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[18]-Annulene, $C_{18}H_{18}$, Structure, Disorder and Hückel's $4n+2$ Rule

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Abstract

An unexpected disorder has been discovered during an X-ray reinvestigation of the crystal structure of the monocyclic hydrocarbon $C_{18}H_{18}$. The study at 80 K by Bregman, Hirshfeld, Rabinovich & Schmidt [*Acta Cryst.* (1965), **19**, 227–234] resulted in an almost planar molecule with 12 inner C—C bonds of mean length 1.382 (3) Å and six outer bonds of 1.419 (4) Å. The 0.037 Å difference was and has remained puzzling. In new work at 111 K, partial disorder has been found. 86.3% of the molecules are in the orientation found by Bregman *et al.* and 13.7% are rotated by approximately 30° in the mean plane. Constrained refinement yields a molecule of approximate D_{6h} symmetry with mean dimensions in the *major* orientation: inner bonds 1.385 (2) Å, outer bonds 1.405 (3) Å, C—C—C ring re-entrant angles 127.9 (4)°, C—C—C ring internal angles 124.0 (2)°. The Bregman data is interpreted by a 6% disorder. The new dimensions agree well with the D_{6h} self-consistent field (SCF) calculations of Schulman & Disch [*J. Mol. Struct. Theochem.* (1991), **234**, 213–225]. One can exclude a 50:50 inversion disorder of D_{3h} molecules with alternating short and long bonds as their calculated ring diameters are up to 0.20 Å too large. Thus, the $4n+2$ π-electron molecule [18]-annulene is confirmed as having an aromatic structure in the crystal. The rotation disorder and small deviations from planarity are explained by the crystal packing. Crystal data: $C_{18}H_{18}$, $M_r = 234.34$, monoclinic, $P2_1/a$, $a = 14.984(5)$, $b = 4.802(2)$, $c = 10.260(3)$ Å, $\beta = 111.52(1)°$, $V = 686.8(4)$ Å^3, $Z = 2$, $D_x = 1.134(1)$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.069$ mm^{-1}, $T = 111$ K, final $R = 0.0398$ for 1256 significant reflections.

Introduction

[18]-Annulene, $C_{18}H_{18}$ (Figs. 1*a*–*d*), was first synthesized by the late Professor Franz Sondheimer and his collaborators (Sondheimer & Wolovsky, 1959; Sondheimer, Amiel & Gaoni 1962). According to Hückel's (1931) $4n+2$ rule, its 18 π-electron system should be delocalized, resulting in a fully conjugated and planar structure with $6/mmm$ (D_{6h}) symmetry. However, it was argued by Mislow (1952) that the interaction of the internal H atoms would prevent a planar structure. Moreover, chemical evidence (Sondheimer, Wolovsky & Amiel, 1962) points to addition rather than substitution reactions and therefore to localized double bonds. A molecule with alternating single and double bonds would be non-centrosymmetric.

The crystal structure of [18]-annulene was determined by photographic X-ray diffraction at 80 K by Bregman, Hirshfeld, Rabinovich & Schmidt (1965) and Hirshfeld & Rabinovich (1965). The analysis yielded a roughly planar centrosymmetric molecule with 12 inner C—C bonds of mean length 1.382 (3) Å and six outer bonds of 1.419 (4) Å. The authors (hereafter BHRS) observed C atoms displaced from the mean molecular plane by amounts up to 0.085 Å. They found an approximate molecular symmetry $\bar{3}$ (C_{3i}) only slightly distorted from the $6/mmm$ expected for a delocalized planar π-system. BHRS explained the slight non-planarity of the molecule by a rather convincing account of intermolecular non-bonded repulsions, but they were unable to find a satisfactory explanation of the 0.037 Å difference between the two types of bonds. BHRS found no evidence for a 1:1 packing disorder of non-centrosymmetric molecules; thus the crystallographic centre of symmetry excluded a molecule with alternating short and long bonds.

Since the work of BHRS in 1965, theoreticians have been in frequent debate as to the ground-state structure of an isolated [18]-annulene molecule (Fig. 1). Is a planar structure of $6/mmm$ (D_{6h}) symmetry with almost equal bonds of lower or higher energy than a structure with alternating short and long bonds [having $\bar{6}m2$ (D_{3h}) symmetry if planar or 32 (D_3) symmetry if non-planar]? However, no $6/mmm$ calculation reproduced the 1.382 Å inner and 1.419 Å outer bonds found by BHRS. References may be traced from the paper by Schulman & Disch (1991), which we will consider later.

We now report a reinvestigation of the crystal structure in Leiden with CAD-4 diffractometer data at 111 K (see Table 1). An unexpected partial disorder, involving molecular rotation, has been discovered. The dimensions of the *major* molecule differ only slightly, but significantly, from those found by BHRS. We have also

