An NMR Study on the Association Stabilities of Thiaheterohelicenes against 7,7,8,8-Tetracyanoquinodimethan. Effect of the Staggered Configuration of Helicene

Hisao Tanaka, Hiroko Nakagawa, Koh-ichi Yamada, and Hiroshi Kawazura*
Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama 350-02

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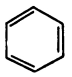
In order to evaluate the influence of the staggered configuration of helicene on complex formation, a ^{1}H NMR technique was applied to the complexing equilibria of thiaheterohelicene homologs with 7,7,8,8-tetracyanoquinodimethan (TCNQ). Formation constants of the complexes showed irregular changes in the case of [5] and [7]-thiaheterohelicenes in which the staggerings occur. This irregularity could be interpreted on the basis of the observed abnormal decrease of the bonding entropy. The reduced bonding entropy was understood in terms of the incomplete quenching of internal freedom, which was expected from the peculiar orientation of the staggered thiaheterohelicene towards planar TCNQ in the charge-transfer complex.

To understand the molecular staggering due to the helical shape of helicenes, it will be useful to examine the thermodynamic stability of their charge-transfer (CT) complexes with an appropriate π-acceptor. In a series of studies$^{1-3)}$ on thiaheterohelicenes with alternating thiophene and benzene rings, we have reported$^{1)}$ that the thiaheterohelicene molecules act as π-donors to give the 1 : 1 CT complexes with a strong π-acceptor, 7,7,8,8-tetracyanoquinodimethan (TCNQ). Formation constants of the complexes, determined preliminarily by a Benesi-Hildebrand (B-H) treatment$^{4)}$ on the CT-band intensities, were in the order of benzo[1,2-*b* : 4,3-*b*′]dithiophene (**3**)<[7]thiaheterohelicene (**5**)<[5]-thiaheterohelicene (**4**). This order was different from the ordinary trend in which formation constants in the complexes of cata-condensed aromatic donors increase with the number of aromatic rings. The reduced stability in the complex of [7]thiaheterohelicene has been considered to reflect its helical configuration, where two terminal thiophene rings are annularly overlapped.$^{5)}$ However, it was difficult to inquire further into the thermal stabilities of the complexes, because of a lower degree of the accuracy of the formation constants which were determined by the B-H method on the weak CT absorptions.

A Hanna-Ashbaugh (H-A) treatment$^{6)}$ on the ^{1}H NMR chemical shifts of interacting molecules was appropriate for the more exact determination of the formation constants and allowed us to estimate the enthalpy and entropy changes on complexation. This paper aims to clarify the steric effect caused by the staggering of helicene. The examination of thermodynamic parameters in the TCNQ complexes of thiaheterohelicene homologs: benzene (**1**), benzo[b]-thiophene (**2**), **3**, **4**, and **5** has led us to appreciate the importance of the entropy factor.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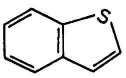
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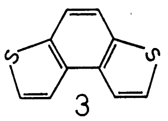
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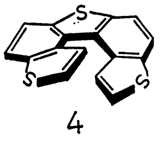
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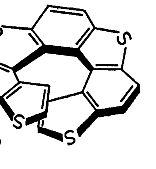
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Experimental

Materials. Benzo[1,2-*b*: 4,3-*b*′]dithiophene(**3**), [5]-thiaheterohelicene(**4**), and [7]thiaheterohelicene(**5**) were synthesized$^{3,7)}$ by photocyclization of the corresponding precursor olefins. Benzene-d_6 (**1**) and benzo[b]thiophene (**2**) were purchased from Merck Co. These compounds were purified as follows. **2** and **3** were column-chromatographed over alumina with hexane as an eluent, then sublimated under vacuum. **4** and **5** were also column-chromatographed over alumina with benzene, followed by recrystallization from benzene.

7,7,8,8-tetracyanoquinodimethan was purchased from Merck Co. and was purified by recrystallization three times from pure acetonitrile. 1,1,2,2-Tetrachloroethane-1,2-d_2 ($C_2D_2Cl_4$) used as an NMR solvent was of the spectroscopic grade (Merck; *Uvasol*).

