Supplementary Information

Existence of Both Blue-Shifting Hydrogen Bond and Lewis Acid-Base Interaction in the Complexes of Carbonyls and Thiocarbonyls with Carbon Dioxide

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Table S5: NBO charge (in 10^{-3} electron) of O, S, X atoms of the XCHZ monomers at MP2/aug-cc-pVTZ

	CH_3CHO	HCHO	FCHO	ClCHO	BrCHO
q(O)	-495	-474	-481	-444	-440
q (X)			-351	-78	-37
	CH_3CHS	HCHS	FCHS	ClCHS	BrCHS
q(S)	-85	-109	-173	-156	-143
q (X)			-329	-31	-10

Table S6.1: Intermolecular hyperconjugation energy (E, in $kJ.mol^{-1}$) and the change of intramolecular hyperconjugation energy (ΔE, in $kJ.mol^{-1}$) at MP2/aug-cc-pVTZ

	$X=CH_3$, Z=O	X=H, Z=O	X=F, Z=O		X=Cl, Z=O		X=Br, Z=O	
	T1	**T1**	**T1**	**T2**	**T1**	**T2**	**T1**	**T2**
E(n(Z3,X4)→σ*(C6O7))	7.7	6.9	4.8	2.6	4.7	3.9	4.9	4.7
E(n(O5)→σ*(C1H2))	0.9	0.7	1.0	2.1	1.7	3.6	0.6	4.0
ΔE(n(O3,X4)→σ*(C1-H2))	-7.5	-7.0	-5.2	-5.4	-11.5	-13.3	-3.5	-5.5
	$X=CH_3$, Z=S	X=H, Z=S	X=F, Z=S		X=Cl, Z=S		X=Br, Z=S	
E(n(Z3,X4) →σ*(C6O7))	6.8	6.3	5.1	2.8	5.3	3.6	5.1	4.4
E(n(O5)->σ*(C1H2)	1.4	1.3	1.2	1.6	1.5	2.1	1.4	2.2
ΔE(n(S3,X4) →σ*(C1H2))	-7.1	-3.1	-8.2	-7.1	-8.2	-8.8	-10.2	-10.6

The n index denotes for lone pairs on the Z and X atoms; the delta (Δ) is symbolized for a change of the complex compared to the monomer.

Table S6.2: The change of occupation (all in 10^{-3} electron) in some lone pairs on some selected atoms for XCHZ···CO_2 at MP2/aug-cc-pVTZ

Parameter		Δn(Z3)	Δn(X4)	Δn(O5)	Δn(O7)
X=F, Z=O	T1	5	-2	24	-1
	T2	-2	5	21	-1
X=Cl, Z=O	T1	7	-5	23	-1
	T2	-5	5	21	-1
X=Br, Z=O	T1	8	-5	22	-1
	T2	-7	4	22	-1
X=H, Z=O	T1	1		21	-1
X=CH_3, Z=O	T1	1		20	-1
X=F, Z=S	T1	1	-2	18	-1
	T2	-3	5	17	-1
X=Cl, Z=S	T1	1	-5	17	-1
	T2	-3	4	16	-1
X=Br, Z=S	T1	1	-5	17	-1
	T2	-5	3	16	-1
X=H, Z=S	T1	3		15	-1
X=CH_3, Z=S	T1	3		15	-1

Cartesian coordinates of complexes at the MP2/aug-cc-pVTZ level

a. The complexes of FCHZ with CO_2 (Z = O, S)

		FCHO···CO_2				**FCHS···CO_2**		
		Cartesian coordinate				Cartesian coordinate		
	Atom	x	y	z	Atom	x	y	z
T1	C	-0.95122	-0.12555	0	C	1.44615	-0.41295	0
	H	-0.63094	-1.16725	0	H	0.85610	-1.32426	0
	O	-0.26601	0.84380	0	S	0.87938	1.08268	0
	F	-2.29388	-0.06343	0	F	2.74972	-0.70970	0
	O	1.97742	-1.23838	0	O	-1.63741	-1.35648	0
	C	2.49103	-0.18450	0	C	-2.20057	-0.32877	0
	O	3.02073	0.85610	0	O	-2.77902	0.68644	0
T2	C	1.72126	-0.30995	0	C	1.67588	-0.38688	0
	H	1.11398	-1.21453	0	H	1.04488	-1.27000	0
	O	2.90069	-0.20786	0	S	3.27116	-0.33641	0
	F	0.89831	0.76692	0	F	-1.51923	0.71212	0
	O	-1.45078	-1.16433	0	O	-1.51923	-1.10272	0
	C	-1.94076	-0.09954	0	C	-1.94609	-0.01135	0
	O	-2.43679	0.95789	0	O	-2.38014	1.07337	0

b. The complexes of ClCHZ with CO_2 (Z = O, S)