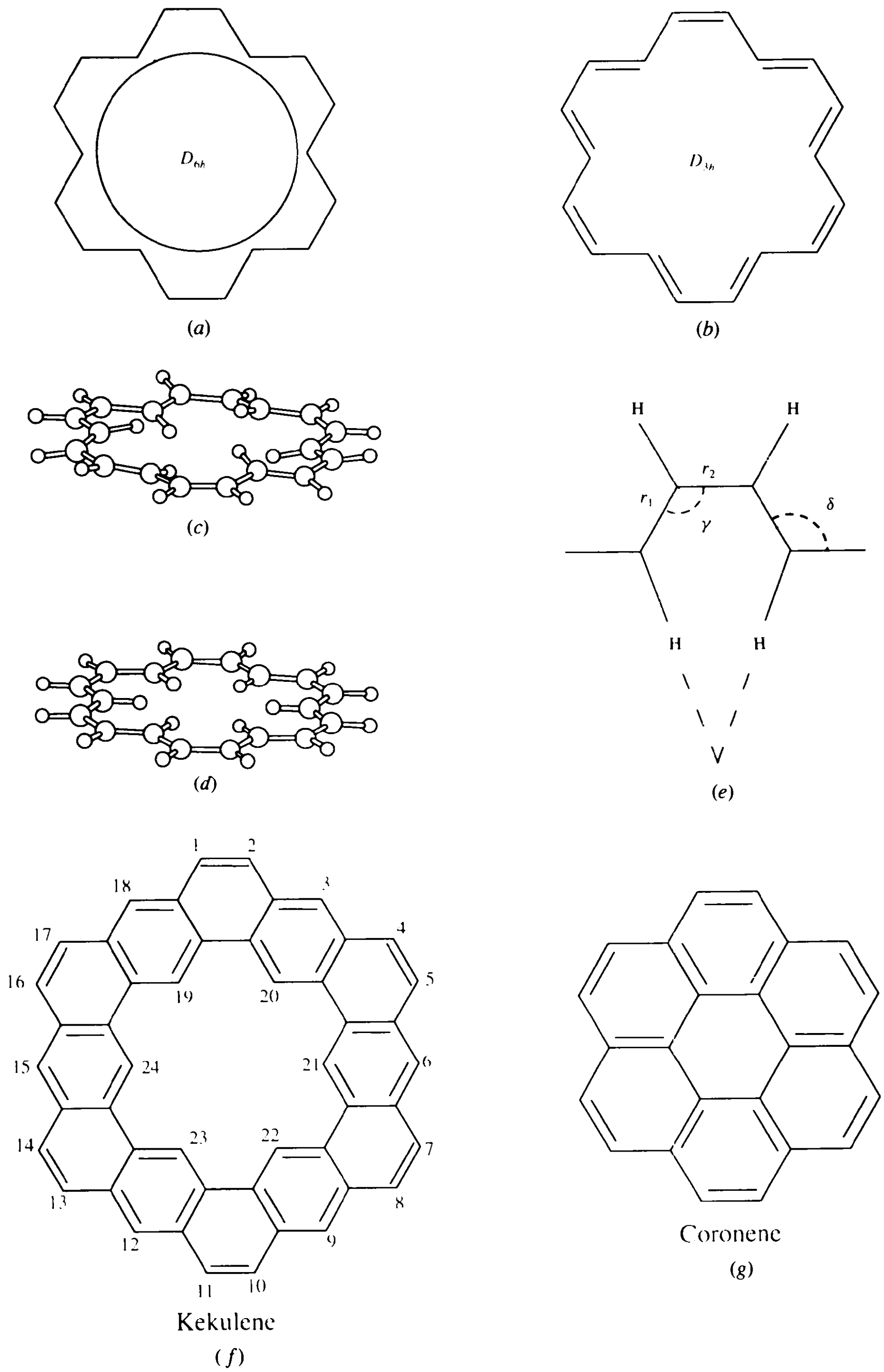

Fig. 1. (a) and (b) Possible bond structures for annulene; (c) and (d) perspective views of D_{3h} and D_{6h} annulene; (e) parameters in constrained refinement; (f) a valence structure for kekulene; (g) a valence structure for coronene.

reanalysed the data of BHRS and find that these can be similarly interpreted. The results agree well with the 6/*mmm* calculations of Schulman & Disch (1991).

Experimental

From Professor Sondheimer we obtained a small sample of the title compound, which was purified by thin-layer chromatography and stored in a dark room at 253 K. A crystal with dimensions 0.50 x 0.40 x 0.30 mm^3 was mounted in a glass capillary and kept at a temperature of 111 K throughout the diffraction experiments. The unit-cell dimensions listed in Table 2 were determined with a least-squares procedure using the $\sin^2\theta$ values of 24 reflections. Table 2 also includes the cell dimensions at 80 K and at room temperature reported by BHRS.

Table 1. *Experimental details*

Crystal data	
Chemical formula	$C_{18}H_{18}$
Chemical formula weight	234.34
Cell setting	Monoclinic
Space group	$P2_1/a$
a (Å)	14.984 (5)
b (Å)	4.802 (2)
c (Å)	10.260 (3)
β (°)	111.52 (1)
V (Å^3)	686.8 (4)
Z	2
D_x (Mg m^{-3})	1.134 (1)
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71069
No. of reflections for cell parameters	24
θ range (°)	12.98–13.94
μ (mm^{-1})	0.069
Temperature (K)	111
Crystal form	Box
Crystal size (mm)	0.50 × 0.40 × 0.30
Crystal colour	Dark brown
Data collection	
Diffractometer	CAD-4
Data collection method	ω,θ mode (zigzag)
Absorption correction	None
No. of measured reflections	4184
No. of independent reflections	2004
No. of observed reflections	1256
Criterion for observed reflections	$I > 2\sigma_I$
$R_{\rm int}$	0.0611
$\theta_{\rm max}$ (°)	27
Range of h, k, l	$-14 \rightarrow h \rightarrow 14$ $-6 \rightarrow k \rightarrow 6$ $0 \rightarrow l \rightarrow 21$
No. of standard reflections	3
Frequency of standard reflections (s)	5400
Variation of standards (%)	$\sigma_1 = 4.8$, $\sigma_2 = 7.5$, $\sigma_3 = 3.3$
Refinement	
Refinement on	F
R	0.0398
wR	0.0525
S	1.2596
No. of reflections used in refinement	1256
No. of parameters used	118
H-atom treatment	x,y,z and isotropic temperature factors refined
Weighting scheme	$w = 1/\sigma^2$
$(\Delta/\sigma)_{\rm max}$	$<1/150$
$\Delta\rho_{\rm max}$ (e Å^{-3})	0.336
$\Delta\rho_{\rm min}$ (e Å^{-3})	−0.208
Extinction correction method	None
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)

The space group is $P2_1/a$ and the unit cell contains two molecules.

Reflection intensities were recorded with a CAD-4 diffractometer using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). A total of 4184 reflections were measured, of which 2004 were symmetry independent. These comprised 1256 intensities with $I > 2\sigma_I$, 244 with $2\sigma_I > I > \sigma_I$, and 504 with $\sigma_I > I$. The (ω,θ) scanning mode was employed in the range $2 < \theta < 27°$. Standard reflections, *i.e.* $0\bar{3}1$, 031 or $10\,0\,\bar{3}$ were scanned every 5400 s to monitor the loss of scattering power during exposure to X-rays. The correction function was a polynomial of the exposure time. The standard errors σ_I and the corresponding weights were estimated from the counting statistics. The intensities were corrected for Lorentz and polarization factors and were reduced to structure factors, but no absorption correction was applied.

Table 2. *Unit-cell dimensions for* [18]-*annulene*

	Present study	BHRS	BHRS
T (K)	111	80	300
a (Å)	14.984 (5)	14.889 (4)	15.33
b (Å)	4.802 (2)	4.800 (2)	4.88
c (Å)	10.260 (3)	10.235 (3)	10.27
β (°)	111.52 (1)	111.60 (14)	111.8
V (Å^3)	686.8 (4)	680.1	713.4

Refinement

All calculations were executed with an Amdahl V7B computer and later on an Amdahl 5890-109E computer of the University of Leiden. The scattering factors of hydrogen were adopted from Stewart, Davidson & Simpson (1965) and those of carbon ($C_{\rm val}$) from *International Tables for X-ray Crystallography* (1974, Vol. 4). The function minimized during the full-matrix least-squares refinement (*KLKWAD*; Rutten-Keulemans, 1995) was $R = \Sigma_h w_h \Delta F_h^2$ with $\Delta F_h = |F_{h,{\rm obs}} - F_{h,{\rm calc}}|$. Discrepancy factors are defined as $R = (\Sigma_h|\Delta F_h|)/(\Sigma_h|F_{h,{\rm obs}}|)$ and $wR = [(\Sigma_h w_h \Delta F_h^2)/(\Sigma_h w_h F_{h,{\rm obs}}^2)]^{1/2}$.

