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CHARGE-TRANSFER ABSORPTION SPECTRA BETWEEN TETRACYCLO[3.2.0.0^{2,7}.0^{4,6}]HEPTANE AND π-TYPE ELECTRON ACCEPTORS

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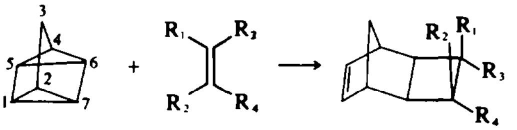
Abstract—Charge-transfer transition energies, association constants, and molar extinction coefficients of complexes between tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane(quadricyclane) and olefine type or quinone type acceptors were measured in methylene chloride at 20°. An excellent linear relationship ($r = 0{\cdot}9938$) with a slope of 0·96 was observed in plots of ν_{max}(CT) for a series of complexes of quadricyclane against ν_{max}(CT) for the corresponding complexes of N,N-dimethyl-aniline, indicating that quadricyclane forms electron donor-acceptor complexes of weak interactions. The first ionization potential, estimated from the hyperbolic relationship between the charge-transfer transition energy (E_{CT}) and the ionization potential, was an exceptionally low value (8·28–8·32 eV) for a saturated hydrocarbon and was indeed in the same order of magnitude with that of norbornadiene, which was well reproduced by EHM and MINDO/1 calculations applying Koopmans' theorem to the calculated HOMO energy.

INTRODUCTION

Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane or quadricyclane (hereafter abbreviated as QC) showed an unusual reactivity toward dienophiles, as was shown by Smith,[1] Prinzbach *et al.*,[2] Rieber *et al.*[3] and the authors.[4] The regio- and stereo-specificity of the cycloaddition (Eqn 1) observed by the authors[4] suggested that the mechanism was concerted, and, therefore, suggested an existence of an unusually effective interaction between two cyclopropane rings in a QC molecule; the major contribution to which was presumed to be the interaction between C_1–C_7 and C_5–C_6 bonds. The considerable theoretical interest in the assumed conjugative interaction of the cyclopropane rings naturally gives rise to questions of the molecular geometry and the ionization potential of QC; the latter is one of the important factor governing the CT interactions.



(1)

The molecular geometry was determined by the gas phase electron diffraction study[5] where the equilibrium geometry in the ground electronic state of QC was depicted as follows, bond lengths[†] were: C_1–C_2, 1·512 (1·503); C_1–C_5, 1·569 (1·562); C_1–C_7, 1·517 (1·518); C_2–C_3, 1·537 (1·560) Å and QC holded C_{2v} symmetry. That the bond lengths in the cyclopropane rings of QC were found to be normal[6] implied negligible or weak conjugative interaction between cyclopropanes was observable in the ground electronic state of QC; the criterion was in accord with the normal total ring strain of QC in which the approximate additivity was still found to hold.[‡]

In most of the works on CT absorption spectra of saturated hydrocarbons (σ-type donors), the use of acceptors has been restricted to σ-type ones such as halogens.[7] The investigations of the CT spectra of the (σ, π) type complexes between saturated hydrocarbons and π-type acceptors have been restricted by the experimental difficulties often encountered in the separation of the weak absorption spectra of the complexes from the strong absorptions of the uncomplexed species. And the experimental difficulties are related to (a) the high ionization potentials of the donors, (b) the quite small equilibrium constants for the formations of the EDA complexes, and/or (c) the absence of ideally rigid configurations in the EDA complexes. Recently Smith reported that QC formed a colored complex (315 nm, ϵ 1000) with maleic anhydride in cyclohexane,[1] but since then there appeared no detailed study involving CT spectra with various π-type acceptors or equilibrium constants in formations of EDA complexes.

In this article the authors report the CT spectra of QC with several olefine type or quinone type acceptors giving some new insights into "normal"[§] EDA complexes of a (σ, π) type. We also report the facile electron donation of QC to the acceptors in the EDA complexes and the assumed conjugative interaction of cyclopropane rings in QC molecule especially in the strongly or moderately perturbed state.

