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CHARGE-TRANSFER COMPLEXATION WITH A NEW CLASS OF ELECTRON ACCEPTORS MADE OF TRIPTYCENEQUINONE UNIT

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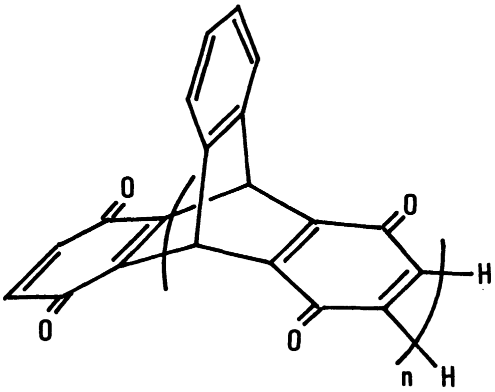
The charge-transfer complex formation has been examined in CH_2Cl_2 solution with 9,10-(o-benzeno)anthracene-1,4,5,8-tetraone and 5,18:7,16:9,14-tri-(o-benzeno)heptacene-1,4,6,8,10,13,15,17-octaone derivatives as electron acceptors. The high formation constants and the relevant thermodynamic parameters were obtained for the 1:2 quinone-TTF complexes.

In previous papers, we have shown that there is an interesting transannular interaction between the benzoquinone rings incorporated in a molecular framework of triptycene.$^{2)}$ The electrochemical reduction potential of the benzoquinone unit is lowered and the trapped electron is found to be rapidly jumping from the one site to the other in the mono- and trianion radicals of triptycenebisquinone $\underset{\sim}{\mathrm{I}}(n = 1)$.$^{3)}$ These results encouraged us to design a series of more extended systems which were expected to show the higher electron affinity and therefore serve as a novel electron acceptor. In line with these ideas, we prepared a series of polyquinones $\underset{\sim}{\mathrm{I}}$ incorporated into the polybenzenopolyacene skeleton.$^{4)}$ In this paper, we would like to report a striking acceptor property of some representative quinones of the series.



$\underset{\sim}{\mathrm{I}}(n = 1,2,3...)$

Bisquinone $\underset{\sim}{\mathrm{I}}(n = 1)$ forms with electron donors the corresponding charge-transfer complexes as revealed by the appearance of charge-transfer (CT) absorptions in the visible/uv regions.$^{5)}$ For example, N,N-dimethylaniline shows with $\underset{\sim}{\mathrm{I}}(n = 1)$ a CT absorption maximum at 555 nm in CH_2Cl_2 in reference to $\lambda_{max} = 513$ nm of the complex of the same amine with benzoquinone in $CHCl_3$.$^{6)}$ The CT absorption maximum with DABCO appears at 520 (in CH_2Cl_2) or 517 nm (in CH_3CN).

When $\underset{\sim}{\mathrm{I}}(n = 1)(C_A^\circ = 6.0 \times 10^{-3}$ M) and 2-(1,3-dithiol-2-ylidene)-1,3-dithiole (TTF)($C_D^\circ = 0.02$ M) in CH_2Cl_2 were mixed, absorptions having maxima at 554 (strong) and 760 nm (weak) appeared. Absorbance at ca. 434 nm increased at the same time, suggesting the formation of $TTF^{+\cdot}$ ($\lambda_{max}(\varepsilon)$, 435 nm(56,000) and 575 nm(16,000) in H_2O).7) The red solution showed a broad ESR signal (ca. 1 G wide and characteristic of electron transfer between $TTF^{+\cdot}$ and TTF present in excess).7)

The donor-acceptor equilibrium was studied by the method of Benesi-Hildebrand and some modification thereof.8) Thus the absorbance (A_{CT}) due to the complex at 760 nm of a series of solutions with constant C_A° (= 1.05×10^{-3} M) and varying C_D° (= 0.052 ~ 0.150 M) in CH_2Cl_2 was measured. The Rose-Drago plot of K^{-1} vs. ε_{CT} thus derived did not give a clear intersection point for a 1:1 CT complex. Only when the 1:2 quinone-TTF complex formation was assumed;

$$A + 2D \overset{K}{\rightleftharpoons} D_2A \quad (1), \qquad \frac{C_A^\circ C_D^{\circ 2}}{A_{CT}} = \frac{1}{K\varepsilon_{CT}} + \frac{C_D^\circ(C_D^\circ + 4C_A^\circ)}{\varepsilon_{CT}} \quad (2)$$

sets of lines with very close intersection points were obtained. The formation constants and molar absorptivities for the **I**(n = 1)-TTF complex at several temperatures are collected in Table 1. The van't Hoff plots corresponding to these values are satisfactorily linear and the thermodynamic constants for the complexation are given in Table 2.

