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Charge-Transfer Interactions of Amines with Tetrahalomethanes. X-ray Crystal Structures of the Donor-Acceptor Complexes of Quinuclidine and Diazabicyclo[2.2.2]octane with Carbon Tetrabromide

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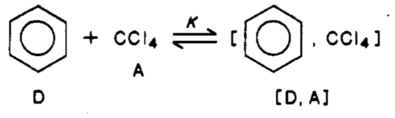
The molecular association of various amines with carbon tetrachloride, tetrabromide, and tetraiodide is examined spectroscopically by observing the charge-transfer (CT) absorption bands. Among the amines, quinuclidine and diazabicyclo[2.2.2]octane (Dabco) afford the most cleancut evidence for the formation of electron-donor-acceptor or EDA complexes. Quantitative evaluation of the formation constant $K = 3.2\ \mathrm{M}^{-1}$ by the Benesi-Hildebrand method indicates a moderately weak 1:1 EDA complex of Dabco and CBr_4. However, the insolubility of the complexes in chloroform allows single crystals suitable for X-ray crystallography to be grown. The molecular structure of the crystalline Dabco complex consists of alternating planes of the diamine and CBr_4 in which each acceptor is bound to two donor units to form a series of juxtaposed, infinite chains. In contrast, the quinuclidine complex consists of discrete pairs of donor-acceptor interactions in which every CBr_4 is bound to only a single donor, the unit cell consisting of four such pairs each residing on a different three-fold axis. The difference between the catenated structure of the Dabco-CBr_4 complex and the pairwise structure of the quinuclidine-CBr_4 complex is manifested in their solid-state CT spectra. The CT interaction in the EDA crystal of Dabco is compared with that of the 1:1 complex in solution by a variety of spectral techniques including UV-vis, infrared, and ^1H and ^{13}C NMR. The charge-transfer photochemistry of the Dabco-CBr_4 complex is also examined briefly.

Introduction

Polyhaloalkanes such as carbon tetrachloride, chloroform, methylene chloride, etc., are commonly used as "inert" solvents. Nonetheless chloroform and dichloromethane have been shown to form hydrogen-bonded complexes with aromatic π-donors.[1-3] Even carbon tetrachloride undergoes molecular association with arenes such as benzene[4,5]—as indicated from freezing-point diagrams, from volumes and heats of mixing, and from measurements of the far infrared spectra.[6-8] Most importantly the electronic spectra of solutions containing these and related polyhaloalkanes and aromatic hydrocarbons show absorption bands that are not present in either component alone.[9] These new bands are associated with the formation of electron-donor-acceptor or EDA complexes in which the polyhaloalkane participates as the electron-acceptor component (A) and the aromatic hydrocarbon as the electron-donor component (D), e.g.



With the EDA complex from carbon tetrachloride and benzene,[3] the optical change is referred to as the charge-transfer (CT) transition by Mulliken,[10,11] and it is observed merely as a small, unresolved shift in the absorption band. This minor spectral variation coupled with the limited magnitude of the association constant $K < 0.1\ \mathrm{M}^{-1}$ results in large experimental uncertainties in the measurements by quantitative spectrophotometry.[12]

In order to delineate the properties of carbon tetrachloride and related haloalkanes as electron acceptors, we sought other types of electron-donor molecules that would form EDA complexes suitable for quantitative study. Among these donors, the strongest EDA complexes are generally formed with lone-pair or n-donors among which are amines, sulfides, ethers, etc.[13] Accordingly we have focused our attention in this study on the CT interaction of various halomethanes with amines, and we have established the molecular structures of the EDA complexes by X-ray crystallography.

Results and Conclusions

Owing to the possibility of hydrogen bonding in the formation of EDA complexes with the haloforms and methylene dihalides as the electron acceptor,[1-5] we have restricted our studies to the tetrahalomethanes—carbon tetrachloride, tetrabromide, and tetraiodide.

I. Charge-Transfer Spectra of Tetrahalomethanes with Amines. When a solution of triethylamine in isooctane is mixed with carbon tetrachloride, a faint yellow coloration is observed immediately. In agreement with the early observation by Stevenson and Coppinger,[4] the color is associated with a nondescript red shift in the electronic absorption spectrum but no distinct band, either resolved or partially resolved, can be discerned. The magnitude of the red shift is successively larger with carbon tetrabromide, in accord with the expectations based on their charge-transfer origin.[9] The quantitative analysis of the absorbance changes that accompany the variations in triethylamine and halomethane concentrations indicated

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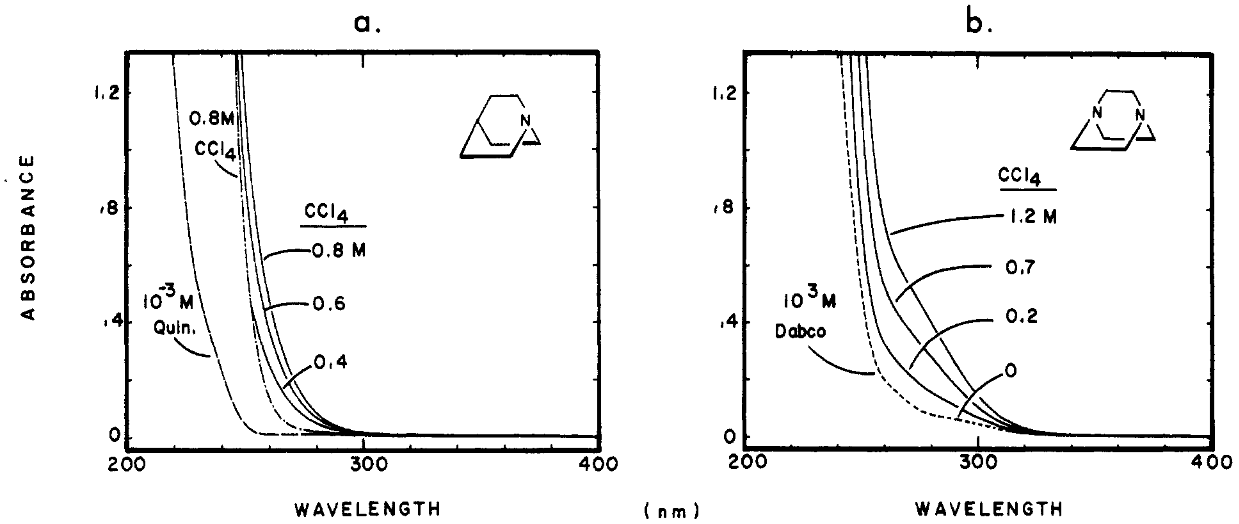


Figure 1. Spectral changes accompanying the molecular association of carbon tetrachloride with amines in isooctane. (a) From left to right: 1.4×10^{-3} M quinuclidine, no CCl_4 (---); 0.78 M CCl_4, no amine (-·-); 1.4×10^{-3} M quinuclidine plus 0.36 M CCl_4; 1.3×10^{-3} M quinuclidine plus 0.58 M CCl_4; 1.3×10^{-3} M quinuclidine plus 0.78 M CCl_4. (b) From left to right: 9×10^{-4} M Dabco, no CCl_4 (---); 9×10^{-4} M Dabco plus 0.23 M CCl_4; 9×10^{-4} M Dabco plus 0.66 M CCl_4; 8×10^{-4} M Dabco plus 1.24 M CCl_4.

