CHEMCOMM
Communication
www.rsc.org/chemcomm

# Noncovalent binding of the halogens to aromatic donors. Discrete structures of labile $Br_2$ complexes with benzene and toluene†

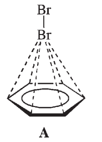
**Aleksandr V. Vasilyev, Sergey V. Lindeman and Jay K. Kochi***

*Department of Chemistry, University of Houston, Houston, Texas, 77204-5641, USA.*
*E-mail: jkochi@pop.uh.edu*

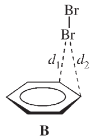
***Received (in Columbia, MO, USA) 14th February 2001, Accepted 4th April 2001***

**Precise molecular structures resulting from the noncovalent interaction of $Br_2$ with benzene (and toluene) reveal the unusual localized bonding to *specific* (one or two) carbon centers in prereactive complexes leading directly to the transition states for electrophilic aromatic brominations.**

Noncovalent interactions of benzene donors with a variety of small molecules including Brønsted acids (*e.g.* HF, HCl, $HOCH_3$), halogens ($X_2 = F_2, Cl_2, Br_2, I_2$) and Lewis acids ($SO_2$, NO, $AlCl_3$), *etc.* are under active investigation.[1,2] Molecular structures of these weak (intermolecular) complexes have been experimentally deduced with the aid of various spectroscopic techniques,[2,3] but their *fine structures* established by X-ray crystallographic methods are largely restricted to the halogen adducts.[4] Since the latter are prereactive intermediates critical to electrophilic aromatic halogenation,[5] it is important to establish the precise location of the noncovalently-bonded halogen relative to the aromatic ring. Unfortunately, the classic X-ray crystallography of the benzene complex of bromine by Hassel and Strømme at −40(−50) °C merely reveals the completely delocalized 'axial' orientation **A**, in which the Br–Br bond (2.28 Å) lies on the six-fold symmetry axis (at a bromine separation of 3.36 Å from the mean plane) of benzene.[6] (In other words, the six π electrons comprising the C–C bonds are all equally involved in the 'bonding' to bromine.) Moreover, the corresponding chlorine complex determined by the same workers at −90 °C shows these noncovalently bound crystals to be isomorphous with **A**[7] (which they also considered as further proof for their interesting axial model).



**A**



**B**

Although the axial model is generally accepted and widely cited, it is at variance with several (recent) theoretical studies which identify a significantly less symmetrical model **B**,[8,9] in which the more localized bonding locates the halogen directly above one C–C bond (*i.e.* $\eta^2$) or above a carbon atom ($\eta^1$).[10] Since a number of detailed IR studies[11,12] have been unable to resolve the ambiguity between the delocalized and localized models of halogen binding to benzene,[13] we sought the more definitive X-ray crystallographic analysis of the bromine complex with benzene as well as with toluene.

Owing to very weak intermolecular interactions, the requisite (1 : 1) bromine complexes with benzene and toluene for our studies were necessarily prepared *in situ* by (low-temperature) crystallization in a glass capillary.[6,7] Very careful temperature modulation was the critical factor in the successful growth of single crystals of the benzene and toluene complexes suitable for X-ray crystallography at −150 °C.†‡

In both the benzene and toluene complexes, dibromine is uniformly oriented perpendicular to the aromatic planes (with slight deviations $\alpha$ of typically < 8°); and the bromine approach occurs at a distance $D$ = 3.01–3.17 Å which is significantly shorter than the sum of the van der Waals radii of 3.55 Å (see Table 1†).[14] Most importantly, the bromine does not coordinate to the benzene ring symmetrically—in striking contrast to the coaxial (delocalized) model **A** reported by Hassel and Strømme.[6] Instead, bromine is positioned over the rim (not above the center) of the benzene ring, being shifted by *ca.* 1.4 Å from the main symmetry axis (see Fig. 1 and $\delta$ in Table 1†). In all cases, there is an asymmetric coordination of bromine as given by the shortest Br···C distances $d_1$ and $d_2$ (see the localized structure **B**). However from the relative values of $(d_1^2 - D^2)^{1/2}$ and $(d_2^2 - D^2)^{1/2}$, we estimate the hapticity of coordination as: $\eta = 1 + 2(d_1^2 - D^2)^{1/2}/[(d_1^2 - D^2)^{1/2} + (d_2^2 - D^2)^{1/2}]$. Indeed, this evaluation leads to $\eta = 1$ if $d_1 = D$ ('over-atom' coordination) and $\eta = 2$ if $d_1 = d_2$ ('over-bond' coordination).