EXPERIMENTAL

Hitachi EPS-3T recording spectrometer and Hitachi Perkin-Elmer 139 spectrometer were used for the measurements of the electronic spectra at 20°. The light-path length of the cell was 0·10 mm for the measurements of three anhydrides and 10·0 mm for four quinones.

Materials. The preparation and usual purification of quadricyc-

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[†] The bond distances determined by the least square analysis on the assumption that the C_1–C_2 distance is equal to the bond length in cyclopropane (1·512 Å). In parentheses are the result on the assumption that the C_2–C_3 distance equals the C_1–C_7 distance of norbornane (1·560 Å) (see Ref 5).

[‡] 18·2 (norbornane) + 2 × 27·6 (cyclopropane) + 26·4 (cyclobutane) = 99·8 kcal/mol. Expl. 95 kcal/mol Ref. 23).

[§] As mentioned in Results and Discussion, plots of ν_{max} (CT) for a series of complexes of QC vs ν_{max}(CT) for the corresponding complexes of N,N-dimethylaniline was found to be linear with a gradient of unity.

lane (QC) was reported in our previous paper.[4] QC for the spectroscopic measurements was purified through repeated fractional distillations and was obtained QC of more than 99·9% purity. Suspected impurities in the sample were norbornadiene, acetophenone (a sensitizer in the photo isomerization of norbornadiene to QC), or iso-pentane (solvent).

But independent experiments demonstrated that the CT spectra observed were not appreciably affected by these impurities. Norbornadiene, the major impurity, and the acceptors investigated formed EDA complexes, the CT absorption maxima of which appeared at shorter wave lengths than those of QC. Although the average Kϵ value of these CT absorptions was 50, the absorbance due to norbornadiene (less than 0·1% in the QC sample) at the absorption maxima of the CT bands of QC was negligible (less than 0·2% of the absorbance of the CT band of QC).

Maleic anhydride was recrystallized from chloroform and sublimed *in vacuo*: m.p. 52·0–52·5° (lit. 52·8°). Chloranil was purified by recrystallization from chloroform: m.p. 292–292·5° (lit.[8] 289–290°). Benzoquinone was recrystallized from light petroleum: m.p. 113·8° (lit.[9] 112·5–113·5°, 112·7°, 114·5°, 115–116°). Dichloromaleic anhydride was purified by successive sublimations *in vacuo*: m.p. 122–123° (lit.[10] 120°). 2,5-dichlorobenzoquinone was recrystallized from chloroform: m.p. 162–163° (lit.[11] 161°). Chloromaleic anhydride was purified by distilation.

The concentration of the acceptor: chloranil, $1{\cdot}261 \times 10^{-3}$ M; 2,5-dichloro-*p*-benzoquinone, $3{\cdot}390 \times 10^{-3}$ M; benzoquinone, $3{\cdot}377 \times 10^{-3}$ M; dichloromaleic anhydride, 0·4025 M; chloromaleic anhydride, 0·504 M; maleic anhydride, 0·4975 M. The mole fraction of the donor (quadricyclane) was varied from 0·0439 to 0·4077. Commercially available methylene chloride of spectrograde was used as a solvent without further purification.

RESULTS AND DISCUSSION

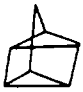
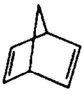
CT absorption spectra. A typical CT spectrum for QC and tetrachloro-*p*-benzoquinone(chloranil) in methylene chloride is shown in Fig. 1. Spectrum *C* in Fig. 1 refers to

Table 1. Charge-transfer absorption maxima, wave numbers, transition energies, molar absorptivities and association constants in methylene chloride at 20°

Acceptor	Donor	λ_{max}(CT) nm	ν_{CT} 10^3 cm^{-1}	E_{CT} eV	ϵ_{DA}	K_x
Maleic anhydride	Quadricyclane	325[a]	30·8	3·82	740	0·61
Chloromaleic anhydride		334	29·9	3·71	1400	0·30
Dichloromaleic anhydride		346	28·9	3·63		
p-Benzoquinone		368	27·2	3·39	1980 ±110	0·21 ±0·01
2,5-dichloro-*p*-benzoquinone		418	23·9	2·99		
Chloranil		464	21·6	2·67	2600 ±600	0·23 ±0·10
2,3-Dichloro-5,6-dicyano-*p*-benzoquinone		536	18·7	2·31		

[a] 315 nm (ϵ 1000) in cyclohexane, see Ref. 1.

