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Halide Recognition through Diagnostic “Anion– π ” Interactions: Molecular Complexes of Cl[–], Br[–], and I[–] with Olefinic and Aromatic π Receptors

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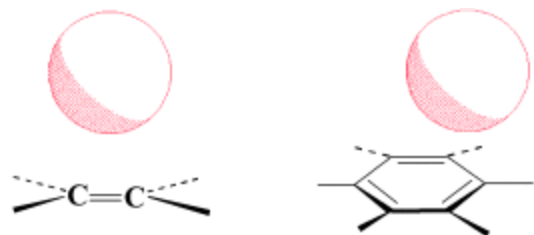
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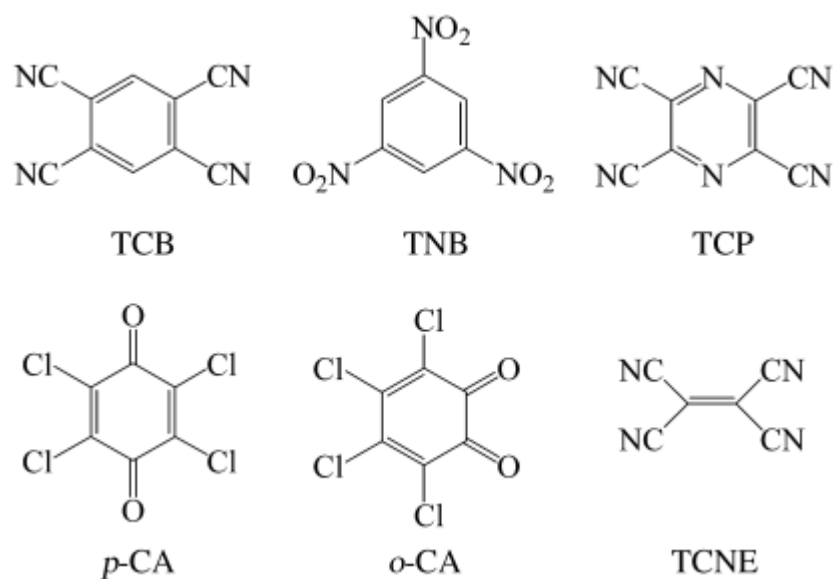
Abstract

Intense colorations and new charge-transfer absorption bands are observed upon addition of a halide (Cl^- , Br^- , I^-) to neutral organic π acceptors with electron-deficient olefinic and aromatic centers. These phenomena results from noncovalent anion- π interactions (shown schematically), which were confirmed by X-ray crystallography.



Noncovalent interactions of anions have become one of the most actively explored areas of supramolecular chemistry.^{1, 2} Indeed, recent quantum-mechanical calculations suggest the possibility of anion binding to uncharged organic π receptors.^{3, 4} However, experimental (X-ray) verification of such direct noncovalent interactions is lacking, and the few observations of anion- π bonding are limited to metal coordination compounds.^{1, 5}

Despite numerous examples of analogous cation- π interactions in a variety of organic and biochemical systems,⁶ anion sensing or recognition have heretofore relied primarily on electrostatic binding or hydrogen bonding to the organic receptor.^{1, 2, 7} Thus, to experimentally characterize direct anion- π interactions in the most unambiguous way, we now turn to a series of neutral organic π acceptors with electron-deficient olefinic and aromatic centers (Scheme 1). The recognition of halide anions X^- ($\text{X}=\text{Cl}$, Br , I) is established by 1) isolation and X-ray structure determination of a series of well-defined 1:1 salt-admixed complexes, and 2) definitive spectral assignments of each of their diagnostic charge-transfer absorption bands.⁸



Scheme 1 Neutral organic π acceptors investigated in this study.

