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THE STRUCTURE OF OCTACHLORO-PENTAFULVALENE[a]

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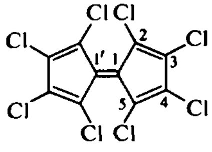
Abstract—The structure of octachloropentafulvalene has been redetermined by a 3-dimensional X-ray crystallographic analysis. The space group is monoclinic, $C2/c$, and cell parameters are $a = 14{\cdot}998$, $b = 7{\cdot}9110$, $c = 11{\cdot}8068$ Å, $\beta = 103{\cdot}38^\circ$. The X-ray intensity data were measured on a computer-controlled diffractometer using Mo radiation. The least-squares structure refinement used anisotropic temperature factors for C and Cl and gave a final R of 0·036. Corrections were applied for absorption, Cl dispersion and secondary isotropic extinction. The central C=C is twisted by 37° as a result of Cl · · · Cl repulsions from one C_5Cl_4 half to the other. The central C=C length, 1·365 Å, is only slightly larger than the standard 1·34 Å ethylenic value. The bond distance increase can be explained in terms of a decrease in π-bond character accompanying the C=C twist. Carbon–carbon distances in the 5-ring have typical values for the cyclopentadienylidene moiety; there is no evidence for single–double bond delocalization.

There has been considerable interest recently in the properties and reactions[1,2] of the blue-violet octachloropentafulvalene (1)†, which was first synthesized by Mark[3] in 1961. Wheatley[4] reported a 2-dimensional X-ray crystallographic investigation of the compound, which showed that the molecule is severely distorted from the simple coplanar arrangement depicted by structure 1. He found a twist of 41° and length of 1·49 Å for the interring C=C bond (C(1)–C(1')). In the aminopentafulvalenes and cyclopentadienylidene-dihydropyridines,[5] the exocyclic C=C distances (*ca* 1·40 Å) and other structural features arise from mesomeric effects which place excess electron density in the 5-ring. However, in octachloropentafulvalene, nonbonded interactions between chlorines clearly are the dominant forces influencing the C=C length and overall molecular conformation. These interactions undoubtedly are responsible for the compound's unusual electronic absorption[1,2] and ^{35}Cl nuclear quadrupole resonance[6] spectra. The compound is a moderately strong π-acid, similar to chloranil,[2] and by virtue of the shielding chlorines, it enjoys much greater chemical stability than its hydrocarbon parent pentafulvalene.



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In a LCAO-SCF-CI investigation of twisting distortions in fulvalenes, Meyer and Yinnon[7] found that the long C(1)–C(1') bond (1·49 Å[4]) and relatively short C(3)–C(4) bond (1·39 Å[4]) alone could account for the spectroscopic properties of 1. They further showed that both stretching and twisting the exocyclic C=C produced a red shift in the absorption spectrum of unsubstituted pentafulvalene, and that calculations—even when based on the reported structure[4]—lead to a set of computed interatomic distances that differed markedly from the input values. These calculated distances, especially the short exocyclic C=C (1·370 Å), are what one would expect in an unstrained molecule.

We have reinvestigated the crystal structure of octachloropentafulvalene to obtain a more accurate picture of the effects of the large Cl · · · Cl interactions on the double bond twist and stretch, and molecular conformation. The results of our study are reported here.

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[a] Fulvenes and Thermochromic Ethylenes. Part 81.

†The *Chem. Abstr.* name is 2,2',3,3',4,4',5,5'-octachlorobi-2,4-cyclopentadien-1-ylidene.

DISCUSSION

An ORTEP-II drawing[8] of the molecule is given in Fig 1. Bond lengths, angles and Cl · · · Cl distances are given for only half of the structure because the two C_5Cl_4 units are related by a C_2 axis perpendicular to C(1)–C(1′). The drawing was made with one C_5Cl_4 unit in the plane of the paper to illustrate the exocyclic C=C twist. The C=C twist angle, 36·7°, defined here as the angle between the two 5-ring planes, is close to the literature value of 41°. The 5-ring is reasonably coplanar: the underlined numbers in Fig 1 give the distances of the atoms from the five C atom least-squares plane.

