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Preparation and Crystal Structure of $S_2I_4^{2+}(AsF_6^-)_2$ containing the Distorted Right Triangular Prismatic Disulphur Tetraiodine(2+) Cation and a Disulphur Unit of Bond Order greater than Two

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Summary $S_2I_4^{2+}(AsF_6^-)_2$ has been prepared and its crystal structure determined in which the $S_2I_4^{2+}$ cation was found to have a distorted right triangular prismatic structure, with one S_2 and two I_2 units joined by weak sulphur–iodine bonds; the sulphur–sulphur bond distance is the shortest reported in an isolated compound, and is indicative of the presence of a 3pπ–3pπ bond and a bond order greater than two.

SULPHUR iodides, until recently regarded as essentially non-existent,[1] are proving to be very different from the other sulphur halides.[2] The neutral binary sulphur–iodine species S_2I_2 has been reported, although it is stable only at low temperatures,[3,4] and attempts to prepare $SI_3^+MF_6^-$ (M = As, Sb), analogous to SX_3^+ (X = F, Cl, Br)[5] led to stable $S_7I^+MF_6^-$ salts.[6,7] Subsequently, $[(S_7I)_2I]^{3+}(SbF_6^-)_3 \cdot 2AsF_3$[8] and $(S_7I^+)_4S_4^{2+}(AsF_6^-)_6$[9] were characterized. In an attempt to prepare $S_2I^+AsF_6^-$ (*cf.* $S_2F^+AsF_6^-$)[10] by the reaction of $S_4^{2+}(AsF_6^-)_2$[9] with an excess of iodine, $S_2I_4^{2+}$-$(AsF_6^-)_2$ was characterized as a product, and then synthesized quantitatively in liquid sulphur dioxide according to equation (1).

$$\tfrac{1}{4}S_8 + 2I_2 + 3AsF_5 \xrightarrow{SO_2} S_2I_4^{2+}(AsF_6^-)_2 + AsF_3 \qquad (1)$$

Crystal Data: $S_2I_4^{2+}(AsF_6^-)_2$, monoclinic, space group C_2/c (C_{2h}^6), $a = 965{\cdot}0(2)$, $b = 1287{\cdot}4(2)$, $c = 1366{\cdot}4(4)$ pm, $\beta = 93{\cdot}79(2)^\circ$, $U = 1694 \times 10^6$ pm^3, $Z = 4$, $D_c = 3{\cdot}72$ g cm^{-3}, μ(Mo-K_α) = 118·81 cm^{-1}. Data were collected for $2\theta \leqslant 50^\circ$, 1498 unique reflections, 965 observed ($I \geqslant 2\sigma$). The data were corrected for absorption and the structure was solved by direct methods. Least-squares refinement, with anisotropic thermal parameters for sulphur, iodine, and arsenic gave a final $R = 0{\cdot}074$, $R_w = 0{\cdot}119$.† The structure consists of discrete $S_2I_4^{2+}$ and AsF_6^- ions with weak anion–cation contacts. Attempts to refine the fluorine thermal parameters anisotropically gave excessively high values indicating some rotational disorder of the AsF_6^- units.

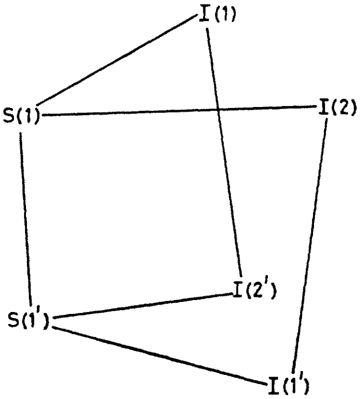

FIGURE 1. Structure of $S_2I_4^{2+}$: S(1)–S(1′), 182·8(1·1); S(1)–I(1), 285·8(6); S(1)–I(2), 319·5(6); I(1)–I(2′), 259·7(2) pm; ∠I(1)–S(1)–I(2), 89·5(2); S(1)–I(1)–I(2′), 87·0(1); I(1)–I(2′)–S(1′), 78·4(1); S(1′)–S(1)–I(2), 92·9(3); S(1′)–S(1)–I(1), 101·6(3)°. Contacts (S–F ⩽ 320; I–F ⩽ 335 pm): S(1)–F(5) 303(2); I(1)–F(3), 323(5); I(1)–F(4), 327(3); I(2)–F(2), 310(4) pm; non-bonding distance I(1)–I(2) 426·7(3) pm.

