Crystal and Molecular Structure of 4,10-Dibromo-1,7-methano[12]annulene [1]

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An X-ray crystal structure determination of the title compound (I) (monoclinic, space group $C2/c$, $a = 14.929(2)$, $b = 4.281(1)$, $c = 18.630(2)$ Å, $\beta = 100.60(1)°$, $Z = 4$) shows systematic alternation of long and short bond distances (means 1.46 and 1.34 Å) in the perimeter ring. The configuration of the double bonds follows the order *trans, cis, cis*. The molecule has a twisted conformation and crystallographic symmetry 2 (C_2), with the two-fold axis running through the carbon atom of the methano-bridge. Simple HMO calculations for the present compound and other [4n]annulenes are in quite good agreement with experimental results. The structure was determined by the heavy-atom method and refined by least-squares techniques to R 0.037 for 1 249 observed reflections measured by diffractometer.

THE role of a bridge overimposed on an annulene ring has been recently emphasized [2] in testing the validity of the Hückel rule. However, for [12]annulene aromatic behaviour cannot be expected, even when the strain is relieved by the presence of a bridge. Recently, the crystal-structure determination of a hydrazino-bridged [12]annulene, namely 8b,8c-diazacyclopent[*fg*]acenaphthylene (II),[3] has shown the bond lengths in the perimeter to be within ±0.03 Å of 1.39 Å in a nearly planar centrosymmetric molecule.

On the other hand, the u.v. spectrum of 1,7-methano-[12]annulene has been interpreted as that of a polyenic compound.[2,4] It therefore seemed to us worthwhile to establish the geometry of a methano-bridged [12]-annulene in the solid state by means of X-ray diffraction. Because of the low m.p. of the hydrocarbon (−6 to −4°) we used its 4,10-dibromo-derivative (I) for the crystal structure determination.

EXPERIMENTAL

Crystals of (I) are orange parallelipipeds elongated along b. After preliminary photographic work a single crystal of dimensions 0.11 × 0.13 × 0.20 mm was chosen and centred on a Syntex $P\bar{1}$ four-circle diffractometer by use of graphite-monochromated Mo-K_α radiation. Cell parameters were obtained from a least-squares fit of 13 reflections (plus their equivalents).

Crystal Data.—$C_{13}H_{10}Br_2$, $M = 326.06$, m.p. 179 °C. Monoclinic, $a = 14.929(2)$, $b = 4.281(1)$, $c = 18.630(2)$ Å, $\beta = 100.60(1)°$, $U = 1\,170$ Å^3, $D_m = 1.845$ (by flotation), $Z = 4$, $D_c = 1.850$ g cm^{-3}, $F(000) = 632$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 73.05 cm^{-1}. Space group $C2/c$ or Cc from systematic absences: hkl when $h + k = 2n + 1$, $h0l$ when $l = 2n + 1$; evidence for $C2/c$ was given by the features of the Patterson map.

Collection of Intensities and Structure Determination.—Diffracted intensities were measured with the θ—2θ scan technique, scan width 2.1° + $\alpha_1\alpha_2$ separation, variable scan-speed between 0.5 and 12° min^{-1}, and dead time for coincidence correction 2.1×10^{-6} s. Background was counted for half the total scanning time on each side of the peak. 3 Standard reflections monitored after every group of 20 showed no significant change during data collection. In the range of measurements ($2\theta_{max.}$ 55°) 1 349 unique reflections were collected, of which 1 249 had intensity above background. The variance $\sigma^2(I_{rel})$ was calculated as $[S + B + (0.02\ S)^2]\ v^2$, with S = scan count, B = total background count, and v = scan speed. Diffraction data were corrected for absorption effects [5] and then for Lorentz and polarization factors.

The structure was solved by interpretation of the Patterson map. After location of the bromine atom, the positions of some carbon atoms became apparent. However, the first structure-factor calculation was carried out with the bromine contributions only; a subsequent difference-Fourier map showed all carbon-atom positions.