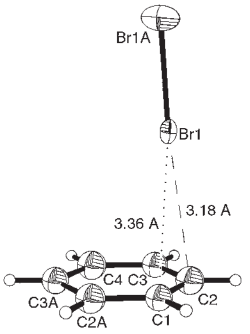


**Fig. 1** ORTEP diagram showing the localized (over-atom/bond) coordination of $Br_2$ to benzene. Thermal ellipsoids of nonhydrogen atoms are shown at 50% probability level.

In the benzene/$Br_2$ complex, the calculated value of $\eta = 1.52$ (Table 1†) corresponds to coordination midway between the 'over-atom' and 'over-bond' configurations. In the toluene complex, the hapticities vary from 1.70 to 1.86 (in four non-equivalent moieties) and thus lie closer to the 'over-bond' coordination model. Moreover, the 'over-bond' coordinated bromine is remarkably shifted toward the *ortho-* or *para-*carbons (see Fig. 2) which correspond to the positions of highest electron density.

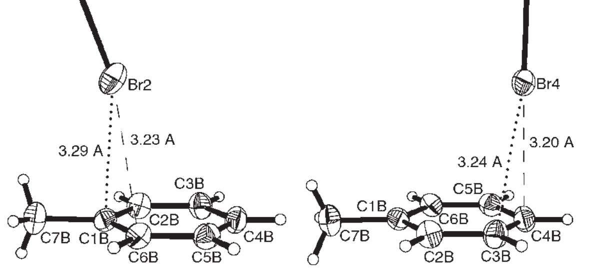


**Fig. 2** Localized bonding of bromine to *ortho-* (left) and *para-* (right) centers of toluene in the charge-transfer complex.

---

† Electronic supplementary information (ESI) available: crystallization of $C_6H_6 \cdot Br_2$ and $C_6H_5Me \cdot Br_2$, crystal data, and their principal geometric parameters. See http://www.rsc.org/suppdata/cc/b1/b102148f/

DOI: 10.1039/b102148f

Such an experimental location of bromine is in a good agreement with the results of high level theoretical calculations which consistently discriminate against the symmetrical coaxial $\eta^6$-coordination, and favor both 'over-atom' and 'over-bond' (*i.e.* $\eta^1$ and $\eta^2$) coordinations without a significant energy barrier between them.[8,9,15] It is also noteworthy that the 'over-rim' coordination modes of $Br_2$ are highly reminiscent of those found in silver(I) complexes, as representing another general class of electron acceptors showing charge-transfer (non-covalent) binding to arene donors.[16,17]

The charge-transfer complex $[C_6H_6,Br_2]$ is presently the weakest EDA complex of dibromine studied in the solid state. Although the C···Br separation of 3.18 Å is 0.37 Å closer than the equilibrium van der Waals distance,[14] the contraction is perceptibly less than those previously reported in a series of complexes with slightly polarizable and weakly nucleophilic donors.[18] [For example, the X···Br distance contraction (relative to the corresponding equilibrium van der Waals separations) is 0.55 Å in the acetone/$Br_2$ complex (O···Br 2.82 Å),[20] 0.56 Å in the acetonitrile/$Br_2$ complex (N···Br 2.84 Å),[21] 0.57 Å in the $[Te_2Cl_{10}]^{2-}/Br_2$ complex (Cl···Br 3.03 Å),[22] and 0.60 Å in the $[Se_2Br_{10}]^{2-}/Br_2$ complex (Br···Br 3.10 Å).[22,23]] Moreover, the average C···Br separation of 3.156 Å in the toluene/$Br_2$ complex is somewhat shorter than that in the benzene complex, as expected from the better donor strength of toluene.[24]

