Acta Cryst. (1974). **B30**, 2407

The Structure of Octabromopentafulvalene

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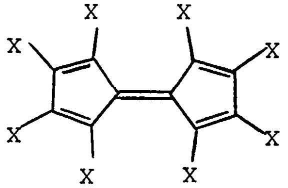
(*Received* 11 *April* 1974; *accepted* 7 *June* 1974)

The crystal and molecular structure of octabromopentafulvalene has been determined by three-dimensional X-ray analysis. The space group is monoclinic, $C2/c$, with $a=15{\cdot}588$ (3), $b=8{\cdot}371$ (1), $c=12{\cdot}164$ (3) Å, $\beta=104{\cdot}78$ (2)°; $D_c=3{\cdot}286$ g cm^{-3} for $Z=4$. Intensity data were measured on a computer-controlled diffractometer with Mo radiation. The compound is isostructural with octachloropentafulvalene, and a starting set of atomic coordinates was derived from the published octachloro coordinates. Corrections for absorption and secondary isotropic extinction were applied to the data. The structure refinement was by least-squares with a Hughes-type weighting scheme and anisotropic temperature factors for all atoms: final $R=0{\cdot}045$. The 37·1° twist of the central C=C, which is caused by Br···Br repulsions from one C_5Br_4 half of the molecule to the other, is only slightly larger than the 34·5° octachloro twist. The central C=C distance is 1·38 (1) Å; the octachloro distance is 1·365 (4) Å. Carbon–carbon bond distances in the five-membered rings, and deviations of the halogens from the five-ring planes, are similar in the Br and Cl compounds. Bond distances in the C=C–C=C portions of the five-rings have typical butadiene-like values. The C–Br and C–Cl distances are shorter than the normal aromatic C(sp^2)-halogen distance. The X···X separations between the C_5X_4 halves, Br···Br = 3·41 Å and Cl···Cl = 3·22 Å, are *ca.* 92% of the respective van der Waals contact distances. Assuming that the van der Waals spheres can interpenetrate by *ca.* 8%, C=C twist angles of 18° and 43·5°, respectively, were calculated for octafluoro and octaiodopentafulvalene.

Introduction

We wish to report the results of an X-ray crystallographic investigation of the crystal and molecular structure of octabromopentafulvalene (I). The study was undertaken to determine the extent of Br···Br induced distortions of the molecule. The structure of octachloropentafulvalene (II) (Ammon, Wheeler & Agranat, 1973) is distorted by Cl···Cl interactions within each of the C_5Cl_4 units, and by interactions from one C_5Cl_4 unit to the other. In view of the 1·85 Å van der Waals radius of Br compared to the 1·75 Å value for Cl (Bondi, 1964), the extent of molecular distortion in (I) was expected to be substantially greater than that observed in (II).



(I) X = Br
(II) X = Cl

Experimental

A *ca.* 0·18 × 0·16 × 0·15 mm deep-blue prism of octabromopentafulvalene, $C_{10}Br_8$ (Kwitowski & West, 1966; West & Kwitowski, 1968), crystallized from Skelley B, was mounted parallel to **a**. Oscillation and Weissenberg photographs suggested that the material was isostructural with the octachloro derivative (II) (Ammon, Wheeler & Agranat, 1973), and subsequent calculations confirmed the similarity. The crystals were monoclinic, space group $C2/c$. A Picker FACS-I diffractometer with Mo radiation (graphite monochromator, $K\alpha$ $\lambda=0{\cdot}71069$ Å) was used for the lattice-parameter and intensity measurements from the crystal with **a*** aligned parallel to the instrument's φ axis. The cell parameters, obtained from a least-squares fit to the 2θ's of 12 reflections manually centered at $\pm 2\theta$, were $a=15{\cdot}588$ (3), $b=8{\cdot}371$ (1), $c=12{\cdot}164$ (3) Å, $\beta=104{\cdot}78$ (2)°. For comparison, the octachloropentafulvalene cell parameters (Ammon *et al.*, 1973) were $a=14{\cdot}998$, $b=7{\cdot}911$, $c=11{\cdot}809$ Å, $\beta=103{\cdot}38$°. The calculated crystal density was 3·286 g cm^{-3} for $Z=4$. The unique structural unit consisted of only one C_5Br_4 segment because the molecular C_2 axis, which is normal to the plane of the paper at the central C=C of structure (I), coincided with a crystallographic dyad. We did not attempt to measure the crystal density. The intensity measurements were made with the θ–2θ scan method with a 2θ rate of 1° min^{-1}, and with two 20 s backgrounds. Three standard reflections, counted at

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100 reflection intervals, were used to correct for intensity fluctuations. 1609 total data were measured to a 2θ of 50°. These data yielded 1361 unique data, 991 of which were 3σ above background.

