

Crystal and Molecular Structure of 1,6:8,13-Propane-1,3-diyldiene[14]-annulene^{1a}

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Initial positional parameters for the crystal structure of 1,6:8,13-propane-1,3-diyldiene[14]annulene (orthorhombic, space group $Fdd2$, $a = 19.455$, $b = 36.358$, $c = 6.572$ Å, $Z = 16$) were obtained by two methods, and the structure refined by least-squares techniques to R 0.062 for 826 observed reflexions. The geometry is compared with that of the isolated molecule calculated by molecular mechanics, and that suggested from consideration of the u.v. spectrum. The molecular symmetry in the crystal is close to $mm2$ within experimental error. In spite of the distortion imposed by the propane bridge, the annulene ring maintains aromatic behaviour.

It has been pointed out² that it would be desirable to study the relationship between chemical and geometrical properties in a series of $[4n + 2]$ annulenes.

For the case $n = 3$ the following molecules have been recently synthesized: *syn*-1,6:8,13-diepoxy[14]annulene,³ *syn*-1,6-epoxy-8,13-methano[14]annulene,⁴ 1,6:8,13-propane-1,3-diyldiene[14]annulene,² 1,6:8,13-butane-1,4-diyldiene[14]annulene,⁵ and *anti*-1,6:8,13-dimethano[14]annulene.⁶ The chemical behaviour and spectral data suggest the presence of an aromatic structure in *syn*-compounds and of an olefinic structure in the *anti*-isomers. It has been inferred⁶ that an explanation for this is to be found in the different deviation from planarity of the annulene ring. We report here our results for 1,6:8,13-propane-1,3-diyldiene[14]annulene.^{1a} X-Ray structure analyses of methyl *anti*-1,6:8,13-dimethano[14]annulene-7-carboxylate and of 1,6:8,13-butane-1,4-diyldiene[14]annulene are in progress.^{1b,c}

EXPERIMENTAL

1,6:8,13-Propane-1,3-diyldiene[14]annulene, m.p. 180–181°, crystallizes from boiling ethanol as yellow-orange piezoelectric crystals elongated along the c axis. Weissenberg and precession photographs taken with $\text{Cu-K}\alpha$ radiation established the space group as $Fdd2$ (C_{2v}^{19}). Cell constants were determined by least-squares treatment of 81 measurements on zero-level Weissenberg photographs taken at 21° about the crystallographic axes a and c ($\text{Cu-K}\alpha$ radiation) with a double-radius camera with the film held in the asymmetric (Straumanis) position. The cell parameters reported in the preliminary communication^{1a} were less accurate.

Crystal Data.— $\text{C}_{17}\text{H}_{14}$, $M = 218.3$, Orthorhombic, $a = 19.4549(4)$, $b = 36.358(2)$, $c = 6.5716(2)$ Å, $U = 4648.4(3)$ Å³, $D_m = 1.248$ (by flotation), $Z = 16$, $D_c = 1.248$, $F(000) = 1856$. $\text{Cu-K}\alpha_1$ radiation, $\lambda = 1.54051$, $\text{Cu-K}\alpha_2$, $\lambda = 1.54433$, $\text{Mo-K}\alpha$, $\lambda = 0.71069$ Å; $\mu(\text{Cu-K}\alpha) = 5.4$ cm⁻¹, $\mu(\text{Mo-K}\alpha) = 0.8$ cm⁻¹. Space group $Fdd2$ (C_{2v}^{19}) from systematic absences.

Diffraction intensities were measured with a linear auto-

¹ (a) Preliminary communication, G. Casalone, A. Gavezzotti, A. Mugnoli, and M. Simonetta, *Angew. Chem. Internat. Edn.*, 1970, **9**, 519; (b) C. M. Gramaccioli, A. Mimun, A. Mugnoli, and M. Simonetta, *Chem. Comm.*, 1971, 796; (c) C. M. Gramaccioli, A. Mugnoli, T. Pilati, M. Raimondi, and M. Simonetta, *Chem. Comm.*, 1971, 973.

² E. Vogel, A. Vogel, H. K. Kübbeler, and W. Sturm, *Angew. Chem. Internat. Edn.*, 1970, **9**, 514.

³ E. Vogel, M. Biskup, A. Vogel, and H. Günther, *Angew. Chem. Internat. Edn.*, 1966, **5**, 734; E. Vogel and H. Günther, *ibid.*, 1967, **6**, 385.

matic diffractometer using $\text{Mo-K}\alpha$ radiation and silicon monochromator in the incident beam. The crystal used was a parallelepiped $0.19 \times 0.26 \times 0.47$ mm. All the 1446 independent reflexions within the copper sphere were measured, of which the 826 reflexions having $I \geq 2\sigma(I)$ were considered 'observed' and used in the subsequent solution and refinement. The data were corrected for Lorentz and polarization factors. No absorption or extinction corrections were applied. Wilson statistics gave an overall isotropic thermal factor $B = 3.6$ Å².

