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Charge-Transfer Character of Halogen Bonding: Molecular Structures and Electronic Spectroscopy of Carbon Tetrabromide and Bromoform Complexes with Organic σ- and π-Donors

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ABSTRACT: *Carbon tetrabromide and bromoform are employed as prototypical electron acceptors to demonstrate the charge-transfer nature of various intermolecular complexes with three different structural types of electron donors represented by (1) halide and pseudohalide anions, (2) aromatic (π-bonding) hydrocarbons, and (3) aromatics with (n-bonding) oxygen or nitrogen centers. UV–Vis spectroscopy identifies the electronic transition inherent to such [1:1] complexes; and their Mulliken correlation with the donor/acceptor strength verifies the relevant charge-transfer character. X-ray crystallography of CBr_4/$HCBr_3$ complexes with different types of donors establishes the principal structural features of halogen bonding.* Heteroatom Chem 17:449–459, 2006; DOI 10.1002/hc.20264

INTRODUCTION

Intermolecular interactions involving various halogen centers, also referred to as halogen bonding [1,2] has recently developed into a powerful methodology for supramolecular design [2]. For example, halogen-bonded complexes are recognized as effective synthons for crystal engineering of nonlinear optic materials, rational drug design, chiral resolution, control of solid-state reactivity, etc. [2–7]. Furthermore, such intermolecular interactions are critical for the reactivity of halogen derivatives [1,8,9] and play important roles in biochemical systems [10]. Thus the nature of halogen bonding has become the focus of numerous experimental and quantum-mechanical studies which concentrate on the relative roles of electrostatic forces, polarization, dispersion, etc. in determining the geometry and stability of such complexes [11–13].

Important insight into the properties of halogen-bonded associates can be provided by recognition of their charge-transfer character. Indeed, the complexes of molecular iodine and bromine acceptors with aromatic donors represent classic examples of charge-transfer compounds [14,15]. In comparison, although intermolecular associates of halocarbons with amines have been known more than a hundred years [16], and complexes of carbon tetrabromide with *p*-xylene were characterized structurally as early as the 1960s [17], only scattered (interim) reports appeared until the end of the 1990s [18–20]. Moreover, a flurry of recent papers have concentrated mainly on iodo- or

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bromoperfluorocarbons, in which the donor interaction with either a polarizable iodine or bromine site is promoted by the fluorine-enhanced acceptor strength [21,22]. Furthermore, halocarbon complexes have been characterized mostly as (solid-state) crystalline compounds, and there are only a few examples of the spectral appearance of new absorption bands for such complexes in solutions [4,19]. As such, the diagnostic features of donor/acceptor associates that are commonly characterized by the Mulliken dependence of their absorption bands [23] are difficult to establish unambiguously. Likewise, the scarce (nonsystematic) literature data do not allow rigorous delineation of the relationship between donor/acceptor properties of the components and the structural characteristics of halogen bonding. As a result, halocarbon interactions have been related mostly to hydrogen bonding, and the charge-transfer nature of their associates has not been so apparent—in contrast to those commonly recognized for the related molecular-dihalogen acceptors.

Accordingly, we now turn to the spectral and structural properties of a series of complexes of carbon tetrabromide and bromoform with three types of donors: (i) halide and pseudohalide anions, (ii) aromatic (π-bonding) hydrocarbons, and (iii) aromatics with (*n*-bonding) oxygen or nitrogen centers. Indeed, the electronic spectroscopy and X-ray crystallography of these intermolecular associates with two representative halocarbons will reveal the effects of the variation of donor/acceptor strengths sufficient to establish the relationship between these halocarbon complexes with those of traditional organic acceptors [23,24]. As a result, we hope to place halogen bonding in the more general context of charge-transfer associations.

RESULT AND DISCUSSION

Electronic Spectra and the Thermodynamics of CBr_4/$CHBr_3$ Bindings in Intermolecular Complexes

UV–Vis absorption studies allow us to establish the spectroscopic and thermodynamic characteristics of intermolecular complexes between bromocarbon acceptors and various donors as follows. Carbon tetrabromide is characterized by a near-UV absorption band at $\lambda_{max} = 225$ nm ($\varepsilon = 6 \times 10^3$ M^{-1} cm^{-1}), and thiocyanate as the tetrabutylammonium salt shows only an absorption band with $\lambda_{max} < 250$ nm such that their separate solutions are colorless. However, when thiocyanate salt was added to the solution of CBr_4 in dichloromethane, a pale yellow coloration was observed immediately. This coloration was related to the appearance of new an absorption band with maximum at $\lambda_{max} = 315$ nm, the intensity of which grew progressively with incremental additions of thiocyanate (Fig. 1). The same effect was observed upon incremental additions of CB_4 to solutions of thiocyanate; and the application of Job's methods to these systems with different molar ratios (see inset in Fig. 1) shows the [1:1] stoichiometry of the complex, i.e.