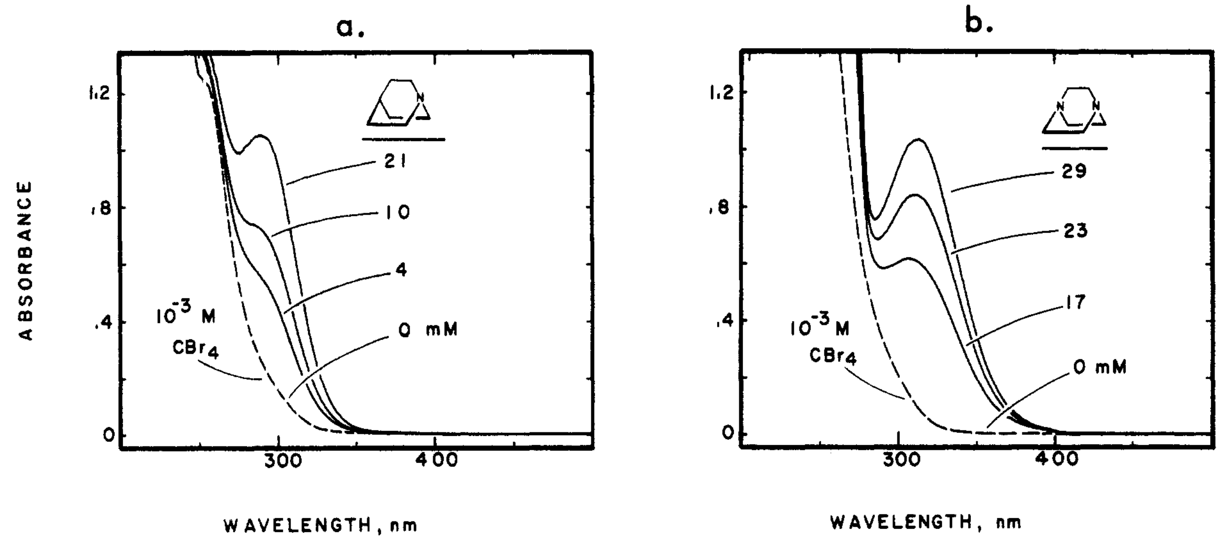
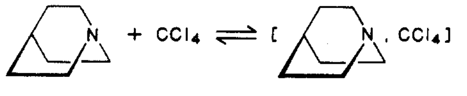


Figure 2. Charge-transfer absorption spectra of the EDA complexes of amines with carbon tetrabromide in isooctane. (a) From left to right: 1×10^{-3} M CBr_4, no amine; 10^{-3} M CBr_4 plus 4×10^{-3} M quinuclidine; 10^{-3} M CBr_4 plus 1×10^{-2} M quinuclidine; 10^{-3} M CBr_4 plus 2×10^{-2} M quinuclidine. (b) From left to right: 1.5×10^{-3} M CBr_4, no amine; 1.5×10^{-3} M CBr_4 plus 1.7×10^{-2} M Dabco; 1.5×10^{-3} M CBr_4 plus 2.3×10^{-2} M Dabco; 1.5×10^{-3} M CBr_4 plus 2.9×10^{-2} M Dabco.

a 1:1 stoichiometry for the formation of the EDA complexes,[4] i.e. eq 1.

$$Et_3N + CCl_4 \rightleftharpoons [Et_3N, CCl_4] \qquad (1)$$

In an effort to increase the donor properties of the amine, we next examined the interaction of carbon tetrachloride with quinuclidine in which the three ethyl groups of triethylamine are tied back to expose the donor center on nitrogen.[14] However the spectral changes accompanying the successive addition of incremental amounts of carbon tetrachloride to quinuclidine in Figure 1a do not lead to a distinctive, new absorption band. It is clear from the measurable red shift in the low-energy tail that a charge-transfer interaction does derive from the molecular association, i.e., eq 2. Accordingly we turned to 1,4-diazabicyclo[2.2.2]octane (hereafter referred to simply as Dabco) as the electron-donor component, since it is known to facilitate charge-transfer interactions with electron acceptors such as triplet benzophenone.[15-19] The spectral changes accompanying the successive addition of Dabco to a solution of carbon tetrachloride in isooctane are shown in Figure 1b. The pronounced shoulders in the spectra obtained at higher concentrations of Dabco indicate that the maximum of the CT band is obscured by the low-en-



(2)

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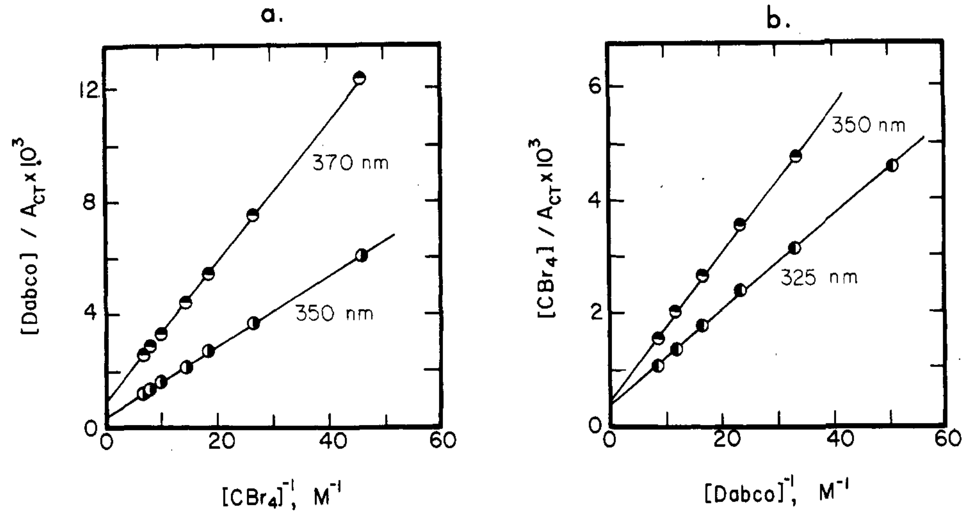
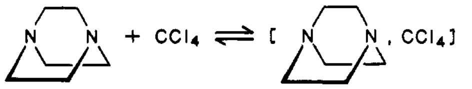


Figure 3. Spectrophotometric determination of the formation constants of the Dabco–CBr_4 complex in acetonitrile at 25 °C according to the Benesi–Hildebrand method at two wavelengths with (a) the electron acceptor in excess and (b) the electron donor in excess.

ergy tails of the components in the molecular association, i.e., eq 3.



(3)

Indeed the charge-transfer bands of the EDA complexes of these amines are clearly resolved with carbon tetrabromide as the electron acceptor in Figure 2. Moreover the red shift in the absorption maximum from λ_{CT} 292 nm in the quinuclidine complex to 313 nm in the Dabco complex follows from their ionization potentials of 8.06 and 7.52 eV, respectively.[20]

The charge-transfer band of the Dabco–CBr_4 complex shifts to lower energy (λ_{CT} 342 nm) when isooctane is replaced by acetonitrile as the solvent. With chloroform and methanol, the hydrogen bonding to Dabco causes a red shift in the donor absorption which is sufficient to obscure the maximum of the CT band of the EDA complex in these solvents. Nonetheless the consistency of the magnitudes of the formation constants (vide infra) indicates the occurrence of a common molecular association in all solvents. The significant shift in the CT band with a solvent change from isooctane to acetonitrile follows the general trend of solvent polarity as given by the Z values.[21]

II. Formation Constants of the EDA Complexes of Amines with Tetrahalomethanes. The formation constant of the EDA complex derived from carbon tetrachloride and triethylamine in isooctane could not be measured reliably by Stevenson and Coppinger.[4] However their estimate of the upper limit as $K < 0.1$ M^{-1} indicates that it is a weak complex at best, and the molecular association may be even described as arising from contact charge transfer.[9b]

Table I. Formation Constant of the Dabco-CBr_4 Complex from the Concentration Dependence of the CT Absorbance[a]

		absorbance[b]	
CBr_4 (M)	Dabco (M)	λ_1	λ_2
	Chloroform		
0	0.00559	0.0095	0.0043
0.168	0.00559	0.4157	0.2305
0.221	0.00559	0.5375	0.2985
0.256	0.00559	0.6119	0.3428
0.325	0.00559	0.7518	0.4257
0.370	0.00559	0.8435	0.4803
0.366	0	0.0631	0.0413
0.00119	0	0.0180	0.0010
0.00396	0.0665	0.7060	0.3447
0.00396	0.0965	0.9570	0.4757
0.00396	0.1173	1.1310	0.5690
0.00396	0.1415	1.3200	0.6758
0	0.1754	0.059	0.008
	Methanol		
0.00554	0	0.0184	0.0110
0.00554	0.132	0.1956	0.1526
0.00554	0.244	0.3561	0.2800
0.00554	0.337	0.4819	0.3830
0.00554	0.416	0.5970	0.4740
0.00554	0.0563	0.8140	0.6480
0	0.571	0.0091	0.0083

[a] Measurements in an optical cell with 1-cm pathlength. [b] Monitoring wavelengths λ_1 325 nm and λ_2 350 nm for first seven entries, 370 and 380 nm for entries 8–12, and 335 and 340 nm for last seven entries.