Solution of the Structure.—The structure was solved by determining in subsequent steps the orientation and the position of a molecular model in the unit cell. This result was achieved following two parallel routes, (A) and (B).

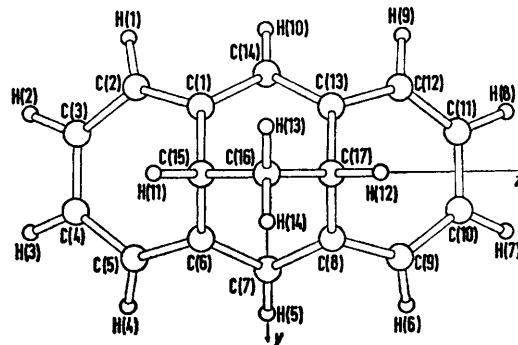


FIGURE 1 Numbering of atoms and molecular axes. The z axis points upwards

Route (A). We constructed the model by referring to a similar compound of known structure, *syn*-1,6:8,13-diepoxy[14]annulene.⁷ The atomic co-ordinates for the carbon atoms in the annulene ring were determined starting from the co-ordinates in the diepoxy-compound, averaged by assuming molecular symmetry $mm2$. Figure 1 shows the orientation of the chosen molecular axes in a Cartesian system and the numbering of the atoms. The co-ordinates for the carbon atoms of the propane bridge were calculated by assuming the bond length C(1)–C(15) and the C(1)–C(15)–C(6) angle to be equal to 1.47 Å and 100° respectively, to be consistent with the corresponding values in 1,6-methano[10]annulene-2-carboxylic acid,⁸ and with the assumed

⁴ E. Vogel, U. Haberland, and J. Ick, *Angew. Chem. Internat. Edn.*, 1970, **9**, 517.

⁵ E. Vogel, W. Sturm, and H. D. Cremer, *Angew. Chem. Internat. Edn.*, 1970, **9**, 516.

⁶ E. Vogel, U. Haberland, and H. Günther, *Angew. Chem. Internat. Edn.*, 1970, **9**, 513.

⁷ P. Ganis and J. D. Dunitz, *Helv. Chim. Acta*, 1967, **50**, 2369.

⁸ M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1965, **48**, 1429.

C(1)···C(6) distance. The distance C(15)···C(17) and the C(15)–C(16)–C(17) angle were assumed to be 2.55 Å and 112° respectively, rounding off the corresponding values for *n*-butane.⁹ The orientation of the molecular model in the unit cell was determined by plotting Buerger's sum function¹⁰ for the model vector-set as a function of rotation about the axes *x*, *y*, *z*.¹¹ Only the region of the Patterson synthesis within 3.2 Å from the origin was explored for this purpose. The rotation range was 0–180° for θ_1 (about *x*), and 0–90° for θ_2 (about *y*) and for θ_3 (about *z* axis), at intervals of 7.5°. The zone of the most prominent maximum was then refined by scanning at intervals of 2°. The maximum in the sum function occurs at $\theta_1 = 83^\circ$, $\theta_2 = 25^\circ$, and $\theta_3 = 82^\circ$.

The positioning of the reference molecule in the unit cell was achieved by shifting the oriented model along *x* and *y* (*z* being a polar axis) and comparing observed and calculated structure factors for a sample of low-order reflexions ($\sin^2 \theta/\lambda^2 \leq 0.08$). The explored region was 0– $\frac{1}{2}a$ along *x* and 0– $\frac{1}{2}b$ along *y*, at intervals of 0.010 and of 0.005 respectively.¹² In the zone of the minimum of discrepancy index the intervals were lowered to 0.004 and 0.002 respectively. From the position of the minimum the shifts $\Delta x = 0.477$ and $\Delta y = 0.316$ were deduced. At this point a structure-factor calculation performed with an isotropic thermal factor $B = 3.6 \text{ \AA}^2$ for all carbon atoms gave $R = 0.282$.

Route (B). The molecular model was obtained by minimizing the sum of bending, stretching, torsional, π -electron, and non-bonding energies. The different energy terms in this sum were calculated (see later).

The orientation of the model in the crystal cell was accomplished through the same method as in route (A). The rotation angles were $\theta_1 = 85^\circ$, $\theta_2 = 23^\circ$, and $\theta_3 = 85^\circ$. The position of the reference molecule in the unit cell was determined in route (B) by shifting the oriented model along *x* and *y* and calculating at each point the sum of the energies of non-bonded interactions between each atom of the model and each atom of the molecules generated by symmetry around the reference one. Intermolecular non-bonded interactions were calculated between atom pairs separated by a distance ≤ 1.54 times the sum of the van der Waals radii, using the same formulae as for the intramolecular contacts. Owing to the rigidity of this molecule, no allowance of change of geometry due to packing effects was thought to be necessary. The unit cell was scanned in the range $\frac{1}{4}$ – $\frac{3}{4}$ along *x* and *y*, at intervals of 0.0250 and 0.0125 respectively.¹³ The position of the oriented model corresponds to translations $\Delta x = 0.470$, $\Delta y = 0.315$, which are in good agreement with those found by route (A).

