (A')	34.07	-24.22	9.84	
13 (A')	1.85	-9.58	-7.73	
14 (A')	3.85	-25.61	-21.76	
15 (A')	1.88	-8.29	-6.41	
16 (A')	4.58	-34.11	-29.53	
17 (A')	-7.87	-54.23	-62.10	
18 (A')	8.21	-8.07	0.14	
19 (A')	13.08	-21.65	-8.57	
20 (A")	-5.28	-19.77	-25.05	
21 (A')	1.51	-3.40	-1.89	
22 (A')	-4.26	-52.51	-56.77	
23 (A")	1.72	-0.79	0.92	
24 (A")	1.90	-1.80	0.10	
25 (A")	5.27	-14.78	-9.51	
Yocc to Yocc		33.17		
total	260.97	-245.45	15.52	

Table S15. The $\sigma^{d}(C)$, $\sigma^{p}(C)$ and $\sigma(C)$ values of C₆H₅OH (C_s), given separately by each ψ_{i} .^{*a*}

^aCalculated with the GIAO method under B3LYP/BSS-A.

$i \rightarrow a^b$	$\sigma^{p_{i \rightarrow a:xx}}(C)$	$\sigma^{\mathbf{p}_{i \to a:yy}}(\mathbf{C})$	$\sigma^{p}_{i \rightarrow a:zz}(C)$	$\sigma^{p}_{i \rightarrow a}(C)$
12→87	2.65	15.40	0.00	6.01
14→28	-26.78	-0.11	0.00	-8.96
16→28	-19.19	-53.50	0.00	-24.23
17→28	-25.53	-12.31	0.00	-12.62
17→87	-24.92	-2.75	0.00	-9.22
18→28	-0.68	-43.06	0.00	-14.58
18→87	-0.18	20.94	0.00	6.92
20→28	-14.26	-18.78	0.00	-11.01
21→28	17.26	3.31	0.00	6.86
22→28	0.60	-17.40	0.00	-5.60
22→38	0.24	-16.23	0.00	-5.33
22→44	-1.68	-28.12	0.00	-9.93
22→54	-0.98	-24.48	0.00	-8.49

Table S16. Main contributions from the $\psi_i \rightarrow \psi_a$ transitions on the $\sigma^p(C)$ of C₆H₅OH (C₈).^{*a,b*}

^{*a*}Calculated with the GIAO method under B3LYP/BSS-A. ^{*b*}The magnitudes of $\sigma^{p_{i\to a}}(C)$ larger than 5 ppm are shown. ^{*c*}In $\psi_i \rightarrow \psi_a$.



Fig. S1 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta \sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S1, calculated with the GIAO-DFT method under B3LYP/BSS-A.



Fig. S2 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta \sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S2, calculated with the GIAO-DFT method under CAM-B3LYP/BSS-A.



Fig. S3 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta \sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S3, calculated with the GIAO-DFT method under PBE/BSS-A.



Fig. S4 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta \sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S4, calculated with the GIAO-DFT method under PBE0/BSS-A



Fig. S5 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta \sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S5, calculated with the GIAO-DFT method under LC- ω PBE/BSS-A.



Fig. S6 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta \sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S6, calculated with the GIAO-DFT method under ω B97X-D/BSS-A.



Fig. S7 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta \sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S7, calculated with the GIAO-DFT method under MP2/BSS-A.



Fig. S8 Plots of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta\sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S8, calculated with the GIAO-DFT method of B3LYP/BSS-A containing the solvent effect of CHCl₃.



Fig. S9 Plot of $\delta(C: S)_{obsd:TMS}$ versus $-\Delta \sigma^t(C: S)_{calcd:TMS}$ for 40 species (54 plots) of the Table S9, calculated with the GIAO-DFT method under B3LYP/def2TZVP.



Fig. S10 Plot of $\Delta \sigma^{t}(C)_{e}$ for CH₃CH₂X versus those of CH₃CH₂X, where X are shown in the figure. (Data for X = F are omitted.).

Origin of the α -X effect

The α -X effect is examined for CH₃–X from CH₄ and CH₃CH₂–X from CH₃CH₃ (X = OH, SH, SeH, SSCH₃, F, Cl, Br, I, CO₂Me, CN, NH₂ and/or NO₂) (see Scheme 3, Table 2 and Table S1 of the ESI†). The ($\Delta\sigma^{d}(C)_{e}$, $\Delta\sigma^{p}(C)_{e}$, $\Delta\sigma^{t}(C)_{e}$) values of (-18.7 ~ 40.3, -76.4 ~ -11.1, -82.3 ~ -4.4 ppm) are calculated for the species.

Table S13 lists the $\sigma^{d}(C)$, $\sigma^{p}(C)$ and $\sigma^{t}(C)$ values for CH₃NH₂ and CH₃NO₂ separately for each MO. In the case of CH₃NH₂, which has a very strong electron donating X of NH₂, the outer Mos of the HOMO–1 (ψ_{8}) ~ HOMO–3 (ψ_{6}) contribute greatly to $\sigma^{p}(C)$. In the case of CH₃NO₂, with the very strong electron accepting group X of NO₂, the somewhat more inner HOMO–3 (ψ_{13}) and HOMO–4 (ψ_{12}) also strongly affect $\sigma^{p}(C)$. Table S14 lists the $\psi_{i} \rightarrow \psi_{a}$ transitions contributing to $\sigma^{p}_{i\rightarrow a:kk}(C: k = x, y \text{ and/or } z)$, which are greater than approximately 20 ppm in magnitude. The contributions to CH₃NH₂ are large for the $\psi_{i} \rightarrow \psi_{a}$ transitions of $\psi_{7} \rightarrow \psi_{26}$ ($\sigma^{p}_{7\rightarrow 26:zz}(C) = -19.9$ ppm), $\psi_{7} \rightarrow \psi_{41}$ ($\sigma^{p}_{7\rightarrow 41:zz}(C) = -18.8$ ppm), $\psi_{8} \rightarrow \psi_{23}$ ($\sigma^{p}_{8\rightarrow 23:yy}(C) = -31.4$ ppm) and $\psi_{8} \rightarrow \psi_{26}$ ($\sigma^{p}_{8\rightarrow 26:xx}(C) = -22.9$ ppm). The contributions from the $\psi_{i} \rightarrow \psi_{a}$ transitions in CH₃NO₂ are large for $\psi_{12} \rightarrow \psi_{28}$ ($\sigma^{p}_{12\rightarrow 28:xx}(C) = -28.7$ ppm) and $\psi_{12} \rightarrow \psi_{29}$ ($\sigma^{p}_{12\rightarrow 29:yy}(C) = -29.2$ ppm) and $\psi_{13} \rightarrow \psi_{28}$ ($\sigma^{p}_{13\rightarrow 28:zz}(C) = -31.6$ ppm).

Figs. S11a and S11b show the $\psi_i \rightarrow \psi_a$ transitions of $\psi_7 \rightarrow \psi_{26}$, $\psi_7 \rightarrow \psi_{41}$, $\psi_8 \rightarrow \psi_{23}$ and $\psi_8 \rightarrow \psi_{26}$ for CH₃NH₂ and those of $\psi_{12} \rightarrow \psi_{28}$, $\psi_{12} \rightarrow \psi_{29}$, $\psi_{13} \rightarrow \psi_{28}$ and $\psi_{13} \rightarrow \psi_{30}$ for CH₃NO₂, respectively. The α -X effect is well visualized both for X of a very good donor and a very good acceptor, employing $\psi_i \rightarrow \psi_a$ transitions.



Fig. S11 Contributions from each $\psi_i \rightarrow \psi_a$ transition to the components of $\sigma^{p}(C)$ in CH₃NH₂ (*C*_s) (a) and CH₃NO₂ (*C*_s) (b), together with the axes with an isovalue of 0.04 au.