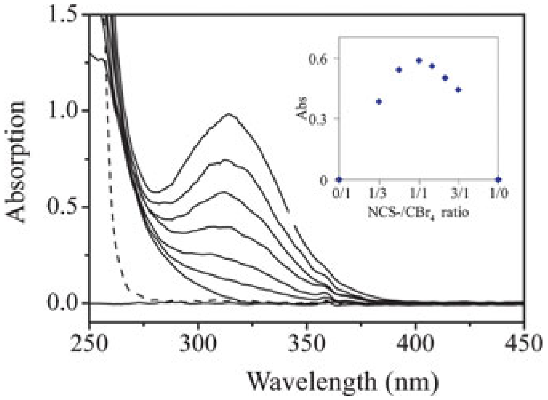

FIGURE 1 Spectral changes (solid lines) attendant upon the addition of $Bu_4N^+SCN^-$ to 10 mM solution of carbon tetrabromide (in CH_2Cl_2, 22°C). Concentration of $Bu_4N^+SCN^-$ (mM): 0, 14, 28, 48, 74, 101, and 132. Dashed line corresponds to (separate) solution of $Bu_4N^+SCN^-$ (133 mM). Inset: Job's plot in solutions with sum of in CBr_4 and SCN^- concentrations of 50 mM showing the formation of [1:1] complex.

$$CBr_4 + Bu_4N^+SCN^- \overset{K}{\rightleftarrows} Bu_4N^+[SCN^- \cdot CBr_4] \qquad (1)$$

The intensity of the absorption band at $\lambda_{max} = 315$ nm was significantly increased upon lowering the temperature (at constant concentrations of components). From the concentration and (reversible) temperature dependences of the absorption intensities, the formation constant, enthalpy, and entropy of complex formation, as well as the extinction coefficient of the complex were determined as described in Experimental; and these data are presented in Table 1.

In a similar manner, the addition of carbon tetrabromide to dichloromethane solutions of iodide, bromide, or chloride anions (and vice versa) resulted in the appearance of new UV-bands to indicate the formation of [1:1] of complexes [halide$^-\cdot$$CBr_4$] [4]; and the concentration/temperature dependences of these bands led to the thermodynamic parameters in Table 1.

The addition of thiocyanate salt to bromoform solutions (and vice versa) also resulted in the appearance of additional absorptions, which were, however, blue shifted to about 250 nm (Unfortunately,

TABLE 1 Thermodynamic Parameters and Spectral Characteristics of Carbon Tetrabromide Complexes with Various Donors

Donor	λ_{max} $(\varepsilon)^a$	K^b	$-\Delta H^c$	$-\Delta S^d$
CNS^-	315 (11)	0.8	2.2	8
TMPD	380 (3.2)	0.3	4.5	14
I^-	292 $(10)^e$	2.8^e	3.2	9
Br^-	345 $(13)^e$	3.2^e	2.7	8

[a] λ_{max} in nm, in parenthesis extinction coefficient ε, in 10^3 $M^{-1}cm^{-1}$.
[b] K in M^{-1}, at 295 K.
[c] $-\Delta H$ in kcal M^{-1}.
[d] $-\Delta S$ in e.u.
[e] From [4].

the intense (local) absorptions of the components prevented quantitative evaluation of complex formation). The interaction of bromoform with iodide anion resulted in the appearance of a new absorption at $\lambda_{max} \approx 280$ nm, which was observed as a shoulder on the absorption tail of bromoform itself. As the result, this new band was characterized by spectral subtraction of the absorption spectra of the individual components from the spectrum of solutions containing both reagents. Furthermore, solutions containing bromoform and either bromide or chloride as tetraalkylammonium salts showed no new bands at wavelengths higher than 250 nm; and the measurements in the far-ultraviolet spectral region ($\lambda < 250$ nm) were barred by strong component absorptions. We similarly carried out UV–Vis spectral measurements of intermolecular interactions of CBr_4 or $CHBr_3$ with various alkyl-substituted benzenes and polycyclic aromatics, as well as alkylamino- and methoxy-substituted benzenes containing both aromatic and heteroatom (*n*-donor) centers. However, only the addition of tetramethyl-*p*-phenylendiamine (TMPD) to the CBr_4 solution in dichloromethane led to the appearance of a clear (new) absorption band with maximum around 380 nm (which was not present in the spectrum of either the separate donor or acceptor). New absorptions band at 300 nm could also be recognized at low temperature in CBr_4 solutions with 9,10-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene (DMA). In other cases, no new bands were observed in the visible region, while strong absorptions of aromatic donors obstructed the UV-spectral measurements. For $TMPD \cdot CBr_4$ solutions, the dependences of the band intensity with reagent concentration and the temperature led to the evaluation of the thermodynamics for formation of [1:1] complexes and extinction coefficients listed in Table 1.

The data in the Table 1 indicated that thermodynamics of complex formation of various donors with carbon tetrabromide with $-\Delta H \sim 2$–5 kcal M^{-1}, and their extinction coefficients of $\varepsilon \sim (1$–$10) \times 10^3$ M^{-1} cm^{-1} were in the range that is characteristic for traditional charge-transfer complexes. To further establish their charge-transfer character, we turned to the relationship between their spectroscopic features and donor/acceptor properties.