Refinement.—The structure was refined by least-squares technique,¹⁴ holding constant the *z* co-ordinate of atom C(1), because of the polarity of *z* axis, and using weights $1/\sigma^2(F_o)$. Atomic scattering factors for carbon and hydrogen atoms were taken from refs. 15 and 16 respectively. For model (B), nine cycles of isotropic full-matrix refinement were per-

formed on carbon atom parameters, starting from the previously calculated co-ordinates with an overall thermal factor $B = 3.5 \text{ \AA}^2$ and without any external intervention between the subsequent cycles; R fell from the initial value of 0.409 to a final value 0.138. The complete refinement was carried out on the model (A), starting from co-ordinates corresponding to $R = 0.282$. After five cycles of isotropic refinement on carbon atoms, hydrogen positions were calculated assuming C–H 1.0 Å. The full-matrix refinement was continued, allowing for anisotropy of carbon atoms and including the hydrogen atoms only in the structure-factor calculations. Some strong low-order reflexions, suspected to be affected by extinction, were given zero weight in the least-squares refinement. After two cycles, a difference Fourier synthesis was computed, using as coefficients $F_o - F_c(\text{carbon})$; the resulting map showed little displacements for the hydrogen atom positions, without significant features otherwise. In the following and last three cycles also the hydrogen atom co-ordinates were allowed to vary. The refinement was then considered complete, the shifts of all parameters being $< 0.16\sigma$. The final value of R was 0.062, with a goodness of fit $\{\sum[w(|F_o| - |F_c|)^2]/(m - n)\}^{1/2} = 1.6$ where m is the number of observations, and n the number of parameters, which indicates that the weights are appropriate and that the experimental data are relatively free from systematic errors. Reasonable values were obtained for the calculated structure-factors of the 152 unobserved reflexions. Carbon atom parameters with standard deviations are collected in Table 1, and hydrogen atom co-ordinates in Table 2. The estimated standard deviations, calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to positional uncertainties of 0.005–0.009 Å for carbon atoms and of 0.03–0.04 Å for hydrogen atoms.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20261 (2 pp., 1 microfiche).*

Minimum-energy Geometry of the Isolated Molecule.—To find the best geometry for the molecule to be used in route (B) we carried out an energy minimization calculation based on the empirical Westheimer method.¹⁷ According to this method the energy of the molecule has been calculated as the difference in energy between the molecule in a given conformation and a hypothetical one with no bond-angle, bending, or bond-stretching strains, no torsional strains, and no steric repulsion, and without loss of π electron energy caused by distortion of the annulene ring.

The total energy difference is given by equation (1) where

$$\Delta E = \Delta E_\pi + E_c + E_a + E_t + E_{nb} \quad (1)$$

ΔE_π represents the variation in π electron energy in the ring, and E_c , E_a , E_t , and E_{nb} represent bond length, bond-angle, torsional, and non-bonded interaction strains. Assuming *mm2* symmetry for the molecule and one value (1.397 Å) for all the C–C bond lengths of the annulene ring, the carbon-atom skeleton has nine degrees of freedom.

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

⁹ R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.*, 1959, **81**, 3491.

¹⁰ M. J. Buerger, 'Vector Space,' Wiley, New York, 1959.

¹¹ G. Filippini and C. M. Gramaccioli, *Ricerca Sci.*, 1969, **39**, 589.

¹² Program written for the IBM 1620 by V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *Ricerca Sci.*, 1963, **33** (II-A), 291.

¹³ Program written for the IBM 7040 by C. Rovere, G. Filippini, and C. M. Gramaccioli, to be published.

¹⁴ We used a modified version of the program ORFLS, by W. R. Busing, K. O. Martin, and H. A. Levy, U.S. Atomic Energy Commission Publication ORNL TM 305, 1962.

¹⁵ D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

¹⁶ J. B. Forsyth and M. Wells, *Acta Cryst.*, 1959, **12**, 412.

¹⁷ F. H. Westheimer in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 12.

All C-H bond lengths were assumed equal to 1.0 Å; however the geometry of minimum energy was found to be almost independent of the value of the C-H bond length if varied in a reasonable range.

Hydrogen atoms bonded to sp^2 carbon atoms were placed on the bisectrix of the pertinent C-C-C angle. Hydrogen atoms H(11) and H(13) (and their equivalent ones), were placed along the direction of maximum strength of hybrid orbitals orthogonal to the hybrids pointing in the direction of the C-C bonds, starting from C(15) and C(16) respectively.

annulene ring were assumed to be orthogonal to the plane formed by $C_{i-1}-C_i-C_{i+1}$, the atoms directly bonded to C_i carbon atom of the ring. The π electron energy was evaluated as the HMO delocalization energy. For the resonance integral β_{i-j} between two bonded atoms i and j in the ring the relation $\beta_{ij} = \beta^\circ \cos \omega$ was used, where ω is the torsional angle around the C_i-C_j bond. The value of β° , the resonance integral between two parallel C_{2p_z} orbitals centered at distance R 1.397 Å, was assumed equal to -20 kcal mol $^{-1}$.