Structure Refinement.—The refinement was carried out by a full-matrix least-squares process,[6] the function minimized being $\Sigma w(\Delta F)^2$ with weights $w = 1/\sigma^2(F)$ and including all observed reflections. In the last two cycles zero weight was given to the low-angle 002 and to the very strong 111 reflections. After some cycles of isotropic and then anisotropic refinement on bromine and carbon atoms, hydrogen atoms (treated as isotropic) were refined together with carbon and bromine, starting from calculated positions and with thermal factors B_H 3.8 Å^2. Scattering factors for carbon and bromine were taken from ref. 7, and for

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hydrogen from ref. 8, the real part of anomalous dispersion being taken into account [9] for bromine. In the final least-squares cycle most shifts were $<0.1\sigma$, the maximum being 0.21σ [for atom H(4)]. The final R value was 0.037 for all observed reflections, with a goodness-of-fit 0.89 $\{[\Sigma w(\Delta F)^2/(n - p)]^{1/2}$, where n is the number of observations and p that of parameters$\}$. Reasonable values were obtained for calculated structure factors of the 100 unobserved reflections. A final difference-Fourier synthesis, calculated with all observed reflections, showed few small peaks of maximum height 0.39 e$Å^{-3}$. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21646 (8 pp., 1 microfiche).*

TABLE 1

Heavy-atom parameters * ($\times 10^4$) and their standard deviations

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	1 642(0)	6 786(1)	546(0)	44(0)	818(2)	27(0)	33(1)	14(0)	−5(0)
C(1)	−713(1)	8 579(6)	2 070(1)	22(1)	385(16)	23(1)	−19(3)	−1(1)	−13(3)
C(2)	−687(2)	9 354(7)	1 380(1)	25(1)	648(21)	24(1)	11(4)	−1(1)	7(3)
C(3)	6(2)	8 347(7)	971(1)	39(1)	664(20)	21(1)	−8(5)	4(1)	−6(4)
C(4)	898(1)	8 430(7)	1 203(1)	34(1)	495(16)	23(1)	11(4)	8(1)	13(3)
C(5)	1 473(2)	9 775(7)	1 851(1)	26(1)	451(17)	30(1)	5(4)	7(1)	9(3)
C(6)	1 396(1)	9 878(7)	2 555(1)	21(1)	441(17)	27(1)	−5(4)	0(1)	−5(3)
C(7)	0(0)	6 522(9)	2 500(0)	28(1)	296(20)	27(1)	0(0)	5(1)	0(0)

* Thermal factors are of the form $\exp[-(B_{11}h^2 + 2B_{12}hk + \ldots)]$.

TABLE 2

Co-ordinates ($\times 10^3$) and thermal factors ($\times$ 10) for hydrogen atoms

	x	y	z	$10B/Å^2$
H(1)	−114(2)	1 066(6)	112(1)	38(5)
H(2)	−17(2)	758(6)	50(1)	47(6)
H(3)	201(2)	1 080(6)	174(1)	46(6)
H(4)	185(2)	1 098(5)	285(1)	35(5)
H(5)	28(1)	513(6)	218(1)	41(5)

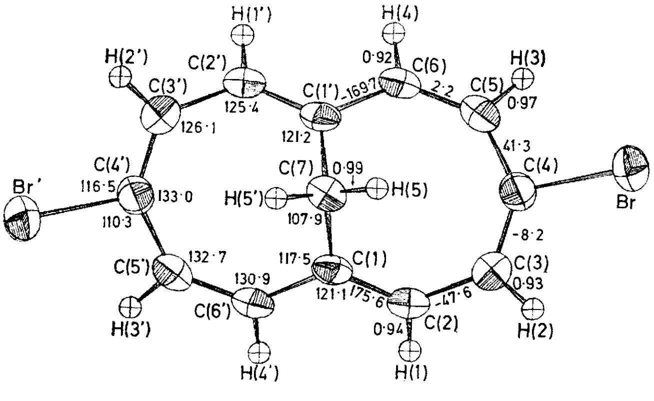

FIGURE 1 One molecule of (I) viewed along its two-fold axis, showing bond angles, torsion angles along the annulene ring, and C–H bond lengths. Thermal ellipsoids are drawn at 0.50 probability, but hydrogen atoms, treated as isotropic, are on an arbitrary scale. Signs for the torsion angles are given following the convention of W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521

Heavy-atom parameters and their standard deviations, as derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, are listed in Table 1, and hydrogen-atom parameters in Table 2. The numbering of atoms, together with bond and torsion angles and C–H bond distances, is shown in Figure 1.[10] The C–C and C–Br bond lengths are reported with their estimated standard deviations in Table 3. Estimated standard deviations in bond angles involving only heavier atoms are *ca.* 0.2°, and those in the torsion angles (calculated according to ref. 11) 0.4°; in C–H bond lengths they are *ca.* 0.03 Å, and in angles involving H atoms between 1.5 and 2° (for the H–C–H).