Typically, an aromatic π acceptor such as tetracyanopyrazine (TCP) shows a characteristic UV/Vis spectrum with a strong absorption at $\lambda=220\text{--}300$ nm (shoulder at 350 nm); in acetonitrile the tetraalkylammonium salts of Cl^- , Br^- , and I^- show no absorption beyond 300 nm. However, when a bromide salt is added to TCP,⁹ a new absorption band appears immediately at $\lambda_{\text{max}}=400$ nm and grows with increasing concentration of halide (Figure 1). Job's procedure¹⁰ reveals the 1:1 stoichiometry of the $[\text{TCP}/\text{Br}^-]$ complex (see the Supporting Information).

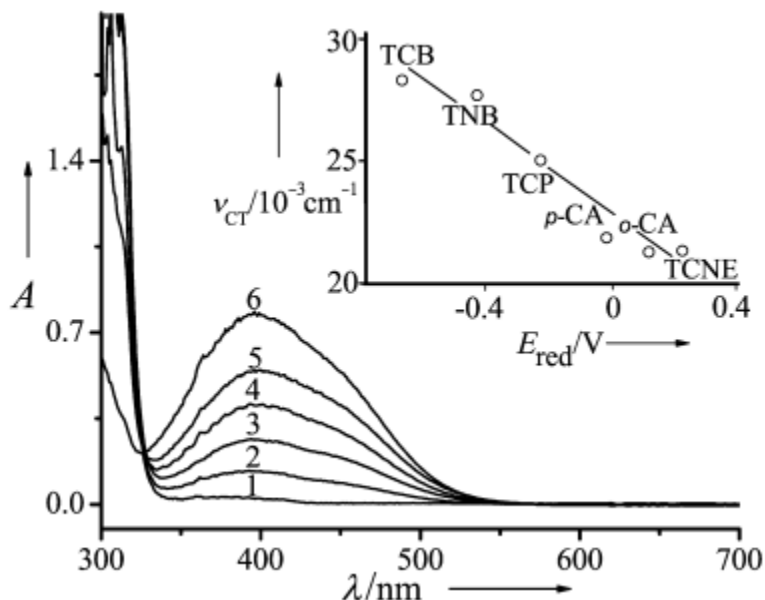


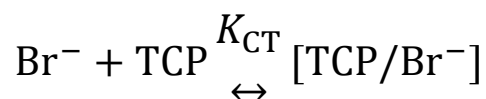
Figure 1 Spectral changes upon incremental addition of $\text{Pr}_4\text{N}^+\text{Br}^-$ —0 mM (line 1), 4.9 mM (line 2), 19 mM (line 3), 46 mM (line 4), 83 mM (line 5), 208 mM (line 6)—to the 5 mM solution of TCP in acetonitrile. Inset: Mulliken dependence of the energy of absorption band (ν_{CT}) with the reduction potential of the π acceptor.

Intense colorations are also observed upon addition of chloride and iodide, and these directly relate to the appearance of new absorption bands that are red-shifted for $[\text{TCP}/\text{I}^-]$ and blue-shifted in $[\text{TCP}/\text{Cl}^-]$ relative to that of $[\text{TCP}/\text{Br}^-]$. Close scrutiny of the spectra of all three complexes reveals that the visible absorption bands consist of two Gaussian components (see the Supporting Information). Most important is the clear Mulliken correlation⁸ between the energy of the low-energy band and the oxidation potential of the anion (see the Supporting Information), which establishes the charge-transfer (CT) character of these complexes.¹¹

In a similar way, addition of halide to the other π acceptors from Scheme 1 results in a change in color from yellow to red and appearance of new absorption bands in the electronic spectra (see the Supporting Information).¹² The increase in acceptor strength (characterized by a positive shift of the reduction potential) is accompanied by the bathochromic shift of this band, and the Mulliken correlation (inset of Figure 1) further confirms the charge-transfer character of these complexes.

