

Supporting Information

The C–H···S–S Hydrogen bonding in Diethyl Disulfide···Difluoromethane: A Combined Microwave Spectroscopic and Computational Study

Wenqi Lv, Jinxi Huang, Haiying Huang, Liuting Wang, Tingting Yang, and Gang Feng*

School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, 401331,

China.

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Figure S1 Shapes and relative energies (ΔE_0 in kJ mol^{-1}) of the five most stable isomers of DEES- CH_2F_2 calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

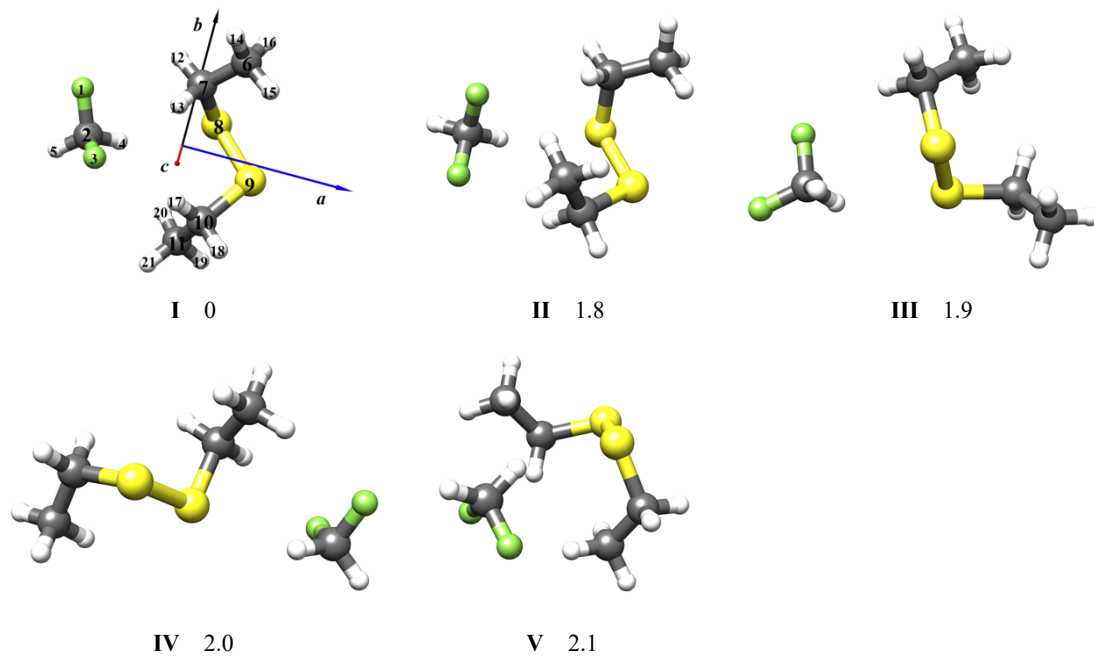


Table S1. Spectroscopic parameters of the energy minima of the DEFS-CH₂F₂ complex calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

isomer	ΔE_0 /kJ·mol ⁻¹	<i>A</i> /MHz	<i>B</i> /MHz	<i>C</i> /MHz	μ_a / Debye	μ_b / Debye	μ_c / Debye
I	0.0	1074	748	513	1.2	1.3	0.1
II	1.8	1212	663	532	0.9	1.0	0.2
III	1.9	1417	509	419	3.2	0.6	0.3
IV	2.0	2011	427	406	1.2	0.4	0.5
V	2.1	1161	721	537	0.9	0.7	0

Table S2 Partial r_0 and B3LYP-D3(BJ)/def2-TZVP calculated geometries of the observed isomer **I** of DEDS-CH₂F₂.

Bond lengths/Å		Angles/°		Dihedral angles/°	
F1C2	1.347				
F3C2	1.344	F3C2F1	107.749		
H4F2	1.097	H4F2C3	108.951	H4F2C3F1	117.742
H5C2	1.099	H5C2H4	113.775	H5C2H4F3	-121.645
C6H5	4.715	C6H5C2	106.343	C6H5C2F3	-55.806
C7C6	1.512	C7C6H5	8.789	C7C6H5C2	16.074
S8C2	3.522(6)	S28C2F1	83.9(3)	S28C2F1F3	98.324
S9S8	2.026	S9S8C7	102.567	S9S8C7C6	67.160
C10S9	1.835	C10S9S8	102.464	C10S9S8C7	90.744
C11C10	1.513	C11C10S9	111.674	C11C10S9S8	71.729
S12C7	1.089	S12C7S8	104.494	S12C7S8S9	-171.955
H13C7	1.089	H13C7S8	107.554	H13C7S8S9	-55.823
H14C6	1.088	H14C6C7	109.942	H14C6C7S8	-179.765
H15C6	1.089	H15C6C7	110.358	H15C6C7S8	-59.922
H16C6	1.087	H16C6C7	110.442	H16C6C7S8	60.101
H17C10	1.089	H17C10S9	107.849	H17C10S9S8	-51.391
H18C10	1.088	H18C10S9	104.250	H18C10S9S8	-167.531
H19C11	1.087	H19C11C9	110.474	H19C11C9S9	61.226
H20C11	1.088	H20C11C10	110.331	H20C11C10S9	-58.658