During minimization with *slack* constraints (Waser, 1963; Flapper, Verschoor, Rutten-Keulemans & Romers, 1977), the sum $\Sigma_v w_v [r_{v,{\rm obs}} - r_{v,{\rm calc}}]^2$ was added to the least-squares residual $\Sigma_h w_h \Delta F_h^2$. The weights w_v were calculated (Rollett, 1970; Flapper *et al.*, 1977) from the expression $w_v = (\Sigma_h w_h \Delta F_h^2)/[\sigma_v^2(M - N)]$, where M is the number of observations and N the total number of variables. The standard errors σ_v (in our case 0.01 Å for C—C distances and 0.04 Å for C···C next-nearest-neighbour distances) determine the leniency of the constraints. The values $r_{v,{\rm obs}}$ are the required constraints and are in general literature values. Distances $r_{v,{\rm calc}}$ are calculated from positional parameters obtained in the previous least-squares cycle.

The starting model of the refinement was based on the coordinates reported by BHRS. As observables only, the reflections with $I > 2\sigma_I$ were used. The initial positions of the hydrogens were derived from difference-Fourier maps. Assuming a molecule with a centre of symmetry, containing nine independent anisotropic C atoms and nine independent isotropic H atoms, the refinement converged to $wR = 0.092$ ($R = 0.104$). The geometry of this model was similar to that found by BHRS. It contained six outer bonds of mean length 1.465 (4) Å and 12 inner bonds of mean length 1.354 (3) Å. Disturbingly, the difference of 0.111 Å is three times that found by BHRS.

A difference-Fourier section was calculated through the mean molecular plane using the Fourier program section Slant Fourier Transform [*SPFT* (de Waal, 1978)]. Contour maps, plotted with the program *FPLOT* (Faber, Rutten-Keulemans & Altona, 1979), are depicted in Figs. 2 and 3. The difference section revealed six significant positive peaks at positions between each pair of the six inner C atoms and 12 smaller though still significant peaks at radial positions for the outer C atoms, but twisted by an angle of approximately 30°. As indicated in Fig. 4, rotation of the molecule by ±±30° hardly changes the positions for the outer H atoms, but introduces new positions for the inner C and H atoms. If we assume a 6/*mmm* molecular shape with nearly equal outer and inner C—C bonds, the observed difference of 0.111 Å between these bonds can be interpreted as an artefact due to the presence of *minor* molecules rotated by ±30° with respect to the orientation of the *major* molecules. The six inner C atoms of the *minor* molecules correspond to the six positive peaks in the difference map. Unfortunately, such a disordered model cannot be refined by conventional least-squares techniques, because the outer C atoms overlap and are only 0.5 Å apart. However, it has been shown (Flapper *et al.*, 1977; de Kok & Romers, 1978, 1980) that disordered, almost coinciding, structures can be refined successfully using *slack* constraints, provided one foregoes the detailed geometrical information available in ordered structures.

We first explored a disordered model in which all the C—C distances were *slackly* constrained to 1.395 Å. During the refinement the occupancy ratios of *major* and *minor* molecules were negatively coupled so that the total occupancy remained equal to one. Since the outer and inner bonds persisted in assuming lengths larger and smaller than 1.395 Å, it was necessary to modify the slack constraints to 1.400 and 1.387 Å, respectively (distances r_2 and r_1, respectively, in Fig. 1*e*). Furthermore, it was necessary, *via* the next-nearest-neighbour distances, to constrain the C—C—C bond angles about the outer C atoms to 124° and about the inner C atoms to 128° (angles γ and δ in Fig. 1*e*). Under these conditions and using $w_h = 1$ the refinement converged to $wR = 0.0379$ ($R = 0.0416$) with occupancies 0.856 and 0.144 for *major* and *minor* molecules.

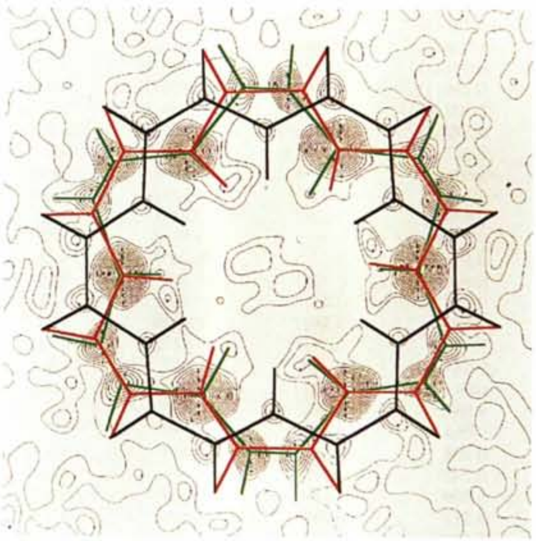

Fig. 3. Difference electron-density map of the section through the molecular plane of the *major* molecule. Black and red as in Fig. 2. The green depicts the starting model for the refinement of the *minor* molecule.

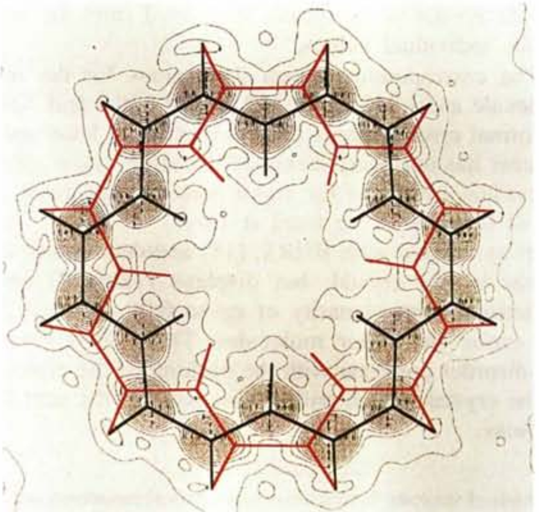

Fig. 2. Electron-density map of the section through the molecular plane of the *major* molecule. The *major* molecule is depicted in black and the *minor* molecule in red. The highest contour level is *ca* 14 e Å^{-3}.