Table S15 lists the $\sigma^{d}(C)$, $\sigma^{p}(C)$ and $\sigma^{t}(C)$ values of C₆H₅OH, separately for each MO. The outer MOs of HOMO–3 (ψ_{22}), HOMO–8 (ψ_{17}) and HOMO–9 (ψ_{16}) contribute greatly to $\sigma^{p}(C)$. Table S16 lists the $\psi_{i} \rightarrow \psi_{a}$ transitions contributing to $\sigma^{p}_{i\rightarrow a:kk}(C: k = x, y \text{ and/or } z)$, which are greater than 18 ppm. The $\psi_{i} \rightarrow \psi_{a}$ transitions of $\psi_{16} \rightarrow \psi_{28}$ ($\sigma^{p}_{16\rightarrow 28:yy}(C) = -53.5$ ppm), $\psi_{17} \rightarrow \psi_{28}$ ($\sigma^{p}_{17\rightarrow 28:xx}(C) = -25.5$ ppm), $\psi_{17} \rightarrow \psi_{87}$ ($\sigma^{p}_{17\rightarrow 87:xx}(C) = -24.9$ ppm) and $\psi_{22} \rightarrow \psi_{44}$ ($\sigma^{p}_{22\rightarrow 44:yy}(C) = -28.1$ ppm) contribute a lot to $\sigma^{p}_{i\rightarrow a:kk}(C: k = x, y \text{ and/or } z)$.

Fig. S12 shows the $\psi_i \rightarrow \psi_a$ transitions of $\psi_{16} \rightarrow \psi_{28}$, $\psi_{17} \rightarrow \psi_{28}$, $\psi_{17} \rightarrow \psi_{87}$ and $\psi_{22} \rightarrow \psi_{44}$, where the transitions of large contributions are omitted if the contributions from ψ_i are small in C₆H₅OH. The *i*-X effect is well visualized through the occupied-to-unoccupied orbital transitions.



Fig. S12 Contributions from each $\psi_i \rightarrow \psi_a$ transition to the components of $\sigma^{p}(C)$ in C₆H₅OH (*C*_s), together with their axes, with an isovalue of 0.04 au.

Optimized structures given by Cartesian coordinates

Optimized structures given by Cartesian coordinates for examined molecules, together with the total energies with the B3LYP/BSS-A method of the Gaussian 09 program.

Symmetry energy	1: C^{4-} O_h E = -36.780	1429 a.u.		
Standard orient	0	0.000000	0.000000	0.000000
Compound Symmetry energy Standard orienta	2 : HC ³⁻ $C_{\infty \vee}$ E = -38.013 ation	0639 a.u.		
6 1	0 0	0.000000 0.000000	0.000000 0.000000	0.156326 -0.937956
Compound Symmetry energy Standard orient	3 : H_2C^{2-} C_{2v} E = -38.977	5351 a.u.		
6 1 1	0 0 0	$\begin{array}{c} 0.000000\\ 0.000000\\ 0.000000\end{array}$	0.000000 0.896970 -0.896970	0.167545 -0.502636 -0.502636
Compound Symmetry energy Standard orient	4 : H ₃ C ⁻ C_{3v} E = -39.860 ation	1650 a.u.		
6 1 1 1	0 0 0 0	$\begin{array}{c} 0.000000\\ 0.000000\\ -0.895648\\ 0.895648\end{array}$	0.000000 1.034205 -0.517103 -0.517103	0.125904 -0.251808 -0.251808 -0.251808
Compound Symmetry energy Standard orient	5: H ₄ C T_d E = -40.537	3993 a.u.		
6 1 1 1 1	0 0 0 0 0 0	$\begin{array}{c} 0.000000\\ 0.628183\\ -0.628183\\ -0.628183\\ 0.628183\end{array}$	$\begin{array}{c} 0.000000\\ 0.628183\\ -0.628183\\ 0.628183\\ -0.628183\\ -0.628183\end{array}$	0.000000 0.628183 0.628183 -0.628183 -0.628183
Compound Symmetry energy Ston dord orient	6 : CH ₃ C ⁻ H ₂ C_s E = -79.181	0665 a.u.		
6	0	-0.057382	0.839127	0.000000
ĩ	ŏ	0.464931	1.234220	0.884887
1	0	0.464931	1.234220	-0.884887
6 1	$\begin{array}{c} 0\\ 0\end{array}$	-0.057382 -0.589406	-0.686321 -1.084501	$0.000000 \\ 0.872860$

1	0	0.937537	-1.216275	0.000000
1	0	-0.589406	-1.084501	-0.872860

Compound Symmetry	7 : CH ₃ CH ₂ / <i>C</i> s	C ⁻ H ₂							
energy	E = -118.51	72821 a.u.							
Standard orientation									
6	0	1.399387	0.032490	0.000000					
1	0	1.684595	-0.508657	0.907410					
1	0	1.684595	-0.508657	-0.907410					
6	0	0.000000	0.561733	0.000000					
1	0	-0.161604	1.210278	0.876171					
1	0	-0.161604	1.210278	-0.876171					
6	0	-1.174732	-0.464023	0.000000					
1	0	-1.115800	-1.109846	0.880568					
1	0	-1.115800	-1.109846	-0.880568					
1	0	-2.162309	0.035245	0.000000					

Compound	8: (CH ₃) ₂ C	HC ⁻ H ₂		
Symmetry	C_1			
energy	E = -157.84	480286 a.u.		
Standard orie	ntation			
6	0	-0.645654	0.747959	-0.239830
1	0	-0.543113	0.882597	-1.312328
1	0	-1.172969	1.563073	0.248472
6	0	0.529049	0.318316	0.433129
1	0	0.545859	0.424163	1.516965
6	0	-1.512463	-0.595847	0.027373
1	0	-1.086021	-1.455442	-0.479282
1	0	-1.650074	-0.797593	1.085885
1	0	-2.475959	-0.347752	-0.416030
6	0	1.677203	-0.308679	-0.179158
1	0	2.478375	0.448376	-0.054683
1	0	1.569485	-0.527819	-1.237330
1	0	2.045611	-1.160098	0.399250

Compound Symmetry	9 : (CH ₃) ₃ C <i>C</i> _s	C ⁻ H ₂		
energy	E = -197.1'	755240 a.u.		
Standard orien	itation			
6	0	-0.852911	-0.111921	0.732602
1	0	-1.064772	0.713692	1.411046
1	0	-1.011118	-1.071652	1.220104
6	0	0.473257	0.000616	0.149778
6	0	-1.855058	0.001601	-0.485944
1	0	-1.763419	0.959101	-0.991756
1	0	-2.853054	-0.079492	-0.061180
1	0	-1.708433	-0.806016	-1.198506
6	0	1.060857	1.314857	-0.102031
1	0	1.915970	1.401209	0.588948
1	0	1.511995	1.369067	-1.095735
1	0	0.386106	2.145125	0.081484
6	0	1.224772	-1.207742	-0.185782
1	0	1.683855	-1.527043	0.766457
1	0	2.025053	-1.053805	-0.904031
1	0	0.572319	-2.034653	-0.468575

Compound	10: CH ₃ (C)	$H_2)_2C^-H_2$		
Symmetry	$C_{\rm s}$			
energy	E = -157.84	425845 a.u.		
Standard orie	ntation			
6	0	1.507664	-1.435026	0.000000
1	0	2.089417	-1.208068	0.902410
1	0	2.089417	-1.208068	-0.902410
6	0	0.138578	-0.809536	0.000000
1	0	-0.433547	-1.160051	-0.875891
1	0	-0.433547	-1.160051	0.875891
6	0	0.000000	0.744578	0.000000
1	0	0.528914	1.137382	-0.874414
1	0	0.528914	1.137382	0.874414
6	0	-1.455368	1.234687	0.000000
1	0	-1.989385	0.863676	0.880373
1	0	-1.989385	0.863676	-0.880373
1	0	-1.536040	2.325907	0.000000