The raw intensities were corrected for absorption prior to intensity averaging: $\mu = 225{\cdot}2\ \text{cm}^{-1}$; Gaussian quadrature method; $8 \times 8 \times 8$ grid; maximum and minimum transmission factors were 0·1380 and 0·0569. An initial set of atomic coordinates was obtained from the octachloro structure in the following way: the carbon fractional coordinates were taken directly from the octachloro structure; the bromine coordinates were approximated by extending the C–Cl bonds in (II) to a distance of 1·9 Å. The initial R value $(\sum||F_o|-|F_c||/\sum|F_c|)$ for the data, with $\sin\theta/\lambda \le 0{\cdot}35$ and with isotropic temperature factors of $U = 0{\cdot}057$ Å^2 ($B = 4{\cdot}5$ Å^2) assigned to all of the atoms, was 0·50. Two cycles of full-matrix least-squares refinement reduced R to 0·11. Subsequent structure refinement was based on the full data set and used anisotropic temperature factors for carbon and bromine, and included corrections for bromine dispersion (Cromer & Liberman, 1970) and secondary isotropic extinction [$r^* = 0{\cdot}020\ (2)\ \text{e}^{-2}$; see equation (22) in Larson (1970)]. The calculations minimized the function $\sum w(F_o - F_c)^2$ [$w = 1$ for $F_o \le 90$, and $w = 90/F_o$ for $F_o > 90$, Hughes (1941)], and included only those reflections for which $I_c \ge 3\sigma(I_o)$ (1118 data were used in the last least-squares cycle). The average and maximum parameter shifts in the last least-squares cycle were 0·1 and 0·4, respectively, and the standard deviation of an observation of unit weight, $\{\sum w(F_o - F_c)^2/[1118 - 83]\}^{1/2}$, was 7·5. The C and Br scattering factors were evaluated from the analytical functions given by Cromer & Mann (1968). The final R and weighted R $[\sum w(F_o - F_c)^2/\sum wF_o^2]$ factors were 0·045 and 0·058, respectively. The atomic parameters are listed in Table 1. All calculations were done on a UNIVAC 1108 computer with the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) of crystallographic programs.*

Discussion

An *ORTEP* drawing of octabromopentafulvalene with bond lengths and angles is given in Fig. 1. The crystal and molecular structures of the octabromo and octachloro compounds are virtually identical. X···X interactions between the two C_5X_4 halves in a molecule have produced similar amounts of central C=C twist in the two fulvalenes. The angle between the two five-ring planes in a pentafulvalene, which can be evaluated from the normals to the planes (39·20° in I, 36·70° in II), contains both C=C twist and tilt components. Whereas the twist component is obvious, the tilt component can be seen as a bending of the C=C bond into a 'V' shape. We have defined these components so that twist occurs about an axis which is coincident with the C(1)–C(1′) direction, whereas the tilt axis is perpendicular to both the C(1)–C(1′) bond and the molecular (and crystallographic) C_2 axis. An algorithm for the calculation of these components has been described by Ammon & Wheeler (1974). The C=C twists and tilts derived from the normals to the three atom units [C(2)–C(1)–C(5) and C(1′)–C(2′)–C(5′)] which define the C=C's are 37·1° (twist) and 3·0° (tilt) in (I), and 34·5° and 4·0° in (II). The twist and tilt angles evaluated from the five-ring normals are 38·5° and 5·1° in (I), and 36·2° and 6·0° in (II). The significance and/or cause of the tilt components are unclear since this motion has relatively little effect, compared to C=C twist, on the inter-ring halogen···halogen distances.