Preparation and Measurement of NMR Samples. 1.77 mg of TCNQ crystals was dissolved in 3500 mm^3 of $C_2D_2Cl_4$ including a trace of tetramethylsilane (TMS). A 500 mm^3 portion of the solution was taken out with a micropipette (Gilson, Pipetman model P, ±0.5% in error), and was put into each of the six 2000 mm^3-sample tubes containing various amounts (3—40 mg) of thiaheterohelicene which were weighed to a precision of 10^{-3} mg by a microbalance. After complete dissolution, a 400 mm^3 portion from each solution was transfered into a 5 mm-diameter NMR tube.

The ^{1}H NMR spectra of six samples thus prepared and of one sample containing only the TCNQ solution originally prepared were successively measured at a fixed temperature, then similarly measured at other temperatures. The measurements were done in the Fourier transform mode on a JEOL PFT-100 spectrometer operating at 100 MHz with an internal deuterium lock. 4096 or 8192 data points were taken over a 1 kHz spectral width at a tilt angle of 45°, repeated at 2.2 or 4.5 s intervals. The accumulation and data reduction of the NMR spectrum were performed on an EC-100 computer attached to the spectrometer. The error in reading the peak position of TCNQ protons was judged to be ±0.3 Hz. The temperature of a given sample was regulated by a VT-3C variable temperature unit and was read from an Ohkura AM-1001 microvoltmeter connected to a copper-constantan thermocouple whose terminal was set in an NMR tube inside the probe. The temperature was constant within *ca.* 1 °C during each series of measurements.

Results

In the samples prepared, TCNQ was held at the low concentration of 2.5×10^{-3} mol/dm^3 to make sure that the amount of the thiaheterohelicene was in a large excess (10 to 100-fold excess to the amount of TCNQ),[8] which was requisite for an application of the H-A method. The ^{1}H NMR signal of TCNQ protons which was not hidden by the intense signals of thiaheterohelicene protons could be detected by 100—200 times of pattern accumulation. The observed signal moved noticeably to the up-field with an increase of the thiaheterohelicene concentration, as exemplified in the spectra of benzodithiophene (**3**)–TCNQ systems (Fig. 1). The net up-field shift $\Delta(=\delta_0-\delta)$, where δ and δ_0 are the chemical shifts of TCNQ protons in the complexing medium and in the uncomplexed state, respectively, was in close relation to the thiaheterohelicene concentration $[D]$, as shown by the fairly linear plots of Δ^{-1} *vs.* $[D]^{-1}$. This is seen in Figs. 2-A, B, and C for benzodithiophene (**3**)–TCNQ, [5]thiaheterohelicene (**4**)–TCNQ, and [7]thiaheterohelicene (**5**)–TCNQ systems, respectively. It is also seen from the figures that the intercepts of the plots at different temperatures show an excellent focussing.

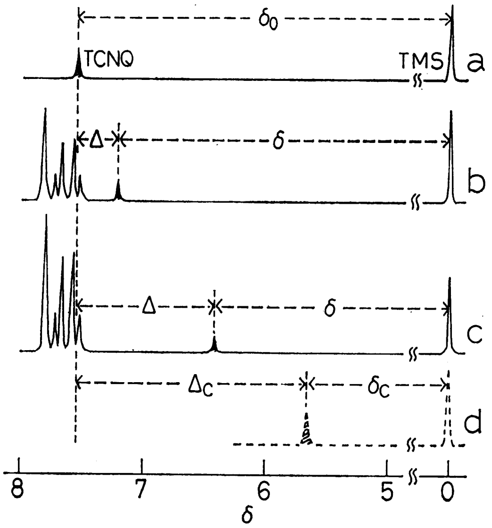

Fig. 1. ^{1}H NMR spectra of the complexing media of benzodithiophene(**3**)–TCNQ at 237 K and the definition of shifts, δ, δ_0, δ_c, Δ, and Δ_c. For $[A]=2.5\times10^{-3}$ mol/dm^3, a): $[D]=0$, b): $[D]=3.92\times10^{-2}$, c): $[D]=2.63\times10^{-1}$ mol/dm^3, d): extrapolated to $[D]=\infty$.