Mulliken Correlations of Charge-Transfer Energies

For donor/acceptor complexes, the energy of the optical (electronic) transition is determined primarily by their HOMO/LUMO separation [23] that is evaluated via redox potentials in solution or ionization potential/electron affinity in the gas phase. As such, the most characteristic feature of charge-transfer complexes with the same acceptor is the linear dependence of their absorption energy with the oxidation potential of the donor; and vice versa, in the series of complexes with the same donor, the linear dependence of the transition energy follows the reduction potential of the acceptor. Accordingly, we consider the spectral properties of complexes of (i) carbon tetrabromide with different donors, and (ii) halide donors with CBr_4 and $CHBr_3$ in comparison with those of traditional organic acceptors.

Figure 2A demonstrates the linear dependence of the absorption energy in the series of CBr_4 complexes and various donors with their oxidation potentials. Similarly, the energies of the optical transitions in the series of iodide or bromide complexes with different acceptors also showed the linear correlation with the reduction potentials (Fig. 2B). (Note: oxidation/reduction waves observed in the cyclic voltammetry of some reactants were not reversible, as described in Experimental, and therefore values of the corresponding potentials are not rigorous.)

Since bromocarbons are relatively weak acceptors, the electronic absorptions of their complexes were observed in the UV region, and most donors were also characterized by strong absorptions in the same range. Therefore, of all the aromatic donors we were able to recognize the charge-transfer absorption band for the CBr_4 complexes only with TMPD and DMA (owing to the combination of their strong donor strength and rather high-energy absorption). The spectral transparency of the halide donors at $\lambda > 250$ nm allowed the characterization of their complexes with CBr_4. However, iodide complexes with the weaker acceptor, $I^- \cdot CHBr_3$, showed clear (new) bands, while the absorption of corresponding chloride and bromide complexes were apparently blue shifted to below 250 nm. It is important to note that (i) the Mulliken correlations in Fig. 2A are valid

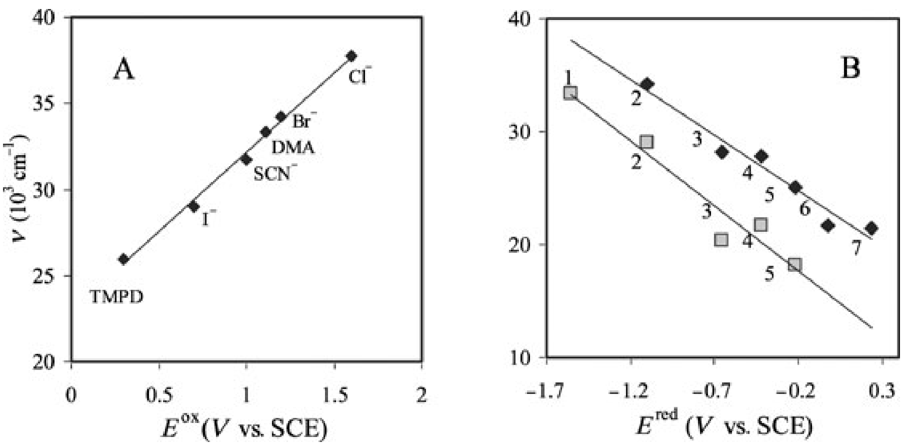

FIGURE 2 Mulliken dependence of energy of charge-transfer transition: (A) in the series of complexes of CBr_4 acceptor on oxidation potential of donors (as indicated); and (B) in the series of complexes of bromide (rombics) and iodide (squares) on reduction potential of acceptor: $CHBr_3$ (1), CBr_4 (2) tetracyanobenzene (3), trinitrobenzen (4), tetracyanopyrazine (5) *p*-chloranile (6), and tetracyanoethylene (7) [25].

in the series of quite different donors; and (ii) $CHBr_3$ and CBr_4 clearly fall on the trend line with the other acceptors in Fig. 2B. As such, these correlations illustrate the charge-transfer character of bromocarbon complexes, and their close relationship to that of other organic acceptors. Accordingly, we now consider the donor/acceptor effects on the structural features of such intermolecular associates.

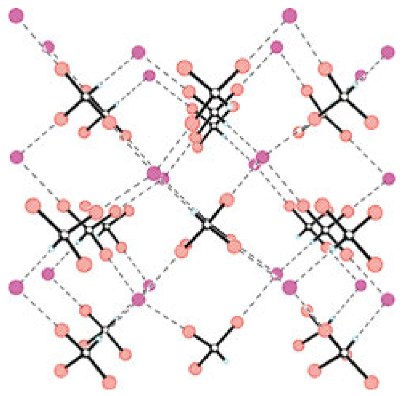

FIGURE 3 The (distorted) diamandoid network in the structure of $Et_4N^+I^- \cdot CHBr_3$ with halogen and hydrogen bonds shown in dashed lines. The Et_4N^+ counterions are omitted for clarity.

Crystallization of CBr_4 and $CHBr_3$ Complexes and an Overview of Their Structures

Complexes of Bromoform with Halides. To prepare crystalline complexes, equimolar quantities of bromoform with iodide or bromide as tetraalkylammonium salts were heated under argon to 60°C. The mixture of bromoform and tetrapropylammonium iodide led to a homogeneous melt; but small amounts of methanol were added to the mixtures of $CHBr_3$ with tetraethyl- and tetramethylammonium salts in order to obtain homogeneous (at 60°C) solutions (see Experimental). Subsequent slow cooling to 0°C resulted in the formation of colorless crystals suitable for X-ray measurements.