The five-ring carbon–carbon distances in the two fulvalenes are very similar to each other, and they have typical values for C(sp^2)–C(sp^2) single and double bonds. For example, the average five-ring C=C and C–C distances in the compounds, 1·340 and 1·463 Å, compare favorably with the C=C's of 1·337 Å in ethylene (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965), 1·341 Å in butadiene (Kuchitsu, Fukuyama & Morino, 1968) and 1·342 Å in cyclopentadiene (Scharpen & Laurie, 1965) and with C–C's of 1·463 Å in butadiene and 1·469 Å in cyclopentadiene. The five-ring distances show no evidence for π-delocalization beyond that normally found in a conjugated diene. The five carbon atom ring in (I) is reasonably planar (deviations are given in Fig. 1).

Although the difference between the central C=C

Table 1. *Fractional coordinates, thermal parameters* (Å^2) *and e.s.d.'s* (*in parentheses*) *for octabromopentafulvalene*

The form of the temperature factors is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots 2klb^*c^*U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	−0·0032 (5)	0·242 (1)	0·3056 (7)	0·026 (4)	0·031 (5)	0·032 (4)	0·000 (4)	0·007 (3)	−0·005 (4)
C(2)	0·0659 (6)	0·201 (1)	0·4077 (7)	0·031 (4)	0·037 (5)	0·031 (4)	0·004 (4)	0·006 (4)	−0·006 (4)
C(3)	0·0325 (6)	0·220 (1)	0·4989 (7)	0·045 (5)	0·037 (5)	0·029 (4)	−0·006 (4)	0·009 (4)	0·000 (4)
C(4)	−0·0573 (6)	0·285 (1)	0·4604 (7)	0·039 (5)	0·030 (5)	0·033 (4)	−0·002 (4)	0·017 (4)	0·004 (4)
C(5)	−0·0796 (6)	0·289 (1)	0·3474 (7)	0·030 (4)	0·035 (5)	0·037 (5)	0·005 (4)	0·012 (4)	0·003 (4)
Br(2)	0·16671 (7)	0·0818 (2)	0·4103 (1)	0·0433 (6)	0·0697 (8)	0·0558 (7)	0·0144 (5)	0·0058 (5)	−0·0089 (6)
Br(3)	0·08325 (9)	0·1592 (2)	0·64600 (9)	0·0673 (8)	0·0799 (9)	0·0338 (6)	0·0018 (6)	0·0036 (5)	0·0010 (5)
Br(4)	−0·11759 (9)	0·3677 (2)	0·5590 (1)	0·0782 (9)	0·0644 (8)	0·0556 (7)	0·0129 (6)	0·0386 (6)	0·0006 (6)
Br(5)	−0·18021 (8)	0·3942 (2)	0·2646 (1)	0·0544 (7)	0·093 (1)	0·0601 (7)	0·0291 (7)	0·0237 (6)	0·0228 (7)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30526 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

distances of 1·382 (13) Å in (I) and 1·365 (4) Å in (II) is not statistically significant, the difference is in the expected direction considering the relative C=C twist angles and the increased severity of Br· · ·Br repulsions compared to Cl· · ·Cl repulsions.

The C–Br distances 1·856, 1·833, 1·839 and 1·853 Å, are significantly shorter than the typical aromatic C(sp^2)–Br distance. James & Williams (1973) reported an average aromatic C–Br distance of 1·8966 (19) Å from a survey of 60 bonds of this type. The octachloropentafulvalene C–Cl distances, 1·710, 1·694, 1·696, and 1·707 Å, are also shorter than the usual aromatic C–Cl bond. Rudman (1970, 1971) reported an average aromatic C–Cl distance of 1·737 Å when the C–Cl bond is not adjacent to other C–Cl bonds, and a distance of *ca.* 1·709 Å when the compound contains two or more *ortho* C–Cl bonds. The C–Br and C–Cl bond lengths in the pentafulvalenes fit the pattern described by Rudman for C–Cl distances, in that C–X bonds [to C(2) and C(5)] which are adjacent to only one other C–X bond are longer than bonds [to C(3) and C(5)] which have two C–X neighbors.