Compression energy. This term was calculated for

TABLE 1
Carbon atom parameters ($\times 10^4$) * and their standard deviations

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	4337(3)	3367(1)	-1750(0)	38(2)	6(0)	153(13)	0(1)	-13(4)	7(2)
C(2)	3725(3)	3333(1)	-2885(10)	48(2)	9(0)	225(15)	2(1)	-30(6)	9(2)
C(3)	3086(3)	3248(1)	-2091(12)	32(2)	10(1)	370(23)	1(1)	-36(5)	0(3)
C(4)	2951(2)	3071(1)	-229(13)	28(2)	10(1)	388(21)	1(1)	7(6)	1(3)
C(5)	3408(2)	2952(1)	1230(12)	29(2)	10(0)	297(17)	3(1)	24(5)	7(3)
C(6)	4093(2)	3075(1)	1418(10)	30(1)	7(0)	144(12)	1(1)	14(4)	-2(2)
C(7)	4617(2)	2861(1)	2193(9)	33(2)	7(0)	129(11)	0(1)	11(4)	7(2)
C(8)	5302(2)	2956(1)	1927(9)	33(2)	6(0)	164(13)	0(1)	-12(4)	2(2)
C(9)	5855(2)	2713(1)	2240(11)	34(2)	8(0)	257(16)	-1(1)	-19(5)	7(2)
C(10)	6483(2)	2735(1)	1241(12)	32(2)	8(0)	404(21)	0(1)	-31(5)	-5(3)
C(11)	6632(2)	2916(1)	-593(13)	27(2)	8(0)	444(23)	-1(1)	10(6)	-10(3)
C(12)	6186(2)	3100(1)	-1857(10)	29(2)	10(0)	317(18)	-4(1)	17(5)	-2(3)
C(13)	5555(2)	3247(1)	-1227(10)	30(2)	5(0)	225(15)	-2(1)	12(4)	1(2)
C(14)	4991(3)	3299(1)	-2516(10)	39(2)	8(0)	191(14)	-2(1)	22(5)	4(2)
C(15)	4255(2)	3443(1)	480(9)	34(2)	5(0)	240(16)	3(1)	-2(4)	-3(2)
C(16)	4906(2)	3603(1)	1379(10)	41(2)	5(0)	225(14)	1(1)	-9(5)	-4(2)
C(17)	5475(2)	3329(1)	1009(9)	32(2)	6(0)	190(14)	-1(1)	-9(4)	-9(2)

* The temperature factor is in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

We carried out our calculations by a computer program according to the steepest descent method. The calculation was stopped when the geometry was unchanged within 0.001 Å and 0.01°; at this stage the energy was constant within 0.001 kcal. mol $^{-1}$. Starting from a planar annulene

C(1)-C(15), C(15)-C(16), and equivalent bonds, according to the expression $E = \frac{1}{2}K(R - R_E)^2$ with R_E 1.533 Å and K 6.48 $\times 10^2$ kcal mol $^{-1}$ Å $^{-2}$ for an sp^2 - sp^3 C-C bond,¹⁸ and R_E 1.505 Å and K 6.91 $\times 10^2$ kcal mol $^{-1}$ Å $^{-2}$ for an sp^2 - sp^3 C-C bond.

Bending energy. This term was evaluated for all the atoms of the ring and of the propane bridge. For the sp^3 type carbons we followed expression¹⁹ (2), the angles being

$$\Delta E = K_{\text{COO}}(\alpha - \tau)^2 + 2K_{\text{HCO}}(\beta - \tau)^2 + 2K_{\text{XCO}}(\delta - \tau)^2 + K_{\text{HOX}}(\gamma - \tau)^2 \quad (2)$$

labelled as shown in Figure 2, where X is a carbon or a hydrogen atom. The values of the parameters are:

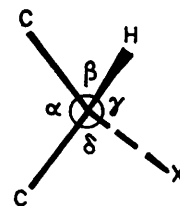


FIGURE 2 Labelling of angles at a carbon atom

τ 109.5°, K_{COO} 0.0175, K_{HCO} 0.0121, and K_{HOX} 0.007 kcal mol $^{-1}$ deg $^{-2}$.

For the atoms in the ring except C(1) and its equivalents, the bending energies were evaluated according to the formula $\Delta E = K_{\text{tot}}(\epsilon - \tau)^2$, with $K_{\text{tot}} = (K_{\text{COO}}^I + \frac{1}{2}K_{\text{HCO}}^I) = 0.034$ kcal mol $^{-1}$ deg $^{-2}$;¹⁷ $K_{\text{COO}}^I = 0.0246$, $K_{\text{HCO}}^I = 0.0188$ kcal. mol $^{-1}$ deg $^{-2}$ where ϵ is the C-C-C angle and τ^I is 120°.