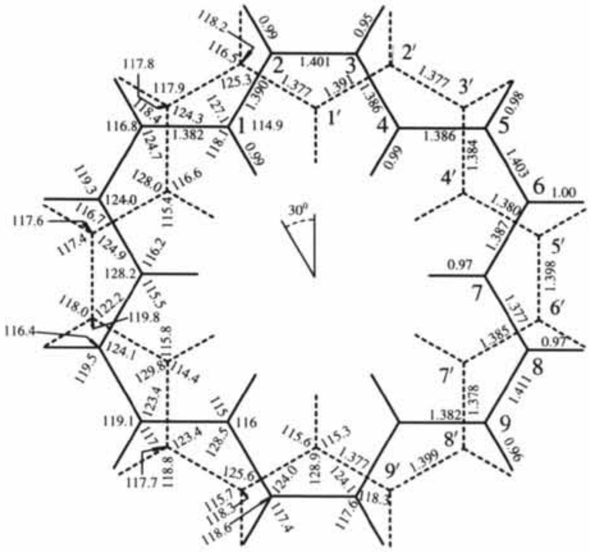

Fig. 4. Schematic view and geometric data (Å and °) of the *major* and *minor* molecules. Numbering of hydrogen is not given for reasons of simplicity. C—H distances in the *minor* molecule are not displayed, because they are all constrained to 1.00 Å.

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$^*B_{eq}$
C(1)	−0.1150 (1)	−0.4547 (2)	0.0434 (1)	2.43 (3)
C(2)	−0.1064 (1)	−0.5076 (2)	0.1807 (1)	2.64 (3)
C(3)	−0.0438 (1)	−0.3638 (2)	0.2973 (1)	2.62 (3)
C(4)	0.0157 (1)	−0.1490 (2)	0.2893 (1)	2.45 (3)
C(5)	0.0847 (1)	−0.0080 (2)	0.3978 (1)	2.71 (3)
C(6)	0.1425 (1)	0.2038 (2)	0.3768 (1)	2.69 (3)
C(7)	0.1415 (1)	0.2838 (2)	0.2464 (1)	2.46 (3)
C(8)	0.1885 (1)	0.5044 (2)	0.2142 (2)	2.70 (3)
C(9)	0.1769 (1)	0.5825 (2)	0.0764 (2)	2.78 (3)
H(1)	−0.072 (1)	−0.309 (3)	0.033 (1)	2.5 (3)
H(2)	−0.145 (1)	−0.659 (4)	0.198 (1)	3.5 (3)
H(3)	−0.043 (1)	−0.418 (3)	0.387 (2)	3.1 (3)
H(4)	0.008 (1)	−0.086 (3)	0.194 (2)	3.6 (3)
H(5)	0.093 (1)	−0.061 (3)	0.494 (2)	3.3 (3)
H(6)	0.186 (1)	0.310 (4)	0.459 (2)	3.9 (4)
H(7)	0.102 (1)	0.172 (4)	0.168 (1)	3.1 (3)
H(8)	0.232 (1)	0.610 (3)	0.292 (2)	3.5 (4)
H(9)	0.217 (1)	0.730 (4)	0.066 (2)	3.8 (3)
C(1′)	−0.0566	−0.3585	0.1848	3.04
C(2′)	−0.0191	−0.2899	0.3263	3.47
C(3′)	0.0549	−0.1062	0.3881	3.32
C(4′)	0.0938	0.0623	0.3132	2.78
C(5′)	0.1659	0.2585	0.3603	4.13
C(6′)	0.1911	0.4285	0.2687	3.00
C(7′)	0.1467	0.4255	0.1241	2.58
C(8′)	0.1665	0.5899	0.0280	4.22
C(9′)	0.1251	0.5543	−0.1172	2.73
H(1′)	−0.034	−0.240	0.122	4.9
H(2′)	−0.041	−0.399	0.392	4.9
H(3′)	0.080	−0.085	0.492	4.9
H(4′)	0.064	0.040	0.209	4.9
H(5′)	0.204	0.275	0.463	4.9
H(6′)	0.242	0.571	0.311	4.9
H(7′)	0.096	0.279	0.085	4.9
H(8′)	0.212	0.748	0.064	4.9
H(9′)	0.148	0.683	−0.176	4.9

* B_{iso} for H atoms.

No e.s.d.'s are given for the *minor* molecule atoms C(1′)–C(9′) due to the use of *slack* constraints. The B values of the H atoms of the *minor* molecule have been coupled.

This unexpected result caused us to reconsider the interpretation of the photographic data given by BHRS. Without the assumption of disorder, using weights w_h = 1 and taking five scaling factors for the reciprocal layers k = 0–4, a model with isotropic C and H atoms refined to wR = 0.097 (R = 0.115). Allowing disorder and using the previous constraints, the model refined to wR = 0.084 (R = 0.102) with occupancies 0.94 and 0.06 for *major* and *minor* molecules. Notwithstanding the less accurate photographic data, Hamilton's (1965) ratio test shows that the ordered model can be rejected at a significance level well below 0.5%.

In the continuation of our refinement and the exploration of several possibilities, we found it was not necessary to apply *slack* constraints to the *major* molecule provided that the previous *slack* constraints were still applied to the *minor* molecule. Two series of refinements were carried out, both with weights derived from the counting statistics. In one, the atomic vibration parameters were restricted to those described by the 24 variables of the **T** and **L** rigid-body tensors for the translational and librational motions of the *major* and *minor* molecules. In the other series, the vibrations of the carbons were described by the usual anisotropic **U** tensor variables. The final residuals were wR = 0.0639 (R = 0.0478) for the **T**,**L** model and wR = 0.0525 (R = 0.0398) for the **U** model. The positional parameters for the *major* molecule in the two models differed by less than 0.01 Å. As described later, the **T** and **L** values for the *major* molecule derived from fitting the **U** model are close to those given directly by the **T**,**L** model. The Hamilton tests showed that the weighted residual for the **U** model is a significant improvement over that given by the **T**,**L** model. The pure **T**,**L** model can be rejected at a significance level well below 0.1%. We took the final parameters as those given by the **U** model with *slack* constraints applied only to the *minor* molecule.

The final positional parameters and the B_{eq} or B_{iso} values derived from the diffractometer data are listed in Table 3. The coordinate e.s.d.s for the C atoms of the *major* molecule are around 0.002 Å or less. The corresponding molecular geometry is depicted in Fig. 4.* A careful analysis of the data in Table 3 reveals that the disorder rotation is 28.9° for the *minor* molecule, which is close to the 30° assumed initially. The orientation is such as to make the *minor* atom C(1′) slightly closer to the *major* atom C(1) than to C(4). (A rotation of 1.1° at an outer radius of 3.78 Å corresponds to a tangential movement of 0.07 Å.) An *ORTEP* plot (a local double precision modification of Johnson, 1965) is shown in Fig. 5. The *major* molecule in Fig. 4 has approximate 6/*mmm* symmetry with almost equal C—C bonds and mean dimensions: inner bonds 1.385 (2) Å, outer bonds 1.405 (3) Å, C—C—C ring re-entrant angles δ = 127.9 (4)° and C—C—C ring internal angles γ = 124.0 (2)°. The occupancies are 0.863 and 0.137 for *major* and *minor* molecules. The values in parentheses are the e.s.d.s of the means as derived from the scatter of the individual values.