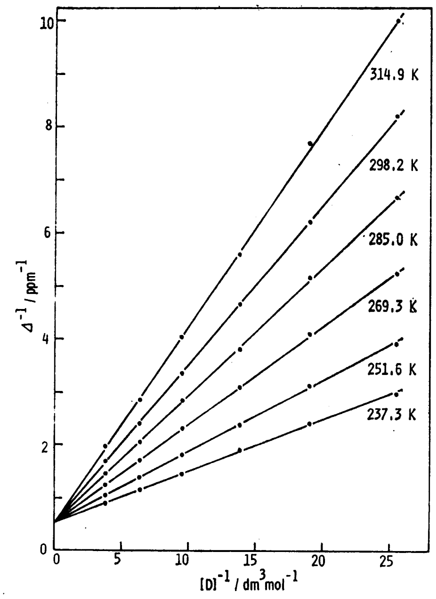

Fig. 2-A. Δ^{-1} *vs.* $[D]^{-1}$ plots for benzodithiophene(**3**)–TCNQ system; $[A]=2.5\times10^{-3}$ mol/dm^3 and $[D]=3.919\times10^{-2}$, 5.252×10^{-2}, 7.228×10^{-2}, 1.055×10^{-1}, 1.576×10^{-1}, and 2.627×10^{-1} mol/dm^3.

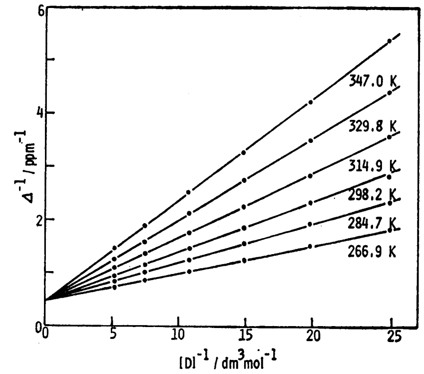

Fig. 2-B. Δ^{-1} *vs.* $[D]^{-1}$ plots for [5] thiaheterohelicene-(**4**)–TCNQ system; $[A]=2.5\times10^{-3}$ mol/dm^3 and $[D]=3.872\times10^{-2}$, 5.046×10^{-2}, 6.742×10^{-2}, 9.309×10^{-2}, 1.384×10^{-1}, and 1.945×10^{-1} mol/dm^3.

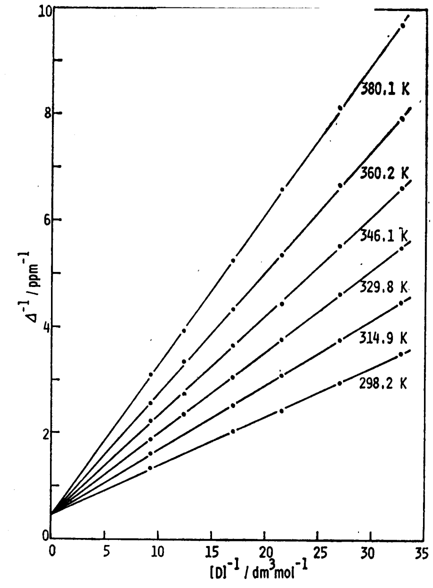

Fig. 2-C. Δ^{-1} *vs.* $[D]^{-1}$ plots for [7]thiaheterohelicene-(**5**)–TCNQ system; $[A]=2.5\times10^{-3}$ mol/dm^3 and $[D]=3.056\times10^{-2}$, 3.720×10^{-2}, 4.644×10^{-2}, 5.909×10^{-2}, 8.076×10^{-2}, and 1.085×10^{-1} mol/dm^3. The ^{1}H NMR signals of TCNQ for $[D]=8.076\times10^{-2}$ mol/dm^3 at 298.2 and 314.9 K were not observed because of overlapping with the donor signals.