Similarly, when a solution of **I**(n = 3)(C_A° = 4.45×10^{-3} M) was mixed with TTF (C_D° = 0.018 M) in CH_2Cl_2, an increase of the absorbance at 456 nm and an appearance of new bands at 543 and 774 nm were observed as shown in Figure 1. The band at 543 nm disappeared gradually on raising the TTF concentration. In the donor concentration range, C_D° = 0.04 ~ 0.1 M with constant C_A° (= 4.45×10^{-4} M), the absorbance (A_{CT}) at 774 nm followed Eq. 2 (see Figure 2). The Rose-Drago intersection plot was consistent with 1:2 stoichiometry of the **I**(n = 3)-TTF complex as shown in Figure 3. From the determination of the formation constants at several temperatures (see Table 1), the enthalpies and entropies of formation of the CT complex were obtained (Table 2).

At higher TTF concentrations, C_D°> 0.1 M, the observed absorbance did not follow Eq. 2 and the Rose-Drago intersection plot was better analyzed in terms of 1:3 and even 1:4 stoichiometry.

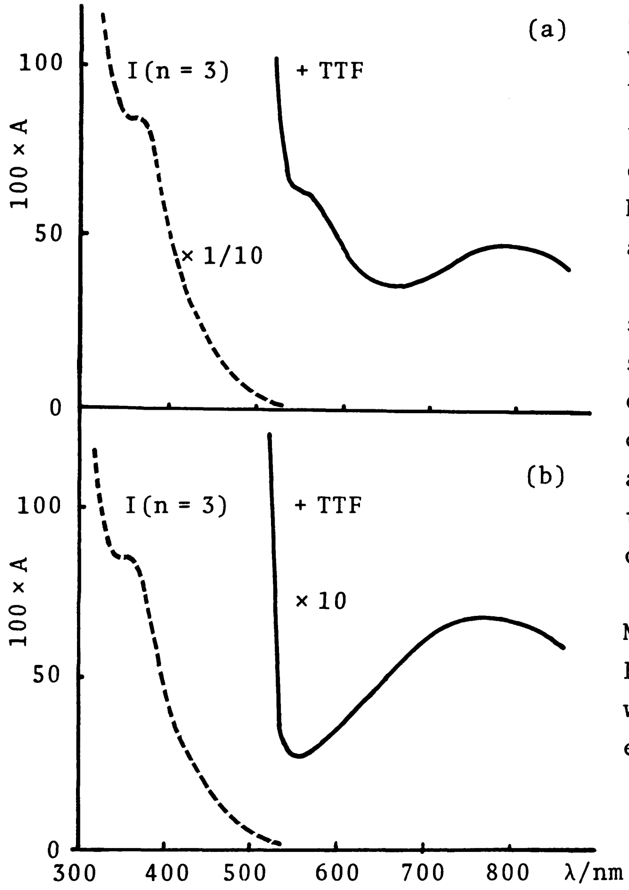


Figure 1. Absorption spectra of **I**(n = 3) with (———) and without (— — —) added TTF. (a) $C_A^\circ = 4.45 \times 10^{-3}$, $C_D^\circ = 1.8 \times 10^{-2}$ M. (b) $C_A^\circ = 4.45 \times 10^{-4}$, $C_D^\circ = 8.0 \times 10^{-2}$ M.

Table 1. Formation constants (K) and molar absorptivities (ε_{CT}) for 1:2 I(n = 1)-TTF and I(n = 3)-TTF complexes at different temperatures[5)]

	I(n = 1)·2TTF			I(n = 3)·2TTF	
T/K	$K/l^2\cdot mol^{-2}$	$\varepsilon_{CT}/l\cdot mol^{-1}cm^{-1}$	T/K	$K/l^2\cdot mol^{-2}$	$\varepsilon_{CT}/l\cdot mol^{-1}cm^{-1}$
284.7	170 ± 1.5	80 ± 6	293.2	367 ± 0.8	227 ± 5
292.6	110 ± 1.0	91 ± 2	297.3	294 ± 1.2	238 ± 4
296.9	88 ± 0.8	90 ± 2	313.8	110 ± 2.5	313 ± 10
304.7	59.5 ± 0.9	105 ± 4			
311.5	43.0 ± 1.6	110 ± 8			

Table 2. Thermodynamic constants for 1:2 I(n = 1)-TTF and I(n = 3)-TTF complexes in CH_2Cl_2