The corresponding mean dimensions for the *minor* molecule are 1.382 and 1.392 Å, and 128.9 and 124.3°. A formal error analysis of the constrained least-squares process has not been attempted; therefore, no e.s.d.s for individual entities of the *minor* molecule are given. The C—H distances were fixed at 1.0 Å.

In agreement with BHRS, [18]-annulene is not quite planar in the crystal, but displays (Table 4) carbon deviations from planarity of up to 0.08 and 0.14 Å in the *major* and *minor* molecules. These deviations and the disorder correlate with the packing of the molecules in the crystal, which will be discussed in the next three sections.

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* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving H atoms have been deposited with the IUCr (Reference: HA0138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The observed deviations from planarity by the carbons in the *major* molecule are very close to those found by BHRS; differences are less than 0.01 Å. This concurrence gives confidence that a discussion of the non-planarity is not invalidated by the constrained refinement. Distance constraints in a nearly planar molecule will have only a second-order effect on the out-of-plane coordinates.

Packing of *major* molecules

The disorder and packing of the molecules in the crystal structure of [18]-annulene, and the geometry of the inner hydrogens, are best understood if considered together with the crystal structures of coronene, $C_{24}H_{12}$ (Robertson & White, 1945; Fawcett & Trotter, 1965), and kekulene, $C_{48}H_{24}$ (Staab, Diederich, Krieger & Schweitzer, 1983).

In coronene, Fig. 1(*g*), the six inner hydrogens of [18]-annulene are replaced by six carbons, so that coronene has a central C_6 benzenoid hexagon surrounded by a $C_{18}H_{12}$ perimeter. In kekulene, Fig. 1(*f*), the 12 outer hydrogens of $C_{18}H_{18}$ are replaced by 12 carbons, which form part of a $C_{30}H_{18}$ perimeter. Kekulene is thus a dodecakisbenzene, in which the cyclic array of 12 annulated benzene rings encloses the same cavity as in [18]-annulene.

A helpful discussion of the crystal structures of polynuclear aromatic hydrocarbons has been given by Desiraju & Gavezzotti (1989). While C···C interactions are best optimized between parallel molecules stacked at van der Waals separation, C···H interactions are most effective between inclined molecules. Part of the molecular free surface can be considered as stack promoting and the rest as glide promoting.

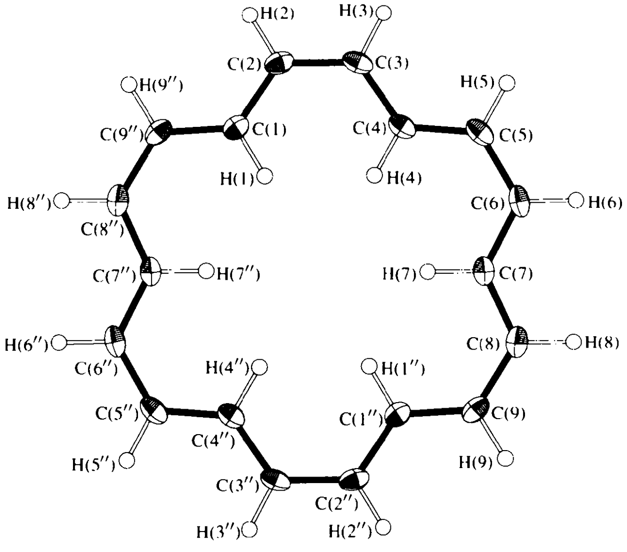

Fig. 5. *ORTEP* (Johnson, 1965) plot of the *major* molecule. Atoms marked with two quotes are generated through the centre of symmetry. The ellipsoids are at the 33% probability level.

Table 4. *Deviations* (Å) *from least-squares planes through* C *atoms of major and minor molecules*

The planes defined with reference to orthogonal axes a^*, b and c are, respectively: $0.7103X - 0.6632Y - 0.2360Z = 0$ and $0.7032X - 0.6640Y - 0.2543Z = 0$.

C(1)	0.055	C(1′)	0.03
C(2)	−0.012	C(2′)	−0.14
C(3)	−0.052	C(3′)	−0.06
C(4)	−0.050	C(4′)	0.04
C(5)	0.010	C(5′)	0.09
C(6)	0.034	C(6′)	0.07
C(7)	0.084	C(7′)	−0.04
C(8)	−0.014	C(8′)	−0.09
C(9)	−0.059	C(9′)	−0.06

As shown by BHRS, [18]-annulene and coronene have very similar crystal structures. The structures are approximately close-packed, for each molecule has 14 near neighbours. A reference molecule *A* at (0,0,0) is surrounded by six neighbours in the (001) plane, whose centres are at ±(0,1,0), $\pm(\frac{1}{2},\frac{1}{2},0)$ and $\pm(\frac{1}{2},-\frac{1}{2},0)$. The upper *z*-positive part of *A* is wedged between four molecules at (0,0,1), $(\frac{1}{2},\frac{1}{2},1)$, $(\frac{1}{2},-\frac{1}{2},1)$ and (0,−1,1), and the lower *z*-negative part is wedged between four corresponding molecules at the $z = -1$ level. It is only the parallel translated neighbours *B* at (0,1,0) and *B* at (0,−1,0) which have C···C interactions in staggered stacking. The other 12 neighbours involve C···H and H···H contacts, essentially as described for [18]-annulene by BHRS.

Since the BHRS geometry is close to that now found for the *major* molecule, the explanations given by them for a slight in-plane elongation of the molecule along one axis (*L*), and compression along another (*M*), and for some out-of-plane distortions due to glide contacts, remain valid. For the *major* molecule the inner diameters C(4)—C(4″) and C(7)—C(7″) are 5.956 and 5.937 Å, whereas C(1)—C(1″) is only 5.831 Å. [C(4″) is the atom generated from C(4) across the centre of symmetry, *etc.*]

However, we now extend the BHRS discussion concerning contacts between the parallel molecules *A* at (0,0,0) and *B* at (0,1,0). The [18]-annulene *b* axis is 4.802 Å in length, but because the *major* molecules are inclined at 48.5° to the *b* axis, the perpendicular distance between mean planes is 3.18 Å. At room temperature the separation between planes is 3.46 Å in coronene and 3.35 Å in both kekulene and graphite. Examination of the out-of-plane distortions in [18]-annulene reveals why the mean plane separation is less than in the other crystals.