The spectral data thus indicate that halide salts form well-defined electron donor–acceptor complexes with organic π acceptors, as typified by Equation (1). Quantitative analyses of the intensity of the new absorption band as a function of the concentration of bromide and π acceptor (by the Drago

procedure⁹) lead to the formation constants $K_{CT}=1-10\text{ M}^{-1}$ and the extinction coefficients $\epsilon_{CT}=500-5000\text{ M}^{-1}\text{ cm}^{-1}$ that are typical of charge-transfer complexes (see the Supporting Information).^{10, 13}



(1)

Slow diffusion of hexane into 1:1 mixtures of TCP with Cl^{-} , Br^{-} , or I^{-} (as alkyl ammonium salts) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ results in the formation of yellow to dark-red crystals. The X-ray crystal-structure analysis reveals that the overall stoichiometry of the $[\text{TCP}/\text{X}^{-}]$ associates varies from 4:1 to 1:1 (Table 1).¹⁴ For example, if chloride is taken in the form of its Pr_4N^{+} salt, the 4:1 $[\text{TCP}/\text{Cl}^{-}]$ complex is isolated in which the anion is surrounded by four acceptors and the cation lies outside the cavity. The same structure is found for $[\text{TCP}/\text{Br}^{-}]$ when propyl- or butylammonium salts are used. If $\text{Et}_4\text{N}^{+}\text{Br}^{-}$ is added, the 3:2 $[\text{TCP}/\text{Br}^{-}]$ complex precipitates with anions surrounded by three TCP molecules. Close TCP– X^{-} contacts with $\text{X}^{-}\cdots\text{C}$ distances of up to 0.4 Å shorter than the sum of the van der Waals radii (Table 1) confirm the strong TCP– X^{-} intermolecular attraction. The solid-state electronic spectra are closely related to those in solution (see the Supporting Information) and thus verify the common charge-transfer nature of the complexes.

Table 1. Solid-state characteristics of halide associates with π acceptors.

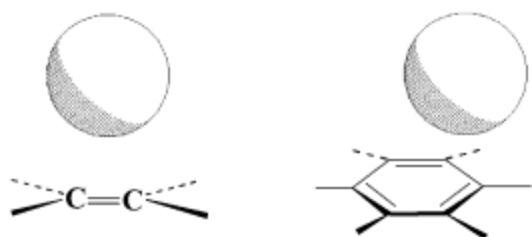
	Molar ratio	Counterion	$\text{X}^{-}\cdots\text{C}$ [Å]^[a]
TCP/ Br^{-}	3:2	Et_4N^{+}	3.16
	4:1	Pr_4N^{+}	3.15
TCP/ I^{-}	2:1	Et_4N^{+}	3.52
	1:1	Bu_4N^{+}	3.49 ^[b]
TCP/ Cl^{-}	4:1	Bu_4N^{+}	3.07
TCNE/ Br^{-}	1:2	Et_4N^{+}	3.20 ^[b]
	1:1	Pr_4N^{+}	3.11
<i>o</i> -CA/ Br^{-}	1:1	Pr_4N^{+}	2.93

[a] The $\text{X}^{-}\cdots\text{C}$ distance in closest contacts; note that the sums of the van der Waals radii are 3.45 Å ($\text{Cl}^{-}\cdots\text{C}$), 3.55 Å ($\text{Br}^{-}\cdots\text{C}$), and 3.68 Å ($\text{I}^{-}\cdots\text{C}$). [b] The average of the distances to the two or three neighboring acceptors is given.

In a similar manner, mixtures of the bromide salt and the olefinic acceptors *o*-CA and TCNE in CH_2Cl_2 yield brown-red crystals. The X-ray structure analysis reveals that in the 1:1 complex with *o*-CA, bromide is located over the center of the $\text{C}=\text{C}$ bond. The $\text{Br}^{-}\cdots\text{C}$ contacts are shortened by as much as 0.6 Å relative to the sum of the van der Waals radii (see the Supporting Information). The location of the anion relative to the acceptor varies in bromide complexes with TCNE. Thus, if $\text{Et}_4\text{N}^{+}\text{Br}^{-}$ is used, the 1:2 $[\text{TCNE}/\text{Br}^{-}]$ complex is isolated in which both anions reside over the olefinic bond, whereas in the 1:1 Pr_4N^{+} complex, the bromide is shifted toward the cyano substituents (see the Supporting

Information). In both cases, however, short intermolecular separations that are characteristic of π - π bonded CT complexes¹³ indicate strong anion-TCNE interactions (Table 1).