	λ_{CT}/nm	$-\Delta H$/kJ mol^{-1}	$-\Delta S$/J deg^{-1} mol^{-1}	$-\Delta G$/kJ mol^{-1} a)
I(n = 1)·2TTF	760	37.7 ± 0.4	90.0 ± 1.5	10.4 ± 0.1
I(n = 3)·2TTF	774	45.1 ± 2.0	104.6 ± 6.5	13.5 ± 0.6

a) at 303 K

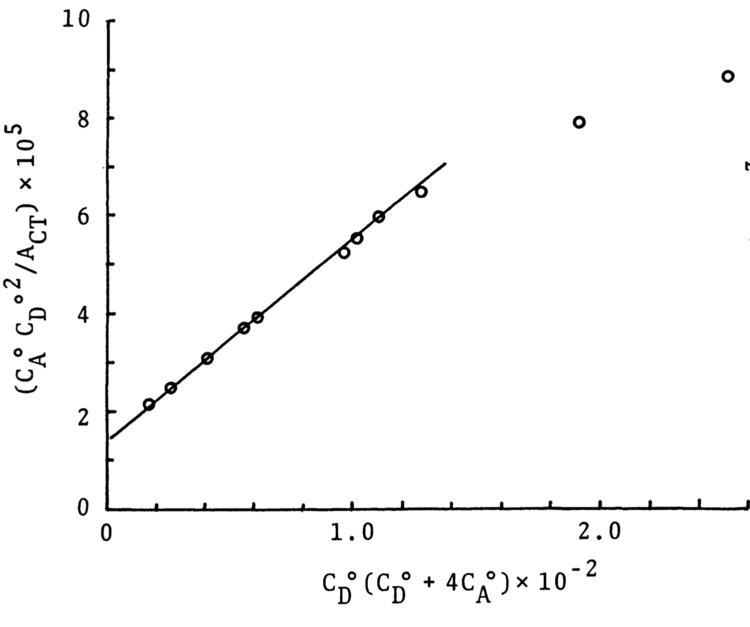


Figure 2. The Rose-Drago plots for 1:2 I(n = 3)-TTF complex in CH_2Cl_2 at 297.3 K.

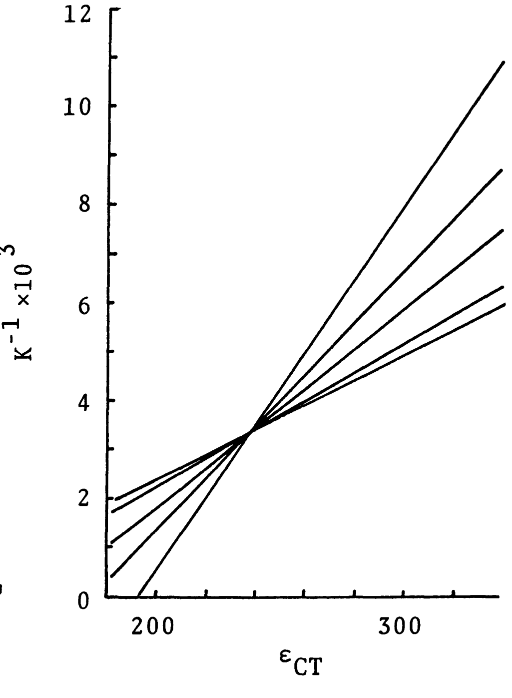


Figure 3. The Rose-Drago intersection for the 1:2 I(n = 3)-TTF complex in CH_2Cl_2 at 297.3 K.

TTF is reported to form CT complexes with p-benzoquinone (λ_{max}^{CT} = 660 nm), chloro-p-benzoquinone (755 nm) and 2,5-dibromo-p-benzoquinone (905 nm) in benzene.$^{9)}$ When compared with these λ_{max} data, polyquinones I are considered to be excellent electron acceptors that do not contain an additional electronegative substituent. The electrochemical half-wave potential suggests that the electron affinity of I(n = 1) may be comparable to that of dichloro-p-benzoquinones.$^{2)}$ Stronger acceptor properties (larger $-\Delta H$ value and longer λ_{CT} wave length) correspond to tighter complex formation (more negative ΔS) for I(n = 3) than I(n = 1).

The structure of complex I(n = 3)·2TTF seems to be of great interest, although it has not yet been obtained as single crystals and structural analyses have not been performed. For one thing, the molecular cavity of the tetraquinone may be serving as an inclusion site for the donor molecules. Secondly, good donor-acceptor orbital overlap may not necessarily be provided in these CT complexes because of steric reasons. In these cases, there is a chance of the electron donors having a segregated stack which is one of the prerequisites for highly conducting organic materials.

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5) Measured on a Hitachi 340 Recording Spectrophotometer equipped with a keyboard attachment. A temperature-regulated cell-holder was used to maintain the constant temperature of 1 cm quartz cells.
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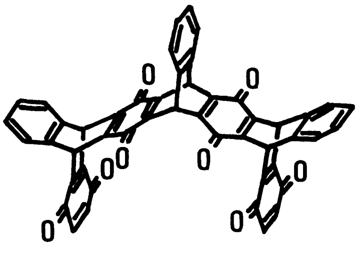

endo-I(n = 3)

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