The X-ray studies of single crystals with the [1:1] general stoichiometry that were formed in $Et_4N^+I^- \cdot CHBr_3$ and $Et_4N^+Br^- \cdot CHBr_3$ systems showed diamandoid three-dimensional networks (Fig. 3) very similar to that observed earlier in the corresponding CBr_4 complexes [4].

The bromoform component in these structures is halogen and hydrogen bonded to four halides (and vice versa); and they alternate in a regular manner with anions at the nodes of adamantane-like cages occupied by tetraethylammonium counterions. Since the symmetry of $CHBr_3$ is lower than that of (tetragonal) CBr_4, their diamandoid networks differ somewhat. Thus in the $Et_4N^+Br^- \cdot CHBr_3$ crystals, the directions of C—H···Br and C—Br···Br contacts interchange statistically, such that bromoform is disordered. By contrast, in the crystals with tetraethylammonium iodide, $CHBr_3$ shows quite regular orientations (Fig. 3). Noticeably, this (trigonal) acceptor is crystallized in *chiral* space group ([$P2_13$])—in comparison with [cubic] *acentric* symmetry of the corresponding crystals with the tetragonal CBr_4.

The variation of the counterion disrupts the diamandoid network. For example, in the bromoform mixture with the tetrapropylammonium iodide, the complex with [2:1] stoichiometry is formed, and the structure shows interchanging bromoform/anion layers (Fig. 4) with two symmetrically nonequivalent

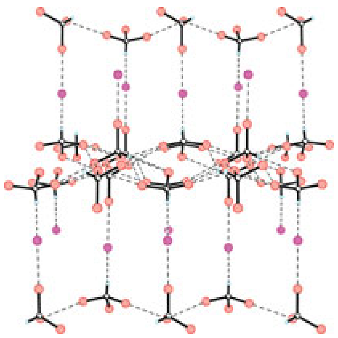

FIGURE 4 The crystal lattice of $Pr_4N^+I^- \cdot CHBr_3$ showing two-dimensional layers with one C—Br···I or C—H···I contact per each molecule of bromoform. The Pr_4N^+ counterions are omitted for clarity.

molecules of bromoform connected to one iodide via C—Br···I and C—H···I short contacts. Interestingly, since each $CHBr_3$ is connected to a donor via only one bromine or hydrogen atom, separate $[I^- \cdot 2CHBr_3]$ complexes can be identified instead of indefinite chains or networks typical for bromocarbon associates (note, however, that shortened Br—Br and H—Br contacts indicate some loose association within bromoform layers).

On the other hand, the crystals of bromoform with the $Me_4N^+I^-$ (which are also of [2:1] acceptor/donor stoichiometry) are characterized by the indefinite 3D networks in which iodide anion is halogen (or hydrogen) bonded with eight molecules of $CHBr_3$.

Carbon Tetrabromide Complex with Thiocyanate. It was crystallized by diffusion of hexane into dichloromethane solutions containing CBr_4 and tetrabutylammonium thiocyanate at −30°C (see Experimental). X-ray measurements revealed that the three-coordinated donors and acceptors form two-dimensional layers (separated by tetrabutylammonium counterions and dichloromethane solvates) consisting of hexagonal (honey-combed) cells (Fig. 5). Noticeably, CBr_4 forms halogen bonds only with the sulfur center of thiocyanates; and SCN^- anions are arranged nearly perpendicular to the $SCN^- \cdot CBr_4$ grid.

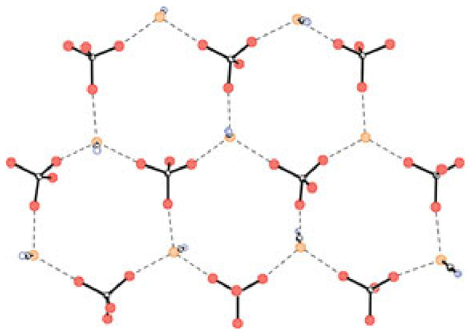

FIGURE 5 Two-dimensional (honey-comb) layers formed by three-coordinated carbon tetrabromide halogen bonded to thiocyanate. The Bu_4N^+ counterions are omitted for clarity.

Complexes of $CHBr_3$/CBr_4 with Methoxy- and Dimethylamino-Substituted Aromatics. Single crystals suitable for X-ray measurements were prepared by isothermal evaporation of the acetone from equimolar donor/acceptor solutions (or by cooling such solutions from +25 to −30°C, see Experimental) for (i) CBr_4 with TMPD and (ii) CBr_4 with 4,4′-bis(dimethylamino)diphenylmethane (DMM), (iii) CBr_4 with DMA, and (iv) $CHBr_3$ with *p*-dimethoxybenzene (DMB) (see Chart 1 in Experimental). In all cases, the structures exhibit similar indefinite chains (Fig. 6), in which the bromocarbon acceptor bridges two donor molecules via halogen bonds with nitrogen or oxygen (similar to indefinite chains formed by the iodo- and bromoperfluorocarbons with molecules containing a pair of *n*-donor centers [2,3].)