Compound	11 : CH ₃ (Cl	H_2) ₃ C ⁻ H_2		
Symmetry	$C_{\rm s}$			
energy	E = -197.17	707841 a.u.		
Standard orie	ntation			
6	0	2.632325	0.653726	0.000000
1	0	2.726921	1.264881	0.904306
1	0	2.726921	1.264881	-0.904306
6	0	1.440253	-0.258483	0.000000
1	0	1.478752	-0.925982	-0.876478
1	0	1.478752	-0.925982	0.876478
6	0	0.000000	0.357618	0.000000
1	0	-0.093093	1.009067	-0.875585
1	0	-0.093093	1.009067	0.875585
6	0	-1.120783	-0.683156	0.000000
1	0	-1.003232	-1.334714	0.873656
1	0	-1.003232	-1.334714	-0.873656
6	0	-2.536313	-0.101305	0.000000
1	0	-2.704396	0.524893	-0.879251
1	0	-2.704396	0.524893	0.879251
1	0	-3.302793	-0.886687	0.000000

Compound Symmetry energy Standard orient	12 : CH ₃ CH D_{3d} E = -79.862 ation	I ₃ 27762 a.u.		
6	0	0.000000	0.000000	0.763656
1	0	0.000000	1.016030	1.160566
1	0	0.879908	-0.508015	1.160566
1	0	-0.879908	-0.508015	1.160566
6	0	0.000000	0.000000	-0.763656
1	0	0.879908	0.508015	-1.160566
1	0	0.000000	-1.016030	-1.160566
1	0	-0.879908	0.508015	-1.160566

Compound
Symmetry**13**: CH₃CH₂CH₃C_{2v}
energyE = -119.1901946 a.u.Standard orientation

6	0	0.000000	0.000000	0.584828
1	0	-0.873548	0.000000	1.241908
1	0	0.873548	0.000000	1.241908
6	0	0.000000	1.273856	-0.259186
1	0	-0.880647	1.318111	-0.903259
1	0	0.880647	1.318111	-0.903259
1	0	0.000000	2.168223	0.365244
6	0	0.000000	-1.273856	-0.259186
1	0	-0.880647	-1.318111	-0.903259
1	0	0.880647	-1.318111	-0.903259
1	0	0.000000	-2.168223	0.365244

Compound	14: (CH ₃) ₃ Cl	H		
Symmetry	C_{3v}			
energy	E = -158.518	3940 a.u.		
Standard orie	ntation			
6	0	0.000000	0.000000	0.371430
1	0	0.000000	0.000000	1.466621
6	0	0.000000	1.458049	-0.095548
1	0	0.000000	1.515410	-1.186954
1	0	-0.882013	1.990442	0.264256
1	0	0.882013	1.990442	0.264256
6	0	-1.262708	-0.729025	-0.095548
1	0	-1.312384	-0.757705	-1.186954
1	0	-2.164780	-0.231375	0.264256
1	0	-1.282767	-1.759067	0.264256
6	0	1.262708	-0.729025	-0.095548
1	0	1.282767	-1.759067	0.264256
1	0	2.164780	-0.231375	0.264256
1	0	1.312384	-0.757705	-1.186954

Compound Symmetry	15 : (CH ₃) ₄ C T_d	1248 0.11		
Chendland amian	E = -197.040	1240 a.u.		
Standard orien	nation			
6	0	0.000000	0.000000	0.000000
6	0	0.886869	0.886869	0.886869
1	0	0.282226	1.529632	1.529632
1	0	1.529632	1.529632	0.282226
1	0	1.529632	0.282226	1.529632
6	0	-0.886869	-0.886869	0.886869
1	0	-0.282226	-1.529632	1.529632
1	0	-1.529632	-1.529632	0.282226
1	0	-1.529632	-0.282226	1.529632
6	0	-0.886869	0.886869	-0.886869
1	0	-0.282226	1.529632	-1.529632
1	0	-1.529632	1.529632	-0.282226
1	0	-1.529632	0.282226	-1.529632
6	0	0.886869	-0.886869	-0.886869
1	0	0.282226	-1.529632	-1.529632
1	0	1.529632	-1.529632	-0.282226
1	0	1.529632	-0.282226	-1.529632

Compound
Symmetry**16**: CH_3CH_2CH_2CH_3
 C_{2h}
energyenergyE = -158.5174535 a.u.
Standard orientation

6	0	-0.420075	0.639038	0.000000
1	0	-1.078107	0.634985	0.874164
1	0	-1.078107	0.634985	-0.874164
6	0	0.420075	1.915190	0.000000
1	0	1.063658	1.962778	0.880689
1	0	1.063658	1.962778	-0.880689
1	0	-0.207795	2.807054	0.000000
6	0	0.420075	-0.639038	0.000000
1	0	1.078107	-0.634985	0.874164
1	0	1.078107	-0.634985	-0.874164
6	0	-0.420075	-1.915190	0.000000
1	0	-1.063658	-1.962778	0.880689
1	0	-1.063658	-1.962778	-0.880689
1	0	0.207795	-2.807054	0.000000

17: CH ₃ (C	H ₂) ₃ CH ₃			
C_{2v}				
E = -197.84	446211 a.u.			
tation				
0	0.000000	0.000000	0.314051	
0	0.874767	0.000000	0.973066	
0	-0.874767	0.000000	0.973066	
0	0.000000	1.280664	-0.521747	
0	0.874141	1.280205	-1.179593	
0	-0.874141	1.280205	-1.179593	
0	0.000000	2.553732	0.323488	
0	0.880636	2.598890	0.967283	
0	-0.880636	2.598890	0.967283	
0	0.000000	3.447961	-0.301044	
0	0.000000	-1.280664	-0.521747	
0	0.874141	-1.280205	-1.179593	
0	-0.874141	-1.280205	-1.179593	
0	0.000000	-2.553732	0.323488	
0	0.880636	-2.598890	0.967283	
0	-0.880636	-2.598890	0.967283	
0	0.000000	-3.447961	-0.301044	
	17 : CH ₃ (C) C_{2v} E = -197.8 tation 0 0 0 0 0 0 0 0 0 0 0 0 0	$\begin{array}{c} \mathbf{17: CH_3(CH_2)_3CH_3}\\ C_{2v}\\ E=-197.8446211 \text{ a.u.}\\ \text{tation}\\ 0 & 0.000000\\ 0 & 0.874767\\ 0 & -0.874767\\ 0 & 0.000000\\ 0 & 0.874141\\ 0 & -0.874141\\ 0 & 0.000000\\ 0 & 0.880636\\ 0 & -0.880636\\ 0 & 0.000000\\ 0 & 0.874141\\ 0 & -0.874141\\ 0 & -0.874141\\ 0 & -0.874141\\ 0 & 0.000000\\ 0 & 0.880636\\ 0 & 0.000000\\ 0 & 0.880636\\ 0 & -0.880636\\ 0 & 0.000000\\ \end{array}$	17 : CH ₃ (CH ₂) ₃ CH ₃ C_{2v} $E = -197.8446211$ a.u.tation00.00000000.8747670.0000000-0.8747670.00000000.0000001.28066400.8741411.2802050-0.8741411.28020500.0000002.55373200.8806362.5988900-0.8806362.59889000.000000-1.28066400.874141-1.2802050-0.874141-1.2802050-0.874141-1.28020500.000000-2.55373200.880636-2.5988900-0.880636-2.5988900-0.880636-2.5988900-0.880636-2.5988900-0.000000-3.447961	17 : CH ₃ (CH ₂) ₃ CH ₃ C_{2v} E = -197.8446211 a.u. tation 0 0.000000 0.000000 0.314051 0 0.874767 0.000000 0.973066 0 -0.874767 0.000000 0.973066 0 0.000000 1.280664 -0.521747 0 0.874141 1.280205 -1.179593 0 -0.874141 1.280205 -1.179593 0 0.000000 2.553732 0.323488 0 0.880636 2.598890 0.967283 0 -0.880636 2.598890 0.967283 0 0.000000 -1.280664 -0.521747 0 0.880636 2.598890 0.967283 0 0.000000 -1.280664 -0.521747 0 0.874141 -1.280205 -1.179593 0 -0.874141 -1.280205 -1.179593 0 0.000000 -2.553732 0.323488 0 0.880636 -2.598890 0.967283 0 0.000000 -2.553732 0.323488 0 0.880636 -2.598890 0.967283 0 0.000000 -2.553732 0.323488 0 0.880636 -2.598890 0.967283 0 0.000000 -3.447961 -0.301044