In order to evaluate the EDA complexes of the amine donors which show more intense and distinct CT bands (vide supra), we measured the formation constants by the Benesi–Hildebrand procedure under conditions in which one component is in 50–100-fold excess. The concentration-dependent change in the CT absorbance A_{CT} for $[x]_0 \ll [y]_0$ is given by[22,23]

$$\frac{[x]_0}{A_{CT}} = \frac{1}{K\epsilon_{CT}} \cdot \frac{1}{[y]_0} + \frac{1}{\epsilon_{CT}} \tag{4}$$

where x and y are either the electron donor or acceptor and ϵ_{CT} is the extinction coefficient of the EDA complex. Typical Benesi–Hildebrand plots at two wavelengths are shown in Figure 3 for the EDA complex of Dabco and carbon tetrabromide in acetonitrile with the acceptor in excess (left) and the donor in excess (right). The limited magnitude of $K = 4.2 \pm 0.3$ M^{-1} evaluated from Figure 3a (see Table I, entries 9–12) indicates that the Dabco–CBr_4 pair can be considered as forming a moderately weak EDA complex. The alternate measurement of K in Figure 1b

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Table II. Solvent Dependence of the Formation Constant of the Dabco-CBr_4 Complex[a]

solvent	K (M^{-1})	conditns[b]	ϵ (M^{-1} cm^{-1}), λ^c (nm)	r^d
CH_3CN	4.5	Dabco	2659 (325)	0.9997
CH_3CN	3.9	Dabco	2003 (350)	0.9998
CH_3CN	3.0	CBr_4	2646 (350)	0.9999
CH_3CN	3.4	CBr_4	2181 (370)	0.9999
$CHCl_3$	2.1	Dabco	1435 (325)	0.9998
$CHCl_3$	1.3	Dabco	1121 (350)	0.9999
$CHCl_3$	0.5	CBr_4	1034 (370)	0.9999
$CHCl_3$	0.3	CBr_4	879 (380)	1.0000
CH_3OH	0.1	Dabco	2758 (335)	0.9999
CH_3OH	0.03	Dabco	6380 (340)	1.0000

[a] Evaluated by the Benesi–Hildebrand method (see text). [b] Component in excess. [c] Extinction coefficient of the complex at the monitoring wavelength λ. [d] Correlation coefficient of the Benesi–Hildebrand plot.

with the acceptor in excess yields $K = 3.2 \pm 0.2$ M^{-1} (entries 2–6). The discrepancy in the two measurements of K may be due to problems associated with the overlap of the CT band with the strong tail absorption of the acceptor CBr_4 when it is present in excess. [Note the extended wavelengths necessitated for the monitoring light in Figure 3a relative to those in Figure 3b]. Alternatively it is possible that competition from the 1:2 complex Dabco–$(CBr_4)_2$ occurs as a result of the availability of two nitrogen sites on Dabco, especially at relatively high concentrations of the electron acceptor.

The formation constant of the EDA complex of carbon tetrabromide and Dabco is not highly solvent-dependent. Thus the magnitude of $K = 1.7 \pm 0.4$ M^{-1} in chloroform (Table I) is only slightly less than that in the polar acetonitrile. Likewise the formation constant $K = 0.06 \pm 0.04$ M^{-1} in the protic methanol indicates that hydrogen bonding is not a dominant factor. The values of the formation constant and extinction coefficient of the Dabco–CBr_4 complex in the various solvents are summarized in Table II.

III. Molecular Structure of the EDA Complex of Dabco and Carbon Tetrabromide by X-ray Crystallography. Crystals of the EDA complex of Dabco and carbon tetrabromide were prepared by mixing nearly saturated solutions of the components at room temperature. A yellow-green solid of the 1:1 complex precipitated rapidly as the temperature of the solution rose to ~35 °C.[15] A single crystal suitable for X-ray analysis was grown by careful recrystallization from chloroform. The pertinent crystal data and the X-ray processing data are included in Table III.

The crystal of the EDA complex is a 1:1 mixture of Dabco and carbon tetrabromide. The packing in the crystal consists of alternating monolayers of infinite two-dimensional planes of Dabco and of carbon tetrabromide. The unit cell is illustrated in Figure 4 which also includes the numbering scheme for the principal atoms. Crystallographically there are two types of independent carbon tetrabromide molecules, labeled as A and B, each showing mirror symmetry in the *ac* plane. Furthermore each CBr_4 is related to another CBr_4 by an inversion operator (*i*) located in the center of a neighboring Dabco.

Every molecule of carbon tetrabromide consists of two crystallographic pairs of bromine atoms—one pair (e.g., Br_4/Br_4' and Br_1/Br_1' which have exceptionally close nonbonded contacts to a nitrogen atom on a neighboring Dabco of 2.88 Å and 2.76 Å for $N_1 \cdots Br_4$ and $N_2 \cdots Br_1$, respectively (see Table IV). The other pairs of bromine atoms (i.e., Br_5/Br_6 and Br_2/Br_3) show no close nonbonded interaction with any other atom in the crystal.

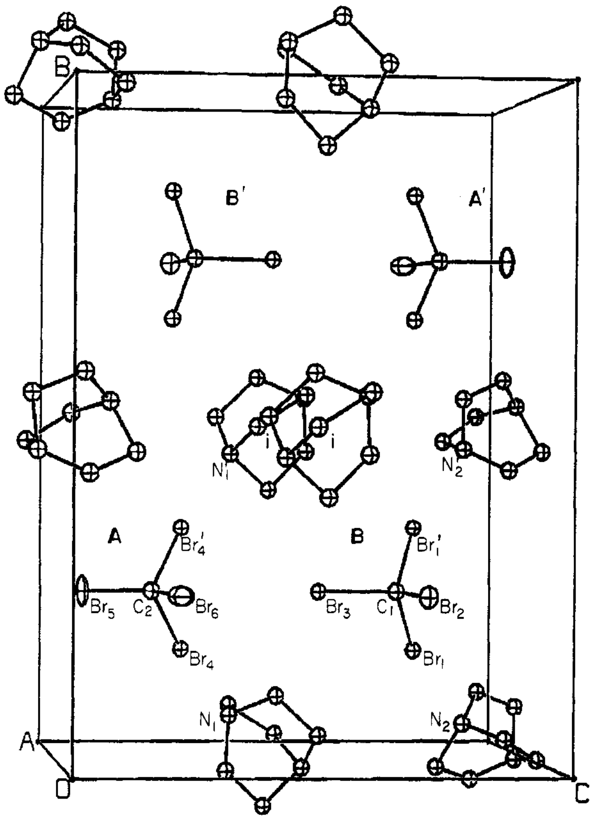


Figure 4. Molecular structure and number scheme of the EDA complex of Dabco and carbon tetrabromide showing only the principal non-hydrogen atoms. The view of the packing in the unit cell shows only one of the two possible orientations of each disordered Dabco molecule.