π-Coordinated Complexes of Carbon Tetrabromide. Slow diffusion of hexane into solutions of CBr_4 and 2,6-dimethylnaphthalene (DMN) in dichloromethane led to colorless crystals with [1:1] donor/acceptor stoichiometry. X-ray analysis showed that each molecule of DMN coordinates a pair of CBr_4 acceptors with the C—Br bond directed to the centers of two different aromatic rings of naphthalene. In turn, each CBr_4 is bonded to two DMN and this leads to the formation of chains (Fig. 7) comparable to that with *n*-donor atoms (vide supra in the previous section).

Similar π-bonding of halogen was observed when the same crystallization methodology was applied to the solution of carbon tetrabromide with

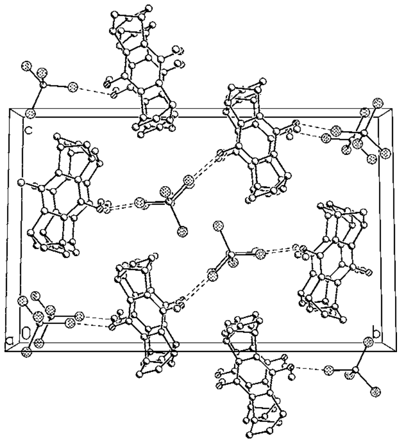

FIGURE 6 Indefinite chains in the structure of $DMA \cdot CBr_4$.

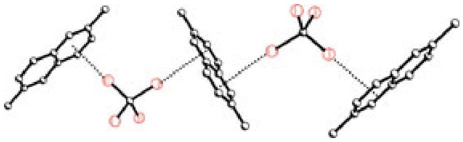

FIGURE 7 Indefinite chains in the structure of DMN · CBr_4.

tribenzylamine (TBA) and octamethyltetraphenylene (OMTP). However in these cases, one carbon tetrabromide interacts with a single donor such that distinct [1:1] complexes can be separated. In each, the direction of C–Br bond is not to the center of the aromatic ring, but off to one side [8b,31].

Finally, the structural parameters that characterize the overall geometry of the halogen bond in various complexes are summarized in Table 2.

Donor/Acceptor (Structural) Effects on Halogen Bondings

The analysis of the data presented in Table 2 together with the earlier reported structures [4,20] allows us to recognize the distinctive features of halogen bonds formed by bromocarbons with *n*- and π-donors, and relate these to the donor/acceptor characteristics. We first note that bromocarbon complexes show structural characteristics of halogen bonding in common with other halocarbons [2b,12b]. In particular, the C—Br···X angles are close to 180°, and the (Br···X) separations between the atoms involved in the halogen bonding are significantly shorter than the sum of their van der Waals radii. Such a shortening is pronounced in bromine bonding with anionic halide or pseudohalide, and with *n*-donor nitrogen or oxygen in aromatic donors, and with π-bonding to benzene rings (in the latter, the C—Br bond is nearly perpendicular and directed to the center of the aromatic ring).

Differences in the nature of electron donors and the effects of (solid-state) crystal forces obscure any global analysis of the interrelationship between donor/acceptor strengths of components evaluated by the corresponding oxidation and reduction potentials (Table 3). However, the separation of structural data into several related series allows us to reveal unambiguously some important correlation between the characteristics of halogen bonding and donor/acceptor properties.

For example, the (counterion induced) differences in the crystal packing result in some variation of the C—Br···Br^- separations in bromide complexes with CBr_4 (entry 1 in Table 3); and the corresponding contractions relative to the sum of the

TABLE 2 Overview of Crystal Structures of Halogen-Bonded Complexes

Formula	*Molecular Aggregate*	*Contacts*[a] *A/D*	*X*[c]	*Br···X*[d] *(Å)*	*C—Br···X*[e] *(in deg)*
$Pr_4NI \cdot 2CHBr_3$	[1:2] Complex	1[b]/2	I^-	3.4722 (13)	179.22 (14)
$Et_4NBr \cdot CHBr_3$	Diamond-like	4/4	Br^-	3.588 (3)	162.82 (6)
$Et_4NI \cdot CHBr_3$	Diamond-like	4/4	I^-	3.5542 (7)	178.49 (12)
$Me_4NI \cdot 2CHBr_3$	3D framework	4[b]/8	I^-	3.5325 (4)	172.93 (11)
				3.5910 (4)	174.49 (11)
				3.8185 (6)	177.05 (11)
$Bu_4NSCN \cdot CBr_4$	Layers	3/3	S	3.2645 (2)	169.66 (14)
				3.157 (2)	171.52 (14)
				3.243 (2)	165.64 (14)
TMPD · CBr_4	Chains	2/2	N	2.774 (2)	169.29 (10)
DAM · CBr_4	Chains	2/2	N	2.819 (6)	170.0 (2)
DMA · CBr_4	Chains	2/2	O	2.860 (2)	172.98 (10)
				2.821 (2)	174.00 (9)
DMB · $CHBr_3$	Chains	2/2	O	2.9891 (18)	179.35 (10)
DMN · CBr_4·	Chains	2/2	Ar[f]	3.324 (2)[g]	173[h]
OMTP · CBr_4	[1:1] Complex	2/2	Ar[f]	3.144 (2)[g]	166[h]
				3.337 (2)[g]	175[h]
TBA · CBr_4	[1:1] Complex	2/2	Ar[f]	3.361 (4)[g]	179[h]

[a] Number of contacts per acceptor and per donor (halogen or hydrogen bond).
[b] Per each independent acceptor.
[c] Donor atom.
[d] Br···X separation.
[e] C—Br···X angle.
[f] Halogen (π-)bonding to benzene ring.
[g] Distance from Br to aromatic plane.
[h] The angle between C—Br bond and normal to aromatic plane.