The weak C(arene)···Br charge-transfer interaction is reflected in an almost unperturbed geometry of the coordinated dibromine. [The Br–Br bond length is actually very sensitive to coordination/polarization effects and readily elongates from 2.284 Å in the non-coordinated molecule (bond order $n = 1$) to 2.53 Å in $[Br_3]^-$ anion[25] (bond order $n = \frac{1}{2}$).] As such, the Br–Br bond lengths of 2.301(2) Å in the benzene complex and an average of 2.302(1) Å in the toluene complex do not exhibit much elongation during complex formation. For comparison, the Br–Br bond lengths vary within a narrow range (2.28–2.33 Å) in the weakly coordinated acetone, acetonitrile, dioxane and methanol complexes.[20,21,26,27]

In the absence of significant polarization, dibromine can be coordinated equally well from either end (owing to the $\sigma^*$-orbital which is localized at both bromine centers); and this explains why dibromine has often been found to be symmetrically coordinated to a pair of donor molecules (in a bridging manner), especially in complexes with weak donors.[4] In the benzene and toluene complexes, dibromine is also positioned symmetrically between the coordinated benzene rings forming infinite (weak) chains ···Ar···Br–Br···Ar···Br–Br···Ar··· through the crystal, and there are no specific interactions other than van der Waals contacts between the chains. Although the chains are highly symmetrical in the benzene/dibromine crystals—with two-fold axes (through the diagonals of the benzene rings and through the centers of the dibromine molecules) across the chains, the chains in the toluene/dibromine crystals are less so. Thus, two of the three dibromines (Br3–Br3A and Br4–Br4A) occupy inversion centers and are thus symmetrically coordinated, but the third dibromine (Br1–Br2) does not show crystallographic symmetry. Indeed, the latter exhibits some signs of larger polarization as a result of a less symmetric coordination (Table 1), and it has the shortest contact C···Br 3.053(4) Å as well as the longest Br–Br bond length 2.307(1) Å in the series. Interestingly, a similar asymmetric coordination of dibromine is found in the complex with methanol,[26] in which the O···Br distance is shorter (2.705 *vs.* 2.723 Å) and the Br–Br bond length is longer (2.324 *vs.* 2.303 Å) than those in the closely related (but symmetric) dioxane complex.[27] This structural effect predicts that polarization in isolated donor/acceptor dyads (as extant in dilute solutions) will be somewhat stronger than that observed in (crystalline) polymeric chains.

We thank the National Scientific Foundation and R. A. Welch Foundation for financial support.

## Notes and references

‡ CCDC 162148 and 162149. See http://www.rsc.org/suppdata/cc/b1/b102148f/ for crystallographic data in .cif or other electronic format.

1 For example, an unusual number (3) of thematic issues of *Chem. Revs.* have been issued in the last dozen years: *viz.* 1988 (vol. **88**), 1994 (vol. **94**) and 2000 (vol. **100**); See, especially: K. S. Kim, P. Tarakeshwar and J. Y. Lee, *Chem. Rev.*, 2000, **100**, 4145.

2 *Molecular Interactions. From van der Waals to Strongly Bound Complexes*, ed. S. Scheiner, Wiley, New York, 1997; P. Hobza and R. Zahradnik, *Intermolecular Complexes*, Elsevier, New York, 1988; H. Ratajczak and W. J. Orville-Thomas, *Molecular Interactions*, Wiley, New York, vol. **1** (1980), vol. **2** (1981), vol. **3** (1982).

3 As observed variously in the gas phase, rare-gas matrix, solution, or the crystalline solid state.

4 O. Hassel and Chr. Rømming, *Quart. Rev. Chem. Soc.*, 1962, **26**, 1; O. Hassel, *Mol. Phys.*, 1958, **1**, 241.

5 M. J. S. Dewar, *The Electronic Theory of Organic Chemistry*, Clarendon Press, Oxford, 1958, p. 168; A. C. Legon, *Angew. Chem., Int. Ed.*, 1999, **38**, 2686; S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, 1981, **103**, 7240.

6 O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, 1958, **12**, 1146 (in this temperature range, significant thermal motion caused a weak diffraction pattern and high angle reflections were absent).