Thus, the plots in Fig. 2 were analyzed by a least-squares method, using the H-A relation:[6]

Table 1. Shifts ($\varDelta_c$) and association constants (K) for the complexes at various temperatures(T)

Complex	T/K	$\varDelta_c{}^{a)}$/ppm	$K^{b)}$/dm^3 mol^{-1}	$SD(\times 10^2)$
1–TCNQ	224.5	1.71	0.177	3.2
	244.9	1.78	0.157	7.4
	264.8	1.62	0.150	10.3
2–TCNQ	227.7	1.77	0.831	3.0
	239.3	1.84	0.725	3.8
	249.7	1.79	0.637	2.9
	264.2	1.75	0.548	4.1
3–TCNQ	237.3	1.84	5.63	3.2
	251.6	1.88	3.96	3.1
	269.3	1.86	2.90	2.4
	285.0	1.86	2.23	4.2
	298.2	1.93	1.73	3.1
	314.9	1.97	1.36	6.5
4–TCNQ	266.9	2.21	8.48	0.6
	284.7	2.16	6.37	1.7
	298.2	2.07	5.28	3.1
	314.9	1.98	4.34	1.9
	329.8	2.07	3.18	1.7
	347.0	2.13	2.48	1.2
5–TCNQ	298.2	2.21	4.85	2.3
	314.9	2.19	3.72	2.0
	329.8	2.34	2.75	2.0
	346.1	2.31	2.29	4.4
	360.2	2.17	2.01	4.5
	380.1	2.27	1.55	4.0

a) The averaged probable error; 3.8% of $\varDelta_c$. b) 4.5% of K.

$$\varDelta^{-1} = (K\cdot\varDelta_c)^{-1}\cdot[D]^{-1} + \varDelta_c{}^{-1} \qquad (1)$$

$$K = [AD]/[A]\cdot[D] \quad (A+D=AD).$$

Here K is the formation constant for the molecular complex and $\varDelta_c(=\delta_0-\delta_c)$ the $\varDelta$ in the pure complex (Fig. 1). Table 1 lists the K and $\varDelta_c$ values, together with the standard deviations (SD) of the least-squares calculations, for the TCNQ complexes of **1**—**5** at various temperatures. Those values for benzene-d_6 (**1**)–TCNQ and benzothiophene (**2**)–TCNQ systems were determined only at lower temperatures owing to the smaller up-field shifts of TCNQ protons.

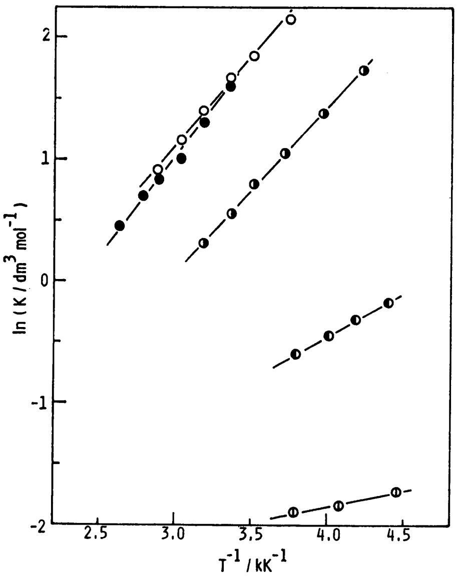

Fig. 3. Plots of ln K vs. T^{-1}. (⦶): **1**-TCNQ, (◐): **2**-TCNQ, (◑): **3**-TCNQ, (○): **4**-TCNQ, (●): **5**-TCNQ.

