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Supplementary Information

Remarkable effects of substitution on stability of complexes and origin of the C-H···O(N) hydrogen bonds formed between acetone's derivative and CO_2, XCN (X = F, Cl, Br)

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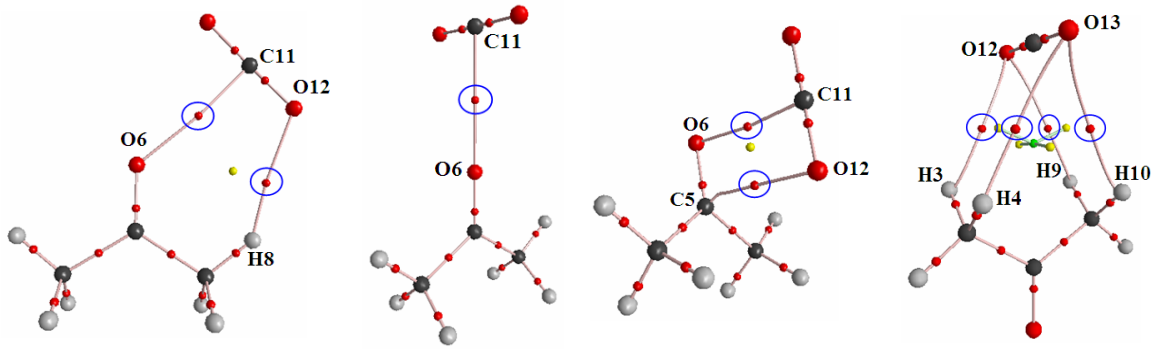
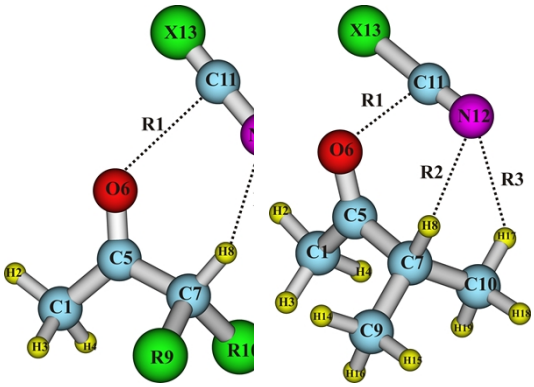


Figure S1. Topological geometries of four complexes **H1**, **H2**, **H3** and **H4**



$CH_3COCHR_2\cdots X$ CN **$CH_3COCH(CH_3)_2\cdots$ XCN**

Figure S2. The stable geometric structures of the complexes between CH_3COCHR_2 (R = F, Cl, Br) and XCN (F, Cl, Br)

Table S1. Electron density and Laplacian at BCPs in the $CH_3COCH_3\cdots CO_2$ complexes (all in electron)

	H1	**H2**	**H3**	**H4**
ρ(>O6···C11)	0.0093	0.0090	0.0084	
ρ(>O12···C5)			0.0081	
ρ(O12···H8)	0.0062			
ρ(O12···H3,9)				0.0041
ρ(O13···H4,10)				0.0041
∇^2(>O6···C11)	0.0384	0.0435	0.0314	
∇^2(>O12···C5)			0.0312	
∇^2(O12···H8)	0.0218			
∇^2 (O12···H3,9)				0.0150
∇^2 (O13···H4,10)				0.0150

Table S2. Electron density and Laplacian at BCP of O···H and >C=O···C intermolecular contacts in the $CH_3COCHR_2\cdots CO_2$ complexes (all in electron)

	$CH_3COCHR_2\cdots CO_2$				
R	H	CH_3	F	Cl	Br
ρ(>O6···C11)	0.0093	0.0098	0.0081	0.0085	0.0086
ρ(O12···H8)	0.0062	0.0054	0.0075	0.0095	0.0099
ρ(O12···H17)		0.0048			
∇^2(>O6···C11)	0.0384	0.0397	0.0332	0.0347	0.0350
∇^2(O12···H8)	0.0218	0.0196	0.0268	0.0342	0.0354
∇^2(O12···H17)		0.0176			

Table S3. An NBO analysis for the $CH_3COCHR_2\cdots CO_2$ complexes at MP2/6-311++G(2d,2p)