Table 2. Ionization potentials of quadricyclane and related molecules (eV)

Molecule	I_p(obsd. CT)[a]	I_p(obsd. PS)	I_p (calcd) EHM[a]	I_p (calcd) MINDO/1[a]	MINDO/2[b]
	1° 8·28[d,e] 8·32[f]	—	11·8	9·09	—
	1° 8·56[g]	8·62[b] 8·42[c] 8·69[i]	12·2	9·70	8·78
	2° 9·51[g]	9·52[b]	—	—	—
	1° 9·18[h]	9·02[b]	—	—	9·46
	1° 8·84[g]	8·82[c] 8·83[b]	—	—	8·91

[a] This work, [b] Ref. 20, [c] adiabatic I_p, Ref. 21, [d] chloranil $C_1 = 5{\cdot}85$, $C_2 = 0{\cdot}58$ in CH_2Cl_2,[19] [e] p-quinone $C_1 = 5{\cdot}15$, $C_2 = 0{\cdot}8$ in CH_2Cl_2,[19] [f] maleic anhydride $C_1 = 4{\cdot}59$, $C_2 = 0{\cdot}37$ in CH_2Cl_2,[19] [g] TCNE $C_1 = 6{\cdot}06$, $C_2 = 0{\cdot}32$ in CH_2Cl_2,[19] [h] iodine $C_1 = 6{\cdot}0$, $C_2 = 3{\cdot}4$ in n-heptane,[19], [i] vertical I_p, Ref. 22.

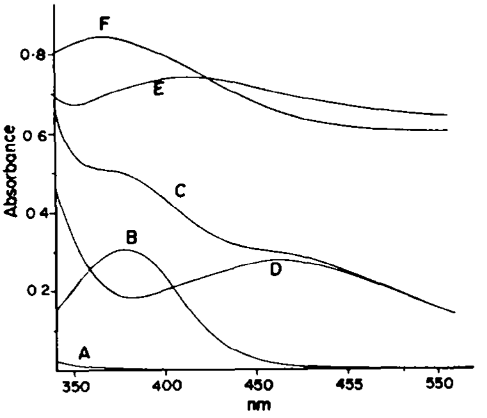


Fig. 1. CT absorption spectra of quadricyclane, (A) quadricyclane 0·4077 (mole fraction); (B) chloranil $1{\cdot}261 \times 10^{-3}$ M; (C) quadricyclane 0·4077 and chloranil $1{\cdot}261 \times 10^{-3}$ M; (D) CT absorption spectrum of quadricyclane-chloranil complex; (E) CT spectrum of quadricyclane-dichlorobenzoquinone complex; (F) CT spectrum of quadricyclane-benzoquinone complex. Spectra E and F are shifted upward by 0·6 unit in absorbance.

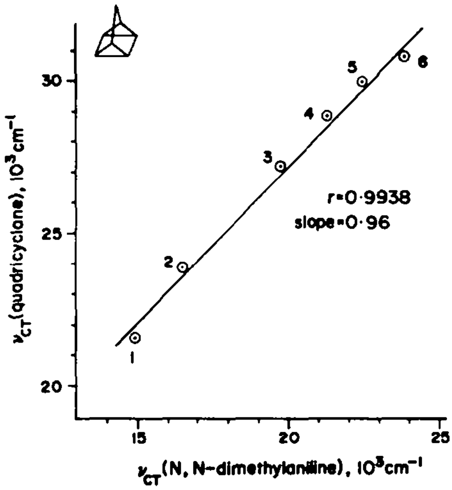


Fig. 2. Plots of the CT transition energies (ν_{CT}) of quadricyclane vs. ν_{CT} of N,N-dimethylaniline: 1, chloranil; 2, 2,5-dichloro-p-benzoquinone; 3, p-benzoquinone; 4, dichloromaleic anhydride; 5, chloromaleic anhydride; 6, maleic anhydride.