TABLE 3

Bond lengths (Å)

	Obs.	Corr.†	Calc.
C(1)–C(2)	1.335(3)	1.339	1.359
C(2)–C(3)	1.459(4)	1.463	1.465
C(3)–C(4)	1.322(3)	1.328	1.352
C(4)–C(5)	1.466(3)	1.473	1.458
C(5)–C(6)	1.337(3)	1.341	1.360
C(6)–C(1')	1.450(3)	1.453	1.442
C(1)–C(7)	1.496(3)	1.503	
C(4)–Br	1.931(2)		

† After rigid-body correction

Rigid-body Motion Analysis.—The rigidity of the molecule was tested by interpreting the anisotropic thermal parameters in terms of molecular rigid-body motion.[12] The tensors $\boldsymbol{T}$, $\boldsymbol{L}$, $\boldsymbol{S}$ were derived from a least-squares treatment.[13] The agreement between observed and calculated values of B_{ij} was fairly good, but significant discrepancies were found for the bromine thermal parameters. A subsequent calculation excluding the bromine atom led to a marked improvement between observed and calculated values, the largest differences being of the order of 3σ [for B_{12} of C(1) and B_{33} of C(4)], and in most cases of the order of 1σ. The mean square rotational displacements about the principal axes of the tensor $\boldsymbol{L}$ amount to 26, 7, and 6 (deg)^2. Values for bond distances corrected under the assumption of rigid-body motion for the carbon atom skeleton are reported in the third column of Table 3. Corrections for bond and torsion angles, of the order of 0.1° or less, have been neglected.

DISCUSSION

The present structure analysis has shown that (I) has in the crystal a twisted conformation, with a molecular (and crystallographic) two-fold axis running through the

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

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[10] C. K. Johnson, ORTEP, U.S. Atomic Energy Commission, Oak Ridge, Tennessee, Report ORNL 3794, 1965.

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[13] Fortran IV program written by Dr. G. Filippini.

carbon atom of the methano-bridge. Geometric parameters are reported in Figure 1 and in Table 3. A striking feature of this structure is the systematic alternation of double- and single-bond lengths along the annulene ring, mean values being 1.34 and 1.46 Å respectively. This is in full agreement with the Hückel rule for a $[4n]$annulene and with the polyenic behaviour predicted on the basis of the u.v. spectrum interpretation.[2,4] Even for $n \neq 3$ (*e.g.* cyclo-octatetraene,[14] and [16]annulene [15]) systematic splitting of the aromatic bond distance in longer and shorter bond lengths has been found, and a derivative of [4]annulene has shown nearly rectangular geometry in the ring.[16]

