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THE ROLE OF SULFUR d-ORBITALS IN THE CHARGE-TRANSFER COMPLEXATION OF CARBONYL CYANIDE WITH ALKYL SULFIDES

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Abstract—Total interaction energies of carbonyl cyanide with methyl sulfide and methyl ether were calculated and the importance of the participation of sulfur d orbitals in charge transfer was emphasized.

We have studied the charge-transfer(CT) complexation of carbonyl cyanide with several sulfur and oxygen donors in the gaseous phase and observed that carbonyl cyanide forms rather strongly bound CT complexes with these donors, especially with alkyl sulfides.[1] It is found that the heat of complexation of ethyl sulfide and tetrahydrothiophene is 2–4 times larger than their oxygen homologs. In order to clarify the origin of the difference shown here, we carried out the intermolecular perturbation study on the interaction of carbonyl cyanide with methyl sulfide and methyl ether which are regarded as the representatives of alkyl sulfides and ethers, respectively.

Total interaction energy, E_{total}, due to mutual interaction is written as sum of five energy terms.[2]

$$E_{total} = E_Q + E_K + E_I + E_D + E_{CT} \qquad (1)$$

where E_Q, E_K, E_I, E_D, E_{CT} denote Coulombic, exchange-repulsion, inductive, dispersion and CT energies, respectively. In evaluating the various energies in eqn (1) numerically, we made use of the CNDO/2 wave functions and orbital energies for the interacting component. For methyl sulfide, both of those obtained with and without inclusion of the sulfur 3d orbitals were used according to sp and spd approximations of Santry and Segal (*sp* and *spd* hereafter).[3] Molecular geometries of the donors were obtained from the literature.[4] Geometry of carbonyl cyanide was assumed to be $\overline{CO} = 1.20$ Å, $\overline{CC} = 1.47$ Å, $\overline{CN} = 1.16$ Å, and $\sphericalangle CCC = 120°$. Spatial geometries of the interacting system considered are depicted in Fig. 1, in which the planes of donor and acceptor molecules are parallel to each other and are separated by the varying intermolecular distance $z = 2.6$–3.4 Å with sulfur or oxygen atom of the former located right above the carbonyl carbon atom of the latter molecule. The plausible value of $z = 3.0$ Å for carbonyl cyanide—n-type donor systems was estimated in Ref. 1. Syn and anti orientations of the donor relative to the acceptor were dealt with. All the calculations were performed on the FACOM Computer at the Kyoto University Computation Center.

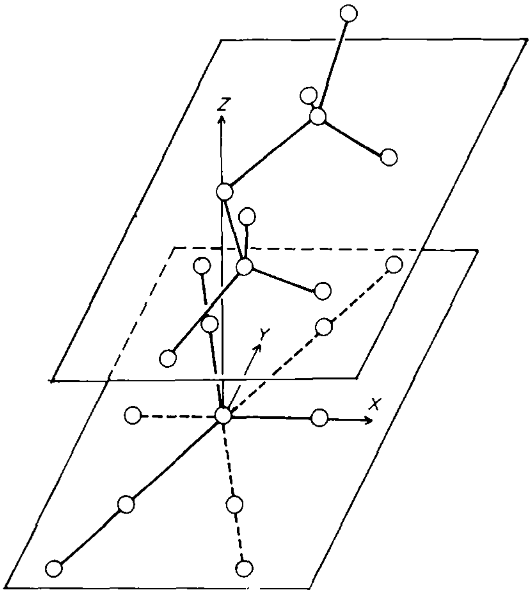

Fig. 1. Models chosen for the interacting system. The spatial arrangements of the acceptor relative to the donor are illustrated for syn (-----) and anti (———) models.

RESULTS AND DISCUSSION

Both the highest occupied(HO) orbitals of the donors and the lowest unoccupied(LU) one of the acceptors are found to be perpendicular to the molecular plane. Thus, our model permits the maximum overlap of these orbitals and is adequate for the present systems. It is noticed that the HO orbital of the acceptor and the second LU ones of donors have also the same orbital symmetry: parallel to the molecular plane and perpendicular to the molecular axis of carbonyl cyanide. It is possible that back-donation of the lone-pair electron of the acceptor onto the vacant orbitals of donor occurs when relative heights of these orbital energies are rather low. Importantly, the inclusion of the sulfur d orbitals in the basis set (*spd*) greatly lowers the vacant levels of methyl sulfide: for example, the LU orbital energy is lowered by 1.26 eV, thus facilitating the inter-orbital interaction mentioned above.