¹⁸ G. Herzberg, 'Molecular Spectra and Molecular Structure', vol. II, p. 193, Van Nostrand, Princeton, New Jersey, 1945.

¹⁹ J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537.

TABLE 2
Parameters for the hydrogen atoms ($\times 10^3$)

	x	y	z
H(1)	375(1)	338(1)	-428(6)
H(2)	267(1)	325(1)	-303(7)
H(3)	243(1)	299(1)	-015(7)
H(4)	326(2)	276(1)	219(6)
H(5)	451(1)	262(1)	281(6)
H(6)	576(1)	250(1)	314(6)
H(7)	685(2)	257(1)	179(7)
H(8)	710(1)	284(1)	-121(6)
H(9)	634(1)	313(1)	-325(7)
H(10)	509(1)	326(1)	-390(6)
H(11)	385(1)	361(1)	079(6)
H(12)	594(1)	341(1)	159(7)
H(13)	503(2)	385(1)	061(6)
H(14)	484(1)	366(1)	291(6)

ring the following parameters were varied: the angle between the C(2)-C(3) bond and the axis through C(3) parallel to axis z , the angle between the C(1)-C(2) bond and the axis through C(2) parallel to the axis z , the angle between the C(1)-C(14) bond and the axis through C(1) parallel to the axis z , the angle of rotation around the C(1)-C(6) axis of the plane C(2)-C(3)-C(4)-C(5), the angle of rotation around the C(1)-C(13) axis of the plane C(1)-C(13)-C(14), the angle of rotation around the C(1)-C(3) axis of the plane C(1)-C(2)-C(3), the angle C(15)-C(16)-C(17), the bond length C(1)-C(15), and the bond length C(15)-C(16). The various energy terms were evaluated as follows.

π *Electron energy.* The $2p_z$ carbon atom orbitals of the

For carbon atom C(1) and its equivalents, both in- and out-of-plane bending energies were evaluated, according to expression (3) where K^{II} is the out-of-plane bending force

$$\Delta E = K^{\text{I}} \cos[(\eta - \tau^{\text{I}})^2 + (\zeta - \tau^{\text{I}})^2 + (\theta - \tau^{\text{I}})^2] + \frac{1}{2} K^{\text{II}} \psi^2 \quad (3)$$

constant (K^{II} 0.0254 kcal deg⁻² mol⁻¹),²⁰ ψ is the angle between the bond C(1)–C(15) and its projection on the plane C(2)–C(1)–C(14), η and ζ are the angles between this projection and the bonds C(1)–C(2) and C(1)–C(14) respectively, and θ is the C(2)–C(1)–C(14) angle.

Torsional energy. This was calculated for the C(15)–C(16) and C(16)–C(17) bonds by means of equation (4)²¹ where ω_{ij} are the torsional angles between each pair of orbitals

$$\Delta E = \frac{K^{\text{III}}}{18 \sin^6 109.5} \sum_{i=1}^3 \sum_{j=1}^3 \sin^3 \theta_i \sin^3 \theta_j (1 + \cos 3\omega_{ij}) \quad (4)$$

starting from the C_i and C_j carbon atoms and θ_i , θ_j are the angles between the same orbitals and the C_i – C_j bond. K^{III} was assumed to be 2.8 kcal mol⁻¹, the torsional barrier of ethane.

Non-bonded interactions. This term was evaluated by means of Bartell's formulae²² (5) (E in kcal mol⁻¹) where R is the interatomic distance. All C–C, C–H, and H–H non-bonded interactions have been taken into account except 1,3-interactions.

$$E_{\text{C-C}} = 2.993 \times 10^5 R^{-12} - 325.2 R^{-6}$$

$$E_{\text{C-H}} = 4.471 \times 10^4 \exp(-2.04R) R^{-6} - 124.9 R^{-6} \quad (5)$$

$$E_{\text{H-H}} = 6591 \exp(-4.08R) - 49.2 R^{-6}$$

Molecular Orbital Calculations.— π Electron energy calculations have been performed for the fourteen-electron system with the experimental annulene ring geometry and with an assumed planar geometry with all C–C–C angles 120° and all C–C bond lengths 1.397 Å.

The standard Hückel technique has been used with the resonance integral $\beta^{\circ} = -20$ kcal mol⁻¹. For both geometries a calculation of the electronic spectrum was also carried out. The standard Pariser–Parr–Pople (PPP)²³ technique was used for the planar geometry. For the case of the distorted ring this technique was modified assuming different β values for different bonds, *i.e.* β was assumed proportional to the overlap according to $\beta = \beta^{\circ} \frac{S}{S^{\circ}}$, while electronic repulsion integrals were evaluated according to the prescriptions given by Hoffmann *et al.*²⁴ S° is the overlap integral for two parallel $2p$ carbon Slater orbitals, at a distance of 1.397 Å.

RESULTS AND DISCUSSION

The geometry of the molecule of 1,6:8,13-propane-1,3-diylidene[14]annulene is described in Tables 3–6. The estimated standard deviations for C–C bond distances and C–C–C bond angles range from 0.006–0.011 Å and from 0.4–0.6° respectively.