The recognition of halides by the π acceptors in Scheme 1 is visually apparent by the color resulting from the diagnostic charge transfer (λ_{CT} , see the Supporting Information). By the same token, the isolation and X-ray crystallography of mixed salts (Table 1) identifies the pertinent separation of the halide donor from the π acceptor, which is responsible for the electronic (charge-transfer) transition. Most importantly, the global Mulliken correlation (inset of Figure 1) underscores the common π -acceptor properties of all the electron-deficient olefinic and aromatic centers. As such, the molecular structure responsible for the color as a result of charge transfer can be gleaned from the X-ray structure data. The composites are schematically presented in Scheme 2 for visualizing the pertinent anion- π interactions.^{13d}



Scheme 2. Schematic drawing of the anion- π interactions. The sphere representing the van der Waals radius of bromide (taken as an example) is drawn to scale relative to the electron-deficient olefinic and aromatic centers.

Thus, the general structural feature of the noncovalent (anion- π) interaction with olefinic acceptors holds the bromide ion at roughly 3 Å over the double bond. Similarly, in anion- π interactions of electron-deficient aromatic π acceptors, the bromide ion lies 3 Å over the periphery of the aromatic ring. Indeed, such structures differ from quantum-mechanical calculations that largely show the anion to lie somewhere along the centroid of the aromatic ring in π complexes with 1,3,5-triazine or hexafluorobenzene.^{3, 15} Furthermore, the possibility of multiple halide- π interactions leads to the formation of three-dimensional solid-state structures in which anions reside in the cavities created by the multiple TCP receptors (Figure 2).

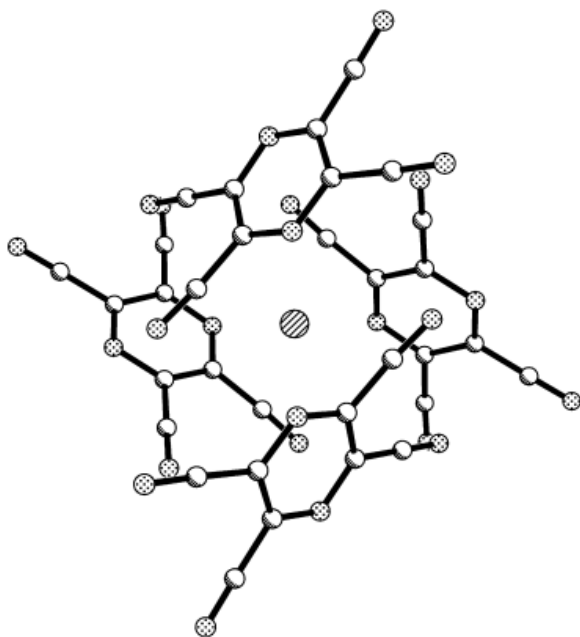


Figure 2. X-ray structure of the 4:1 [TCP/Cl⁻] complex (counterions omitted for clarity).

In summary, the formation constants of the halide complexes with neutral π acceptors, together with the intense absorptions and compression of the intermolecular separations found by X-ray structural analysis,¹⁴ indicate the existence of substantial anion– π interactions. Spectral, thermodynamic, and structural properties of these associates are closely related to those of the classical donor–acceptor complexes,^{10, 13} which indicates the common charge-transfer origin of the seminal anion– π interactions. The formation of relatively strong complexes together with the distinctive colorations of various anion– π interactions encourage their use in the design of anion-sensing receptors, provided systems with multicentered binding sites are chosen for optimum recognition (compare the Venus fly trap).¹⁶ X-ray crystallography of the halide complexes with TCP (see Figure 2 and the Supporting Information) provides insight into the desirable features of such π receptors.