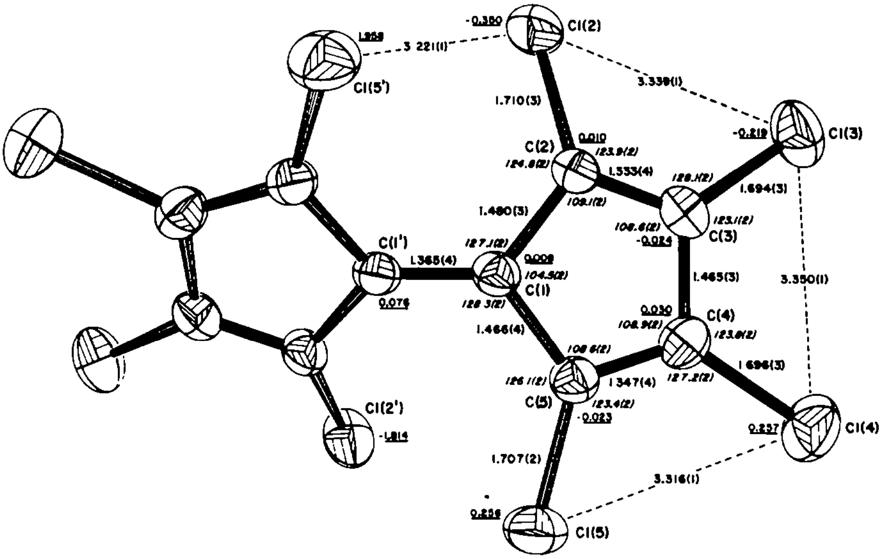

Fig 1. ORTEP-II drawing of octachloropentafulvalene normal to the plane of one 5-ring. Bond lengths (Å), angles (deg) and deviations (Å, underlined) from the unprimed 5-ring plane are shown, Esd's are given in parentheses.

The C—C bond lengths in the 5-ring are very similar to the distances obtained recently from a microwave investigation of pentafulvene,[9] and the distances in the C(2)=C(3)–C(4)=C(5) portion of the ring are close to the values reported for cyclopentadiene[10] and hexachlorocyclopentadiene.[11] The single and double bond lengths have typical values for C(sp^2)–C(sp^2) and C=C connections, and show little evidence of single–double bond delocalization beyond that in cyclopentadiene. The C—C distances reported for two tetrachlorotriapentafulvalene derivatives[12,13] differ somewhat from the corresponding octachloropentafulvalene values. A comparison of the triapentafulvalene distances with the cyclopentadiene-like bond length pattern in **1** points out that there is reduced single–double bond alternation and thus enhanced π-electron delocalization in the tetrachlorotriapentafulvalenes.

The four Cl atoms in each C_5Cl_4 unit are displaced from their 5-ring planes in a way which reduces both the Cl · · · Cl contacts between adjacent Cl's in the same ring, and from ring to ring. The two pairs of Cl atoms attached to the two C=C's are found on opposite sides of the 5-ring: Cl(2) and Cl(3) are below while Cl(4) and Cl(5) are above. This places the two Cl's farthest from the exocyclic C=C (Cl(3) and Cl(4)) on opposite sides of the 5-ring, an arrangement which permits the exocyclic angles Cl(3)–C(3)–(4) and Cl(4)–C(4)–C(3) to have smaller values than they would have if both Cl's were in the plane or on the same side of the 5-ring plane. The angle reduction is accompanied, of course, by an increase in the exocyclic Cl(3)–C(3)–C(2) and Cl(4)–C(4)–C(5) angles. The bond angle increase may be responsible for permitting the C=C Cl's to locate on the same side of the 5-ring.

The interring Cl(2) · · · Cl(5′) and Cl(5) · · · Cl(2′) contacts are clearly responsible for the 37° C=C twist and probably also for the out-of-plane pattern of Cl displacements discussed in the preceeding paragraph. The twist can be credited with increasing the interring Cl · · · Cl distance from the impossibly short 2·2–2·3 Å that would occur in a hypothetical planar octachloropentafulvalene to the more reasonable value of about 3·1 Å. The last 0·1 Å increment in the separation, reaching the 3·22 Å final value, is achieved by displacing the opposing Cl's to different sides of their respective rings. In all cases, the Cl · · · Cl distances remain below the 3·5 Å van der Waals distance.[14] It should be emphasized that the ring-to-ring contacts (Cl(2) · · · Cl(5′)) are the shortest Cl · · · Cl contacts in the molecule.

The most important difference between our results and those previously reported[4] is in the C(1)–C(1′) bond length. Whereas our 1·365 Å value corresponds to a slightly elongated C=C, the 1·49 Å literature value is appropriate for the length of a C(sp^2)–C(sp^2) single bond. The latter distance is unlikely since it would require the symmetrical octachloropentafulvalene to exist as a diradical – a circumstance which does not accord with the compound's chemical stability. Double bond twisting would be a more effective means of increasing the ring-to-ring Cl · · · Cl contacts than stretching. For example, a relatively expensive (energetically) increase in the C=C distance of 0·1 Å would only increase the Cl · · · Cl contacts by the same amount, whereas a C=C twist of about 40° would increase the Cl · · · Cl separation by 1 Å.

The increase in the octachloropentafulvalene C=C distance from the *ca* 1·34 Å expected for planar pentafulvalene* to 1·365 Å can be accounted for in terms of the loss of π-bond character accompanying the 37° twist. HMO calculations† for the planar and twisted form of the molecule show a 0·04 decrease in C=C π-bond order which can be translated into a 0·02 Å increase in bond length. Our results show that steric interactions across a C=C will preferentially twist rather than stretch the bond, and that any increase in the bond length from normal values can be related to the degree of twist. Since a C=C twist of 40° corresponds to a 0·02–0·03 Å bond distance increase, any additional bond lengthening can be ascribed to electronic factors such as dipolar or diradical‡ character or hybridization effects.