the absorption spectrum of QC and chloranil in methylene chloride; there apparently exists a new absorbing species in the solution. To obtain the absorption spectrum of the QC-chloranil complex, the absorption of the uncomplexed chloranil and QC were subtracted from observed spectrum C. Thus spectrum D was obtained, which showed the absorption maximum of the first CT band at 464 nm ($21{\cdot}57 \times 10^3\,\text{cm}^{-1}$) and the tail of the secondary CT absorption.[†] The observed CT bands of QC with *p*-benzoquinone and 2,5-dichloro-*p*-benzoquinone are also shown in Fig. 1 and the absorption maxima of the CT bands of QC with the acceptors investigated are listed in Table 1. It was found difficult to observe clear CT spectra of QC with several other π-acceptors on account of (1) poor separation of the CT band from the absorptions of the uncomplexed species (this was the case for tetrachlorophthalic anhydride, 2,3-dichloro-1,4-naphthoquinone, fumaronitrile, or maleonitrile) or (2) rapid cycloaddition reaction of acceptors to QC.[4] The typical example of the latter was seen for tetracyanoethylene(TCNE), which was observed to react rapidly with QC giving a cycloadduct at the moment of the mixing of two solutions and any attempt to observe the CT spectrum of the TCNE-QC complex at 20° was unsuccessful.

Figure 2 shows plots of ν_{CT} of QC vs ν_{CT} of N,N-dimethylaniline, giving a good linear relationship ($r = 0{\cdot}9938$, slope $= 0{\cdot}96$).[‡] This linearity is equivalent to a linear relationship between ν_{CT} of QC and E_a with a slope of about unity, where E_a refers to the electron affinity of the acceptor. Therefore, the present results strongly suggest that the interaction is the CT and that QC behaves as a donor forming normal EDA complexes of weak interaction, the structures of which do not appreciably vary with the change of the acceptor.

Molar extinction coefficients (ϵ_{DA}) *and association constants* (K_x). Under the circumstance that the donor concentration is much greater than that of the acceptor, it is demonstrated that at any wavelength the equilibrium constant (K_x) for the complex formation is related to the mole fraction of the donor (D),[12] as shown in Eqn (2), where ϵ is related to the measured optical density (d) and the total molar concentration $[A_t]$ of both free and complexed acceptor by the equation $d = \log(I_0/I) = \epsilon[A_t]$. Plots of $1/(\epsilon - \epsilon_A)$ vs $1/(D)$ for CT spectra of QC gave a straight line as shown for chloranil (Fig. 3) as a typical example. Determination of the slope and the intercept of the plot was made with the least square method. K_x values determined at several wavelengths coincided to each others within 10%.[§] ϵ_{DA} and K_x thus obtained are listed in the last two columns in Table 1. Molar extinction coefficients in Table 1 showed the tendency expected from Mulliken's theoretical description of CT absorption spectra,[13] i.e. the increase in the electron affinity, E_a, of the acceptor afforded the increased ϵ_{DA}. But the increased E_a was accompanied by the decreased K_x in contrast to the theory. The observed K_x were such small values that be explained by, e.g. van der Waals interaction between the donor (QC) and the acceptors. Therefore, it is quite difficult to elucidate what is a major factor determining the change in small K_x value observed.

$$\frac{1}{\epsilon - \epsilon_A} = \frac{1}{K_x \cdot (D) \cdot (\epsilon_{DA} - \epsilon_A)} + \frac{1}{\epsilon_{DA} - \epsilon_A} \qquad (2)$$

Following four different explanations had been given

[†] The absorption maximum of the secondary CT band between QC and chloranil was estimated to be shorter than 330 nm, if any.