7 O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, 1959, **13**, 1781.

8 F. C. Grozema, R. W. J. Zijlstra, M. Swart and P. Th. Van Duijhen, *Int. J. Quantum Chem*, 1999, **75**, 709.

9 A. M. Mebel, H. L. Lin and S. H. Lin, *Int. J. Quantum Chem*, 1999, **72**, 307.

10 The descriptor $\eta$ is the arene hapticity as defined by F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988, p. 38; In structural comparisons discussed hereinafter, for convenience we make no distinction among the various halogens ($Cl_2$, $Br_2$ or $I_2$)

11 H. Bai and B. S. Ault, *J. Phys. Chem.*, 1990, **94**, 199; E. E. Ferguson, *J. Chem. Phys.*, 1956, **25**, 577; L. Fredin and B. Nelander, *J. Am. Chem. Soc.*, 1974, **96**, 1672.

12 S. A. Cooke, C. M. Evans, J. H. Holloway and A. C. Legon, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2295; L. Fredin and B. Nelander, *Mol. Phys.*, 1974, **27**, 885; W. B. Person, C. F. Cook and H. B. Friedrich, *J. Chem. Phys.*, 1967, **46**, 2521.

13 See also: J. Collin and L. D'Or, *J. Chem. Phys.*, 1955, **23**, 397; H. B. Friedrich and W. B. Person, *J. Chem. Phys.*, 1966, **44**, 2161; G. DeBoer, J. W. Burnet, A. Fujimoto and M. A. Young, *J. Phys. Chem.*, 1996, **100**, 14 882; P. Y. Cheng, D. Zhong and A. H. Zewail, *J. Chem. Phys.*, 1996, **105**, 6216; J. T. Su and A. H. Zewail, *J. Phys. Chem. A*, 1998, **102**, 4082.

14 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

15 S. S. C. Ammal, S. P. Ananthavel, P. Venuvanalingam and M. S. Hegde, *J. Phys. Chem. A*, 1998, **102**, 532; A. Matsuzawa and Y. Osamura, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1531. However, see: G. Milano, G. Guerra and L. Cavallo, *Eur. J. Inorg. Chem.*, 1998, 1513; E. Kochanski and J. Prissette, *Nouv. J. Chem.*, 1980, **4**, 509; I. Jano, *Theor. Chim. Acta*, 1985, **66**, 341; E. G. Cook and J. C. Shug, *J. Chem. Phys.*, 1970, **53**, 723.

16 S. V. Lindeman, R. Rathore and J. K. Kochi, *Inorg. Chem.*, 2000, **39**, 5707.

17 The halogen/arene complexes have also been discussed as charge-transfer complexes. For reviews, see: J. Andrews and R. M. Keefer, *Molecular Complexes in Organic Chemistry*, Holden-Day, San Francisco, 1964; R. Foster, *Organic Charge-Transfer Complexes*, Academic, New York, 1969; S. Fukuzumi and J. K. Kochi, *J. Org. Chem.*, 1981, **46**, 4116.

18 According to Mulliken,[19] the dative contribution from $[Br_2^-,C_6H_6^+]$ plays a role in the noncovalent interaction. As such for charge-transfer complexes, the contraction is largely due to Coulombic and dispersion forces. See also: H. O. Hooper, *J. Chem. Phys.*, 1964, **41**, 599.

19 R. S. Mulliken, *J. Am. Chem. Soc.*, 1950, **72**, 600; R. S. Mulliken, *J. Am. Chem. Soc.*, 1952, **74**, 811; R. S. Mulliken and W. B. Person, *Molecular Complexes, A Lecture and Reprint Volume*, Wiley, New York, 1969.

20 O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, 1959, **13**, 275.

21 K.-M. Marstokk and K. O. Strømme, *Acta Crystallogr., Sect. B*, 1968, **24**, 713.

22 S. Hauge and K. Maroy, *Acta Chem. Scand.*, 1996, **50**, 1095.

23 V. Janickis, *Acta Chem. Scand.*, 1999, **53**, 188.

24 J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3968.

25 Cambridge Crystallographic Database, Release Fall 2000.

26 P. Groth and O. Hassel, *Acta Chem. Scand.*, 1964, **18**, 402.

27 O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, 1954, **8**, 873.