Compound	18 : (CH ₃) ₂	CHCH ₂ CH ₃		
Symmetry	C_1			
energy	E = -197.84	440349 a.u.		
Standard orie	ntation			
6	0	0.480203	-0.002963	-0.327738
6	0	0.664189	1.450098	0.121208
1	0	1.555482	1.887583	-0.331413
1	0	-0.184071	2.076500	-0.154180
1	0	0.782805	1.506691	1.206422
6	0	1.734302	-0.823998	-0.013200
1	0	1.915030	-0.859177	1.064125
1	0	1.636356	-1.851736	-0.366771
1	0	2.619518	-0.391558	-0.482369
1	0	0.343244	-0.004042	-1.415429
6	0	-0.763812	-0.657067	0.294454
1	0	-0.667202	-0.630343	1.385068
1	0	-0.771412	-1.715134	0.017916
6	0	-2.097067	-0.031970	-0.116498
1	0	-2.186523	1.001019	0.220300
1	0	-2.215593	-0.038161	-1.202172
1	0	-2.934516	-0.586236	0.309143

Compound	19 : (CH ₃) ₃ (CCH ₂ CH ₃		
Symmetry	$C_{\rm s}$			
energy	E = -237.16	599657 a.u.		
Standard orie	ntation			
6	0	1.169577	0.270459	0.000000
1	0	1.487243	0.847637	0.873662
1	0	1.487243	0.847637	-0.873662
6	0	1.908541	-1.068650	0.000000
1	0	1.672908	-1.666295	-0.880970
1	0	1.672908	-1.666295	0.880970
1	0	2.986876	-0.904205	0.000000
6	0	-0.377216	0.217889	0.000000
6	0	-0.899202	-0.498742	-1.255581
1	0	-0.597420	-1.546139	-1.280662
1	0	-1.989991	-0.471618	-1.288530
1	0	-0.527260	-0.020297	-2.163996
6	0	-0.899202	-0.498742	1.255581
1	0	-1.989991	-0.471618	1.288530
1	0	-0.597420	-1.546139	1.280662
1	0	-0.527260	-0.020297	2.163996
6	0	-0.899202	1.663902	0.000000
1	0	-0.553525	2.206864	0.881942
1	0	-0.553525	2.206864	-0.881942
1	0	-1.990568	1.687195	0.000000

Compound	20: CH ₃ (C	$H_2)_4CH_3$		
Symmetry	$C_{2\mathrm{h}}$,		
energy	E = -237.1	717998 a.u.		
Standard orie	ntation			
6	0	0.005749	0.764488	0.000000
1	0	-0.542528	1.129769	0.874767
1	0	-0.542528	1.129769	-0.874767
6	0	1.410752	1.368804	0.000000
1	0	1.958605	1.004624	0.874085
1	0	1.958605	1.004624	-0.874085
6	0	1.410752	2.896907	0.000000
1	0	0.899126	3.290481	0.880585
1	0	0.899126	3.290481	-0.880585
1	0	2.425514	3.296781	0.000000
6	0	-0.005749	-0.764488	0.000000
1	0	0.542528	-1.129769	0.874767
1	0	0.542528	-1.129769	-0.874767
6	0	-1.410752	-1.368804	0.000000
1	0	-1.958605	-1.004624	0.874085
1	0	-1.958605	-1.004624	-0.874085
6	0	-1.410752	-2.896907	0.000000
1	0	-0.899126	-3.290481	0.880585
1	0	-0.899126	-3.290481	-0.880585
1	0	-2.425514	-3.296781	0.000000
Commonwed	31 . (CIL.).			
Compound	21 : (CH3)2	CHCH(CH3)2		
Symmetry	C2h	(07022		
energy	E = -23/.1	08/932 a.u.		
Standard orie	ntation	0 001 40 4	0.720007	0.000000
6	0	0.231406	0.739007	0.000000
1	0	1.328494	0.732030	0.000000

6	0	-0.231406	1.496844	1.250973
1	0	-1.321298	1.480548	1.334257
1	0	0.180049	1.078541	2.167942
1	0	0.077704	2.541917	1.201349
6	0	-0.231406	1.496844	-1.250973
1	0	0.077704	2.541917	-1.201349
1	0	0.180049	1.078541	-2.167942
1	0	-1.321298	1.480548	-1.334257
6	0	-0.231406	-0.739007	0.000000
1	0	-1.328494	-0.732030	0.000000
6	0	0.231406	-1.496844	-1.250973
1	0	1.321298	-1.480548	-1.334257
1	0	-0.180049	-1.078541	-2.167942
1	0	-0.077704	-2.541917	-1.201349
6	0	0.231406	-1.496844	1.250973
1	0	-0.077704	-2.541917	1.201349
1	0	-0.180049	-1.078541	2.167942
1	0	1.321298	-1.480548	1.334257

Compound	22 : (CH ₃) ₃	$CCH(CH_3)_2$		
Symmetry	$C_{\rm s}$			
energy	E = -276.4	927327 a.u.		
Standard orier	ntation			
6	0	0.594102	0.761242	0.000000
1	0	1.667444	0.538519	0.000000
6	0	0.312734	1.606711	1.250275
1	0	-0.739922	1.886456	1.318385
1	0	0.584575	1.094524	2.171695
1	0	0.889440	2.532104	1.211275
6	0	0.312734	1.606711	-1.250275
1	0	0.889440	2.532104	-1.211275
1	0	0.584575	1.094524	-2.171695
1	0	-0.739922	1.886456	-1.318385
6	0	-0.117075	-0.634080	0.000000
6	0	0.312734	-1.435826	-1.242271
1	0	1.400475	-1.510201	-1.306258
1	0	-0.048594	-0.987031	-2.166715
1	0	-0.086337	-2.450492	-1.195233
6	0	0.312734	-1.435826	1.242271
1	0	-0.086337	-2.450492	1.195233
1	0	-0.048594	-0.987031	2.166715
1	0	1.400475	-1.510201	1.306258
6	0	-1.649604	-0.505311	0.000000
1	0	-2.013421	0.022046	-0.882169
1	0	-2.110042	-1.495062	0.000000
1	0	-2.013421	0.022046	0.882169

23: (CH ₃) ₂	CHCH ₂ CH ₂ CH ₃		
C_1			
E = -237.10	587932 a.u.		
ation			
0	1.071996	-0.012812	-0.332282
0	1.023359	0.045039	-1.425819
0	2.151316	-1.036715	0.032678
0	1.916952	-2.022764	-0.371833
0	2.241858	-1.135939	1.117216
0	3.127305	-0.739243	-0.354260
0	1.450613	1.375198	0.195296
	$23: (CH_3)_2 (CH_3)(CH_3)_2 (CH_3)_2 (CH_3)_2 (CH_3)_2 (CH_3)_2 (CH_3)_2 (CH_3)_2 $	23 : (CH ₃) ₂ CHCH ₂ CH ₂ CH ₃ C_1 E = -237.1687932 a.u. ation 0 1.071996 0 1.023359 0 2.151316 0 1.916952 0 2.241858 0 3.127305 0 1.450613	23 : (CH ₃) ₂ CHCH ₂ CH ₂ CH ₃ C_1 E = -237.1687932 a.u. ation 0 1.071996 -0.012812 0 1.023359 0.045039 0 2.151316 -1.036715 0 1.916952 -2.022764 0 2.241858 -1.135939 0 3.127305 -0.739243 0 1.450613 1.375198