The parameters in bold have been modified to reproduce the experimental values of rotational constants, uncertainties (in parentheses) are given in units of the last digit. Their theoretical values are: 3.522 Å, and 83.9°.

Table S3. NBO stabilization energy contributions (≥ 0.21 kJ/mol) for the isomer **I** of the DEDES- CH_2F_2 complex calculated at B3LYP-D3(BJ)/def2-TZVP level of theory.

Donor NBO	Acceptor NBO	$E^{(2)}$ [kJ·mol ⁻¹]
From DEDES to CH_2F_2		
BD(1)C11-H20	BD*(1)C2-H4	0.33
BD(1)C10-H17	RY*(1)F3	1.72
BD(1)C7-H13	RY*(1)F3	0.25
BD(1)C7-H13	RY*(2)F3	0.50
BD(1)C7-H12	RY*(1)F1	0.25
LP(1)S8	BD*(1)C2-H4	1.17
LP(2)S8	BD*(1)C2-H4	6.07
From CH_2F_2 to DEDES		
BD(1)C2-H4	RY*(5)S8	0.33
BD(1)C2-H4	BD*(1)C10-H17	0.33
BD(1)C2-H4	BD*(1)C7-C6	0.25
LP(2)F3	BD*(1)C10-H17	0.84
LP(2)F3	BD*(1)C7-H13	0.38
LP(2)F1	BD*(1)C7-C6	0.33

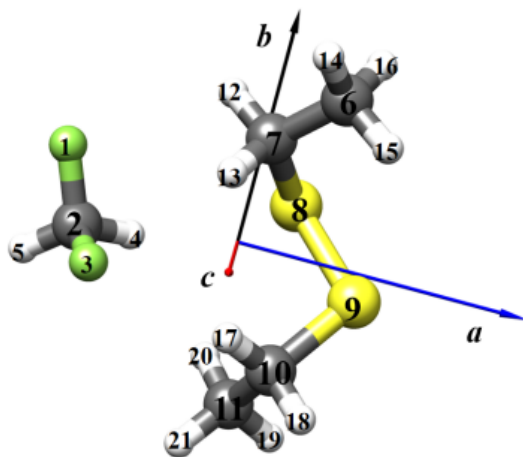


Table S4. Experimental transition frequencies of the observed parent species of isomer I of the DEFS-CH₂F₂ complex.

J'	K_a'	K_c'	J''	K_a''	K_c''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}} (\text{MHz})$
6	0	6	5	1	5	6454.4444	-0.0026
6	1	6	5	1	5	6457.6650	0.0022
6	0	6	5	0	5	6465.0527	0.0037
6	1	6	5	0	5	6468.2651	0.0004
4	3	2	3	2	1	7133.3544	-0.0027
6	1	5	5	2	4	7037.2080	-0.0002
6	2	5	5	2	4	7136.8978	0.0012
6	1	5	5	1	4	7275.9995	0.0013
7	0	7	6	1	6	7474.4051	-0.0016
7	1	7	6	1	6	7475.3351	-0.0033
7	0	7	6	0	6	7477.6210	-0.0014
7	1	7	6	0	6	7478.5536	-0.0005
4	3	1	3	2	2	7614.4579	-0.0045
6	3	4	5	3	3	7588.4754	0.0003
6	4	3	5	4	2	7718.1304	0.0016
6	4	2	5	4	1	7831.1746	0.0005
6	2	4	5	2	3	8033.6522	-0.0005
4	4	1	3	3	0	8263.2720	-0.0040
4	4	0	3	3	1	8286.4284	0.0007
7	1	6	6	2	5	8151.9806	-0.0021
7	2	6	6	2	5	8188.7413	0.0030
6	3	3	5	3	2	8145.0869	-0.0013
7	1	6	6	1	5	8251.6710	0.0000
7	2	6	6	1	5	8288.4266	0.0000
7	2	5	6	3	4	8307.7745	0.0015
8	0	8	7	1	7	8491.1707	-0.0004
8	1	8	7	1	7	8491.4350	0.0027
8	0	8	7	0	7	8492.1016	-0.0011
8	1	8	7	0	7	8492.3657	0.0017
7	3	5	6	3	4	8757.3007	-0.0026
7	4	4	6	4	3	9011.2919	-0.0017
7	2	5	6	2	4	9130.8605	-0.0006
7	5	2	6	5	1	9046.6522	0.0006
8	1	7	7	2	6	9207.2809	-0.0033
8	2	7	7	2	6	9219.7757	0.0018
8	1	7	7	1	6	9244.0413	0.0015
8	2	7	7	1	6	9256.5298	0.0004
5	4	2	4	3	1	9462.1007	0.0000

