Structurally recognizable electron density transfer in the donor–acceptor complex $\{1,2,4,5\text{-tetra(thioethyl)benzene}\cdots\text{bromine}_2\}_\infty$

Hans Bock,* Zdenek Havlas, Andreas Rauschenbach, Christian Näther and Markus Kleine

Department of Chemistry, University of Frankfurt, Marie-Curie-Str. 11, D-60439 Frankfurt/Main, Germany

The crystal structure determination of a sulfur lone pair donor complex with bromine reveals an increase of the Br–Br bond length from 228 pm (gas-phase) to 241 pm, for which density functional theory calculations predict a −0.25 charge transfer in the ground state.

During our investigations of the interactions in molecular crystals such as cation solvation, hydrogen bridge bonding or van der Waals forces,[1] we also studied the effects of donor–acceptor complex formation by selecting suitable donors, *e.g.* tetra- and hexa-methyl benzenes,[2] pyrene or perylene,[3] amino benzenes[4] or 2,3,6,7-tetramethoxythianthrene,[5] and acceptors of the same skeletal symmetry and π overlap area, *e.g.* tetrahalogen-*p*-benzoquinones,[2] tetracyano- hydroquinone,[3] 1,3,5-nitro/cyano substituted benzenes[4] or terephthalic acid anhydride,[5] and succeeded in exclusively crystallizing mixed stack aggregates. None of the 21 structures determined for the deeply coloured complexes with charge transfer excitation energy shifts of up to 2 eV showed any significant geometry change of the donor and acceptor components due to π stacking with interplanar distances of around 340 pm *i.e.* double π radius of 170 pm.[2–5] Semiempirical calculations based on the crystal structure data did not show any donor ⟶ acceptor polarization at all.

In order to reduce the acceptor size the two-centre molecule bromine was chosen as a search in the Cambridge Structural Database revealed evidence for a possible significant Br–Br distance elongation.[6] For an electron-rich multifunctional donor with full substituent perturbation [Σ ($c_{j\mu}^2$) = 1],[7] 1,2,4,5-tetra(thioethyl)benzene was synthesized.[8] Its cyclovoltammogram in aprotic acetonitrile showed two oxidation potentials at +1.10 V (rev.) and +1.50 V (irrev).[9] UV–VIS spectra in pure dichloromethane showed band maxima for the donor at 30 800 cm^{-1}, for Br_2 at 24 450 cm^{-1} and in their combined 1:4 stoichiometric solution additional charge transfer maxima at 13 200 cm^{-1} and 25 500 cm^{-1}.[7] Red–brown needles with a reddish lustre were crystallized by isothermic gas-phase diffusion of bromine between CCl_4 solutions, Fig. 1.

Structure determination† confirmed the elemental analysis, which suggested a 1:2 complex $\{(H_5C_2S)_4C_6H_2\cdots(BrBr)_2\}_\infty$ (Fig. 2). In the monoclinic unit cell containing two formula units, the benzene donor is located around a centre of inversion. The tetra(thioalkyl) substituted six-membered rings are closely packed in layers parallel to the X, Y diagonal and staggered along the X axis. They are bridged alternatingly by two adjacent Br–Br acceptors in a staircase lattice motive, which allows for an insertion of the subunits S···Br–Br···S between each of the donors and, therefore, an optimally dense packing.

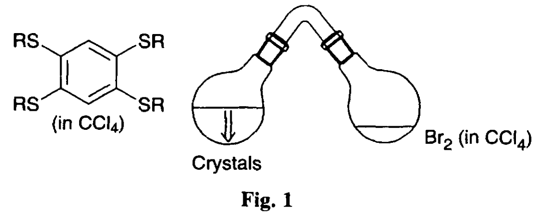

Fig. 1

The contact distances S···Br of 281 and 324 pm differ by 43 pm but are both well within the sum of the van der Waals radii, $r_S^{vdW} + r_{Br}^{vdW}$ = 180 + 195 = 375 pm. The shorter bond distance is perpendicular to the planes of the six-membered rings, the longer one deviates by 15°. There are, within the precision of measurement, no structural changes detected for the donor molecule[8] due to complex formation.‡ In contrast, the Br–Br bond length is elongated from the gas-phase electron diffraction value of 228 pm[6] to 241 pm.

In order to elaborate upon this unique observation, density functional calculations of B3LYP type with 6–31G** basis sets, further optimized for the Br centres by additional polarization functions, were performed for the model system $Me_2S\cdots Br–Br\cdots SMe_2$ based on the experimentally determined structural coordinates $C_2S\cdots Br–Br\cdots SC_2$.‡ For complex formation, a total energy difference of −10 kJ mol^{-1} results relative to the three components as well as the charge distribution shown in Fig. 3.