1	0	0.741430	2.141584	-0.116614
1	0	2.436020	1.673667	-0.166125
1	0	1.485015	1.376656	1.287887
6	0	-0.304462	-0.478471	0.168271
1	0	-0.457042	-1.513826	-0.153000
1	0	-0.293506	-0.501268	1.264165
6	0	-1.495295	0.356029	-0.307823
1	0	-1.399469	1.383061	0.051014
1	0	-1.479952	0.411427	-1.400626
6	0	-2.838553	-0.210332	0.152209
1	0	-2.989039	-1.224207	-0.224005
1	0	-2.895944	-0.252293	1.241708
1	0	-3.670670	0.400720	-0.199796

Compound	24: (CH ₃) ₂	CH(CH ₂) ₃ CH ₃		
Symmetry	C_1			
energy	E = -276.4	927327 a.u.		
Standard orient	ation			
6	0	-1.641597	0.030984	-0.342312
1	0	-1.545445	0.112775	-1.431169
6	0	-2.816460	-0.906571	-0.047225
1	0	-3.749044	-0.514340	-0.456163
1	0	-2.652738	-1.896605	-0.475998
1	0	-2.953762	-1.030073	1.029942
6	0	-1.922364	1.432157	0.210570
1	0	-2.860372	1.826165	-0.184061
1	0	-1.135036	2.140140	-0.046824
1	0	-2.006679	1.407685	1.300192
6	0	-0.329577	-0.562475	0.195347
1	0	-0.388847	-0.616496	1.288500
1	0	-0.249761	-1.596927	-0.153807
6	0	0.943737	0.184851	-0.206394
1	0	0.974847	0.284056	-1.296808
1	0	0.923692	1.202771	0.191547
6	0	2.223983	-0.504688	0.269671
1	0	2.256815	-1.520758	-0.134356
1	0	2.190608	-0.612612	1.357838
6	0	3.496105	0.242554	-0.128244
1	0	3.509267	1.249967	0.292428
1	0	3.573815	0.338122	-1.213127
1	0	4.389674	-0.274748	0.223384

Compound	25 : H ₃ C ⁺			
Symmetry	C_{3v}			
energy	E = -39.49422	274 a.u.		
Standard orient	ation			
6	0	0.000000	0.000000	0.000002
1	0	0.000000	1.090611	-0.000004
1	0	0.944497	-0.545306	-0.000004
1	0	-0.944497	-0.545306	-0.000004
Compound	26 : CH ₃ C ⁺ H ₂			
Symmetry	$C_{\rm s}$			
energy	E = -78.89056	578 a.u.		
Standard orient	ation			

uru orientut	IOII				
6	0	-0.064110	0.688210	0.000000	
1	0	-0.072782	1.243215	0.932457	

1	0	-0.072782	1.243215	-0.932457
6	0	-0.064110	-0.688210	0.000000
1	0	-0.072783	-1.243214	0.932457
1	0	1.060452	-0.000001	0.000000
1	0	-0.072783	-1.243214	-0.932457

Compound	27: CH ₃ CH	$I_2C^+H_2$		
Symmetry	$C_{\rm s}$			
energy	E = -118.22	376403 a.u.		
Standard orie	ntation			
6	0	0.000000	0.897191	0.000000
1	0	0.249432	1.406255	0.919802
1	0	0.249432	1.406255	-0.919802
6	0	0.811234	-0.628973	0.000000
1	0	1.375984	-0.577683	0.922625
1	0	1.375984	-0.577683	-0.922625
1	0	0.305039	-1.605513	0.000000
6	0	-0.944838	-0.117440	0.000000
1	0	-1.377123	-0.478150	0.924466
1	0	-1.377123	-0.478150	-0.924466
Compound	28 $(CH_2)_2$	$CHC+H_2$		
Symposites	$\mathbf{L}_{\mathbf{C}}$			

Symmetry	C_1			
energy	E = -157.58	374653 a.u.		
Standard orie	ntation			
6	0	-0.645654	0.747959	-0.239830
1	0	-0.543113	0.882597	-1.312328
1	0	-1.172969	1.563073	0.248472
6	0	0.529049	0.318316	0.433129
1	0	0.545859	0.424163	1.516965
6	0	-1.512463	-0.595847	0.027373
1	0	-1.086021	-1.455442	-0.479282
1	0	-1.650074	-0.797593	1.085885
1	0	-2.475959	-0.347752	-0.416030
6	0	1.677203	-0.308679	-0.179158
1	0	2.478375	0.448376	-0.054683
1	0	1.569485	-0.527819	-1.237330
1	0	2.045611	-1.160098	0.399250

Compound Symmetry energy	29 : (CH ₃) ₃ (C_1 E = -196.93	CC+H2 399794 a.u.		
Standard orie	ntation			
6	0	-0.852911	-0.111921	0.732602
1	0	-1.064772	0.713692	1.411046
1	0	-1.011118	-1.071652	1.220104
6	0	0.473257	0.000616	0.149778
6	0	-1.855058	0.001601	-0.485944
1	0	-1.763419	0.959101	-0.991756
1	0	-2.853054	-0.079492	-0.061180
1	0	-1.708433	-0.806016	-1.198506
6	0	1.060857	1.314857	-0.102031
1	0	1.915970	1.401209	0.588948
1	0	1.511995	1.369067	-1.095735
1	0	0.386106	2.145125	0.081484
6	0	1.224772	-1.207742	-0.185782
1	0	1.683855	-1.527043	0.766457

1	0	2.025053	-1.053805	-0.904031
1	0	0.572319	-2.034653	-0.468575

Compound Symmetry	30 : (CH ₃) ₂ (C ₂ E = 118.25	C+H		
	E = -110.2	59125 a.u.		
Standard orier	ntation			
6	0	0.000000	0.000000	0.451823
1	0	0.000000	0.000000	1.541900
6	0	0.000000	1.277873	-0.197414
1	0	-1.035947	1.642690	-0.003286
1	0	0.162796	1.257899	-1.270705
1	0	0.608421	2.017445	0.332058
6	0	0.000000	-1.277873	-0.197414
1	0	1.035947	-1.642690	-0.003286
1	0	-0.162796	-1.257899	-1.270705
1	0	-0.608421	-2.017445	0.332058

Compound	31 : CH ₃ CH	$I_2C^+HCH_3$		
Symmetry	C_1			
energy	E = -157.5	867293 a.u.		
Standard orien	ntation			
6	0	-0.597922	-0.372526	-0.133580
1	0	-0.452372	-1.423226	-0.387732
6	0	-1.951305	0.059178	0.112242
1	0	-2.195921	-0.419541	1.084209
1	0	-2.081169	1.132649	0.213873
1	0	-2.665675	-0.399848	-0.576627
6	0	0.562372	0.457246	-0.128531
1	0	0.390846	1.439521	0.313252
1	0	0.474887	0.645017	-1.245309
6	0	1.935740	-0.156335	0.141574
1	0	2.060946	-0.309202	1.212375
1	0	2.060124	-1.111267	-0.366544
1	0	2.715027	0.520514	-0.197729

Compound	32 : (CH ₃) ₂	CHC+HCH ₃		
Symmetry	C_1			
energy	E = -196.92	216377 a.u.		
Standard orie	ntation			
6	0	0.608998	-0.367371	0.379704
1	0	0.451038	-0.550398	1.439334
6	0	1.996597	-0.421462	-0.109030
1	0	2.102442	-0.123105	-1.148987
1	0	2.683789	0.130694	0.531605
1	0	2.289851	-1.477102	-0.023469
6	0	-0.534708	-0.173260	-0.406213
1	0	-0.379205	-0.192354	-1.480168
6	0	-1.901239	-0.613488	0.058084
1	0	-2.039252	-1.664135	-0.197920
1	0	-2.021367	-0.505174	1.135500
1	0	-2.681459	-0.044874	-0.444019
6	0	-0.161927	1.428089	0.044879
1	0	0.404463	1.880312	-0.757887
1	0	-1.176980	1.806167	0.136388
1	0	0.320358	1.624923	1.005078