Table III. X-ray Data Collection and Processing Parameters for the EDA Complexes of CBr_4

	[Dabco, CBr_4]	[quinuclidine, CBr_4]
space group	$P2_1/m$, monoclinic	$P2_13$, cubic
cell constants		
a, Å	6.126 (1)	10.906 (8)
b, Å	16.800 (3)	
c, Å	12.634 (4)	
β, deg	101.82 (2)	
V, $Å^3$	1245	1297
mol form	$C_7H_{12}N_2Br_4$	$C_8H_{13}NBr_4$
form wt	443.8	442.8
Z	4	4
ρ, $g \cdot cm^{-3}$	2.39	2.27
μ, cm^{-1}	129.1	122.6
λ(Mo Kα), Å	0.71073	0.71073
collectn range	$4° \gtrsim 2\theta \gtrsim 44°$	$4° \lesssim 2\theta \lesssim 40°$
scan width	$\Delta\theta = (1.00 + 0.35 \tan\theta)°$	$\Delta\theta = (0.90 + 0.35 \tan\theta)°$
maximum scan time, s	120	90
scan speed range	0.7 to 5.0° min^{-1}	0.9 to 7.0° min^{-1}
total data collected	1751	287
independent data, $I > 3\sigma(I)$	775	200
total variables	90	26
$R = \sum \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \sum \lvert F_o \rvert$	0.090	0.048
$R_w = [\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \sum w \lvert F_o \rvert^2]^{1/2}$	0.095	0.050
weights	$w = \sigma(F)^{-2}$	$w = \sigma(F)^{-2}$

Every Dabco molecule exists in the crystal as a completely disordered "pseudo molecule" illustrated in Figure 5, in which the crossed atoms (⊗) belonging to one Dabco set are related to the open atoms (○) of the other set by a $\pi/3$ radian rotation about the $N_1 \cdots N_2$ axis. Such a true

Table IV. Close Nonbonded Interactions in the Dabco-CBr_4 Crystal

atom···atom	distance (Å)
$N_1 \cdots N_1'$	2.56 (3)
$N_1 \cdots Br_4$	2.88 (1)
$N_2 \cdots N_2'$	2.50 (3)
$N_2 \cdots Br_1$	2.76 (1)
atom···atom···atom	**angle (deg)**
$N_1 \cdots N_1' \cdots Br_4$	154 (1)
$N_2 \cdots N_2' \cdots Br_1$	163 (1)

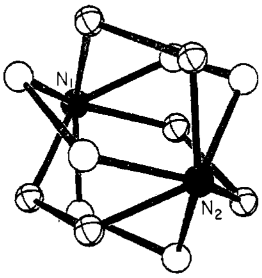


Figure 5. ORTEP diagram of the statistically disordered Dabco molecule represented as the superposition of two units (○ and ⊗) which differ by a 60° rotation.

statistical disorder of the Dabco molecules reduces the accuracy of the final refinement. Thus the carbon–bromine distances and angles on each CBr_4 as listed in Tables V and VI, respectively, are merely crystallographically relevant and do not necessarily reflect actual differences in bond lengths and angles. Nonetheless the root-mean-square amplitudes for thermal vibration of the bromine atoms on each CBr_4 are sufficiently different to distinguish them into 2 pairs (see Table VII). In particular, it is the motion of those pairs of bromine atoms (Br_5/Br_6 and Br_2/Br_3) having no close contacts that show relatively large thermal amplitudes. By contrast, the relevant pairs of bromines (i.e., Br_4/Br_4' and Br_1/Br_1') having close nonbonded contacts to a neighboring Dabco are thermally constrained. Each molecule of Dabco is thus formally associated with a pair of CBr_4 molecules at each nitrogen center to form essentially a doubly bridged entity. The

Table V. Selected Bond Distances (Å) in the EDA Complexes of Carbon Tetrabromide and Amines[a]

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
[Dabco, CBr_4]								
C_1	Br_1	2.117 (11)	N_1	C_6	1.42 (3)	C_3	C_7	1.58 (4)
C_1	Br_2	1.88 (2)	N_1	C_7	1.46 (3)	C_4	C_6	1.56 (5)
C_1	Br_3	1.90 (2)	N_1	C_8	1.47 (3)	C_5	C_8	1.60 (4)
C_2	Br_4	1.740 (9)	N_2	C_9	1.46 (3)			
C_2	Br_5	2.04 (2)	N_2	C_{10}	1.46 (3)	C_9	C_{14}	1.58 (4)
C_2	Br_6	1.98 (2)	N_2	C_{11}	1.45 (4)	C_{10}	C_{12}	1.57 (4)
N_1	C_3	1.45 (4)	N_2	C_{12}	1.48 (4)	C_{11}	C_{13}	1.54 (4)
N_1	C_4	1.45 (4)	N_2	C_{13}	1.47 (4)			
N_1	C_5	1.46 (3)	N_2	C_{14}	1.45 (3)			
[Quinuclidine, CBr_4]								
C_1	Br_1	2.243 (9)	C_2	C_4	1.47 (2)	N	C_2	2.616 (10)
C_1	Br_2	1.857 (2)	C_3	C_4	1.51 (3)			
N	C_3	1.52 (2)	N	Br_1	2.531 (6)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Principal Bond Angles (deg) in the EDA Complexes of CBr_4 and Amines[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
[Dabco, Br_4]											
Br_1	C_1	Br_1	101.9 (8)	C_6	N_1	C_7	116 (2)	N_1	C_7	C_3	105 (2)
Br_1	C_1	Br_2	110.3 (7)	C_6	N_1	C_8	107 (2)	N_1	C_7	C_4	59 (2)
Br_1	C_1	Br_3	108.4 (7)	C_7	N_1	C_8	102 (2)	C_3	C_7	C_4	69 (2)
Br_1	C_1	Br_2	110.3 (7)	C_9	N_2	C_{10}	112 (2)	N_1	C_8	C_5	117 (2)
Br_1	C_1	Br_3	108.4 (7)	C_9	N_2	C_{11}	112 (2)	N_2	C_9	C_{12}	59 (2)
Br_2	C_1	Br_3	116.4 (9)	C_9	N_2	C_{12}	64 (2)	N_2	C_9	C_{14}	97 (2)
Br_4	C_2	Br_4	121 (1)	C_9	N_2	C_{13}	49 (2)	C_{12}	C_9	C_{14}	88 (2)
Br_4	C_2	Br_5	109.0 (7)	C_9	N_2	C_{14}	142 (2)	N_2	C_{10}	C_{12}	124 (3)
Br_4	C_2	Br_6	108.9 (7)	C_{10}	N_2	C_{11}	108 (2)	N_2	C_{10}	C_{13}	58 (2)
Br_4	C_2	Br_5	109.0 (7)	C_{10}	N_2	C_{12}	140 (2)	C_{12}	C_{10}	C_{13}	88 (2)
Br_4	C_2	Br_6	108.9 (7)	C_{10}	N_2	C_{13}	65 (2)	N_2	C_{11}	C_{13}	99 (2)
Br_5	C_2	Br_6	97.8 (8)	C_{10}	N_2	C_{14}	49 (2)	N_2	C_{11}	C_{14}	59 (2)
C_3	N_1	C_4	112 (2)	C_{11}	N_2	C_{12}	49 (2)	C_{13}	C_{11}	C_{14}	66 (2)
C_3	N_1	C_5	105 (2)	C_{11}	N_2	C_{13}	137 (2)	N_2	C_{12}	C_9	57 (2)
C_3	N_1	C_6	34 (2)	C_{11}	N_2	C_{14}	61 (2)	N_2	C_{12}	C_{10}	93 (2)
C_3	N_1	C_7	134 (2)	C_{12}	N_2	C_{13}	107 (2)	C_9	C_{12}	C_{10}	79 (2)
C_3	N_1	C_8	75 (2)	C_{12}	N_2	C_{14}	108 (2)	N_2	C_{13}	C_{10}	57 (2)
C_4	N_1	C_5	105 (2)	C_{13}	N_2	C_{14}	109 (2)	N_2	C_{13}	C_{11}	117 (3)
C_4	N_1	C_6	136 (2)	N_1	C_3	C_7	110 (3)	C_{10}	C_{13}	C_{11}	79 (2)
C_4	N_1	C_7	61 (2)	N_1	C_4	C_6	117 (3)	N_2	C_{14}	C_9	121 (3)
C_4	N_1	C_8	42 (1)	N_1	C_4	C_7	60 (2)	N_2	C_{14}	C_{11}	59 (2)
C_5	N_1	C_6	74 (2)	C_6	C_4	C_7	86 (2)	C_9	C_{14}	C_{11}	102 (3)
C_5	N_1	C_7	47 (2)	N_1	C_5	C_8	99 (2)				
C_5	N_1	C_8	136 (2)	N_1	C_6	C_4	102 (3)				
[Quinuclidine, CBr_4]											
Br_1	C_1	Br_2	101.1 (3)	Br_2	C_1	Br_2	116.4 (2)	C_4	C_2	C_4	105 (1)
Br_1	C_1	Br_2	101.1 (6)	C_3	N	C_3	109.0 (9)	C_4	C_2	C_4	105.2 (9)
Br_1	C_1	Br_2	101.1 (1)	C_3	N	C_3	109.0 (7)	N	C_3	C_4	107 (2)
Br_2	C_1	Br_2	116.4 (4)	C_3	N	C_3	109 (1)	C_2	C_4	C_3	117 (2)
Br_2	C_1	Br_2	116.4 (7)	C_4	C_2	C_4	105 (1)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