		ClCHO···CO_2				**ClCHS···CO_2**		
		Cartesian coordinate				Cartesian coordinate		
	Atom	x	y	z	Atom	x	y	z
T1	C	-0.95708	-0.12351	0	C	0.19078	1.01836	0
	H	-0.61604	-1.16096	0	H	1.13833	0.48990	0
	O	-0.26011	0.84419	0	S	-1.24128	0.28953	0
	Cl	-2.71770	-0.04931	0	Cl	0.43861	2.73056	0
	O	1.96597	-1.23701	0	O	1.42317	-1.96101	0
	C	2.48432	-0.18551	0	C	0.45980	-2.62829	0
	O	3.01845	0.85299	0	O	-0.48849	-3.31115	0
T2	C	1.76425	-0.26463	0	C	1.79398	-0.21836	0
	H	1.03261	-1.07473	0	H	1.08574	-1.03995	0
	O	2.94883	-0.35915	0	S	3.38970	-0.37711	0
	Cl	0.91267	1.29916	0	Cl	0.94048	1.29841	0
	O	-1.40746	-1.17063	0	O	-1.37999	-1.17427	0
	C	-2.04141	-0.18446	0	C	-2.01375	-0.18852	0
	O	-2.68165	0.79236	0	O	-2.65397	0.78899	0

c. The complexes of BrCHZ with CO_2 (Z = O, S)

		BrCHO···CO_2				**BrCHS···CO_2**		
		Cartesian coordinate				Cartesian coordinate		
	Atom	x	y	z	Atom	x	y	z
T1	C	0.10780	0.18908	0	C	0.05198	0.33004	0
	H	1.14712	-0.14863	0	H	1.02674	-0.14577	0
	O	-0.85815	-0.50877	0	S	-1.33861	-0.47306	0
	Br	0.02743	2.11045	0	Br	0.23465	2.20541	0
	O	1.23790	-2.71300	0	O	1.45646	-2.55420	0
	C	0.19186	-3.24235	0	C	0.53637	-3.28001	0
	O	-0.84141	-3.78655	0	O	-0.36757	-4.02061	0
T2	C	1.80509	-0.27854	0	C	1.80520	-0.22580	0
	H	1.04346	-1.06163	0	H	1.06479	-1.01838	0
	O	2.98463	-0.41276	0	S	3.39252	-0.44435	0
	Br	0.92983	1.45789	0	Br	0.92693	1.45470	0
	O	-1.35777	-1.15081	0	O	-1.37582	-1.15092	0
	C	-2.02226	-0.18467	0	C	-2.03972	-0.18509	0
	O	-2.69536	0.76961	0	O	-2.71200	0.77059	0

d. The complexes of HCHZ with CO_2 (Z = O, S)

		HCHO···CO_2				**HCHS···CO_2**		
		Cartesian coordinate				Cartesian coordinate		
	Atom	x	y	z	Atom	x	y	z
T1	C	-0.23551	2.12824	0	C	-0.28655	2.26478	0
	H	-1.25972	1.72946	0	H	-1.18435	1.65346	0
	O	0.73033	1.39160	0	S	1.18514	1.59898	0
	H	-0.12199	3.22169	0	H	-0.4226	3.34248	0
	O	-1.24183	-0.87868	0	O	-1.23018	-0.86185	0
	C	-0.15031	-1.30551	0	C	-0.20974	-1.43755	0
	O	0.92426	-1.76393	0	O	0.7935	-2.03744	0

e. The complexes of CH_3CHZ with CO_2 (Z = O, S)

		CH_3CHO···CO_2				**CH_3CHS···CO_2**		
		Cartesian coordinate				Cartesian coordinate		
	Atom	x	y	z	Atom	x	y	z
T1	C	1.47871	-0.17393	0	C	1.47634	-0.37829	0
	H	1.08856	-1.20662	0	H	0.84521	-1.26698	0
	O	0.70199	0.76351	0	S	0.764975	1.07763	0
	C	2.96782	-0.03234	0	C	2.94571	-0.62559	0
	O	-1.51787	-1.24966	0	O	-1.65559	-1.38128	0
	C	-1.94709	-0.15911	0	C	-2.23383	-0.36222	0
	O	-2.41357	0.91211	0	O	-2.83932	0.63765	0
	H	3.37640	-0.53743	0.87656	H	3.21637	-1.21975	0.87594
	H	3.37640	-0.53743	-0.87656	H	3.21637	-1.21975	-0.87594
	H	3.25517	3.25517	1.01488	H	3.50557	0.30565	