Compound	33 : (CH ₃) ₃	CC ⁺ HCH ₃		
Symmetry	C_1			
energy	<i>E</i> = -236.2	700082 a.u.		
Standard orient	ation			
6	0	-0.669180	-0.282559	-0.417256
1	0	-0.654808	-0.907723	-1.312420
6	0	-1.720797	0.818813	-0.526293
1	0	-1.863293	1.353468	0.411568
1	0	-1.461425	1.538852	-1.301684
1	0	-2.675261	0.370507	-0.795032
6	0	0.694916	0.107610	-0.089571
6	0	1.815543	-0.739763	-0.502786
1	0	1.517705	-1.680433	-0.955571
1	0	2.373320	-0.155207	-1.252537
1	0	2.528582	-0.889556	0.311064
6	0	0.975540	1.338336	0.651094
1	0	0.207436	1.559180	1.392784
1	0	1.971515	1.374756	1.081798
1	0	0.887427	2.154459	-0.084993
6	0	-1.008213	-1.275640	0.780368
1	0	-0.319201	-2.113778	0.841714
1	0	-1.035362	-0.748562	1.731091
1	0	-2.003492	-1.656742	0.558882

Compound Symmetry	34 : (CH ₃) ₃ C ⁺ C ₁			
energy	E = -157.6094	1446 a.u.		
Standard orient	ation			
6	0	-0.002204	-0.000237	-0.005383
6	0	0.992254	-1.067584	-0.008699
1	0	1.492337	-1.033415	0.972915
1	0	1.797888	-0.836142	-0.713801
1	0	0.588860	-2.060822	-0.176052
6	0	0.428343	1.391674	0.014457
1	0	1.478616	1.535523	0.250514
1	0	-0.226685	2.011692	0.630529
1	0	0.253662	1.754471	-1.015183
6	0	-1.423586	-0.323618	-0.010236
1	0	-2.079107	0.532168	-0.138408
1	0	-1.644037	-1.122184	-0.723855
1	0	-1.630374	-0.782701	0.972511
Compound	35 : CH ₃ CH ₂ C	2 ⁺ (CH ₃) ₂		
Symmetry	C_1			
energy	E = -196.9401	1512 a.u.		
Standard orient	ation	a 53 0000	0.0000.50	0.0070.00
6	0	0.530990	-0.000863	-0.00/060
6	0	1.808/17	-0.710332	0.015809
1	0	2.330957	-0.424498	0.940742
1	0	1 77/160	1 701020	1 1 1 1 1 1 1 1 1 1 1 1
	0	1.724100	-1./91030	-0.041290
l	0	2.457485	-0.323039	-0.041290
6	0 0	2.457485 0.519631	-0.323039 1.456411	-0.041290 -0.778495 -0.008121
1 6 1	0 0 0	$\begin{array}{c} 1.724100\\ 2.457485\\ 0.519631\\ 1.503569\end{array}$	-0.323039 1.456411 1.912840	-0.041290 -0.778495 -0.008121 0.008895
1 6 1 1	0 0 0 0	$\begin{array}{c} 1.724100\\ 2.457485\\ 0.519631\\ 1.503569\\ -0.049990\\ 0.049990\end{array}$	-1.791030 -0.323039 1.456411 1.912840 1.800969	-0.041290 -0.778495 -0.008121 0.008895 -0.882240
6 1 1 1	0 0 0 0 0	$\begin{array}{c} 1.724100\\ 2.457485\\ 0.519631\\ 1.503569\\ -0.049990\\ -0.088232\\ 0.088232\end{array}$	-1.791030 -0.323039 1.456411 1.912840 1.800969 1.806600	-0.041290 -0.778495 -0.008121 0.008895 -0.882240 0.836638
6 1 1 1 6	0 0 0 0 0 0	$\begin{array}{c} 1.724100\\ 2.457485\\ 0.519631\\ 1.503569\\ -0.049990\\ -0.088232\\ -0.713103\\ 0.612422\end{array}$	-0.323039 1.456411 1.912840 1.800969 1.806600 -0.766702	-0.041290 -0.778495 -0.008121 0.008895 -0.882240 0.836638 -0.030859

1	0	-0.621214	-1.392266	-0.938511
6	0	-2.052055	-0.048764	0.026399
1	0	-2.166012	0.518022	0.949987
1	0	-2.187851	0.629535	-0.815058
1	0	-2.855532	-0.780580	-0.010320

Compound	36 : (CH ₃) ₂	$CHC^{+}(CH_3)_2$		
Symmetry	C_1			
energy	E = -236.27	700082 a.u.		
Standard orie	ntation			
6	0	0.694917	0.107613	-0.089571
6	0	0.975533	1.338335	0.651096
1	0	1.971509	1.374768	1.081797
1	0	0.887407	2.154458	-0.084991
1	0	0.207426	1.559177	1.392784
6	0	1.815548	-0.739758	-0.502785
1	0	2.528580	-0.889555	0.311068
1	0	1.517710	-1.680426	-0.955574
1	0	2.373326	-0.155203	-1.252536
6	0	-0.669179	-0.282561	-0.417257
1	0	-0.654805	-0.907727	-1.312420
6	0	-1.008210	-1.275641	0.780368
1	0	-2.003487	-1.656750	0.558882
1	0	-0.319191	-2.113774	0.841716
1	0	-1.035364	-0.748562	1.731091
6	0	-1.720796	0.818809	-0.526295
1	0	-1.863303	1.353457	0.411569
1	0	-1.461423	1.538855	-1.301680
1	0	-2.675257	0.370502	-0.795044

Compound	37 : (CH ₃) ₃	$CC^{+}(CH_{3})_{2}$		
Symmetry	C_1			
energy	E = -275.59	958819 a.u.		
Standard orient	ation			
6	0	-0.848508	0.005958	-0.078007
6	0	-1.628735	-1.235100	-0.090714
1	0	-2.522622	-1.155552	0.528276
1	0	-2.005353	-1.322132	-1.124446
1	0	-1.066961	-2.135086	0.126537
6	0	-1.600460	1.267669	-0.095511
1	0	-2.659976	1.144757	0.104150
1	0	-1.163674	2.014393	0.568283
1	0	-1.473802	1.693601	-1.102254
6	0	0.616272	0.000998	-0.047509
6	0	0.812336	-0.152774	1.534165
1	0	1.893488	-0.147132	1.669257
1	0	0.388985	0.681017	2.088897
1	0	0.416932	-1.091318	1.913253
6	0	1.272617	-1.207738	-0.742641
1	0	0.944664	-2.165598	-0.347723
1	0	1.080732	-1.188330	-1.815002
1	0	2.348991	-1.147330	-0.595813
6	0	1.279745	1.308461	-0.503651
1	0	1.087290	1.495972	-1.560189
1	Ō	0.955126	2.176306	0.066134
1	Õ	2.356574	1.221587	-0.376153

Compound 38: CH₃OH Symmetry $C_{\rm s}$ *E* = -115.7743176 a.u. energy Standard orientation 0 -0.046432 0.664807 0.000000 6 1 0 0.438471 1.075495 0.890506 0 1 0.438471 1.075495 -0.890506 1 0 -1.087885 0.979086 0.000000 8 0 -0.046432 -0.756172 0.000000 1 0 0.860988 -1.069539 0.000000 39: CH₃SH Compound $C_{\rm s}$ E = -438.7536229 a.u. Symmetry energy Standard orientation 0 0.047843 1.157308 0.000000 6 1 0 1.092597 1.459044 0.000000 1 0 -0.4307701.551802 0.892164 1 0 -0.430770 1.551802 -0.892164 0.047843 -0.666819 0.000000 0 16 0 -1.283610 -0.837392 0.000000 1 **40**: CH₃SeH Compound Symmetry $C_{\rm s}$ energy E = -2442.0836083 a.u. Standard orientation

