CHEMISTRY LETTERS, pp. 933-936, 1978. Published by the Chemical Society of Japan

CHARGE TRANSFER COMPLEXES OF THIAHETEROHELICENES WITH 7,7,8,8-TETRACYANOQUINODIMETHANE.
A NEWLY FASHIONED STERIC EFFECT

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The title effect in the charge transfer complexes of thiaheterohelicenes and tetracyanoquinodimethane was characterized by their spectroscopic and electrical properties.

It seemed intriguing to investigate how helicenes and heterohelicenes with their screw-like structures interact with π-acceptors in charge transfer (CT) complexes. Hitherto no CT complexes of this class of compounds as donors have been reported although 2-(2,4,5,7-tetranitro-9-fluorenylideneamino-oxy)propionic acid acts as a π-acceptor and has found utility in the optical resolution of helicenes[1] and heterohelicenes[2]. We wish to report here that the thiaheterohelicenes containing alternant thiophene nucleus (i.e. benzodithiophenes(I), trithia[5]heterohelicenes(II), and tetrathia[7]heterohelicene(III)) yield well-defined solid state CT complexes with 7,7,8,8-tetracyanoquinodimethane(TCNQ). Peculiar spectroscopic and electrical properties are observed which are thought to arise from the characteristic skeleton of the helicenes. Addition of hot acetonitrile solutions of Ia, Ib, IIa, IIb, and III (for the structures, refer to Figure 1) to a hot acetonitrile solution of TCNQ under nitrogen atmosphere, followed by cooling, all gave complexes[3] of crystalline black needles. The complexes contained donor and acceptor components in equimolar amount as determined by elemental analyses.

The absorption spectra of the complexes in benzene and in dichloromethane and also the diffuse reflection spectra of the complexes diluted with NaCl exhibited the CT absorption maxima ($\bar{\nu}_{CT}$) listed in Table 1. As the number of aromatic rings in the donors increased, the absorption maxima shifted to the lower wave numbers with both solution and solid. Thus, the ionization potentials (IP) of the donors decrease with number of aromatic rings[4]. Table 1 also contains the molecular extinction coefficients (ε_{CT}) and equilibrium constants (K_{CT}) of the complexes in dichloromethane, which were determined by applying the Benesi-Hildebrand equation[5] to the variation of CT absorbance as a function of the donor concentration.

Table 1

Spectroscopic Properties of Thiaheterohelicene-TCNQ (1:1) Complexes

Donor	Solution				Solid	IP of Donor[a]
	C_6H_6	CH_2Cl_2				
	$\bar{\nu}_{CT}$ kK	$\bar{\nu}_{CT}$ kK	$\log\varepsilon_{CT}$	K_{CT} mol^{-1}	$\bar{\nu}_{CT}$ kK	e.V.
Ia	17.9	17.8	3.08	4.7	18.9	8.18
IIa	15.1	14.9	2.91	15.8	15.6	7.80
III	†	13.7	2.86	11.9	14.3	7.64
Ib	17.5	17.4	3.02	6.6	18.0	8.04
IIb	-	14.5	3.33	6.2	14.5	7.70

[a] Calculated from the equation $h\bar{\nu}_{CT}=IP-C_1+[C_2/(IP-C_1)]$ where the values of constants, C_1 and C_2 were quoted from ref. 4.

† Maximum was not determined owing to a poor solubility of the complex.

Although usually the lower the IP of donor, the more easily it engages in CT complexation, the K_{CT} of III is smaller than that of IIa. This reverse ordering as regard the value of K_{CT} may be interpreted in terms of a steric effect arising from the helical configuration of the donors. Molecular models show that IIa and III have similar diameters (about 8.5 Å), but the latter has a wider pitch (Figure 1). The "intramolecular staggering" of III could prevent effective overlapping with the acceptor and reduce the stability of the complex. This appears to be a new type of steric effect on CT interaction.

This staggering effect was confirmed by the introduction of methyl group to Ia and IIa. Methyl derivative Ib, which retains molecular planarity, gives a lower IP and thus a larger K_{CT}. On the other hand, IIb, in which the methyl groups sterically impede planarity, displays a marked decrease in K_{CT} despite a lowering in IP. Clearly, the staggering effect is different from a simple bulk effect[6] which has been frequently observed in CT complexation in the past.