Table 2. The enthalpy(ΔH) and entropy change(ΔS) in the complex formation

Complex	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
1–TCNQ	-2.0 ± 0.8	-23.5 ± 3.2
2–TCNQ	-5.7 ± 0.5	-26.7 ± 2.0
3–TCNQ	-11.2 ± 0.2	-33.1 ± 0.6
4–TCNQ	-11.7 ± 0.5	-25.7 ± 1.6
5–TCNQ	-13.0 ± 0.4	-30.5 ± 1.0

Figure 3 shows the plots of ln K to T^{-1}. The enthalpy (ΔH) and entropy changes (ΔS) collected in Table 2 were determined from the least-squares fitting of the plots to the van't Hoff equation:

$$\ln K = -(\Delta H/R)\cdot T^{-1} + \Delta S/R. \qquad (2)$$

Discussion

$\varDelta_c$ and K for the 1 : 1 Complex. The nice fit of the plots of $\varDelta^{-1}$ vs. $[D]^{-1}$ to the H-A Eq. 1, which is judged from the small SD's in Table 1, allows us to assume[6,9] that only the 1 : 1 molecular complex is formed in the donor-acceptor equilibrium in the concentration range used for the present study. Table 1 also indicates that the intrinsic shifts $\varDelta_c$'s for the 1 : 1 complex scatter independently of temperature and fall into a small range and that the averages are ordered as follows: 1.70 (**1**-TCNQ) $<$ 1.79 (**2**-TCNQ) $<$ 1.89 (**3**-TCNQ) $<$ 2.12 (**4**-TCNQ) $<$ 2.25 ppm (**5**-TCNQ). This ordering may be understood on the basis of the idea[10] that the shift $\varDelta_c$ of TCNQ molecule facing the donor molecule is induced by the long range shielding due to the ring current which is accumulated with an increase of the number of rings of the donor. Thus, the parameter $\varDelta_c$ exhibits a natural profile of the cata-condensed aromatic donors; however, it does not give a direct indication of the staggered configuration characteristic of helicenes.

On the other hand, an anomaly is observed for the association constants in the complex series: K's in $C_2D_2Cl_4$ at 25 °C are in the order of 0.13 (**1**-TCNQ) $<$ 0.41 (**2**-TCNQ) $<$ 1.73 (**3**-TCNQ) $<$ 4.85 (**5**-TCNQ) $<$ 5.28 dm^3/mol (**4**-TCNQ), where the values for **1**-TCNQ[11] and **2**-TCNQ are obtained by extrapolating the van't Hoff plots in Fig. 3 to 298.2 K. We can note again a reduction of the K in **5**-TCNQ like that preliminarily found[1] from the B-H treatment of the CH_2Cl_2 solution. Interestingly, a similar result was also obtained[12] from a high performance liquid chromatography (HPLC) with a column of silica gel bonded with a strong π-acceptor, 2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid (TAPA). The elution order of the donors was **1**, **2**, **3**, **5**, and **4** giving the inversion of **4** to **5**, contrary to the absence of inversion in the case which used a column of silica gel only. Evidently, the CT interaction between donor molecule

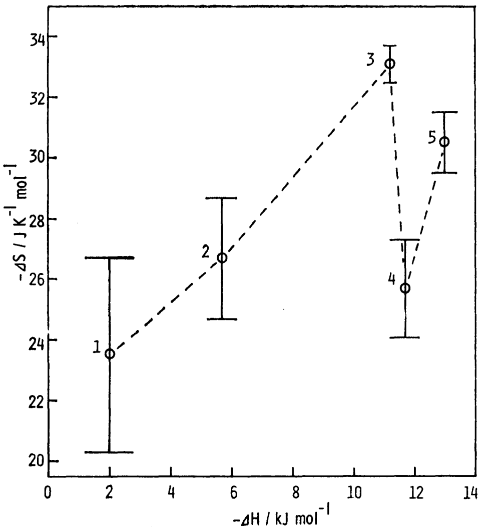

Fig. 4. Plots of $-\Delta S$ *vs.* $-\Delta H$. 1): **1**-TCNQ, 2): **2**-TCNQ, 3): **3**-TCNQ, 4): **4**-TCNQ, 5): **5**-TCNQ.

and fluorenylidene moiety of TAPA may produce this inversion. The inverse order is independent of solvent, detection method, or aromatic acceptor used, and so must be related to the inherently helical configuration of the donor.