6 34 1 1 1	0 0 0 0 0	0.031553 0.031553 -1.432546 -0.453229 -0.453229	1.546876 -0.423773 -0.563131 1.923810 1.923810	0.000000 0.000000 0.000000 0.894191 -0.894191
1	Ő	-0.453229	1.923810	-0.894191
1	0	1.076890	1.842548	0.000000

Compound	41: CH ₃ SS	CH ₃		
Symmetry	C_2			
energy	E = -876.31	114452 a.u.		
Standard orie	ntation			
6	0	0.966120	1.648448	0.788556
1	0	0.782868	1.232418	1.775956
1	0	0.228330	2.411204	0.554989
1	0	1.963302	2.088181	0.765415
16	0	0.966120	0.347540	-0.489231
16	0	-0.966120	-0.347540	-0.489231
6	0	-0.966120	-1.648448	0.788556
1	0	-0.782868	-1.232418	1.775956
1	0	-0.228330	-2.411204	0.554989
1	0	-1.963302	-2.088181	0.765415

Compound	42 : CH ₃ F			
Symmetry	C_{3v}			
energy	E = -139.800	2847 a.u.		
Standard orient	ation			
6	0	0.000000	0.000000	-0.636070
9	0	0.000000	0.000000	0.752737
1	0	1.031653	0.000000	-0.986072
1	0	-0.515827	0.893438	-0.986072

Compound	43: CH ₃ Cl			
Symmetry	C_{3v}			
energy	E = -500.159	98382 a.u.		
Standard orie	ntation			
6	0	0.000000	0.000000	-1.133585
17	0	0.000000	0.000000	0.660275
1	0	-1.029529	0.000000	-1.474386
1	0	0.514764	0.891598	-1.474386
1	0	0.514764	-0.891598	-1.474386

Compound	44: CH ₃ Br			
Symmetry	C_{3v}			
energy	E = -2614.0	0807337 a.u.		
Standard orienta	ation			
6	0	0.000000	0.000000	-1.535565
35	0	0.000000	0.000000	0.422953
1	0	0.000000	1.032294	-1.863318
1	0	-0.893993	-0.516147	-1.863318
1	0	0.893993	-0.516147	-1.863318

45 : CH ₃ I			
$C_{3\mathrm{v}}$			
E = -6960.4	728009 a.u.		
ation			
0	0.000000	0.000000	-1.831482
0	0.000000	0.000000	0.329498
0	0.000000	1.032342	-2.158165
0	-0.894034	-0.516171	-2.158165
0	0.894034	-0.516171	-2.158165
	45 : CH ₃ I C_{3v} E = -6960.4 ation 0 0 0 0 0 0 0	45 : CH ₃ I C_{3v} $E = -6960.4728009$ a.u. ation 0 0.000000 0 0.000000 0 0.000000 0 0.000000 0 0.000000 0 0.000000 0 0.894034 0 0.894034	45 : CH ₃ I C_{3v} $E = -6960.4728009$ a.u. ation 0 0.000000 0 0.000000 0 0.000000 0 0.000000 0 0.000000 0 0.000000 0 0.000000 0 0.000000 0 0.000000 0 0.516171 0 0.894034 -0.516171

Cf: The basis set of the Sapporo-TZP with diffuse functions of the 1s1p type (Sapporo-TZP + 1s1p) was employed for Iodine atom, implemented from Sapporo Basis Set Factory.^{*Ref*} *Ref*T. Noro, M. Sekiya and T. Koga, *Theor. Chem. Acc.*, 2012, **131**, 1124.

Compound	46 : CH ₃ C(=	=O)OCH ₃		
Symmetry	Cs	,		
energy	E = -268.49	952145 a.u.		
Standard orier	ntation			
6	0	1.126869	1.492588	0.000000
1	0	1.754996	1.344233	0.877931
1	0	1.754996	1.344233	-0.877931
1	0	0.720578	2.498624	0.000000
6	0	0.000000	0.495099	0.000000
8	0	-1.173541	0.763356	0.000000
8	0	0.470706	-0.768723	0.000000
6	0	-0.518727	-1.808865	0.000000
1	0	-1.146688	-1.737895	-0.885991
1	0	-1.146688	-1.737895	0.885991
1	0	0.036636	-2.741299	0.000000

Compound	47 : CH ₃ CN
Symmetry	$C_{3\mathrm{v}}$
energy	E = -132.8056202 a.u.

Standard orie	ntation			
6	0	0.000000	0.000000	-1.174036
1	0	0.000000	1.022326	-1.549601
1	0	-0.885360	-0.511163	-1.549601
1	0	0.885360	-0.511163	-1.549601
6	0	0.000000	0.000000	0.280619
7	0	0.000000	0.000000	1.429901
Commonwead	49. CIL.NIL			
Summetru	40 : $CH_{31}NH_{2}$			
Symmetry	$C_{\rm s}$	1752 0.11		
Standard aria	$E = -93.901^{2}$	+/35 a.u.		
		0.040020	0 706320	0.00000
0	0	-0.049039	1.065154	0.000000
1	0	-0.387090	1.005154	0.877309
1	0	-0.387090	1.005154	-0.877309
1 7	0	0.944033	0.757106	0.000000
1	0	0.047037	-0.737170 -1.1197/8	0.812978
1	0	0.433415	-1 119248	-0.812978
1	0	0.435415	1.11/2+0	0.012770
Compound	49 : CH ₃ NO ₂			
Symmetry	$C_{\rm s}$			
energy	E = -245.109	96821 a.u.		
Standard orien	ntation			
6	0	0.000236	-1.323947	0.000000
1	0	-0.491705	-1.663804	0.903474
1	0	1.044526	-1.626712	0.000000
1	0	-0.491705	-1.663804	-0.903474
7	0	-0.009474	0.174306	0.000000
8	0	0.000236	0.729866	1.083481
8	0	0.000236	0.729866	-1.083481
Compound	50 : CH ₃ CH ₂	ОН		
Symmetry	$C_{\rm c}$	011		
energy	$\vec{E} = -155.106$	5985 a.u.		
Standard orie	ntation			
6	0	-1.176718	-0.399986	0.000000
1	0	-1.152216	-1.037957	0.883327
1	0	-1.152216	-1.037957	-0.883327
1	0	-2.115220	0.155476	0.000000
6	0	0.000000	0.553216	0.000000
8	0	1.199561	-0.220669	0.000000
1	0	1.956530	0.370327	0.000000
1	0	-0.036528	1.198039	0.885102
1	0	-0.036528	1.198039	-0.885102
Compound	51· H₂∩=∩¤	- In		
Symmetry	D_{2h}	12		
energy	E = -78 6720)932 a u		
Standard origi	L = -70.0220	<i>552</i> a.u.		
6	0	0.000000	0 000000	0 662352
6	ŏ	0.000000	0.000000	-0.662352
1	ŏ	0.000000	0.920632	1.231614
1	ŏ	0.000000	-0.920632	1.231614
1	Õ	0.000000	0.920632	-1.231614
1	0	0.000000	-0.920632	-1.231614