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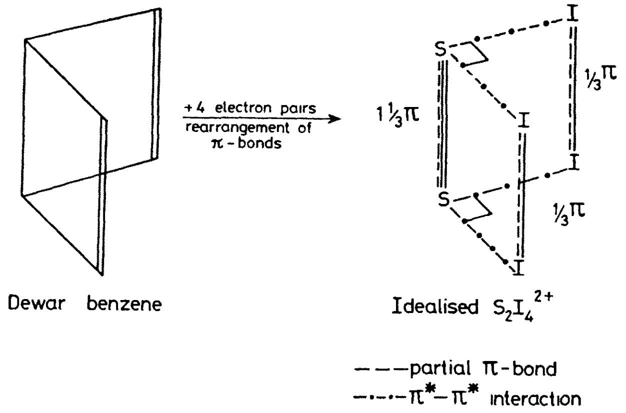
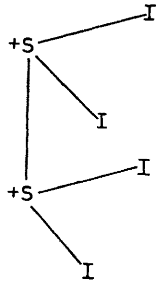
† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institute fur Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

The $S_2I_4^{2+}$ cation (of C_2 symmetry), represents the first reported example of a hexa-atomic species whose structure approximates to that of a right triangular prism (Figure 1), and, unexpectedly, does not have the structure of the isoelectronic P_2I_4.[11] The sulphur–sulphur bond distance of 182·8(1·1) pm [*cf.* S_2, 189·2,[12] and S_2^+ (calculated from photoelectron spectra) 182·5 pm[13]] and the two equal iodine–iodine bond distances of 259·7(2) pm [*cf.* $I_2(g)$, 266·2,[14] and I_2^+ 255·7(4) pm[15]] are consistent with a $+2/3$ charge on each dimer unit and the essentially equal ionization potentials of S_2 [9·36 ($\pm$0·02)] and I_2 [9·3995 ($\pm$0·0012) eV].[16] The sulphur–sulphur bond distance is the shortest so far reported in an isolable compound and corresponds to a bond order of $2\frac{1}{3}$; the iodine–iodine bond distance is consistent with a bond order of $1\frac{1}{3}$. Therefore, like S_4^{2+},[9] $S_2I_4^{2+}$ is an example of a stable species containing $3p\pi$–$3p\pi$ bonds, and is an exception to the generalization[17] that second-row elements do not form isolable compounds containing homoatomic $p\pi$–$p\pi$ bonds.

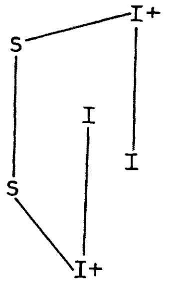
The two planar S_2I_2 units are joined at the sulphur–sulphur bond with a torsional angle between the planes of 89·9°. The S–I distances of 285·8(6) and 319·5(6) pm are comparable with sulphur–iodine distances in sulphur–iodine charge transfer complexes,[18] but are longer than that in $[(H_2N)_2CS]_2I^+$ (262·9 pm)[19], which has a formal sulphur–iodine bond order of 0·5, and are less than the sum of the van der Waals' radii (400 pm).[17] The two mutually perpendicular π^* orbitals on the S_2 unit may therefore bond to each I_2^+ unit *via* a 4-centre 2 electron π^*–π^* bond, in an asymmetric manner, resulting in preferential bonding between one sulphur and one iodine. A similar bonding scheme has been proposed for the bond linking $[S_3N_2]^+$ units in $[S_6N_4]^{2+}$[20] and $[Se_2(C_2F_5)_2]^+$ units in $[(C_2F_5)_2Se_2]_{2n}^{2n+}$.[21]

It is of interest to note that the structure of $S_2I_4^{2+}$ (containing 13 electron pairs), in which π-bond formation is maximised, can be formally derived[22] from Dewar benzene (9 bonding pairs), as indicated in Figure 2. The all-σ-bonded isomers (**1**) and (**2**), like Te_6^{4+},[23] are related[22,24] to prismane.





(1)



(2)

FIGURE 2.

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