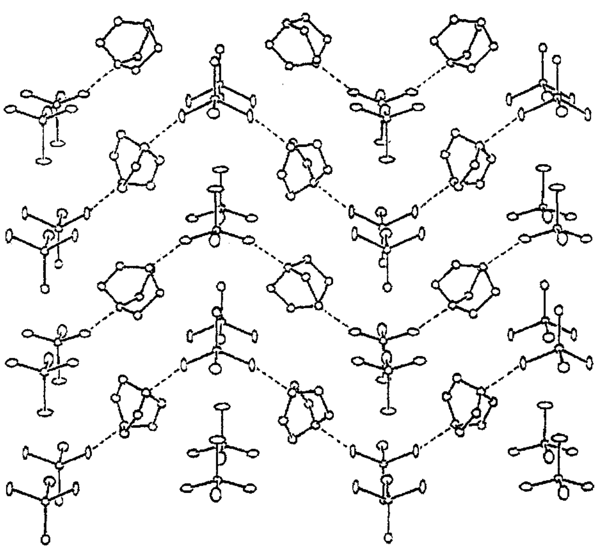


Figure 6. Molecular structure of the EDA complex showing the continuous series of relevant charge-transfer interactions between Dabco and carbon tetrabromide.

Table VII. Root-Mean-Square Amplitudes of Thermal Vibration of the Bromine Atoms in the Dabco–CBr_4 Crystal[a]

atom	min	int med	max
	Carbon Tetrabromide A		
Br_4	0.149	0.253	0.295
Br_5	0.131	0.354	0.366
Br_6	0.223	0.245	0.343
	Carbon Tetrabromide B		
Br_1	0.029	0.243	0.287
Br_2	0.128	0.203	0.261
Br_3	0.085	0.250	0.254

[a] In angstroms.

result is a series of sinuous chains comprised of alternating 1:1 molecular associations of Dabco and carbon tetrabromide, as illustrated in Figure 6. It is reasonable to conclude that these are indeed the sites of the charge-transfer interactions extant in this EDA complex. If so it raises the interesting question as to the electronic nature of the CT excitation. The time-resolved spectroscopic studies have established the donor–acceptor ion pair as the CT excited state.[24-26] As applied to the amine–CBr_4 complexes, the relevant CT excitation can thus be depicted as shown in eq 5.[27-29] In the case of Dabco, the cation is

$$[{>}N, CBr_4] \xrightarrow{h\nu_{CT}} [{>}N^{\bullet+}, CBr_4{}^{\bullet-}] \qquad (5)$$

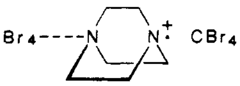
stabilized relative to that of quinuclidine by the transannular interaction of two nitrogens, as established from its ESR spectrum.[30,31] This added interaction no doubt is responsible for the substantial red shift in the CT spectrum (compare Figure 2). The extent to which both nitrogen atoms in a Dabco moiety are involved in the formation of the crystalline EDA complex will affect the unitary process depicted in eq 5, as presented in the following section.

IV. Comparison of the Dabco–CBr_4 Complex in the Crystal and in Solution. The properties of the crystalline EDA complex of Dabco and carbon tetrabromide were compared with those of the complex in solution by the examination of the electronic, infrared, and ^1H and ^{13}C NMR spectra.

A. The UV–vis absorption spectrum of the crystalline Dabco–CBr_4 complex shown in Figure 7a was determined in a Nujol mull. For comparison, the absorption spectrum of the EDA complex obtained in isooctane solution is superimposed. The broadening of the CT band in the solid-state spectrum may be partially understandable as scattering from the microcrystalline surface. However the rather pronounced shift in the absorption maximum of the CT band from 313 nm in isooctane to 343 nm in the crystalline material reflects the contributions from the intercomplex interactions extant in the solid which are absent in solution. The theoretical problems associated with the consideration of a variety of intermolecular forces in infinite molecular stacks in crystalline EDA complexes have been considered.[32] Suffice it to mention at the simplest level that the binary CT interaction in the 1:1 complex of Dabco and carbon tetrabromide in solution is different from the additional multiple CT interactions possible in the unit cell as emphasized in the ORTEP diagram (see Figure 6).

The ramification of the catenated structure resulting from the difunctional Dabco in Figure 6 is also shown by a comparison with the CT properties of the analogous complexes from the monodentate quinuclidine—both in the crystal as well as in solution. Thus the canary-yellow crystals of the EDA complex of quinuclidine and carbon tetrabromide are collected from chloroform solution as a stoichiometric 1:1 mixture. The X-ray crystal structure in Figure 8 shows the stereoscopic view of the unit cell to consist of a multitudinous array of discrete quinuclidine–CBr_4 pairs, each with axial three-fold symmetry. Unlike the crystal of the Dabco–CBr_4 complex, there is no evidence for any type of extended CT interaction (i.e., non van der Waals) beyond each donor–acceptor pair of quinuclidine and CBr_4. As a result, the charge-transfer spectrum of the EDA complex of quinuclidine and CBr_4 in solution (λ_{CT} 292 nm) is essentially the same as that (λ_{CT} 296 nm) obtained from the crystal in a Nujol mull (see Figure 7b).

Despite the dissimilarity in the gross structural features of the crystalline EDA complexes of CBr_4 with Dabco and quinuclidine in Figures 4 and 8, respectively, the principal charge-transfer spectra in Figure 7 remain basically the same, differing only in detail. Thus let us initially consider the CT excitation of a unitary interaction (as in the 1:1 complex). Following the formulation in eq 5, we must then consider how complexation of the transannular nitrogen affects the Dabco–CBr_4 ion pair, i.e.



We suspect that in a single photon excitation, the properties of such an extended complex ion pair are not fundamentally different from those obtained by the CT excitation of a simple 1:1 complex such as those formed in solution. Such secondary interactions no doubt contribute

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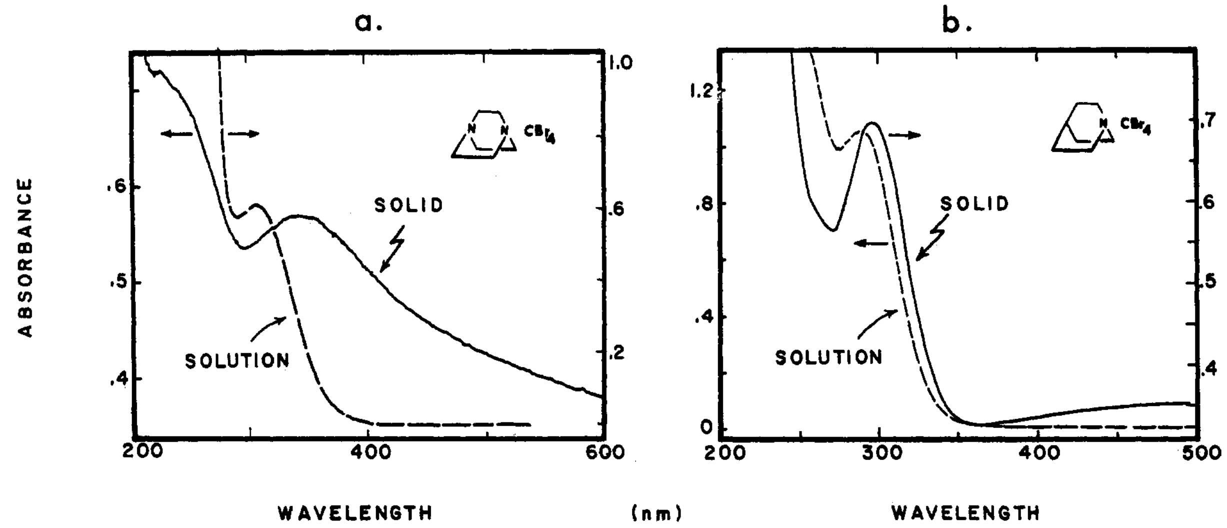

Figure 7. Comparison of the CT spectra of crystalline EDA complex (left scale) with those in isooctane solution (right scale) from carbon tetrabromide with (a) Dabco and (b) quinuclidine.