We further observed the higher wave number shifts of $\bar{\nu}_{CT}$(solid) compared with $\bar{\nu}_{CT}$(soln.). The higher shifts in the solid are probably due to (1) a delocalization of excited electron from a donor molecule, over some extent of crystal lattice[7] and (2) to an inadequate stacking of CT molecules upon crystallization, both leading to a decrease of coulombic energy in CT interaction. In the complexes with smaller K_{CT} values, the first effect may be predominant since there exists a larger amount of non-charge-transfered structure which may provide more places of accomodating the excited electron and hence afford its delocalization.

In the complexes with larger K_{CT} values, the second effect may be operative to cause still higher shifts. Thus, the staggering effect explains the higher shifts.

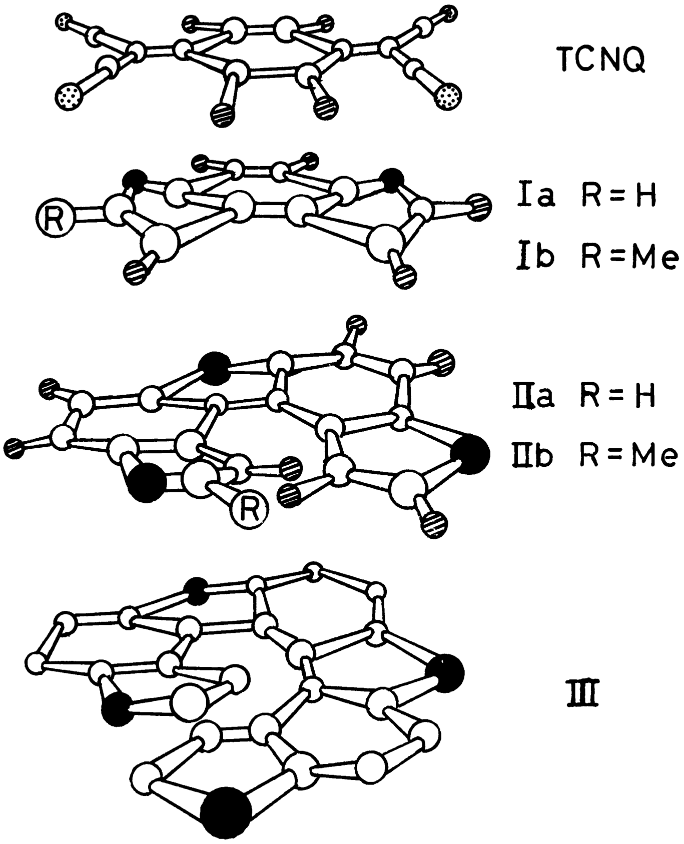

Figure 1
Perspective drawing of TCNQ and thiahetero-helicene molecules in approximately the same dimension, where ○ carbon, ◌ nitrogen, ● sulfur, and ◍ hydrogen. Hydrogens are omitted in III for clarity.

Table 2
Electrical Conductivity of Thiaheterohelicene-TCNQ (1:1) Complexes

Donor	Resistivity ρ_{15}, Ωcm	Activation Energy ΔE, e.V.
Ia	6.0×10^{12}	0.73
IIa	5.3×10^{11}	0.69
III	8.3×10^{7}	0.60
Ib	7.4×10^{10}	0.47
IIb	$4.9 \times 10^{10\dagger}$	0.45

† At 0°C,

Temperature dependences of d.c. electrical conductivity[8] of the complexes were measured along the needle axis of their single crystals with an ordinary two-probe method (Table 2). Note that the resistivity decreases as the number of rings in the donors increases, as if the staggering effect does not influence the conductivity. Indeed, large increase of resistivity by an introduction of a bulky substituent to a planar component in an ordinary CT complex has been often observed[9]. On the other hand, our staggering effect could be explained by the fact that the reduction in ΔE for the complexes with larger conjugation are not as large as expected from a well documented relation between $2\Delta E$ and $h\bar{\nu}_{CT}$ in planar aromatic donor and acceptor series[7]. Although a detailed interpretation on this point must await a further study, we believe that the staggering effect is unique and exists quite apart from an ordinary steric effect.

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education.

References and Notes

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3. Ia-TCNQ and IIa-TCNQ both give monoclinic crystals with the space group A2/m and Cc respectively. For the former a=6.912, b=13.311, c=10.769 Å, β=106.15°, and Z=2 and for the latter a=21.478, b=8.548, c=13.841 Å, β=114.86°, and Z=4. We owe the data to Professor Y. Saito, the University of Tokyo to whom our thanks are due.
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8. Good linear relationships between the logarithmic resistivity and the reciprocal of temperature were obtained in a range -70 to 50°C for all the specimens to give the activation energies described in the Table 2.
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(Received June 13, 1978)