The Br· · ·Br distances between adjacent Br's are appreciably smaller than the van der Waals contact distance of 3·70 Å (2 × 1·85 Å; Bondi, 1964), and these contacts give rise to the major elements of distortion in the molecule. The Br(2)· · ·Br(5′) contacts from one C_5Br_4 unit to the other are responsible for the C=C twist, while Br(2)· · ·Br(3)· · ·Br(4)· · ·Br(5) contacts within a C_5Br_4 unit are primarily responsible for out-of-plane displacements of the halogen atoms. The 3·411 Å Br(2)· · ·Br(5′) distance is the shortest contact of this type that we are aware of. Similar distortion effects were reported (Ammon *et al.*, 1973) for the octachloro structure.

We have calculated hypothetical Br positions from the octachloro structure by lengthening the C–Cl bonds to the observed C–Br values. The hypothetical Br· · ·Br distances within a C_5Br_4 unit, Br(2)–Br(3) = 3·505 Å, Br(3)–Br(4) = 3·508 Å and Br(4)–Br(5) = 3·485 Å, differ only slightly from the real values. The actual out-of-plane Br displacements are larger by 0·02–0·08 Å than the hypothetical ones, Br(2) = 0·380 Å, Br(3) = 0·236 Å, Br(4) = −0·276 Å and Br(5) = −0·280 Å, and the displacements are in directions which increase the Br· · ·Br distances. The *ca.* 0·14 Å difference between the real and hypothetical (3·268 Å) Br(2)–Br(5′) distances is primarily due to an increase in central C=C twist in the Br compound over the Cl derivative.

There are three Br· · ·Br intermolecular contacts, ranging from 3·52 to 3·67 Å, which are shorter than the 3·7 Å van der Waals value. These are common values for the Br· · ·Br distance, and no extraordinary Br· · · Br interactions can be inferred from the contacts.

The lowest energy bands in the electronic absorption spectra of the pentafulvalenes are: fulvalene, 416 nm (Doering, 1959), octafluoropentafulvalene, 578 nm* (Banks, Bridge, Haszeldine, Roberts & Tucker, 1970); octachloropentafulvalene, 610 nm; octabromopentafulvalene, 637 nm (Kwitowski & West, 1966). The

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* The octafluoro compound has not been isolated in a pure state. A blue contaminant in an octafluoronapthalene sample absorbing at 578 nm has been ascribed to the pentafulvalene.

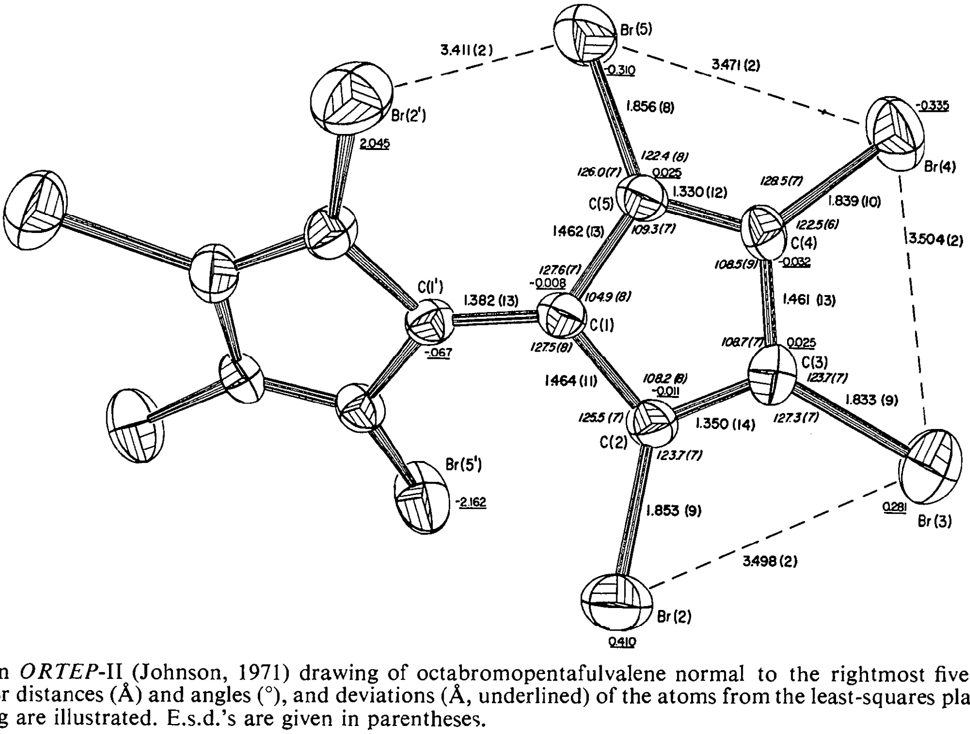

Fig. 1. An *ORTEP*-II (Johnson, 1971) drawing of octabromopentafulvalene normal to the rightmost five-ring. Bond lengths, Br· · ·Br distances (Å) and angles (°), and deviations (Å, underlined) of the atoms from the least-squares plane of the right-hand five-ring are illustrated. E.s.d.'s are given in parentheses.