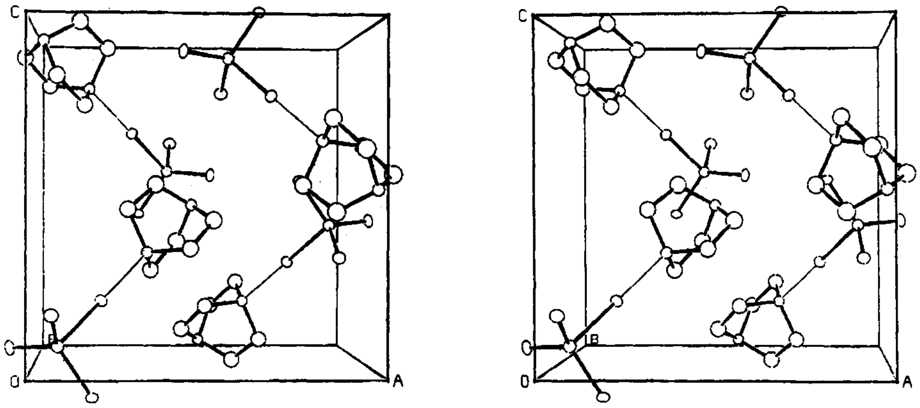

Figure 8. Stereoscopic ORTEP diagram of the unit cell of the EDA complex of quinuclidine and CBr_4 showing only the principal non-hydrogen atoms. Note the axial three-fold symmetry of each donor–acceptor pair about the individual C–Br···N axis which exists in three separate orientations.

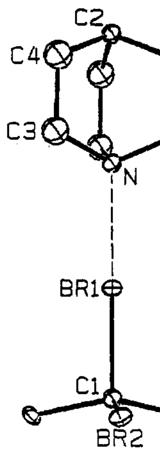

Figure 9. ORTEP diagram of the discrete CT chromophore in the 1:1 EDA comples of quinuclidine and carbon tetrabromide.

to the prolonged low-energy tail in Figure 7a.

B. **The infrared spectrum** of the crystalline Dabco–CBr_4 complex in a Nujol mull is essentially the same as the superposition of the individual spectra of the components (see Experimental Section), with one apparent exception. There is a slight shift in the carbon–bromide stretching band from 670 cm^{-1} in carbon tetrabromide to 659 cm^{-1} in the Dabco–CBr_4 complex. However the band shift is significantly less pronounced when the IR spectra are measured in a CBr_4 pellet, the carbon–bromine band in CBr_4 being shifted from 662 cm^{-1} to only 660 cm^{-1} in the EDA complex. At this juncture we are unable to determine whether these differences arise from the (partial) solubility of the crystalline complex in the matrices.

C. **The ^{13}C NMR spectrum** of the crystalline Dabco–CBr_4 complex measured in the cross-polarization magic angle spin (CPMAS) mode consists of a single, slightly broadened asymmetric resonance at δ 49.08. The latter compares with an unsymmetric doublet (from the ^{14}N quadrupolar splitting[33]) with δ 48.04 in the crystalline Dabco under the same conditions. The ^{13}C resonance of the CBr_4 moiety in the EDA complex is not observed, although a crystalline sample of carbon tetrabromide alone shows a pair of resonances at δ −26.08 and −26.51 apparently due to two distinct environments in the crystal. By comparison, a saturated solution (0.2 M) of the Dabco–CBr_4 complex in chloroform-*d* shows ^{13}C resonances at δ 47.19 (t, J_{CH} = 138 Hz) and 28.13 (s). These ^{13}C resonances compare with δ 46.99 and −29.49 obtained in comparable solutions of Dabco and carbon tetrabromide alone, respectively. If the formation constant $K \sim 1$ M^{-1} (vide supra) is used for the Dabco–CBr_4 complex dissolved in chloroform, about 86% is dissociated. Thus the observed shift of 1.36 ppm in the ^{13}C resonance of the CBr_4 moiety roughly translates into a molar shift of ~9.1 ppm in the EDA complex (see Experimental Section). This compares

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[33] Compare Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*; Academic: New York, 1969.

with a corresponding molar shift of only ~1.3 ppm for the ^{13}C resonance of the Dabco moiety. The significantly larger shift in the ^{13}C resonance associated with CBr_4 compared to Dabco may reflect its charge-transfer interaction in the EDA complex.

Taken all together, the accumulated results indicate that the crystalline EDA complex of Dabco and carbon tetrabromide is similar to that formed in solution with 1:1 stoichiometry. Moreover the electron donor and acceptor maintain their essential structural integrity—with the greatest perturbation occurring along with the C–Br bond in the acceptor moiety, as qualitatively indicated from X-ray crystallography and to a limited extent from minor variations in the IR and NMR spectra.

V. Comments on the Charge-Transfer Photochemistry of the Dabco–CBr$_4$ Complex. In order to determine whether the absorption bands in Figures 1, 2, and 6 are to be truly ascribed to the charge-transfer transition, a saturated solution (2 mL) of the EDA complex of Dabco and carbon tetrabromide in acetonitrile was irradiated with a 450-W xenon lamp. A sharp cutoff filter at $\lambda < 380$ nm ensured that only the CT band was excited, both components being otherwise completely transparent beyond this wavelength. The course of the photochemistry was monitored by following the gradual downfield shift of the methylene proton at δ 2.64 in the ^{1}H NMR spectrum to δ 3.04, at which point (15 min) the yellow solution was bleached. Addition of diethyl ether to the photolysate yielded a white precipitate which was the same as Dabco·HBr synthesized independently [^{1}H and ^{13}C NMR at δ 3.04 and 45.16, respectively.] Further product studies are required to establish the fate of the residual tribromomethyl moiety which is unaccounted for and the source of the proton in Dabco·HBr. Nonetheless the apparently facile formation of Dabco·HBr by the CT excitation of the EDA complex suggests an efficient photochemical process. Although there is insufficient experimental information at this juncture to provide a detailed mechanistic formulation, the charge-transfer origin suggests a partial mechanism consistent with previous time-resolved spectroscopic studies (Scheme I). Further quantitative studies of products and quantum yields will allow the details of this interesting CT photochemical process to be established.[34,36]

Scheme I

$$\text{Dabco} + CBr_4 \rightleftharpoons [\text{Dabco}, CBr_4] \qquad (6)$$

$$[\text{Dabco}, CBr_4] \xrightarrow{h\nu_{CT}} [\text{Dabco}^{\bullet+}, Br^-, CBr_3^{\bullet}] \qquad (7)$$

$$\text{Dabco}^{\bullet+} + SH \rightarrow \text{DabcoH}^+ + S^{\bullet}, \text{ etc.} \qquad (8)$$

VI. Structural Relevance of the Halogen Bond in EDA Complexes of Polyhaloalkanes. The formation of crystalline EDA complexes of polyhaloalkanes provides evidence for the existence of a halogen bond if the structural determinations show that the separation of the acceptor atoms from those of the donor is less than the sum of their van der Waals radii.[37] Indeed the earliest crystallographic report of an EDA complex of an organic halide was the establishment of an essentially linear C–I···N interaction between iodoform and quinoline, the I···N distance of 2.99 Å being 0.66 Å shorter than the sum of the van der Waals radii.[38] Creighton and Thomas characterized by X-ray diffraction the single crystals of 33 complexes of tetramethylammonium halides with various tetrahalomethanes and ethylenes as having C–X···Y$^-$ contacts which were 0.4 to 0.8 Å shorter than the sum of the van der Waals' radii of the components.[39] The crystal structure of the Dabco complex with the brominating reagent *N*-bromosuccinimide (NBS) features short, linear N–Br···N interactions at each end of the Dabco donor similar to that shown in Figure 4.[40] Moreover, the mean N–Br distance of 2.14 Å (av) compares with 1.82 Å in the uncomplexed NBS. Similar elongations have been observed in (quinoline)$_2$Br$^+$,ClO$_4^-$ and (quinuclidine)$_2$Br$^+$,BF$_4^-$.[41]

In each of the crystalline EDA complexes, the structural studies establish the interaction of the halogen atom with the donor moiety to lie along their atomic centers. Whether this linear atomic arrangement applies to all EDA complexes of halogen acceptors is not known. Furthermore the relationship of such a geometric arrangement with the nature of the CT excitation remains to be established.[42]

Experimental Section

Materials. 1,4-Diazabicyclo[2.2.2]octane or Dabco (Aldrich) was purified by the removal of water during azeotropic distillation of a benzene solution.[43] The colorless solid was recrystallized twice from anhydrous diethyl ether under an argon atmosphere and stored in a Schlenk flask under argon until use. Quinuclidine (Aldrich) was resublimed prior to use. Carbon tetrachloride, chloroform, and methanol were spectrograde solvents and stored under 3A molecular sieves and used without further purification. Carbon tetrabromide and tetraiodide (Aldrich) were sublimed in vacuo prior to use. Acetonitrile-d_3 (Biorad) was distilled from phosphorus pentoxide and stored over 3A molecule sieves, as were the other deuteriated solvents.