[‡] N,N-dimethylaniline is one of typical π-donors, since a similar plot of ν_{CT}(N,N-dimethylaniline) vs ν_{CT} (another π-donor) usually gives a straight line with unit gradient. Therefore, the linearity in Fig. 2 signifies that QC serves as a normal electron donor, the interaction of which with π-acceptor closely resembles to those between π-donors and π-acceptors.

[§] Person reported a criterion for reliability of formation constants (K) of weak complexes; the donor concentration in the most concentrated solution must be greater than $0{\cdot}1(1/K)$ in order to obtain the most accurate value of K, in applying Benesi-Hildebrand's method or its modifications; W. B. Person, *J. Am. Chem. Soc.* **87**, 167 (1965). See also D. A. Derenlau, *Ibid.* **91**, 4044, 4050 (1969). The donor concentration in the present system sufficed the condition mentioned above: in the cases for acceptors other than chloranil, the donor concentration in the most concentrated solution was 0·4077 in mole fraction, which was greater than $0{\cdot}1(1/K)$. At least 5% of chloranil is complexed in the most concentrated solution employed, even when the smallest K_x value 0·13 is taken.

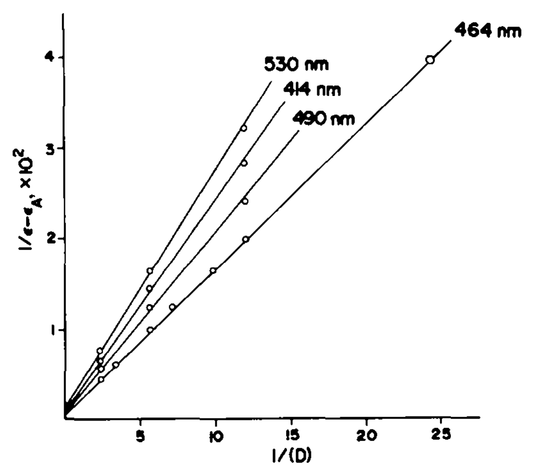


Fig. 3. The plot of Eqn (2) for the QC-Chloranil complex in methylene chloride, 20°.

for the disagreement between the deduction from Mulliken's theoretical description[13] and Keefer and Andrews' observation of alkylbenzene-iodine complexes,[14] where the decrease in the ionization potential of the donor afforded the decreased ϵ_{DA} and the increased K_x; (a) experimental error, (2) contamination with the contact CT,[15] (3) competition of the solvation of the donors and the acceptors with the formation of the EDA complex,[16] (4) discrepancy from the Beer's law.[17] All of these, of course, must be considered also in the present case. Furthermore, a steric effect (due to the bulkiness of the acceptor) on K_x is to be considered, since the intermolecular distance in a (σ, π) type complex may be shorter than that in a (π, π) type complex to cause a sufficient overlap between the donor and the acceptor.

Quadricyclane as an electron donor. It is concluded from the above discussion that QC forms normal electron donor-acceptor complexes, probably not a loose contact pair. The present case is classified as the (σ, π) type complex.

It is most likely that the remarkably low ionization potential of QC (see next paragraph) made it possible to observe the CT absorption spectra of complexes between QC and π type acceptors. Considerably stable complex formation of QC with a π-acceptor was reasonably expected from the low ionization potential of QC, comparable to that of aromatic donor xylene or mesitylene. However, the observed association constants were smaller than those of (π, π) type complexes which implied, therefore, a somewhat smaller overlap (S_{DA}) of QC than that of π-donors.