Signs for the torsion angles are given following the

²⁰ J. R. Scherer, *Spectrochim. Acta*, 1967, **23B**, 1489.

²¹ R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, 1966, **44**, 3054.

²² E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, 1967, **47**, 3736.

TABLE 3
Bond lengths (Å)

	Found	Corr. ^a	Mean ^b	Calc.
C(1)–C(2)	1.410	1.416	1.413	1.397
C(5)–C(6)	1.411	1.417		
C(12)–C(13)	1.402	1.407		
C(8)–C(9)	1.407	1.413		
C(2)–C(3)	1.383	1.389	1.387	1.397
C(4)–C(5)	1.377	1.383		
C(9)–C(10)	1.389	1.396		
C(11)–C(12)	1.375	1.381		
C(3)–C(4)	1.407	1.416	1.414	1.397
C(10)–C(11)	1.404	1.412		
C(6)–C(7)	1.380	1.385	1.395	1.397
C(7)–C(8)	1.388	1.394		
C(13)–C(14)	1.399	1.405		
C(14)–C(1)	1.391	1.396		
C(1)–C(15)	1.500	1.508	1.517	1.487
C(15)–C(6)	1.507	1.514		
C(13)–C(17)	1.507	1.516		
C(17)–C(8)	1.522	1.529		
C(15)–C(16)	1.514	1.520	1.518	1.533
C(16)–C(17)	1.509	1.515		

^a After rigid-body correction. ^b Mean of *mm2* related bonds.

TABLE 4
Bond angles (deg)

	Found	Mean ^a	Calc.
C(1)–C(2)–C(3)	125.4	124.7	123.6
C(4)–C(5)–C(6)	124.8		
C(8)–C(9)–C(10)	124.6		
C(11)–C(12)–C(13)	124.1		
C(2)–C(3)–C(4)	126.7	127.9	127.5
C(3)–C(4)–C(5)	128.9		
C(9)–C(10)–C(11)	127.9		
C(10)–C(11)–C(12)	128.1		
C(5)–C(6)–C(7)	123.5	124.0	124.1
C(7)–C(8)–C(9)	124.0		
C(12)–C(13)–C(14)	124.0		
C(14)–C(1)–C(2)	124.4		
C(6)–C(7)–C(8)	121.5	121.5	118.6
C(13)–C(14)–C(1)	121.5		
C(2)–C(1)–C(15)	116.3	116.6	116.2
C(5)–C(6)–C(15)	116.3		
C(12)–C(13)–C(17)	117.0		
C(9)–C(8)–C(17)	116.6		
C(14)–C(1)–C(15)	118.9	119.2	119.7
C(7)–C(6)–C(15)	119.8		
C(14)–C(13)–C(17)	118.9		
C(17)–C(8)–C(7)	119.0		
C(1)–C(15)–C(16)	111.3	111.2	110.6
C(6)–C(15)–C(16)	110.9		
C(8)–C(17)–C(16)	111.2		
C(13)–C(17)–C(16)	111.3		
C(1)–C(15)–C(6)	105.0	104.3	105.8
C(13)–C(17)–C(8)	103.5		
C(15)–C(16)–C(17)	107.3		105.9

^a Mean of *mm2* related angles.

convention of Klyne and Prelog.²⁵ The standard deviations of the torsion angles along the annulene ring were calculated according to Huber.²⁶ Their values range between 0.7 and 1.5°. The six four-atom mean

²³ R. G. Parr, 'The Quantum Theory of Molecular Electronic Structure,' Benjamin, New York, 1963.

²⁴ R. Hoffmann, A. Imamura, and G. A. Zeiss, *J. Amer. Chem. Soc.*, 1967, **89**, 5215.

²⁵ W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

²⁶ P. J. Huber, *Helv. Chim. Acta*, 1961, **44**, 2032.

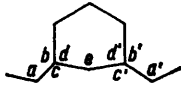
planes in the annulene ring were calculated according to ref. 27. Distances of the relevant atoms from the respective mean plane never exceed the positional standard deviation. In Table 6 dihedral angles between adjacent planes are given. Torsion angles along the annulene ring measure the amount of the distortion of p_z orbitals from parallelism. The maximum misalignment occurs for

TABLE 5
Torsion angles (deg)

	Found	Mean ^a	Calc.
C(14)-C(1)-C(2)-C(3)	151.7	151.8	162.7
C(4)-C(5)-C(6)-C(7)	-150.5		
C(7)-C(8)-C(9)-C(10)	151.7		
C(11)-C(12)-C(13)-C(14)	-153.3		
C(1)-C(2)-C(3)-C(4)	-21.5	20.9	25.5
C(3)-C(4)-C(5)-C(6)	19.0		
C(8)-C(9)-C(10)-C(11)	-20.0		
C(10)-C(11)-C(12)-C(13)	22.9		
C(2)-C(3)-C(4)-C(5)	1.8	2.3	0.0
C(9)-C(10)-C(11)-C(12)	-2.8		
C(5)-C(6)-C(7)-C(8)	164.9	164.6	158.1
C(6)-C(7)-C(8)-C(9)	-164.3		
C(12)-C(13)-C(14)-C(1)	165.4		
C(13)-C(14)-C(1)-C(2)	-163.7		

Mean of absolute values of $mm2$ related angles.