Instrumentation. The UV–vis absorption spectra were measured on a Hewlett-Packard 8450A diode array spectrophotometer with 2 cm^{-1} resolution. The ^{1}H and ^{13}C NMR spectra in solution were obtained on a JEOL FX 90Q FT NMR spectrometer. The CPMAS ^{13}C NMR spectra were measured on a Nicolet NT 360 wide-bore spectrometer at the Colorado State University Regional NMR Center. The infrared spectra were recorded on a Nicolet 10DX FT-IR spectrometer.

Determination of the Formation Constants. In a typical study, a 2-mL aliquot of a standard solution of carbon tetrabromide was transferred to a 1-cm precision quartz cell equipped with a magnetic stir bar. All spectra were measured relative to the pure solvent as reference. Successive additions of a preweighed amount of Dabco to the solution were followed by thorough stirring. The volume change attendant upon the addition of Dabco was assumed to be negligible. After the final spectrum was measured, the solution was allowed to stand for ~10 min as a check for stability. A spectrum of Dabco at its highest concentration was always measured to insure that there was no complication arising from the interference with the relevant CT band.

Charge-Transfer Photochemistry of the Dabco–CBr$_4$ Complex. A saturated solution of the EDA complex from Dabco

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[34] Although the anion radical of CBr$_4$ may be the first-formed species in eq 7, it undergoes rapid fragmentation.

[35] See: Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; Chapter 17.

[36] Dabco differs from other amines in that its cation radical does not readily render its α-hydrogens, see: Griller, D.; Howard, J. A.; Marriott, P. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619.

[37] E.g., see: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell Univ. Press: Ithaca, NY, 1973.

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[42] Compare: Ramasubbu, N.; Parthasarathy, R.; Murray-Rust, P. *J. Am. Chem. Soc.* **1986**, *108*, 4308.

[43] Blair, L. K.; Baldwin, J.; Smith, W. C., Jr. *J. Org. Chem.* **1977**, *42*, 1816.

and carbon tetrabromide was prepared by dissolving the yellow crystals in 2 mL of acetonitrile to make an apparent 0.02 M solution. It was irradiated for 15 min with light from a 450-W xenon lamp using a Pyrex cutoff filter at $\lambda < 380$ nm (Corning No. CS 375). The CT absorbance at 310 nm was bleached completely in this time interval. Inspection of the ^{1}H NMR spectrum revealed that the Dabco resonance at δ 2.64 diminished in intensity as it moved downfield to δ 3.04. Addition of diethyl ether led to a colorless precipitate, the ^{1}H and ^{13}C NMR spectra of which showed singlet resonances at δ 3.04 and 45.18, respectively. These resonances coincided with that of an authentic sample of Dabco·HBr prepared from a solution of Dabco in acetonitrile and concentrated hydrobromic acid.

X-ray Crystallography of the EDA Complex of Dabco and Carbon Tetrabromide. A large yellow plate of approximate dimensions 0.50 × 0.50 × 0.20 mm was mounted on a glass fiber in a random orientation on an Enraf-Nonius CAD-4 automatic diffractometer. As the crystals were being examined, a strong odor of chloroform was detected.[15] The radiation used was Mo Kα monochromatized by a dense graphite crystal assumed for all purposes to be 50% imperfect.

Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table I. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown to be either $P2_1$ or $P2_1/m$. Intensities were measured by using the θ–2θ scan technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and during the first 8 h of the experiment one standard lost 75% intensity while the other only lost 20%. There was no way to correct for such anisotropic decay, and so this data was abandoned; however since the decay seemed to be leveling off a new data collection was begun from this point using the same crystal. Now the intensity decay was isotropic and occurred at a rate of only 0.75% per h. In reducing the data, Lorentz and polarization factors were applied, as well as an empirical absorption correlation based on the measurement of five reflections having ψ values near 90°.

Since the unitary structure factors exhibited centric statistics, space group $P2_1/m$ was initially chosen. The structure was solved by MULTAN,[44] which revealed the positions of two ordered, independent CBr$_4$ molecules on mirror sites and two heavily disordered Dabco molecules situated about inversion centers. Naturally, it would be impossible for an ordered Dabco molecule to lie around a $\bar{1}$, but two staggered ones there only 50% of the time each is allowable. When all of the non-hydrogen atoms had been located, the space group was switched to $P2_1$ in the hopes that the forced disorder about the $\bar{1}$ sites would disappear. Unfortunately the problem remained and thus indicated a true statistical disorder of the Dabco molecules. Therefore the final refinement was made in $P2_1/m$. No attempts were made to position hydrogen atoms ideally, and only the bromine atoms were refined anisotropically. The Dabco carbon atoms were given 50% population factors each and refined with rather strict distance constraints based on normal C and N geometry. Thus we were unable to determine whether the Dabco molecules are twisted or straight, except possibly by the examination of the N···N′ separations (avg = 2.53 Å). The crystal structure of this compound seems reasonably well determined, consisting of infinite chains of alternating CBr$_4$ and Dabco molecules along the b axis, with close Br···N contacts. All calculations were made by using the SHELX-76 series of crystallographic programs. The final fractional positional parameters for the Dabco–CBr$_4$ complex are included in Table VIII.

Table VIII. Final Fractional Coordinates of the Amine–CBr$_4$ Crystals[a]

atom	x	y	z	B A^2
		[Dabco, CBr$_4$]		
Br$_1$	0.6723 (8)	0.1521 (3)	0.7788 (4)	3.7 (1)
Br$_2$	0.494 (1)	0.250	0.5478 (5)	3.3 (2)
Br$_3$	0.2024 (9)	0.250	0.7362 (5)	3.5 (2)
Br$_4$	0.6766 (8)	0.1600 (4)	0.2759 (4)	4.5 (1)
Br$_5$	0.514 (2)	0.250	0.0574 (5)	7.3 (3)
Br$_6$	0.239 (1)	0.250	0.2345 (7)	6.0 (2)
N$_1$	0.052 (4)	0.545 (2)	0.585 (2)	2.5*
N$_2$	0.115 (5)	0.535 (2)	0.081 (2)	3.0*
C$_1$	0.489 (8)	0.250	0.699 (4)	2.5*
C$_2$	0.56 (1)	0.250	0.225 (5)	2.5*
C$_3$	0.119 (9)	0.579 (4)	0.489 (5)	2.5*
C$_4$	0.113 (9)	0.461 (4)	0.600 (5)	2.5*
C$_5$	−0.19 (1)	0.546 (7)	0.558 (7)	2.5*
C$_6$	0.01 (1)	0.403 (6)	0.506 (5)	2.5*
C$_7$	0.12 (1)	0.513 (5)	0.399 (5)	2.5*
C$_8$	−0.228 (9)	0.508 (4)	0.437 (4)	2.5*
C$_9$	0.28 (1)	0.516 (4)	0.017 (5)	3.0*
C$_{10}$	−0.08 (1)	0.577 (5)	0.015 (5)	3.0*
C$_{11}$	0.03 (1)	0.465 (5)	0.128 (5)	3.0*
C$_{12}$	−0.21 (1)	0.545 (5)	−0.099 (6)	3.0*
C$_{13}$	−0.14 (1)	0.438 (5)	0.028 (6)	3.0*
C$_{14}$	0.12 (1)	0.471 (5)	−0.080 (5)	3.0*
		[Quinuclidine, CBr$_4$]		
Br$_1$	0.2040 (3)	0.204	0.204	3.74 (4)
Br$_2$	0.0726 (3)	−0.0549 (3)	0.1811 (3)	4.00 (7)
N	0.338 (2)	0.338	0.338	2.4 (9)*
C$_1$	0.085 (2)	0.085	0.085	4 (1)*
C$_2$	0.477 (3)	0.477	0.477	4 (1)*
C$_3$	0.281 (3)	0.351 (3)	0.465 (3)	8 (1)*
C$_4$	0.366 (3)	0.433 (3)	0.539 (3)	9 (1)*
H$_2$	0.5291	0.5291	0.5291	7*
H$_3$A	0.2738	0.2681	0.5026	7*
H$_3$B	0.1982	0.3887	0.4563	7*
H$_4$A	0.3903	0.3844	0.6142	7*
H$_4$B	0.3156	0.5052	0.5668	7*

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Asterisk identifies atom refined isotropically.