Essentially the reason is that the thickness of an [18]-annulene molecule is much less in its central region, since the van der Waals radius of a H atom is 0.4 Å or so less than that of a C atom. When the *major* molecule *B* at (0,1,0) is projected onto the mean plane of the *major* molecule *A* at (0,0,0), the projected molecular centres are 3.59 Å apart (Fig. 6), so that the *major* molecule

A at the origin approximately half overlaps the *major* molecule *B*. More specifically, atoms C(6)–C(4″) of *A* lie above atoms C(6″)–C(4) of *B*. The ring crossover points occur where the bond C(6)—C(7) of *A* crosses over the bond C(3)—C(4) of *B*, and where C(3″)—C(4″) of *A* crosses C(6″)—C(7″) of *B*. At these crossover points the atoms deviate from the mean molecular planes to increase the C···C distances. C(6) and C(7) are 0.03 and 0.08 Å above the plane of *A*, while C(3) and C(4) are both 0.05 Å below the plane of *B*. The intermolecular C···C distances are: C(6)···C(3) 3.33, C(6)···C(4) 3.58, C(7)···C(3) 3.45 and C(7)···C(4) 3.43 Å. All these are approximately 0.1 Å greater than they would be if the atoms were exactly in the mean planes and thus are comparable with the distances in graphite and coronene [C(8)···C(4) 3.40 Å].

The portion of ring *A* at (0,0,0) between C(8) and C(2″) lies over the central cavity of molecule *B*, but is underneath atom H(9″) of the inclined molecule *E* at $(\frac{1}{2},-\frac{1}{2},0)$, which makes H···C contacts with ring *A* at (0,0,0). Because of the cavity in molecule *B*, it is not surprising that atoms C(9) and C(1″) of *A* are both 0.06 Å below the mean plane.

In the other half of the *major* molecule *A*, deviations with opposite signs occur from C···C contacts with the parallel molecule *B* at (0,−1,0) and H···C contacts with molecule *E* at $(-\frac{1}{2},\frac{1}{2},0)$.

Disorder and packing of *minor* molecules

As stated earlier (de Kok & Romers, 1980), the packing of alternative molecules in disordered structures (*a*) must obey the packing rules that exist in the original structure and (*b*) the alternative atomic positions in the disturbed part must not violate the packing rules in the undisturbed part of the structure. If these conditions are fully met one expects a 1:1 disorder. Since the final positions for the outer hydrogens are almost equal for the *major* and *minor* molecules, there are no large changes in the close H···H contacts. The shortest contacts between a molecule at the origin and the glide molecules at $(\frac{1}{2},\pm\frac{1}{2},1)$ are 2.58 Å between *major* molecules, 2.47 Å between a *major* and a *minor* molecule, and 2.37 Å between two *minor* molecules. Between a molecule at the origin and those at (0,−1,±1) the corresponding shortest H···H contacts are 2.33, 2.32 and 2.32 Å. The shortest C···H contacts between a molecule at (0,0,0) and the glide molecules at $\pm(\frac{1}{2},\frac{1}{2},0)$ decrease only slightly from 2.81 Å between *major* molecules to 2.72 Å between a *major* and a *minor* molecule (or 2.72 Å between two *minor* molecules).

The normals to the mean carbon planes of the *major* and *minor* molecules differ by only 1.1°. The r.m.s. deviations of the *major* and *minor* atoms from the *major* plane are 0.048 and 0.09 Å and of the *minor* atoms from the *minor* plane 0.08 Å. Examination of Fig. 7 shows that the contacts between stacked molecules at (0,0,0) and (0,1,0) are less efficient between *major* and *minor* molecules than between pairs of *major* molecules. Whereas the smallest C···C distance between *major* molecules is 3.33 Å, between *major* and *minor* molecules there are contacts of 3.34 for C(6)—C(2′) and 3.28 Å for C(7)—C(1′), and 3.43 Å for C(5′)—C(2′) between pairs of *minor* molecules.

Thus, the insertion of rotated *minor* molecules into the crystal structure of annulene does not cause any great anomalies, but it is not surprising that the observed disorder deviates considerably from a 1:1 distribution. The possibility of rotated *minor* molecules was suggested for coronene by Boyd, Fyfe & Wright (1974). However, Pawley & Rayment (1979), using the observed structure factors of Fawcett & Trotter (1965), showed that disorder in coronene is less than 2%, if any.

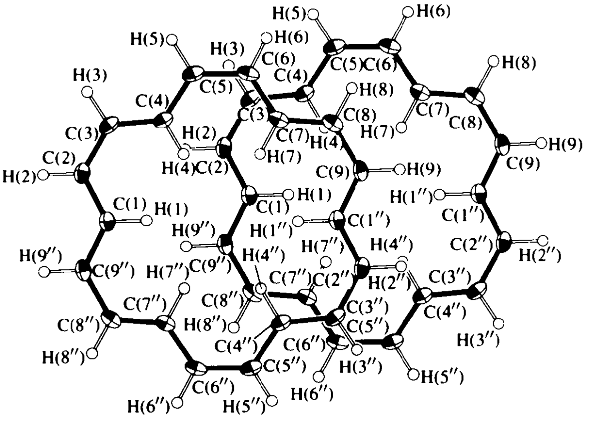

Fig. 6. Projected overlap of two adjacent parallel *major* molecules. Molecule *A* (0,0,0) is to the left and is depicted above molecule *B* (0,1,0) to the right.

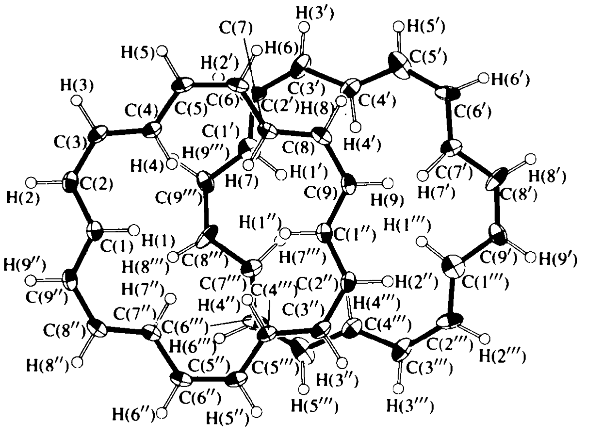

Fig. 7. Projected overlap of a *major* molecule and an adjacent *minor* molecule. *Minor* molecule atoms marked with triple quotes are generated through the centre of symmetry from those marked with a single quote.