TABLE 6
Dihedral angles (deg)



	Found	Mean ^a	Calc.
a	163.0	162.4	158.2
a'	161.8		
b	114.3	114.4	113.8
b'	114.5		
c	139.4	139.6	144.3
c'	139.8		
d	106.3	106.0	101.9
d'	105.7		
e	148.6		158.9

^a Mean of symmetry-related values.

C(1), C(2), C(3), and symmetry-related p_z orbitals, the mean deviation angles being quite similar, ϕ_{12} 28 and ϕ_{23} 21°. This behaviour is analogous to that found in *syn*-1,6:8,13-diepoxy[14]annulene ⁷ (ϕ_{12} 26°, ϕ_{23} 18°). As pointed out by Ganis and Dunitz,⁷ this corresponds to a trend of the molecule to subdivide the distortion, as imposed by the presence of bridges, on the annulene perimeter. In spite of this distortion, all the carbon atoms in the annulene ring lie at a distance of <0.6 Å from the least-squares plane through atoms C(2), C(5), C(9), and C(12).

The rigidity of the molecule suggests the interpretation of thermal parameters in terms of rigid-body motion.²⁸ Experimental and calculated²⁹ thermal parameters are in good agreement for all the 17 carbon atoms, the

²⁷ V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

²⁸ V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B24**, 63.

²⁹ Program written for the IBM 7040 by G. Filippini and C. M. Gramaccioli.

differences being of the order of the standard deviations. The mean-square rotational displacements of the molecule amount to 22, 17, and 7 (deg)² about the principal axes of the libration tensor. The transformation matrix relating principal libration axes x_L to the molecular inertial axes x_I shown in Figure 1 is:

$$x_L = \begin{pmatrix} -0.0521 & 0.0542 & 0.9972 \\ 0.9568 & -0.2834 & 0.0654 \\ 0.2861 & 0.9575 & -0.0371 \end{pmatrix} x_I$$

The bond distances corrected by rigid-body motion are collected in Table 3; they are longer by 0.006–0.009 Å than the uncorrected values. The effect of the correction on bond and torsion angles is negligible ($\leq 0.1^\circ$). A thermal ellipsoid plot³⁰ of the molecule at the end of the least-squares refinement is shown in Figure 3.

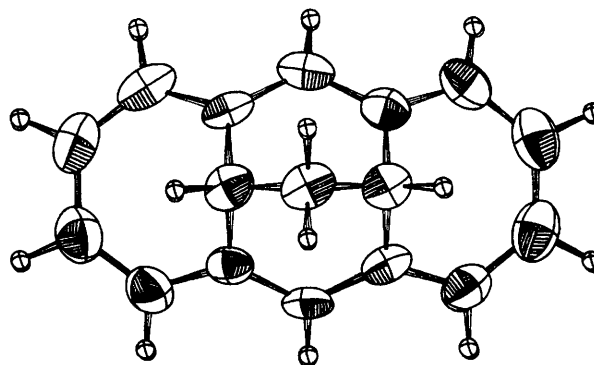


FIGURE 3 Thermal ellipsoids plot at a probability 0.50. Hydrogen atoms, treated as isotropic, are on an arbitrary scale

The C-C bond distances along the annulene perimeter are in the range 1.381–1.417 Å (values corrected for libration; mean 1.401 Å). This is an even narrower range than that found for anthracene (1.366–1.433 Å).³¹ A significant variation of carbon-carbon bond lengths in $[4n + 2]$ annulene derivatives was found in 1,6-methano[10]annulene-2-carboxylic acid,⁸ and in 11,11-difluoro-1,6-methano[10]annulene,³² whereas in *syn*-1,6:8,13-diepoxy[14]annulene⁷ all the bonds along the perimeter are equal within the experimental errors. In 1,6:8,13-propane-1,3-diylidene[14]annulene the presence of 'longer' and 'shorter' bond distances is observable along the ring. In fact, the χ^2 test³³ showed, assuming for the considered bond distances σ 0.008 Å, that the 14 bonds are not equal at a significance level $\alpha < 0.005$. On the other hand, considering the perimeter bond lengths as grouped according to $mm2$ molecular symmetry, the bond distances within each group are found to be all equal at a significance level $\alpha \geq 0.25$. Considering the $mm2$ groups of observed bond and torsion angles

³⁰ Program ORTEP, by C. K. Johnson, U.S. Atomic Energy Commission Publication, ORNL 3794, 1965.

³¹ D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 915.

³² C. M. Gramaccioli and M. Simonetta, *Tetrahedron Letters*, 1971, 173; *Acta Cryst.*, 1971, **B27**, 2231.