5	3	2	4	2	3	9359.5440	0.0014
7	4	3	6	4	2	9310.9200	-0.0013
5	4	1	4	3	2	9618.8327	0.0007
9	0	9	8	1	8	9506.9530	-0.0008
9	1	9	8	1	8	9507.0269	0.0016
9	0	9	8	0	8	9507.2120	-0.0029
9	1	9	8	0	8	9507.2882	0.0018
7	3	4	6	3	3	9560.1412	-0.0013
8	2	6	7	3	5	9665.0760	0.0008
8	3	6	7	3	5	9872.5057	-0.0001
8	2	6	7	2	5	10114.6078	0.0021
5	5	1	4	4	0	10455.6556	-0.0009
5	5	0	4	4	1	10460.1060	-0.0016
8	3	6	7	2	5	10322.0376	0.0012
9	1	8	8	2	7	10236.6801	0.0009
9	2	8	8	2	7	10240.6904	0.0013
9	1	8	8	1	7	10249.1685	-0.0002
9	2	8	8	1	7	10253.1814	0.0027
6	4	3	5	3	2	10516.9884	-0.0022
10	1	10	9	1	9	10522.4672	0.0019
10	0	10	9	0	9	10522.5190	0.0014
8	5	3	7	5	2	10457.9832	-0.0037
8	3	5	7	3	4	10848.7675	0.0004
9	2	7	8	3	6	10859.3692	-0.0009
8	4	4	7	4	3	10837.5268	0.0017
9	3	7	8	3	6	10943.4428	0.0029
6	4	2	5	3	3	11083.2073	-0.0022
9	2	7	8	2	6	11066.7987	-0.0021
9	3	7	8	2	6	11150.8754	0.0048
10	1	9	9	2	8	11256.2717	-0.0021
10	2	9	9	2	8	11257.5089	0.0006
10	1	9	9	1	8	11260.2818	-0.0019
10	2	9	9	1	8	11261.5190	0.0007
6	5	2	5	4	1	11707.1621	0.0000
9	4	6	8	4	5	11466.8408	-0.0006
6	5	1	5	4	2	11746.4158	-0.0010
11	0	11	10	0	10	11537.8637	-0.0006
11	1	11	10	0	10	11537.8637	-0.0056
9	5	5	8	5	4	11663.5509	-0.0001
8	4	5	7	3	4	12089.0137	0.0004
9	3	6	8	3	5	11980.8194	0.0007
10	2	8	9	3	7	11953.5133	-0.0015
10	3	8	9	3	7	11984.6674	0.0026
10	2	8	9	2	7	12037.5865	0.0019

10	3	8	9	2	7	12068.7353	0.0008
9	5	4	8	5	3	11953.8897	0.0028
11	1	10	10	2	9	12272.5607	0.0010
11	2	10	10	2	9	12272.9282	0.0006
11	1	10	10	1	9	12273.7947	0.0005
11	2	10	10	1	9	12274.1626	0.0006
6	6	1	5	5	0	12640.1312	-0.0002
6	6	0	5	5	1	12640.9101	0.0026
10	3	7	9	4	6	12246.1777	-0.0009
9	4	5	8	4	4	12312.3439	0.0019
9	4	6	8	3	5	12707.0899	0.0022
12	0	12	11	1	11	12553.2012	0.0008
12	1	12	11	1	11	12553.2012	-0.0004
12	0	12	11	0	11	12553.2012	-0.0041
12	1	12	11	0	11	12553.2012	-0.0055
10	4	7	9	4	6	12609.3577	0.0002
7	5	3	6	4	2	12890.4032	0.0014
7	4	3	6	3	4	12805.6563	0.0004
7	5	2	6	4	3	13074.9384	-0.0012
10	3	7	9	3	6	12972.4481	0.0004
10	7	4	9	7	3	12900.5822	0.0025
11	2	9	10	3	8	12998.7861	-0.0004
10	5	6	9	5	5	12946.6713	-0.0012
10	7	3	9	7	2	12908.8714	-0.0017
11	3	9	10	3	8	13009.6217	0.0024
11	2	9	10	2	8	13029.9359	-0.0005
11	3	9	10	2	8	13040.7722	0.0030
10	6	5	9	6	4	12980.5440	-0.0002
10	4	7	9	3	6	13335.6279	0.0014
12	1	11	11	2	10	13287.8447	-0.0041
12	2	11	11	2	10	13287.9552	-0.0004
12	1	11	11	1	10	13288.2160	-0.0007
12	2	11	11	1	10	13288.3269	0.0033
13	0	13	12	1	12	13568.5211	0.0012
13	1	13	12	1	12	13568.5211	0.0009
13	0	13	12	0	12	13568.5211	0.0000
13	1	13	12	0	12	13568.5211	-0.0003
7	6	2	6	5	1	13907.3695	-0.0024
7	6	1	6	5	2	13915.7728	-0.0001
8	5	4	7	4	3	13925.0661	0.0000
10	5	5	9	5	4	13514.2689	-0.0030
10	4	6	9	4	5	13656.8496	-0.0021
11	4	8	10	4	7	13700.0514	-0.0012
11	3	8	10	3	7	13904.1832	-0.0021