TABLE 3 The Relationship between the Halogen-Bond Driven Shortening of the Halogen Bonds (Δl^a) on the Donor/Acceptor Strengths

No.	Complex	Donor Atom	E_A^{red} $(V)^b$	E_D^{ox} (V)	Δl (Å)
1	$Br^- \cdot CBr_4$	Br^-	−1.0	0.96[c]	0.37—0.55[c,d]
2	$Br^- \cdot CHBr_3$	Br^-	−1.5	0.96[c]	0.146
3	$I^- \cdot CBr_4$	I^-	−1.0	0.42[c]	0.41—0.53[c,d]
4	$I^- \cdot CHBr_3$	I^-	−1.5	0.42[c]	0.24—0.36[d]
5	$TMPD \cdot CBr_4$	N	−1.0	0.10[e]	0.63
6	$DAM \cdot CBr_4$	N	−1.0	0.75[f]	0.58
7	$DMA \cdot CBr_4$	O	−1.0	1.11[g]	0.53
8	$DMB \cdot CHBr_3$	O	−1.5	1.50[h]	0.38

[a] Relative to the sums of van der Waals radii, which are 3.70, 3.83, 3.40, and 3.37 Å for bromine contacts with Br, I, N, and O, respectively.
[b] In V vs. SCE.
[c] From [4].
[d] In structures with different counterions.
[e] From [26].
[f] From [27].
[g] From [28].
[h] From [29].

van der Waals radii vary in the 0.37–0.55 Å range. Most important, however, is the fact that the weaker bromoform acceptor affords noticeably smaller contractions of the C—Br···Br separation (entry 2). The same tendency toward smaller contractions with weaker acceptors is observed in the carbon tetrabromide and bromoform complexes with iodide (entries 3 and 4). Moreover, according to the literature data on bromocarbon complexes with hexamethylenetetramine, (HMT), the Br···N bond in the much shorter (2.606 Å) in the $HTM \cdot CBr_4$ complex [20], than in bromoform associate $HTM \cdot CHBr_3$ (3.062 Å [30]).

The halogen bonding also correlates clearly with the change of the donor strength. For example, among the complexes with the same carbon tetrabromide acceptor the C—Br···N separation is shorter in the CBr_4 associate with the stronger TMPD donor (entries 5 and 6). In the similar manner, the contraction of the C—Br···O contact relative to the sum of van der Waals radii is more pronounced in the $DMA \cdot CBr_4$ than in $DMB \cdot CHBr_3$ in accord with the fact that CBr_4 is a better acceptor than $CHBr_3$, and DMA is a better donor than DMB.

A similar tendency is observed in carbon tetrabromide complexes with π-type (aromatic) donors. Thus, the separation between the bromine atom and the benzene plane is decreased from 3.34 Å in the CBr_4 complex with the weak *p*-xylene donor [17], to 3.21 Å in the associate with the stronger durene donor [31] and further to 3.144 Å in the complex with OMTP (oxidation potentials for these donors are 2.01, 1.84, and 1.75, respectively, [32]).

Thus, both spectral and structural data are consistent with the charge-transfer nature of the bromocarbon complexes with different types of donors. Moreover, we noted earlier [4] that the association of the carbon tetrabromide with halide anions is accompanied by the (average) elongation of C—Br bond length from ~1.93 Å to ~1.96 Å—in accord with the σ* nature of the acceptor LUMO. In this respect, it is interesting to compare the C—Br bondlengths with bromine involved in halogen bonding versus uncoordinated ones and to establish the localization of the charge transferred to a bromocarbon. Unfortunately, in the most of (diamondoid) X-ray structures, all bromine atoms are bonded to donors or disordered, which precludes such a comparison. Still, we could find a few examples featuring both bonded and nonbonded bromines. Importantly, they do reveal the differences in C—Br bondlengths to indicate the localization of charge transferred mainly to that carbon bond with a halogen-bonded bromine. For example, such an effect is clear in the $Pr_4NI \cdot CHBr_3$ systems, in which only one of the bromine atoms is involved in the bonding with iodide. Noticeably, the relevant C—Br bond is lengthened to 1.942 Å, while the other C—Br bondlengths are 1.920 ± 0.005 Å. In the same way, the "localized" lengthening the C—Br bond can be detected in carbon tetrabromide complexes with alkyl aniline donors. Thus in $TMPD \cdot CBr_4$, the C—Br bonds with N-coordinated bromine are 1.950(2) Å, as compared to the bondlength of 1.932(4) Å involving the noncoordinated bromine; and in $DAM \cdot CBr_4$, the corresponding values are 1.952(4) and 1.935(4) Å. The most pronounced effect is observed in the carbon tetrabromide complex with 1,4-diazabicyclo[2,2,2]octane (DABCO), in which two C—Br bonds (nitrogen coordinated to bromine) are 2.118 Å, while those with uncoordinated bromine are 1.904 and 1.876 Å ([19c], compare also [19e]). (Note that in bromocarbon complexes with weaker methoxy-substituted aromatic donors, the C—Br bonds are equivalent: 1.938 ± 0.005 Å in $DMA \cdot CBr_4$ and 1.926 ± 0.003 Å in $DMB \cdot CHBr_3$.)