Inner hydrogens

The six inner H atoms of a molecule (*major* or *minor*) make no close contacts with any other molecule (all distances are above 3.0 Å). The inner hydrogens of the *major* molecule deviate alternately up and down from the mean plane: +0.10, −0.11, +0.19, −0.10, +0.11, −0.19 Å. If the hydrogen positions are assumed to lie in the planes of their three adjacent carbons [*e.g.* H(4) in the plane of C(4), C(3) and C(5)], the predicted hydrogen deviations are +0.11, −0.09, +0.20, −0.11, +0.09 and −0.20 Å. Thus, evidently the senses and rough magnitudes of the hydrogen deviations found are real, and are related to the intermolecular forces, which slightly distort the C_{18} ring.

Within a molecule of [18]-annulene the average H···H distance between inner hydrogens is only 1.98 Å, which is much less than the supposed 'standard' van der Waals contact distance of 2.4 Å. This annulene distance is slightly larger than the 1.92 Å found for the six inner hydrogens of kekulene, $C_{48}H_{24}$, where the 12 fused rings hold the carbon framework rather rigid and the mean deviation from planarity of the C atoms is only 0.03 Å. The close approach to planarity in kekulene includes the six internal hydrogens, whose deviations are +0.04, −0.08, −0.10, −0.04, +0.08, +0.10 Å. Note that these deviations are not alternating. They also correlate with the deviations of each set of three adjacent C atoms.

The existence of very small H···H distances was also shown in the neutron diffraction study of triphenylene (Ferraris, Jones & Yerkess, 1973). Here in the three 'bays' distances of 1.93, 1.90 and 1.91 ±0.02 Å were found with proton deviations from planarity of: +0.04, −0.07; −0.04, +0.03; −0.04, +0.07 Å. (Because C—H distances determined by X-rays are shorter than those found by neutrons, the inter-proton distances in [18]-annulene are probably *ca* 1.90 Å.)

Thus, the standard intermolecular H···H van der Waals distance of 2.4 Å is evidently not an applicable limit in sideways intramolecular contacts, and Mislow's (1952) concern that the internal hydrogen interactions would prevent planarity is not realized.

Rigid-body vibration analyses

For a centrosymmetric molecule (Cruickshank, 1956*a*; Schomaker & Trueblood, 1968), one can test to see how well the individual atomic anisotropic displacement tensors **U** are fitted by molecular tensors **T** and **L**, representing the mean square translational and librational displacements. A good fit suggests rigidity of the molecule; a poor fit suggests non-rigidity or unallowed for disorder. For the *major* molecule, the atomic **U**s were transformed first to tensors **V**, defined with respect to orthogonal crystal axes, and then to tensors **W**, referred to orthogonal molecular axes. The molecular axes were taken as axis 3 perpendicular to the mean carbon plane, axis 2 through the projection of C(1) on the plane, and axis 1 mutually perpendicular. The calculations were carried out by the least-squares procedure described by Cruickshank (1956*a*).

Results, referred to the molecular axes, are shown in Table 5. Also shown are the **T**,**L** values from the **T**,**L** *model* refinement. The two sets of **T**,**L** values are in good agreement. The **T** tensors have reasonable values, as do the L_{33} elements of L, *viz.* 6.1 (3) and 5.8 (5) deg^2. However, L_{11} and L_{22}, the oscillations about axes in the molecular plane, are effectively zero. Dynamically this is unreasonable. The result shows that librations about the axes 1 and 2, which will cause the outer carbons to have a greater vibration perpendicular to the molecular plane than the inner carbons, must be counteracted either by an excess disorder of the inner carbons or by their greater intramolecular vibrations perpendicular to the plane. In view of the relative flexibility of a single-strand C_{18} ring and of the previous discussion on packing, and especially on the non-involvement of the inner hydrogens in any intermolecular contacts, it seems probable that the cause of the near-zero L_{11} and L_{22} is a greater internal vibration of the inner carbons. Examination of the individual W_{33}, the m.s. amplitudes perpendicular to the molecular plane, also shows an effect of packing. The larger W_{33}s, 0.0311 and 0.0287 Å^2, are for the cavity atoms C(9) and C(1), while the smallest W_{33}s, 0.0258–0.0273 Å^2, are for the ring crossover atoms C(3), C(4), C(6) and C(7).

Effectively zero L_{11} and L_{22} values were also reported for [18]-annulene by Hirshfeld & Rabinovich (1965). However, for isostructural coronene, where the 'thin' inner hydrogens are replaced by carbons, Fawcett & Trotter (1965) found appreciable L_{11} and L_{22}, *i.e.* greater than half L_{33}. A similar dynamically reasonable result for coronene was found by Filippini (1990) in a lattice-dynamical calculation.

For the *major* molecule of [18]-annulene the r.m.s. difference between the observed W_{ij} components of the **U** *model* and those calculated from the corresponding **T**,**L** analysis of the **U** *model* was 0.0016 Å^2. BHRS reported 0.0018 Å^2 in their study. The **T** and **L** of the **T**,**L** *model* refinement also provide a good fit to the observed W_{ij} of the **U** *model* refinement, with an r.m.s. difference of 0.0017 Å^2. (In Table 5 the e.s.d.s of T_{ij} and L_{ij} are derived in the **U** model from W_{ij}, whereas in the **T**,**L** model they are derived directly from ΔF_h and the least-squares refinement.)

For a perfectly rigid molecule, the components of **U** along the line joining any two atoms should be equal within experiment error (Rosenfield, Trueblood & Dunitz, 1978; Hirshfeld, 1976). This rigid-molecule test provides another possible way of detecting disorder or non-rigidity within the molecular plane. Between all pairs of C atoms in the major molecule, the r.m.s. difference is 0.0020 Å. This is only slightly larger than the r.m.s. difference for the W_{ij} components.

Some examination was made of U_{ij} of the 13.7% of *minor* molecules. The values were clearly of lower consistency than those for the major molecules and, although

Table 5. *Components of rigid-body molecular vibration tensors* **T** (Å^2) *and* **L** (deg^2) *for major molecule referred to orthogonal molecular axes.*

Axis 3 is perpendicular to the plane of the molecule. Axis 2 passes through the projection of C(1) on the plane, and axis 1 is mutually perpendicular. The upper set are those calculated from the atomic **U**. The lower set are those found directly in the **T**, **L** refinement of the structure factors.