ΔH and ΔS in the Complexation. Figure 4 shows the plots of $-\Delta H$ and $-\Delta S$ in the complex series. The enthalpy changes $-\Delta H$'s, *i.e.* bonding energies, tend to increase in the order of **1**, **2**, **3**, **4**, and **5**, although the increments among **3**, **4**, and **5** are smaller than those among **1**, **2**, and **3**. The above order may be interpreted in terms of the electron-donative abilities of the donors, which increase with ring accumulation. In fact, their ionization potentials[1)] decrease in the same order as the above. As a result, the enthalpy changes suggest the effect of the staggering of **4** and **5**, but fail to explain the inversion in the K values.

The behavior of the entropy changes $-\Delta S$'s, *i.e.* degrees of bonding restriction, as seen in Fig. 4, is extraordinary: the $-\Delta S$ value reduces abruptly in the complex of **4** and still does not recover, in the complex of **5**, to the value in the complex of **3**. The inversion in the K values corresponds to the abnormal decrease of the $-\Delta S$.

It is known[13)] that an increase of bonding energy causes an increase of bonding entropy in consequence of the stronger restriction between complexing species. This correlation may be valid in the case of absence of sterical hindrance, as demonstrated[13)] in the iodine–alkylbenzene series. Indeed, the relation of the $-\Delta H$ and $-\Delta S$ among the complexes of planar molecules **1**, **2**, and **3** seems to follow the above general criterion. The abnormal decrease of the bonding entropy $-\Delta S$ in the complex of **4** should be a most direct proof for the existence of the sterical hindrance within the complex and certainly corresponds to the appearance of the staggered configuration in **4**, as revealed[2)] by our X-ray structural analysis on the **4**-TCNQ complex. The change from **4** to **5** in Fig. 4 can be explained by the same criterion as in the case of **1**—**3**. This line of reasoning leads us to infer that a contribution of the staggering effect to the $-\Delta S$ approaches a limit against the ring accumulation, in so far as helicene and TCNQ molecules face each other.

Finally, we wish to comment on the decrease of bonding entropy, *i.e.* the gain of additional freedom, brought about by the staggering: the present complexes may be divided into two types with respect to the orientation manner of the donors towards planar TCNQ. In the complexes of planar **1**—**3**, the aromatic planes of donor and TCNQ molecules orient nearly parallel. But in the complexes of staggered **4** and **5**, both planes are much inclined[2)] to each other. Hence the intensity distribution in the bonding interaction between aromatic planes is far from uniform. Thus, in the latter case, a possible displacement at the weakly interacting locus where both planes are widely separated may not change so steeply the total stabilization energy. This is a possible explanation for the existence of the additional freedom in the complexes of **4** and **5**, though the details must await an energy calculation of the complex system.

Here it should be noted that the staggering effect was visualized by looking not at the helicenes themselves, but at their molecular complexes. The influence of the staggering on the intramolecular properties; ionization potentials, transition energies,[14)] and even spin densities of the radical anions[15)] is not so easy to detect.

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8) Only in **1**-TCNQ and **2**-TCNQ systems, TCNQ was held at 5.0×10^{-3} mol/dm^3 and the donor was in 40 to 350-fold excess to the amount of TCNQ.

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10) R. Foster, "Organic Charge-transfer Complexes," Academic Press, London and New York (1969), pp. 115—118. ^{1}H NMR signals of the donor also shifted to the up-field. This means that the partial charges induced by a CT interaction do not significantly contribute to the Δ_c.

11) The K for the benzene-TCNQ complex has been reported as 0.06 dm^3/mol in dioxane at 310 K (Ref. 6).

12) The HPLC experiments were performed according to the procedure of Mikes; see F. Mikes and G. Boshart, *J. Chromatogr.*, **149**, 455 (1978).

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