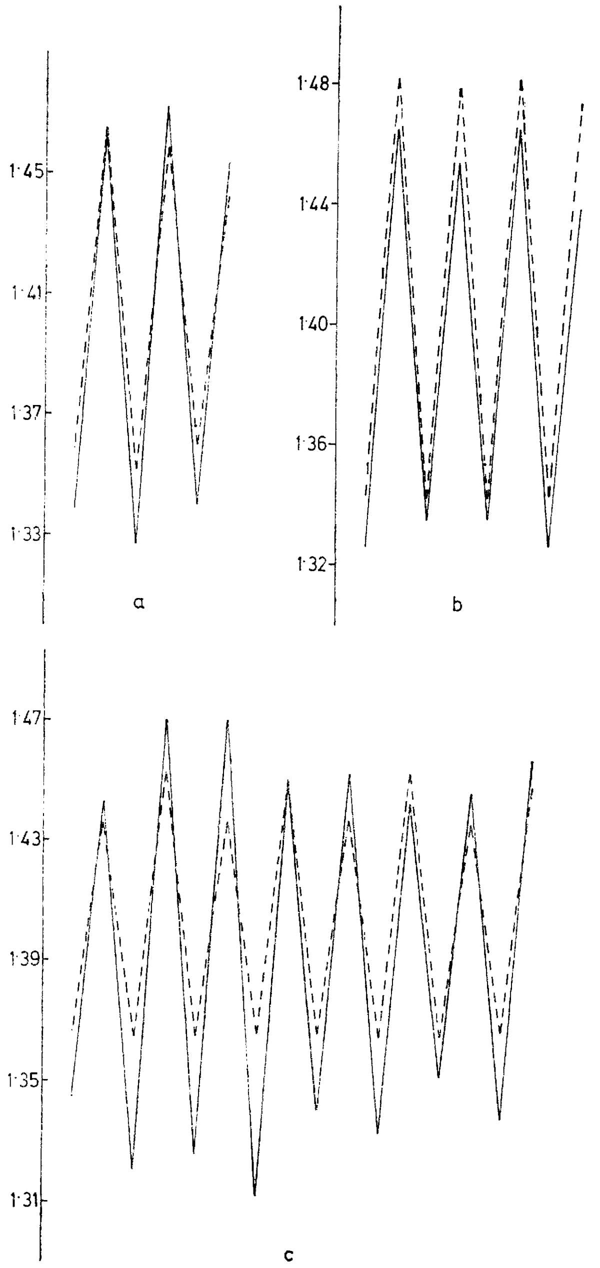

FIGURE 2 Experimental (solid line) and calculated (dashed line) bond lengths (Å) along the perimeter ring, starting from the bond C(1)–C(2) for (a) (I), (b) cyclo-octatetraene, and (c) [16]-annulene

We know of only one other crystal-structure determination of a bridged [12]annulene derivative, namely that of 8b,8c-diazacyclopent[*fg*]acenaphthylene (II),[3] in which all the perimeter bond lengths are near to the aromatic value; however, both the flattening of the molecule (all carbon atoms being within 0.02 Å from the least-squares molecular plane) and the lack of single- and double-bond localization could be ascribed, at least in part, to the presence of the two sp^2 nitrogen atoms of the bridge and to their influence on the electron distribution along the perimeter ring. This could contradict the presumed absence of effects of the hydrazino-bridge on the periphery, as claimed [3] by analogy with results of calculations for pyracylene.[17]

According to simple Hückel molecular orbital (HMO) calculations, values of bond distances in $[4n]$annulenes are in good agreement with the experimental bond distances, when considering the misalignments of adjacent p_z orbitals along the perimeter. Our calculations were performed with the same procedure and parameters as described elsewhere,[18] starting from bond distances all set equal to 1.40 Å and experimental torsion angles. Results at convergence are compared with experimental values of bond lengths for (I) in the last two columns of Table 3 and Figure 2(a), for cyclo-octatetraene [14] in Figure 2(b), and for [16]annulene [15] in Figure 2(c).

The perimeter ring of the present compound does not deviate very much from planarity, as shown in Figure 3. In fact, p_z orbital misalignments, and therefore torsion angles, more than deviation from planarity [18] can be correlated with ring bond lengths. The configuration of the double bonds in the annulene ring follows the order *trans, cis, cis*. The central non-bonded distance C(1) $\cdots$ C(1′) is 2.42 Å.

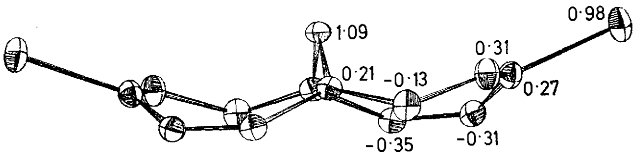

FIGURE 3 Side view of the molecule of (I) with distances of atoms from the least-squares plane through the annulene ring. Thermal ellipsoids are drawn at 0.20 probability

Figure 4 shows the molecular packing in the crystal. Intermolecular distances can be considered to lie in the expected range; there are only four contacts appreciably