From the **U** model refinement

$$\mathbf{T} = \begin{bmatrix} 0.0217\ (8) & -0.0002\ (6) & -0.0022\ (8) \\ - & 0.0268\ (8) & 0.0004\ (8) \\ - & - & 0.0268\ (29) \end{bmatrix} \qquad \mathbf{L} = \begin{bmatrix} 0.6\ (8) & 0.2\ (2) & -0.3\ (3) \\ - & -0.1\ (8) & -0.5\ (3) \\ - & - & 6.1\ (3) \end{bmatrix}$$

From the **T**, **L** model refinement

$$\mathbf{T} = \begin{bmatrix} 0.0217\ (3) & -0.0005\ (3) & -0.0020\ (3) \\ - & 0.0273\ (6) & 0.0008\ (6) \\ - & - & 0.0259\ (6) \end{bmatrix} \qquad \mathbf{L} = \begin{bmatrix} 0.6\ (4) & 0.2\ (2) & 0.0\ (2) \\ - & 0.4\ (4) & -0.4\ (3) \\ - & - & 5.8\ (5) \end{bmatrix}$$

of plausible magnitudes, are not worth discussing in detail. The in-plane components of **U**, but not the out-of-plane ones, were roughly 0.01–0.03 Å^2 larger than for the *major* molecule.

Comparison with molecular theory and benzene

Ab initio calculations for [18]-annulene have been made at the 6–31 G* level by Schulman & Disch (1991). Provided RMP2 electron correlation is included, but not otherwise, a planar D_{6h} structure with almost equal bonds is more stable than planar D_{3h} or non-planar D_3 structures with bond alternation (by 64 and 48 kJ mol^{-1}, respectively). The theoretical D_{6h} dimensions are: inner bonds 1.387 Å, outer bonds 1.402 Å, C—C—C ring re-entrant angles 128.6 Å. These are in excellent agreement with the new experimental dimensions: 1.385, 1.405 and 127.9 Å (*major* molecule).

Conceivably the crystallographic centre of symmetry could be satisfied by a 1:1 inversion disorder of D_{3h} molecules with alternating bond lengths. However, the theoretical D_{3h} C—C—C re-entrant angle is 132.2°, and the resultant C···C distances across the C_{18} ring are up to 0.20 Å too *large* compared with the experiment. The diameters between inner carbons are: experiment 5.91 (*major* average), D_{6h} 5.93, D_{3h} 6.11 Å; between outer carbons: experiment 7.54, D_{6h} 7.56, D_{3h} 7.68 Å. 1:1 disorder of the D_{3h} model would not reproduce the experimental electron-density peak positions.

Schulman & Disch (1991) calculate that the standard enthalpy of formation of D_{6h} $C_{18}H_{18}$ is 322 kJ mol^{-1} greater than the enthalpy of formation of three benzenes, so the resonance stabilization of three benzenes greatly exceeds that of [18]-annulene. Their results for all-*trans* acyclic polyenes, where a constant energy increment is found for each additional (—CH═CH—) group, enable them to estimate the energy of an imaginary unstrained all-*trans* $C_{18}H_{18}$ ring, with all hydrogens outside the ring and with alternating single and double bonds. The energy is 82 kJ mol^{-1} below that of D_{3h} [18]-annulene and is thus an estimate of the strain energy in D_{3h} annulene due to the *cisoid* arrangements of six of the 18 C—C bonds and to the repulsions between the six inner hydrogens.

The relatively modest size of this 82 kJ mol^{-1} provides a quantitative answer to Mislow's (1952) fears regarding inner H···H repulsions, making a planar structure for [18]-annulene impossible. The strain energy in D_{6h} annulene may be slightly larger because of the smaller diameters between inner carbons.

Schulman & Disch's (1991) D_3 structure (Fig. 1*c*), with inner carbons and hydrogens out-of-plane by ±0.1 and ±0.4 Å, is 16 kJ mol^{-1} below the D_{3h} form due to the reduction of the H···H repulsions.

The comparison of the enthalpies of [18]-annulene and benzene, the prototype aromatic molecule, suggest further comparisons between them. For annulene the 1965 problem regarding the apparent 0.037 Å difference in C—C bond lengths has been resolved by the present discovery that the apparently straightforward electron-density maps concealed a rotational disorder. The preliminary account by Cox & Smith (1954) of the X-ray analysis of benzene at 270 K showed a C—C length of 1.378 (6) Å, which was significantly different from the 1.397 (1) Å obtained by Stoicheff (1954) in a very precise study of the rotational Raman spectra of the vapour. This difference was quickly resolved by further analysis of the electron density, which showed anisotropic atomic vibrations and led to the discovery of librational corrections (Cox, Cruickshank & Smith, 1955, 1958; Cruickshank, 1956*b*). These increased the X-ray length to 1.392 (4) Å. In [18]-annulene, with L_{33} = 6.1 deg^2 (Table 5), the librational correction increases the C—C lengths by only 0.001 Å.

A very thorough neutron diffraction analysis of deuterated benzene at 15 and 123 K has been carried out by Jeffrey, Ruble, McMullan & Pople (1987). This yielded a mean C—C length of 1.398 (1) Å in close agreement with the results from gas electron diffraction and rotational spectra. In the same paper, geometry-optimized MP2/6–31 G* calculations gave a bond length of 1.395 Å in good agreement with the experiments, whereas without the MP2 electron-correlation treatment the length was 1.386 Å. The increase in length with MP2 is typical.

In Schulman & Disch's (1991) work on [18]-annulene, RMP2 geometries were not optimized but were taken from the best 6–31 G* geometries. Thus, the D_{6h} annulene theoretical bond lengths may need increasing by approximately 0.01 Å. For comparable 6–31 G* calculations, the mean C—C length in [18]-annulene is 1.392 Å compared with 1.386 Å in benzene, so theoretically the C—C bond length may be marginally longer in [18]-annulene. With the librational correction of 0.001 Å, the mean experimental length in [18]-annulene is 1.393 Å, marginally below 1.398 Å of benzene. The important point, however, is that theory and experiment both show that *the mean* C—C *length in* [18]-*annulene is close to that in benzene.*

In summary, the present work confirms the $4n + 2$ π-electron molecule [18]-annulene as having an essentially planar aromatic structure in the crystal.

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Structural Properties of Synthetic Ionophore GL_2E_4 Diastereomers, 18-Membered Cyclic Lactone Tetraepoxides, by X-ray Crystal Analyses: Possible Relation Between Crystal Structure and Ca^{2+}-Transportation Ability

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Abstract

GL_2E_4s, $C_{20}H_{28}O_8$, $M_r = 396.2$, synthetic cyclic lactone tetraepoxides, are classified into six diastereomers according to the relative configuration of four epoxy groups and exhibit the Ca^{2+} ion-transport activity in membranes with each different potential. Three crystal structures of these diastereomers have been analyzed by