SUMMARY

The spectral and structural study of the halogen-bonded complexes of two representative halocarbons (bromoform and carbon tetrabromine) with various donors shows

(i) a direct relationship of the spectral characteristics of these complexes with those of traditional organic acceptors; and most importantly, the

Mulliken dependence of the absorption band as the most characteristic feature of charge-transfer complexes;

(ii) thermodynamics of the complex formation in the same range as that of classic donor/acceptor associates;

(iii) clear correlation between halogen-bond length and donor/acceptor strengths—the stronger donor and/or acceptor leading to more significant shortening of the $Br\cdots X$ separation (relative to the sum of van der Waals radii) is observed for the each type of donor atom;

(iv) a lengthening of the C—Br bond in the bromocarbons involved in halogen bonding (both overall and particular to that coordinated bromine)—in accord with charge transfer to the σ^*-orbital of the acceptor.

Such data clearly relate bromocarbon complexes to traditional charge-transfer associates, and place halogen bonding within the general context of donor/acceptor (charge-transfer) interactions. Moreover, these results provide an additional insight into the supramolecular design based on the halogen bonding between halocarbons and variety of donors. We also hope that this combined structural and spectroscopic study will provide the basis for further quantitative evaluations of the charge-transfer characteristics in the intermolecular bondings of various halogens.

EXPERIMENTAL

Materials

CBr_4 and TMPD were purified by sublimation under vacuo. Bromoform was washed with H_2SO_4(conc) solution of NaOH, dried over $CaCl_2$, and distilled under vacuo. All other chemicals were used without additional purification. For convenience, the structures and notations of the different aromatic donors are presented in Chart 1.

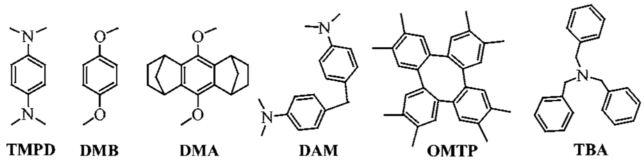

CHART 1

Spectral measurements were carried out in a 1-mm quartz cuvette on HP-845 UV–Vis spectrophotometer; and a Dewar equipped with quartz windows was used for low- temperature experiments. The extinction coefficients of the complexes and the thermodynamics for complex formation were evaluated via the quantitative treatment of the dependences of the absorption intensity (which appeared upon incremental additions of the donor to the bromocarbon dissolved in dichloromethane or vice versa) on the concentration of the reactants and temperature as described earlier [4].

Cyclic voltammetry (CV) was performed in dichloromethane solutions (with Bu_4NPF_6 supporting electrolyte under argon) using on a BAS 100A electrochemical analyzer equipped with platinum electrode, as previously described [4]. Owing to the high reactivity of reduced bromocarbons, their reversible redox potentials were not accessible; and for the evaluation of their acceptor strength, we used the irreversible cathodic reduction waves which were observed at −1.0 and −1.5 V in the cyclic voltammograms of solutions of CBr_4 and $CHBr_3$, respectively. Although these waves were affected by kinetic terms, and deviated from strict thermodynamic values of the redox potential, the reduction potentials measured for different acceptors under the same conditions reasonably reflected the change of their relative values, and was used in the various correlations [4]. The same reasoning was applied in extracting the oxidation potentials from irreversible (in some cases) anodic CV waves of the donors.

Crystallization of Bromocarbon Complexes with Various Acceptors

Single crystals of the bromoform complexes with halide anions were obtained by the heating suspensions of the corresponding alkylammonium salts in $CHBr_3$. For example, 400 mg of $Pr_4N^+I^-$ was added under argon to 0.6 mL of bromoform. Heating this mixture to 60°C resulted in a homogenous liquid, and subsequent slow cooling to 0°C led to colorless crystals (mp 52°C) suitable for X-ray measurements. Single crystals of the bromoform complexes with bromide and iodide as ethyl- and methylammonium counterions were prepared in the similar way. However, to obtain homogeneous liquid at 60°C, small amounts of methanol were added to $Et_4N^+I^- \cdot CHBr_3$ and $Et_4N^+Br^- \cdot CHBr_3$ suspensions, and small amounts of a $MeOH/H_2O$ mixture to the $Me_4N^+I^- \cdot CHBr_3$ system.

The carbon-tetrabromide complex with thiocyanate anion was crystallized (as the solvate containing two molecules of CH_2Cl_2) by slow diffusion of hexane into 3 mL of dichloromethane solution containing 332 mg of CBr_4 and 38 mg of tetrabutylammonium thiocyanate at −30°C. (Note that CH_2Cl_2 solvates do not show any shortened contacts with thiocyanate donor.)