Compound Symmetry	52 : HC≡CH <i>D</i> ∞h <i>E</i> = 77 36233	276 a u				
Standard orier	E = -77.3023.	570 a.u.				
6	0	0.000000	0.0	00000	0.5	598143
6	Ő	0.000000	0.0)000000	-0.5	98143
1	Ő	0.000000	0.0	000000	1.6	59887
1	0	0.000000	0.0	000000	-1.6	59887
Compound	53 : CaHa					
Symmetry	D _{6h}					
energy	E = -232.3293	3476 a.u.				
Standard orier	ntation					
6	0	0.000000	1.3	390962	0.0	00000
6	Õ	1.204608	0.6	595481	0.0	000000
6	0	1.204608	-0.6	95481	0.0	00000
6	0	0.000000	-1.3	90962	0.0	00000
6	0	-1.204608	-0.6	95481	0.0	00000
6	0	-1.204608	0.6	95481	0.0	00000
1	0	0.000000	2.4	172877	0.0	00000
1	0	2.141574	1.2	236438	0.0	00000
1	0	2.141574	-1.2	36438	0.0	00000
1	0	0.000000	-2.4	72877	0.0	00000
1	0	-2.141574	-1.2	36438	0.0	00000
1	0	-2.141574	1.2	36438	0.0	00000
Compound	54 : C ₆ H ₅ OH					
Symmetry	$C_{\rm s}$					
energy	E = -307.5829	9283 a.u.				
Standard orier	ntation					
6	0	1.215	737	-1.1356	590	0.000000
6	0	1.212	675	0.251	937	0.000000
6	0	0.000	000	0.936	403	0.000000
6	0	-1.200.	396	0.2305	572	0.000000
6	0	-1.1834	473	-1.1595	74	0.000000
0	0	0.021	631 926	-1.8510	125	0.000000
l 1	0	2.160	830	-1.0022	262	0.000000
1	0	2.134	207	0.810	830 700	0.000000
1	0	-2.1420	100		00	0.000000
1	0	-2.120	190 171	-1./000	202	0.000000
1	0	0.031	424 081	2.9510	030	0.000000
1	0	-0.8443	358	2.6603	331	0.000000
Compound Symmetry	55 : HC(= O)H C _{2v}	I				

Symmetry	$C_{2\mathrm{v}}$			
energy	E = -114.54	199452 a.u.		
Standard orier	ntation			
6	0	0.000000	0.000000	-0.526024
8	0	0.000000	0.000000	0.672428
1	0	0.000000	0.938212	-1.111639
1	0	0.000000	-0.938212	-1.111639

Compound **56**: HC(=O)OH

Symmetry	$C_{\rm s}$			
energy	E = -189.84	16527 a.u.		
Standard orier	ntation			
6	0	0.000000	0.420408	0.000000
8	0	1.157012	0.116930	0.000000
1	0	-0.382893	1.447570	0.000000
8	0	-1.026765	-0.445362	0.000000
1	0	-0.659085	-1.342561	0.000000

Appendix

Procedure to draw the selected contributions from each ψ_i to σ^d and σ^p and each $\psi_i \rightarrow \psi_a$ transition, using molecular orbitals

(The procedure, analyzing the output of Gaussian program, with the utility program, is explained, exemplified by CH₄: The output format below is the same as that from the program.)

OutputSP: $B3LYP/6-311++G(3df,3pd)$ Number of Basis Functions=Number of Orbitals=121Number of Atoms=5Multiplicity=1Number of Electrons=					
Dia	magnetic MO co	ntribution			
	200 27845	200 27845	200 27845		
$\frac{1}{2}$	200.27843	200.27845	200.27843		
$\frac{2}{3}$	0.81211	0.81211	10 10126		
5 4	0.81211	10 10126	0.81211		
5	10 10126	0.81211	0.81211		
SUM	238.97591	238.97591	238.97591		
 Para	magnetic MO co	ntribution			
$OCC \times OCC$	125 55119	125 55119	125 55119		
1	0.00002	0.00002	0.00002		
2	0.33164	0.33164	0.33164		
3	-87.47495	-87.47495	-0.59302		
4	-87.47495	-0.59302	-87.47495		
5	-0.59302	-87.47495	-87.47495		
SUM	-49.66007	-49.66007	-49.66007		

Contributions from each $\psi_i {\rightarrow} \psi_a$ transition to $\sigma_i{}^p$

Output SP: B3LYP/6- Number of B Number of O Number of A Multiplicity Number of E	311++G(3df,3pd) asis Functions = rbitals = toms = lectrons =	121 121 5 1 10	
Di	iamagnetic MO con	ntribution	
1 2 3 4 5 SUM	200.27845 26.97198 0.81211 0.81211 10.10126 238.97591	200.27845 26.97198 0.81211 10.10126 0.81211 238.97591	$\begin{array}{c} 200.27845\\ 26.97198\\ 10.10126\\ 0.81211\\ 0.81211\\ 238.97591 \end{array}$
Pai	ramagnetic MO co	ntribution	
OCC>OCC	125.55119	125.55119	125.55119
$\begin{array}{c} 1 &> & 6 \\ 1 &> & 7 \\ 1 &> & 8 \\ 1 &> & 9 \\ 1 &> & 10 \end{array}$	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ \end{array}$	0.00000 0.00000 0.00000 0.00000 0.00000	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\end{array}$
1>121	0.00000	0.00000	0.00000
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 0.00000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.$	$\begin{array}{c} 0.00000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.00$	$\begin{array}{c} 0.00000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.0000\\ 0.000\\ 0$
$2 \rightarrow 13$ $2 \rightarrow 14$ $2 \rightarrow 15$ $2 \rightarrow 16$ $2 \rightarrow 17$ $2 \rightarrow 18$ $2 \rightarrow 19$	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ \end{array}$	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ \end{array}$	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ \end{array}$
2> 20 2> 21 2> 22 2> 23 2> 24 2> 25 2> 26	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.08601\\ 0.00000\\ 0.00000\\ 0.00000\end{array}$	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.08601\\ 0.00000\end{array}$	$\begin{array}{c} 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.00000\\ 0.08601 \end{array}$
2>121	0.00000	omitted 0.00000	0.00000
3 - > 6 3 - > 7	0.00000 -10.57648	0.00000 0.00000	0.00000 0.00000

3> 8	0.00000	0.00000	0.00000	
3> 9	0.00000	-10.57648	0.00000	
3>10	-0.81361	0.00000	0.00000	
3>11	0.00000	0.00000	0.00000	
3>12	0.00000	-0.81361	0.00000	
		omitted		
3>121	0.00000	0.00000	0.00000	
4> 6	0.00000	0.00000	0.00000	
4> 7	0.00000	0.00000	0.00000	
4> 8	-10.57648	0.00000	0.00000	
4> 9	0.00000	0.00000	-10.57648	
4>10	0.00000	0.00000	0.00000	
4>11	-0.81361	0.00000	0.00000	
4>12	0.00000	0.00000	-0.81361	
4>13	0.00000	0.00000	0.00000	
4> 14	-33.27102	0.00000	0.00000	
4> 15	0.00000	0.00000	0.00000	
4>16	0.00000	0.00000	-33.27102	
4> 17	0.00000	0.00000	0.00000	
		omitted		
4>121	0.00000	0.00000	0.00000	
5> 6	0.00000	0.00000	0.00000	
5> 7	0.00000	0.00000	-10.57648	
5> 8	0.00000	-10.57648	0.00000	
5> 9	0.00000	0.00000	0.00000	
5>10	0.00000	0.00000	-0.81361	
5>11	0.00000	-0.81361	0.00000	
5> 12	0.00000	0.00000	0.00000	
5>13	0.00000	0.00000	0.00000	
5>14	0.00000	-33.27102	0.00000	
5>15	0.00000	0.00000	-33.27102	
5>16	0.00000	0.00000	0.00000	
		omitted		
5>119	0.00000	-0.67620	0.00000	
5>120	0.00000	0.00000	0.00000	
5>121	0.00000	0.00000	0.00000	
SUM	-49.66007	-49.66007	-49.66007	

Drawing steps:

- 1. Selecting transitions in the above output terms, of which contributions are larger than a certain value.
- 2. Drawing the molecular orbitals in the selected transitions using GaussView with an isovalue of 0.04 au.
- 3. Completing the transition maps of interest, using the molecular orbitals drawn above. (See Figs. 6–13 in the text.)

The input section of this utility program is as follows, although it is not shown in the Appendix:

Input FChk file: CH4Td-B6G6NMR.FChk CH4Td-B6G6NMR NMR B3LYP/6-311++G(3df,3pd) SCF=(Direct,Tight) IOp(10/21=11) IOp(10/33=1) IOp(10/75=1) 6D 10F FChk=All POP=Full GFInput