11	4	8	10	3	7	14063.2327	0.0013
12	2	10	11	3	9	14023.6359	0.0022
12	3	10	11	3	9	14027.2247	-0.0012
12	2	10	11	2	9	14034.4684	0.0020
12	3	10	11	2	9	14038.0582	-0.0004
11	5	7	10	5	6	14177.0312	0.0002
13	1	12	12	2	11	14302.8788	-0.0022
13	2	12	12	2	11	14302.9068	-0.0046
13	1	12	12	1	11	14302.9817	-0.0061
13	2	12	12	1	11	14303.0122	-0.0060
11	7	5	10	7	4	14256.2751	-0.0030
8	5	3	7	4	4	14521.6317	-0.0012
11	6	6	10	6	5	14319.6627	-0.0017
9	5	5	8	4	4	14751.0905	-0.0015
7	7	1	6	6	0	14822.8989	0.0048
7	7	0	6	6	1	14823.0258	0.0045
14	0	14	13	1	13	14583.8047	0.0033
14	1	14	13	1	13	14583.8047	0.0032
14	0	14	13	0	13	14583.8047	0.0029
14	1	14	13	0	13	14583.8047	0.0028
12	3	9	11	4	8	14689.5769	-0.0008
12	4	9	11	4	8	14752.8438	-0.0007
11	6	5	10	6	4	14592.5027	-0.0033
11	4	7	10	4	6	14833.0469	0.0020
12	3	9	11	3	8	14848.6210	-0.0028
12	4	9	11	3	8	14911.8927	0.0020
8	6	3	7	5	2	15150.2324	-0.0007
8	4	4	7	3	5	14885.8772	-0.0003
8	6	2	7	5	3	15198.6238	-0.0009
13	2	11	12	3	10	15040.9585	-0.0004
13	2	11	12	2	10	15044.5530	0.0017
13	3	11	12	2	10	15045.7002	0.0013
10	5	6	9	4	5	15385.4174	-0.0052
11	5	6	10	5	5	15046.0991	0.0019
8	4	4	7	2	5	15335.4112	0.0032
12	5	8	11	5	7	15346.3259	-0.0025
15	0	15	14	0	14	15599.0409	0.0000
15	0	15	14	1	14	15599.0409	0.0001
15	1	15	14	0	14	15599.0409	0.0000
15	1	15	14	1	14	15599.0409	0.0001
12	6	7	11	6	6	15628.1182	-0.0029
8	7	1	7	6	2	16095.7944	0.0009
12	4	8	11	4	7	15844.6333	0.0019
13	4	10	12	4	9	15782.8168	0.0025

13	3	10	12	3	9	15822.5878	0.0033
13	4	10	12	3	9	15846.0794	-0.0017
12	7	5	11	7	4	15718.3724	0.0032
9	6	4	8	5	3	16324.1189	0.0019
9	5	4	8	4	5	16209.5654	0.0054
9	6	3	8	5	4	16517.8337	0.0004
15	1	14	14	2	13	16332.8482	0.0093
15	2	14	14	2	13	16332.8482	0.0069
15	1	14	14	1	13	16332.8482	0.0008
15	2	14	14	1	13	16332.8482	-0.0015
8	8	1	7	7	0	17005.2561	0.0004
8	8	0	7	7	1	17005.2696	-0.0060
16	0	16	15	0	15	16614.2342	0.0008
16	0	16	15	1	15	16614.2342	0.0009
16	1	16	15	0	15	16614.2342	0.0008
16	1	16	15	1	15	16614.2342	0.0009