shift of this transition to longer wavelength from the presumably planar pentafulvalene to the highly twisted octabromopentafulvalene can be related to an increase in conjugative effects and central C=C twist accompanying halogen substitution. The conjugative effects are thought to be small, and thus the principal cause of the bathochromic shift has been ascribed to C=C twist (West & Kwitowski, 1968; Meyer & Yinnon, 1972). We have attempted to estimate the amounts of C=C twist in the unknown octafluoro and octaiodopentafulvalenes from computations with models of the octahalopentafulvalenes. The calculations started with a planar model for the X(2)–C(2)–C(1)=C(1′)–C(5′)–X(5′) portion of an octahalopentafulvalene, which was constructed from average bond lengths and angles from the octachloro and octabromopentafulvalene data. The model parameters were C(1)–C(2) = C(1′)–C(5′) = 1·468 Å; C(1′)=C(1)–C(2) = C(1)=C(1′)–C(5′) = 127·65°; C(1)–C(2)–X(2) = C(1′)–C(5′)–X(5′) = 125·4°; C(1)=C(1′), C(2)–X(2) and C(5′)–X(5′) were varied depending on the halogen. The planarity of this six-atom fragment was altered by displacing the C(2)–X(2) and C(5′)–X(5′) bonds on opposite sides of the C(2)–C(1)=C(1′)–C(5′) plane by 11·25° [*i.e.*, X(2) and X(5′) were displaced from the four-central-atom plane by a distance of $d_{\text{C-X}}$ sin 11·25°]. The optimum X(2)···X(5′) separation in a twisted fulvalene, expressed as a fraction of the ideal van der Waals contact distance, was estimated from a comparison of the actual Cl···Cl and Br···Br distances in the octachloro and octabromo compounds with the appropriate van der Waals distances of 3·50 Å for Cl and 3·70 Å for Br (Bondi, 1964). The observed Cl···Cl and Br···Br distances were, respectively, 0·920 and 0·922 of the ideal contact distances, and, thus, it was assumed that the optimum X(2)···X(5′) distance in an octahalofulvalene would be 0·921 times the van der Waals contact distance. The data for the four octahalopentafulvalenes are given in Table 2. The calculated Cl and Br C=C twists, 36 and 40°, respectively, are close to the observed values of 34·5 and 37·1°. The F value is 18° and the I twist is 43·5°. A slight increase in the angular displacement of the C–I bond from the C(2)–C(1)=C(1′)–C(5′) plane, coupled with a somewhat softer van der Waals sphere for the polarizable halogen, could easily reduce the C=C twist to close to 40°. In view of this conservative twist, we would expect octaiodopentafulvalene to be a reasonably stable compound.

Table 2. *Octahalopentafulvalene model calculations*

	C=C distance	C–X distance	Ideal* X···X	Effective† X···X	C=C twist
F	1·35 Å	1·311 Å	2·94 Å	2·70 Å	18°
Cl	1·365	1·7085	3·50	3·20	36
Br	1·382	1·8545	3·70	3·40	40
I	1·40	2·05	3·96	3·64	43·5

* Two times van der Waals halogen radii reported by Bondi (1964).

† Effective = 0·921 times ideal X···X.

The model calculations have pointed out that at C=C twist angles in the 40° range, the C(2)–X(2) and C(5′)–X(5′) bond vectors are pointing away from, not toward, each other, so that an increase in the C–X distance leads to a larger X···X separation. At 40°, for example, with C–X = 1·8545 Å the X···X distance is 3·40 Å, whereas the X···X distance is 3·50 Å for a C–X of 2·05 Å.

Financial support from the National Science Foundation (GP-15791 and GP-37528) and a grant of computer time from the University of Maryland's Computer Science Center are gratefully acknowledged.

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