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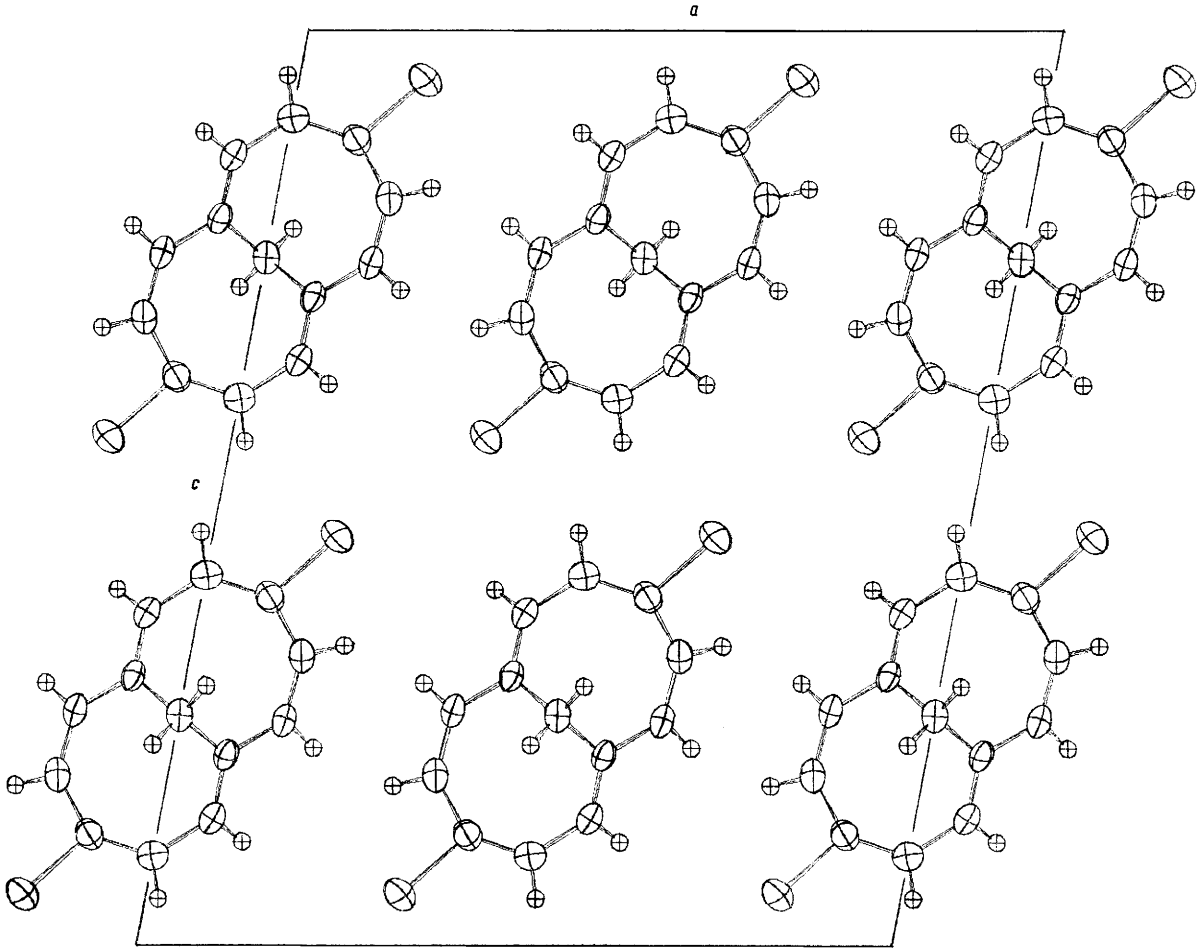

FIGURE 4 Packing of the molecules as seen along the y axis

shorter than the sum of van der Waals radii (C 1.7, CH_2 2.0, H 1.2, Br 1.95 Å):[19] $Br \cdots Br^{I}$ 3.60, $C(1) \cdots C(7^{II})$ 3.61, $C(6) \cdots C(7^{II})$ 3.52, and $C(6) \cdots H(5^{II})$ 2.81 Å (I at $1/2 - x$, $3/2 - y$, $-z$, II at x, $1 + y$, z). The contact between the bromine atoms appears to be quite tight; however this feature has been observed frequently, *e.g.* in octabromopentafulvalene,[20] where there are three $Br \cdots Br$ intermolecular contacts in the range 3.52—3.67 Å. It seems that the quoted value of the van der Waals radius for bromine[19] is overestimated; a value of 1.85 Å has been suggested.[21]

We thank Professor E. Vogel for a gift of crystals of the examined compound.

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