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9. In form of the Pr₄N⁺Br⁻ salt; values for Et₄N⁺Br⁻ or Bu₄N⁺Br⁻ are within the error limit (Table S2).
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11. 11a. High-energy components are tentatively assigned to the transition from the subjacent HOMO-1 of the halide since the difference between two components in the [TCP/Br⁻] absorption of 3.5×10³ cm⁻¹ is comparable to the difference (3.9×10³ cm⁻¹) between the two highest Br⁻ levels (4p_{3/2} and 4p_{1/2}); 11b. J. Overton, J. P. Hernandez, *Phys. Rev. B* 1973, **7**, 778.
12. 12a. Use of KBr leads to the same absorption maximum for the [TCNE/Br⁻] complex (see the Supporting Information); 12b. if TCNE and Pr₄N⁺Br⁻ are simply ground together under an argon atmosphere, the colorless mixture changes to dark purple. The diffuse reflectance spectrum confirms the presence of [TCNE/Br⁻].
13. 13a. *Organic Charge-Transfer Complexes* (Ed.:), Academic, New York, 1969; 13b. *Molecular Complexes* (Ed.:), Crane, Russak, 1973; 13c. A. V. Vasilyev, S. V. Lindeman, J. K. Kochi, *New J. Chem.* 2002, **26**, 582; 13d. for the precise location of the halide anions in the CT complexes, see the Cartesian coordinates in the X-ray (CIF) files.^[14]
14. The intensity data for all compounds were collected with a Siemens SMART APEX diffractometer using MoK_α radiation (λ=0.71073 Å) at -150 °C. Structures were solved by direct methods and refined by full matrix least-squares procedure with IBM Pentium and SGI O2 computers. Crystal data for [(TCP)₄Cl⁻]Bu₄N⁺ (C₄₈H₃₆ClN₂₅): M=998.47, tetragonal space group I4, a=b=13.181(1), c=15.288(1) Å, V=2656.0(1) Å³, ρ_{calcd}=1.248 g cm⁻³, Z=2, 2θ_{max}=63.71. Of 14 580 reflections measured 4309 were symmetrically nonequivalent. R1=0.057 and wR2=0.153 for 4132 reflections with I>2σ(I). For the crystal data of the other complexes from Table 1, see the Supporting Information. CCDC 236236 ([[(TCP)₄Br⁻]Pr₄N⁺·CH₂Cl₂], 236 237 ([[(o-CA)Br⁻]Pr₄N⁺], 236 238 ([[(TCNE)Br⁻]Pr₄N⁺], 236 239 ([[(TCNE)(Br⁻)₂](Et₄N⁺)₂], 236 240 ([[(TCP)₃(Br⁻)₂](Et₄N⁺)₂], 236 241 ([[(TCP)I⁻]Bu₄N⁺], 236 242 ([[(TCP)₂I⁻]Et₄N⁺], 236 243 ([[(TCP)₄Cl⁻]Bu₄N⁺]) 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) 1223-336-033; or deposit@ccdc.cam.ac.uk).

15. 15a. However, the energy difference between the over-ring versus over-center structures in arene π complexes is likely to be small and subject to crystal-packing forces. This has been noted in other donor–acceptor pairs, see: 15b. S. M. Hubig, S. V. Lindeman, J. K. Kochi, *Coord. Chem. Rev.* 2000, **200–202**, 831; 15c. ref [13c] and G. Fukin, S. V. Lindeman, J. K. Kochi, *J. Am. Chem. Soc.* 2002, **124**, 8329; 15d. theoretical calculations^[3b] of 1,3,5-triazine and fluoride, chloride and azide anions also show this ambiguity.
16. See, for example, S. V. Rosokha, S. V. Lindeman, R. Rathore, J. K. Kochi, *J. Org. Chem.* 2003, **68**, 3947.