Total interaction energies were calculated and the results are shown in Fig. 2. It is observed that anti model always gives larger $|E_{total}|$ than the corresponding syn one does. The main source of the destabilization of the latter lies in the increasing E_K term. Anti model can thus be regarded as a useful approximation to the present system. In this model, it is seen that, as z decreases, methyl sulfide system in both *sp* and *spd* tends to be stabilized increasingly, whereas methyl ether system first to be stabilized, giving a shallow minimum at $z = 3.2$ Å, under

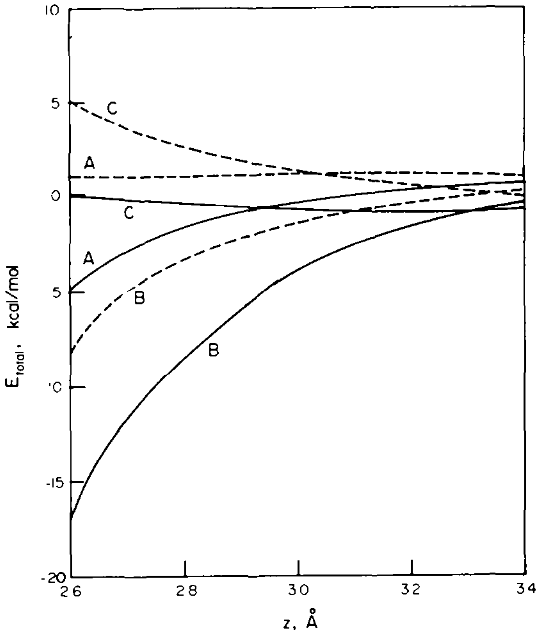

Fig. 2. Dependence of total interaction energies on the intermolecular distance for the donor and acceptor systems. ———, anti model; -----, syn model. A, methyl sulfide (*sp*); B, methyl sulfide (*spd*); C, methyl ether.

Table 1. Interaction energies for anti approaches of carbonyl cyanide toward methyl sulfide and methyl ether

z (Å)	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
			Methyl sulfide (sp)			
2.6	-9.011	15.820	-0.137	-1.751	-9.767	-4.846
2.8	-3.177	8.316	-0.074	-1.295	-5.369	-1.599
3.0	-1.632	4.228	-0.048	-0.972	-2.845	-1.269
3.2	0.505	2.087	-0.028	-0.737	-1.458	0.369
3.4	0.957	1.003	-0.019	-0.567	-0.725	0.649
			Methyl sulfide (spd)			
2.6	-9.286	15.874	-0.165	-1.917	-21.366	-16.860
2.8	-3.399	8.350	-0.092	-1.414	-11.577	-8.132
3.0	-1.816	4.247	-0.061	-1.058	-6.042	-4.730
3.2	0.348	2.096	-0.036	-0.801	-3.049	-1.442
3.4	0.833	1.008	-0.024	-0.615	-1.492	-0.290
			Methyl ether			
2.6	-4.929	10.948	-0.072	-1.911	-4.059	-0.023
2.8	-2.488	5.667	-0.048	-1.393	-2.099	-0.361
3.0	-1.321	2.871	-0.032	-1.030	-1.072	-0.584
3.2	-0.742	1.426	-0.022	-0.771	-0.542	-0.651
3.4	-0.452	0.696	-0.015	-0.585	-0.271	-0.627

* Energies given in units of kcal/mol.

Table 2. Contribution of donation and back-donation terms to charge-transfer energy in anti approach

	Methyl sulfide (sp)		Methyl sulfide (spd)		Methyl ether	
z (Å)	E^d_{CT}	E^{bd}_{CT}	E^d_{CT}	E^{bd}_{CT}	E^d_{CT}	E^{bd}_{CT}
2.6	-9.286	-0.481	-10.523	-10.843	-3.135	-0.924
2.8	-5.123	-0.246	-5.771	-5.806	-1.573	-0.526
3.0	-2.720	-0.125	-3.046	-2.996	-0.783	-0.289
3.2	-1.394	-0.064	-1.554	-1.495	-0.388	-0.154
3.4	-0.693	-0.032	-0.768	-0.724	-0.191	-0.080

* Energies given in units of kcal/mol.

which it slowly destabilized. The values of $|E_{total}|$ near z = 3.0 Å are not so large as the observed heat of complexation for both alkyl sulfide and alkyl ether systems. Such disagreement may be inevitable in the approximate treatment of the molecular interaction given here. However, several significant conclusions can be deduced from the present calculation.

The various types of energies in eqn (1) for anti model are summarized in Table 1. E_{total} obtained consists mostly of four energy terms: E_Q, E_K, E_D and E_{CT}. Among them, the main source of the stabilization is both E_Q and E_{CT}. Charge-transfer energies were further divided into two terms: E^d_{CT} and E^{bd}_{CT}, in Table 2, where the former means the charge-transfer energy due to the donation of donor electron to the acceptor and the latter, vice versa. It is found that the inclusion of sulfur d orbitals in the basis set importantly participates in E_{CT}, especially in back-donation term, resulting in the additional stabilization of the interacting system. Thus, it is proposed that the main source that sulfur donors always give larger heat of complexation than the corresponding oxygen homologs will be due to the back-donation of the lone-pair electron of carbonyl cyanide to the donor vacant orbitals whose energy levels are considerably lowered by the participation of sulfur d orbitals.

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