	$CH_3COCHR_2\cdots CO_2$				
R	EDT/e	Δσ*(C7-H8)/ e	Δ%s(C7)	E(n(O6)→ π*(C11=O12,13)), kJ.mol^{-1}	E(n(O12)→σ*(C7H8)), kJ.mol^{-1}
H	0.0014	0.0009	0.34	6.5	2.3
CH_3	0.0012	0.0004	0.12	6.4	1.0
		0.0001[a)]	0.19[b)]		0.6*
F	-0.0002	-0.0002	0.44	4.6	4.4
Cl	-0.0009	-0.0003	0.61	5.1	4.8
Br	-0.0012	-0.0002	0.66	5.1	5.2

[a)]for the C10-H17 bond and [b)]for the C10(H17) atom

Table S4. Electron density and Laplacian at BCP of O···H and >C=O···C intermolecular contacts in the $CH_3COCHR_2\cdots XCN$ complexes (all in electron)

			$CH_3COCHR_2\cdots FCN$		
R	H	CH_3	F	Cl	Br
ρ(>O6···C11)	0.0104	0.0109	0.0095	0.0100	0.0101
ρ(N12···H8)	0.0075	0.0060	0.0092	0.0119	0.0125
ρ(N12···H17)		0.0056			
∇^2(>O6···C11)	0.0410	0.0422	0.0358	0.0375	0.0379
∇^2(N12···H8)	0.0254	0.0200	0.0320	0.0413	0.0432
∇^2(N12···H17)		0.0188			
			$CH_3COCHR_2\cdots ClCN$		
ρ(>O6···C11)	0.0074	0.0075	0.0068	0.0072	0.0072
ρ(N12···H8)	0.0077	0.0063	0.0098	0.0128	0.0134
ρ(N12···H17)		0.0059			
∇^2(>O6···C11)	0.0297	0.0290	0.0253	0.0264	0.0265
∇^2(N12···H8)	0.0259	0.0210	0.0338	0.0443	0.0463
∇^2(N12···H17)		0.0197			
			$CH_3COCHR_2\cdots BrCN$		
ρ(>O6···C11)	0.0072	0.0073	0.0065	0.0068	0.0068
ρ(N12···H8)	0.0079	0.0066	0.0101	0.0132	0.0137
ρ(N12···H17)		0.0061			
∇^2(>O6···C11)	0.0264	0.0265	0.0235	0.0245	0.0245
∇^2(N12···H8)	0.0263	0.0218	0.0348	0.0456	0.0475
∇^2(N12···H17)		0.0202			

Table S5. An NBO analysis for all the complexes at MP2/6-311++G(2d,2p)

	$CH_3COCHR_2\cdots XCN$				
	EDT/e	Δσ*(C7-H8)/e	Δ%s(C7)	E(n(O6) →π*(C11=N12)), kJ.mol^{-1}	E(n(N12) →σ*(C7H8)), kJ.mol^{-1}
R = H, X = F	0.0021	0.0018	0.64	8.4 (1.6)	3.4
R = H, X = Cl	-0.0026	0.0022	0.68	3.5	3.5
R = H, X = Br	-0.0025	0.0021	0.63	3.3	3.7
R = CH_3, X = F	0.0022	0.0005	0.26	7.8 (1.5)	1.5
		0.0001[a)]	0.34[b)]		
R = CH_3, X = Cl	-0.0024	0.0006	0.31	3.3	1.7
		0.0002[a)]	0.31[b)]		
R = CH_3, X = Br	-0.0026	0.0006	0.33	3.0	2.1
		0.0002[a)]	0.31[b)]		
R = F, X = F	-0.0011	0.0003	0.86	6.4 (1.0)	7.4
R = F, X = Cl	-0.0048	0.0008	0.94	3.0	7.5
R = F, X = Br	-0.0050	0.0009	0.97	2.6	7.7
R = Cl, X = F	-0.0033	0.0007	1.23	6.9 (1.1)	11.0
R = Cl, X = Cl	-0.0077	0.0014	1.36	3.2	11.7
R = Cl, X = Br	-0.0081	0.0015	1.42	2.8	12.1
R = Br, X = F	-0.0039	0.0010	1.36	7.1 (1.1)	11.3
R = Br, X = Cl	-0.0082	0.0017	1.48	3.2	11.5
R = Br, X = Br	-0.0085	0.0019	1.53	2.7	11.8

Note: The values in brackets for intermolecular hyperconjugation interaction E(n(O6)→π(C11-F13), [a)]for the C10-H17 bond and [b)]for the C10(H17) atom*