Spectral Studies of the Dabco–CBr$_4$ Complex. The infrared spectrum of Dabco in a KBr pellet showed bands at 2965 (s), 2942 (s), 2874 (s), 2248 (w), 1680 (m), 1459 (m), 1352 (w), 1317 (m), 1298 (w), 1060 (s), 994 (s), 905 (m), 891 (w), 836 (m), 775 (s), and 750 (m) cm^{-1} in the 400–3000 cm^{-1} region. The infrared spectrum of carbon tetrabromide in a KBr pellet showed a single strong band at 662 cm^{-1}. By comparison, a KBr pellet of crystalline Dabco–CBr$_4$ showed bands at 2958 (s), 2934 (s), 2869 (s), 1455 (m), 1353 (m), 1317 (m), 1300 (w), 1058 (s), 987 (w), 900 (w), 831 (m), 774 (s), 753 (m), and 660 (s) cm^{-1}.

The chemical shifts of the ^{1}H and ^{13}C NMR resonances of the Dabco–CBr$_4$ complex in a saturated (~0.2 M) solution in chloroform was estimated by the following procedure. The observed change $\Delta\delta = 0.5$ ppm in the ^{1}H NMR spectrum is attributed to the time-averaged resonance arising from 15 mol % complex and 85 mol % uncomplexed Dabco by using a value of $K \simeq 1.2$ M^{-1}. On this basis, the calculated change is estimated to be $\Delta\delta \sim 0.33$ ppm for the pure complex (δ ~3.0). Likewise, the chemical shifts of the ^{13}C NMR resonance of the Dabco–CBr$_4$ complex can be estimated as δ 48.3 and −20.4 for the donor and acceptor moieties, respectively, from the observed change $\Delta\delta = 1.33$ and 9.07 ppm.

The electronic spectrum of the crystalline Dabco–CBr$_4$ recorded in the transmission mode of a finely divided powder showed two bands with maxima at 239 and 301 nm. The latter represents a shift of ~5 nm from that shown in Figure 7b.

X-ray Crystallography of the EDA Complex of Quinuclidine and Carbon Tetrabromide. A single crystal of the 1:1 EDA complex was prepared from quinuclidine (50 mg, 0.45 mmol) and carbon tetrabromide (155 mg, 0.47 mmol) in 2 mL of acetonitrile at −20 °C in the dark. A large clear block having a slight yellow tinge, size 0.60 × 0.50 × 0.50 mm, was mounted on the diffractometer and otherwise treated as described above. The Laue symmetry was determined to be $m3$, and from the systematic absences noted the space group was shown unambiguously to be $P2_13$. The intensities were measured by using the θ–2θ scan technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these decayed isotropically by 37% over a 6-h period of data

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collection. A linear decay correction was made to account for this change. In reducing the data, Lorentz and polarization factors were applied, as well as an empircial absorption correction based on the measurement of five reflections having ψ values near 90°.[45] The structure was solved by MULTAN,[44] which revealed the positions of the two Br atoms in the asymmetric unit. The latter was comprised of $^1/_3$ CBr_4 and $^1/_3$ quinuclidine, both lying on three-fold axes and thus forming a 1:1 complex. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses; however the least-squares refinement was found to be quite insensitive to the positional or thermal parameters of the non-bromine atoms. They were accordingly refined isotropically. The CBr_4 appears to be significantly different from ideal sp^3 geometry due probably to poor positioning of C_1. An attempt to idealize it by holding C_1 fixed at 0.101, 0.101, 101 resulted in essentially no change in the R value. Thus the true geometry of this acceptor molecule is unsure. The hydrogen atoms were entered in ideal locations, with isotropic temperature factors estimated on the basis of the thermal motion of the associated carbons. After all shift/esd ratios were less than 0.2, convergence was reached at the agreement factors listed in Table III. No unusually high correlations were noted between any of the variables in the last cycle of least-squares refinement, and the final difference density map showed no peaks greater than 0.90 e Å^{-3}. The correct absolute configuration was determined by refining the inverse structure to $R = 0.052$, indicating the reported atomic coordinates to be correct. All calculations were made by using Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS series of programs. The final fractional positional parameters for the quinuclidine–CBr_4 complex are included in Table VIII.

The donor and acceptor components of the EDA complex of quinuclidine and CBr_4 are well-defined in the crystal. The ORTEP diagram in Figure 8 shows one of the discrete donor–acceptor pairs in isolation. The relevant N···Br distance of 2.53 Å is about an angstrom less than the sum of the van der Waals radii of 3.5.[37] Furthermore it is significantly shorter than the corresponding nonbonded contacts of 2.88 and 2.76 Å in the Dabco–CBr_4 complex. The difference between quinuclidine and Dabco may reside in the extra ground-state stabilization of the latter as a result of the transannular interaction of the two nitrogens[46] and indicated by its weaker base strength.[47] The linear C–Br···N arrangement emphasizes the optimum CT interaction of the n-HOMO centered on nitrogen with the σ^* LUMO of the Br–C bond. Thus the CT chromophoric unit in the EDA complex of quinuclidine and CBr_4 consists essentially of the same close nonbonded interaction between nitrogen and bromine as it is in the Dabco–CBr_4 complex (vide supra). Otherwise the comparison of the solid-state CT spectra in Figure 7 merely reflects quantitative differences in these amine donors. The quinuclidine moiety is well-resolved in the crystal of the EDA complex in contrast to the extensive disorder in the crystal of quinuclidine itself.[49] However, there is some ambiguity of the carbon location in the acceptor (vide supra), unlike that in the crystal of CBr_4 itself.[50]

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Supplementary Material Available: Tables of the observed and calculated structure factors for the Dabco–CBr_4 and quinuclidine–CBr_4 complexes (5 pages). Ordering information is given on any current masthead page.

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Permanganate Ion Oxidations. 18. Kinetics and Mechanism of the Oxidation of (*E*)-3-(2-Pyridinyl)-, (*E*)-3-(3-Pyridinyl)-, and (*E*)-3-(4-Pyridinyl)-2-propenoates[1]

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The kinetics and mechanism of the permanganate ion oxidation of (*E*)-3-(2-pyridinyl)-, (*E*)-3-(3-pyridinyl)-, (*E*)-3-(4-pyridinyl)-, (*E*)-6-methyl-3-(2-pyridinyl)-, (*E*)-2-methyl-3-(3-pyridinyl)-, and (*E*)-2-cyano-3-(3-pyridinyl)-2-propenoate have been studied at 418 nm and 526 nm in phosphate-buffered solutions (pH 6.83 ± 0.03). The rate law $v = k[MnO_4^-][\text{substrate}]$ was observed. The structure of the activated complex, the influence of substituents on the rate of oxidation, the philicity of permanganate ion, and the possible autocatalytic role of soluble (colloidal) manganese dioxide are discussed.

Although the permanganate ion oxidation of alkyl-substituted and phenyl-substituted alkenes has received considerable study,[3-12] there is only one report that involves heterocycle-substituted olefins.[1] None of these studies has presented direct or unambiguous evidence for existence of the long-sought elusive four-membered metallacyclooxetane (1; [2 + 2] cycloaddition) or cyclic manganate(V)

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