EXPERIMENTAL

Crystals of octachloropentafulvalene were grown from xylene. A preliminary X-ray photographic survey revealed the same monoclinic space group ($C2/c$) previously reported[4] for the compound. A crystal with maximum dimensions of 0·4 mm was aligned with b^* parallel to the ϕ axis of a Picker FACS-I diffractometer equipped with a Mo X-ray source and graphite monochromator. The cell parameters were refined by least-squares using 16 2θ's determined manually on the diffractometer at $\pm 2\theta$(Mo$K\alpha$, $\lambda = 0{\cdot}71069$ Å; the average value of $|2\theta_0 - 2\theta_c|$ was 0·002°). These data are: $a = 14{\cdot}998(1)$, $b = 7{\cdot}9110(5)$, $c = 11{\cdot}8068(7)$ Å, $\beta = 103{\cdot}38(1)°$. The intensity data were measured in the $2\theta - \theta$ scan mode, at a 2θ speed of 1° min^{-1} and with 20 sec backgrounds. Three standard reflections were monitored every 100 data. There were 1570 unique data in a total of 1867 intensities measured to a 2θ maximum of 55°, 1382 of which were 3σ above background and coded "observed."

The atomic parameters given by Wheatley[4] were used as the starting point for our calculations. The least-squares structure refinement used anisotropic temperature factors for C and Cl and included corrections for absorption, Cl dispersion and isotropic secondary extinction. The calculations minimized the function $\Sigma w(F_0 - F_c)^2$, where $w^{1/2} = 0{\cdot}2/\text{MAX}(\sigma(F), 0{\cdot}004F)$. The C and Cl scattering factors were evaluated from the analytical functions given by Cromer and Mann.[17] The final R index $(\Sigma|F_0 - F_c|/\Sigma F_0)$ was 0·036; the weighted R index $([\Sigma w(F_0 - F_c)^2/\Sigma w F_0^2]^{1/2})$ was 0·042. The atomic parameters are listed in Table 1. The extinction factor, Larson's r^*,[18] was 0·0095(1). A list of the observed and calculated structure factors may be obtained on request from the authors.

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Table 1. Atomic fractional coordinates and temperature factors (Å²) for octachloropentafulvalene. The temperature factors are in the form exp $[-2\pi^2(U_{11}h^2a^{*2} + \text{---} 2U_{23}kl b^* c^*)]$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
C(1)	−0·0046(2)	0·2442(3)	0·3062(2)	0·028(1)	0·036(1)	0·036(1)	−0·002(1)	0·008(1)	−0·002(1)
C(2)	0·0668(2)	0·2035(3)	0·4119(2)	0·030(1)	0·040(1)	0·035(1)	−0·001(1)	0·005(1)	−0·003(1)
C(3)	0·0321(2)	0·2233(3)	0·5052(2)	0·041(1)	0·038(1)	0·035(1)	−0·003(1)	0·002(1)	−0·002(1)
C(4)	−0·0618(2)	0·2873(3)	0·4672(2)	0·038(1)	0·037(1)	0·043(2)	−0·002(1)	0·017(1)	−0·002(1)
C(5)	−0·0850(2)	0·2911(3)	0·3500(2)	0·030(1)	0·044(2)	0·038(1)	0·004(1)	0·011(1)	0·005(1)
Cl(2)	0·16543(4)	0·0946(1)	0·41272(7)	0·0351(4)	0·0645(5)	0·0560(5)	0·0128(3)	0·0049(3)	−0·0021(4)
Cl(3)	0·08035(6)	0·1716(1)	0·64516(6)	0·0633(5)	0·0760(6)	0·0331(4)	−0·0026(4)	0·0003(3)	0·0012(4)
Cl(4)	−0·12449(6)	0·3592(1)	0·55978(7)	0·0685(5)	0·0603(5)	0·0542(5)	0·0078(4)	0·0360(4)	−0·0020(4)
Cl(5)	−0·18206(5)	0·3860(1)	0·27177 (7)	0·0401(4)	0·0771(6)	0·0561(5)	0·0215(4)	0·0164(3)	0·0135(4)

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*The central C=C in perchloroheptafulvalene ($C_7Cl_6 = C_7Cl_6$) was 1·332 Å.[15]

†The bond order difference was obtained from ω-HMO calculations on planar and twisted pentafulvalene, and octachloropentafulvalene. C—C and C=C resonance integrals of $0{\cdot}9\beta$ and $1{\cdot}06\beta$, respectively, were used for the planar molecules. A C(1)–C(1′) resonance integral of $\cos(37°) \times 1{\cdot}06\beta$ was used in the twisted molecule calculations.

‡Bailey and Hull[16] reported a C=C twist of 40° and length of 1·40 Å for 1,1′-bisisopropoxycarbonyl-9,9′-bisfluorenylidene. They ascribed partial diradical character to the bond.

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