TABLE 4 Crystallographic Parameters and the Details of the Structure Refinements

Compound	$Pr_4NI\cdot 2CHBr_3$	$Et_4NI\cdot CHBr_3$	$Et_4NBr\cdot CHBr_3$	$Me_4NI\cdot 2CHBr_3$	$Bu_4NSCN\cdot CBr_4\cdot 2CH_2Cl_2$	$TMPD\cdot CBr_4$	$DAM\cdot CBr_4$	$DMA\cdot CBr_4$	$DMB\cdot CHBr_3$	$DMN\cdot CBr_4$	$TBA\cdot CBr_4$	$OMTP\cdot CBr_4$
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Orange	Yellow	Colorless	Colorless	Colorless	Colorless	Colorless
M	818.8	509.9	462.9	706.5	802.4	495.9	586.0	602.0	390.9	488.8	619.0	1284.2
Space group	$Pna2_1$	$P2_13$	F-43m	$Pnma$	$Pbca$	$P2_1/m$	$C2$	$P2_1/n$	$Pnma$	$Pnma$	$P2_1/c$	P-1
a (Å)	23.070 (8)	11.718 (2)	11.5725 (5)	15.559 (1)	17.17 (1)	5.917 (2)	8.7049 (3)	6.118 (2)	6.400 (3)	12.218 (3)	6.1387 (8)	10.5494 (2)
b (Å)	9.052 (2)	11.718 (2)	11.5725 (5)	12.3825 (9)	14.29 (1)	21.641 (7)	8.2444 (2)	23.110 (10)	26.516 (8)	20.072 (5)	41.407 (6)	15.8626 (2)
c (Å)	12.306 (2)	11.718 (2)	11.5725 (5)	8.7093 (6)	26.30 (1)	6.000 (2)	14.3469 (4)	14.616 (5)	7.264 (4)	6.112 (1)	9.2180 (12)	18.8187 (3)
α (°)	90	90	90	90	90	90	90	90	90	90	90	100.15 (1)
β (°)	90	90	90	90	90	97.36 (1)	95.89 (1)	96.94 (3)	90	90	105.80 (3)	93.46 (1)
γ (°)	90	90	90	90	90	90	90	90	90	90	90	107.135 (1)
V (Å^3)	2570	1609	1550	1678	6453	762	1024	2051	1233	1499	2254	29.41
F (000)	1536	960	888	1280	3184	472	568	1168	744	920	1200	1304
μ (mm^{-1})	10.57	9.41	10.36	16.17	5.40	10.54	7.862	7.86	9.79	10.72	7.147	2.913
ρ (g/cm^3)	2.116	2.105	1.984	2.797	1.651	2.161	1.900	1.949	2.107	2.162	1.824	1.450
Refls	22800	25019	13740	20981	97795	11676	3537	31291	18937	22948	34135	42681
Indpndt	7586	1708	271	2713	9449	2398	3536	6258	1947	2387	6567	25599
Obsd (F ¿ 4σ)	5201	1437	232	2123	4113	1927	2805	4321	1456	1774	4154	16629
Parameters	272	41	23	67	274	84	112	226	67	82	244	674
R_1 (F ¿ 4σ)	0.0332	0.0303	0.0338	0.0312	0.0410	0.0300	0.0540	0.0321	0.0292	0.0297	0.0381	0.0597
wR_2	0.0630	0.0803	0.0898	0.0873	0.1114	0.0714	0.1231	0.0712	0.0728	0.0716	0.0947	0.1569
GooF	0.823	0.969	1.055	1.028	0.815	0.966	1.019	0.906	0.947	0.930	0.861	1.011

The crystals of the bromocarbon complexes with alkylamino- and methoxy-substituted aromatics (TMPD, DMA, DMB, and DAM) were prepared by the isothermal evaporation of the acetone from the equimolar donor/acceptor solutions. Complex TMPD $\cdot$ CBr_4 was alternatively prepared by the slow cooling of the solutions from +25 to −30°C.

Slow diffusion of hexane into the solution of 50 mg of CBr_4 and 50 mg of 2,6-dimethylnaphtalene (DMN) in dichloromethane led to the formation of colorless crystals with [1:1] donor/acceptor stoichiometry. The crystals of the carbon tetrabromide complexes with OMTP and TBA were prepared in the similar way.

X-Ray Crystallography

The intensity data were collected with aid of a Siemens SMART Apex diffractometer equipped with a CCD detector using Mo Kα radiation ($\lambda = 0.71073$ Å), at −150°C or −100°C. The structures were solved by direct method and refined by full matrix least-squares procedure with IBM Pentium and SGI O_2 computers [29]. Structural data are presented in Table 4; CCDC 279660 ($Pr_4NI \cdot 2CHBr_3$), 279661 ($Et_4NI \cdot CHBr_3$), 279662 ($Et_4NBr \cdot CHBr_3$), 279663 ($Me_4NI \cdot 2CHBr_3$), 279664 ($DMA \cdot CBr_4$), 279665 ($TMPD \cdot CBr_4$), 279666 ($DMB \cdot CHBr_3$), 279667 ($DMN \cdot CBr_4$), 279668 ($Bu_4NSCN \cdot CBr_4$), 279669 ($DAM \cdot CBr_4$), 279670 ($OMTP \cdot CBr_4$), and 279671 ($TBA \cdot CBr_4$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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