The DFT calculation suggests that (−0.10) + (−0.15) = −0.25 negative charges are transferred to the Br–Br acceptor and allows us to rationalize why the electron-rich molecule with 14 valence electrons is stretched by 13 pm. The unsymmetrical donation of −0.10 and −0.15 negative charges from the sulfurs of each of the more distant bromine centres can be rationalized

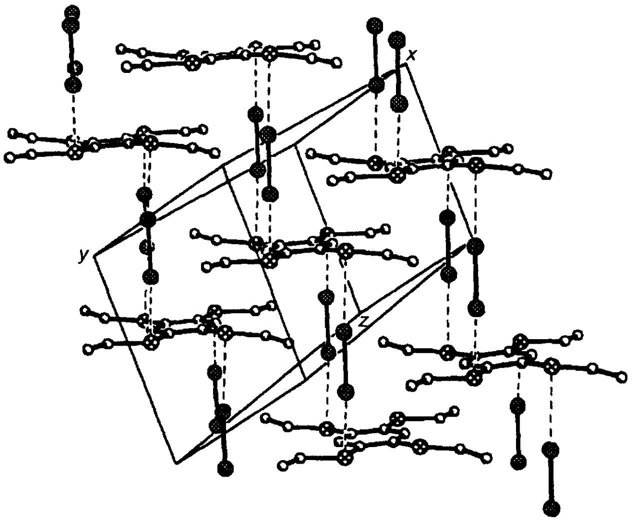

Fig. 2 Single crystal structure of the 1:2 complex of 1,2,4,5-tetra(thioethyl)benzene and bromine†,‡

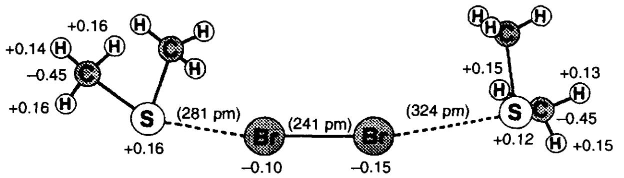

Fig. 3

by distance correlation as also verified by the corresponding iodine complex $\{(H_7C_3S)_4H_2C_6\cdots(I_2)_3\}$:[8] the longer the contact distance S···halogen, the shorter the halogen···halogen bond.

In general, charge transfer complexes are discussed as potential intermediates in local energy minima along microscopic reaction pathways.[9–12] In complexes between electron-rich donors and halogen acceptors such as the one presented here, heterolytic Br–Br dissociation may well be preformed.

$$R_2X + Br_2 \rightleftarrows \{R_2X\cdots Br^{\delta+}\cdots Br^{\delta-}\} \rightleftarrows R_2X\text{–}Br^+ + Br^-$$

Footnotes

† *Crystal data* for $C_{14}H_{22}S_4\cdot 2Br_2$, M = 638.2, a = 677.45(6), b = 1987.7(2), c = 848.6(1) pm, β = 105.569(8)°, V = 1100.8(2) × 10^6 pm^3, 295 K, D_c = 1.925 g cm^{-3}, monoclinic, $P2_1/c$, Z = 2, STOE AED-II-four-circle diffractometer, Mo-Kα-radiation, μ = 7.60 mm^{-1}, numerical absorption correction, 5155 measured reflections in the range of $3° \leqslant 2\theta \leqslant 55°$, of which 2524 independent (R_{int} = 0.0250) and 1661 with $[I > 2.0\sigma(I)]$ used for refinement, structure solution by direct methods and difference Fourier technique (SHELXTL-PC). Refinement with full matrix least-squares (SHELXTL-PC). 106 parameters, $w = 1/\sigma^2(F) + 0.0001\,F^2$, R = 0.0419, R_w = 0.0403, R_g = 0.0454, GOF = 2.0736, residual electron density 1.63/−1.24 e Å^{-3}. C, S, Br are refined anisotropically and all H are geometrically ideally positioned and refined according to the riding model using isotropic displacement parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/97.

‡ Selected bond lengths (Å) and angles (°). S(1)–C(1) 176.2(5), S(1)–C(4) 182.3(5), S(2)–C(2) 177.0(4), S(2)–C(6) 181.1(5), C(1)–C(2) 141.5(6), C(1)–C(3A) 139.5(6), C(2)–C(3) 137.1(7), C(3)–C(1A) 139.5(6), C(4)–C(5) 150.9(8), C(6)–C(7) 153.3(7), Br(1)–Br(2) 240.7(1); C(1)–S(1)–C(4) 103.6(2), C(2)–S(2)–C(6) 102.4(2), S(1)–C(1)–C(2) 118.1(3), S(1)–C(1)–C(3A) 123.5(3), C(2)–C(1)–C(3A) 118.4(4), S(2)–C(2)–C(1) 118.1(4), S(2)–C(2)–C(3) 122.9(3), C(1)–C(2)–C(3) 118.9(4), C(2)–C(3)–C(1A) 122.6(4), S(1)–C(4)–C(5) 109.6(3), S(2)–C(6)–C(7) 107.8(4).

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6 A CSD search (March 1995) for fragments BrBr provided 48 entries with an average bond length of $\overline{267}$ pm and 6 with $\overline{230}$ pm for uncharged compounds. Relative to an average gas-phase electron diffraction distance for Br_2 of $\overline{228}$ pm, the largest elongation to 233 pm was observed in the acetonitrile complex {MeCN···BrBr···NCMe} (ACTNBM; O. Hassel and K. O. Stromme, *Acta Chem. Scand.*, 1959, **13**, 275).

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