Ionization potential of quadricyclane. An ionization potential of a donor can be estimated empirically from the CT absorption maximum. According to simple perturbation theory, the CT transition energy (E_{CT}) was shown to be related to the ionization potential of the donor (I_p) and the electron affinity of the acceptor (E_a) for weak interactions (Eqn 3), where β_0 and β_1 refer to the matrix elements ($H_{01} - S_{01}W_{01}$) and ($H_{01} - S_{11}W_1$), respectively, G_0 is the "no bond" interaction energy and G_1 is the interaction of D^+ and A^- in the excited state.[18] For

$$E_{CT} = I_p - (E_a + G_1 - G_0) + \frac{\beta_0^2 + \beta_1^2}{I_p - (E_a + G_1 - G_0)} \quad (3)$$

$$= I_p - C_1 + \frac{C_2}{I_p - C_1} \quad (4)$$

a series of complexes of different donors with a given acceptor, the simple hyperbolic relationship (Eqn 4) was shown to be applied,[19] indicating that two terms ($E_a + G_1 - G_0$) and ($\beta_0^2 + \beta_1^2$) in Eqn (3) were independent on the donor species and were replaced by constants C_1 and C_2, respectively. On the assumption that Eqn (4) is also valid for QC, ionization potentials of QC and related compounds were evaluated as shown in Table 2.

It is noteworthy that the first I_p of QC was estimated to be remarkably lower† than other saturated hydrocarbons‡, and especially that it was in the same order of magnitude with that of norbornadiene. This means that the highest energy level of the σ-electrons in QC is similar to that of the homoconjugated π-electrons in norbornadiene. It was well reproduced by extended Hueckel (EHM) and MINDO/1 calculations that σ-electrons of QC had considerably high energies. Applying Koopmans' theorem to the energy of the highest occupied molecular orbital, the first I_p of QC was calculated and compared with that of norbornadiene (Table 2). It was shown again that QC had the first I_p of the same order of magnitude with norbornadiene. The remarkable decrease in the first I_p in passing from nortricyclane (9·02, 9·17 eV) to QC (*ca.* 8·3 eV from CT) is rationalized as the result of (a) the increased ring strain from nortricyclane (43 kcal/mol) to QC (95 kcal/mol)[23] and/or (b) a kind of conjugative interaction between two cyclopropane rings in QC similar to homoconjugation in norbornadiene. The latter would be more important than the former on the basis of the following reasons; (i) the total ring strain of QC is smaller than that of cubane (157 kcal/mol),[24] while I_p of QC is still considerably lower(by *ca* 0·5 eV) than that of cubane (I_p = 8·74 eV),[20] (ii) the conjugative interaction assumed is compatible with the regio and stereospecificity in the cycloaddition reaction of QC with some dienophiles.[4] Another example of such an interaction (b) was found in bicyclopropyl (IV) by Bodor *et al.* from the photoelectron spectroscopic studies that the decrease in the first I_p from cyclopropane (10·06 eV) to bicyclopropyl (9·04 eV) was much greater than that from cyclohexane (9·81 eV) to bicyclohexyl (9·41 eV).[20] QC molecule in EDA complexes is not strictly the same as the uncomplexed QC in its electronic state. Appearance of the conjugative interaction in QC molecule seems to require

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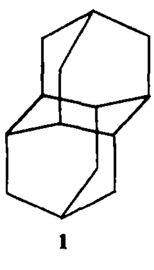
†Prof. Hans Bock of Frankfurt Univ carried out a preliminary experiment of photoelectron spectrum of QC and observed that QC has the first ionization potential of 8·65 eV. Ip(QC): 8·65, 9·70, 10·75, 11·0, 12·0, 13·30, 14·50 eV, Hans Bock, private communication.

‡Most of the first I_p of cyclic or acyclic saturated hydrocarbons fall into the range of 9–11 eV, and only a few hydrocarbons have I_p lower than 9 eV: diamantane (**1**), 8·92 eV; cubane (**2**), 8·74 eV; tricyclo[3.2.1.0^{3,6}] octane (**3**), 8·75 eV. See Ref. 20.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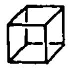
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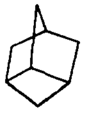
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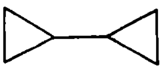
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moderate or a strong perturbation such as the CT interaction or the interaction leading to the cycloaddition.

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