³³ W. C. Hamilton, 'Statistics in Physical Science,' Ronald Press, New York, 1964.

the differences within each group are in some cases more remarkable, but they become possibly significant ($0.025 > \alpha > 0.010$) only in one case: for the group of C(2)-C(3)-C(4) bond angles ($\bar{\sigma} 0.5^\circ$). It may therefore be concluded that the observed molecular geometry fits as a whole the $mm2$ symmetry within experimental errors,

the compression by the two bridges on the C(15)-C(16) and C(17)-C(16) bond distances. The C(15)-C(16)-C(17) bond angle is reduced to 107.3° .

Carbon-hydrogen bond distances are in the range $0.93-1.07 \text{ \AA}$ ($\sigma \approx 0.04 \text{ \AA}$), the longer distances being for the hydrogen atoms in the propane bridge. The

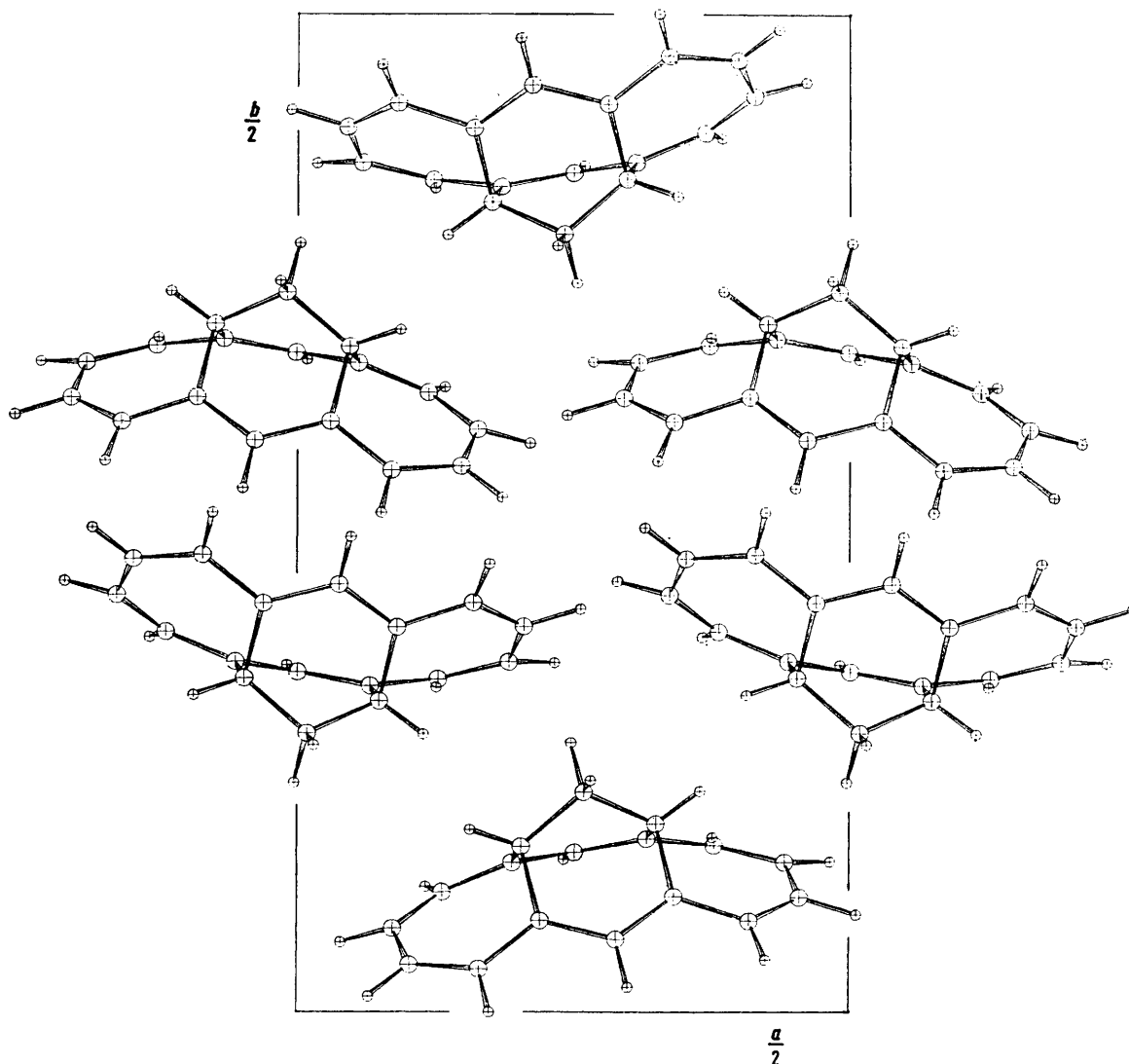


FIGURE 4 Packing of molecules as viewed along the c axis

the differences within each group being probably not significant.

Mean values for bond distances (corrected by libration), and bond, torsion, and dihedral angles are reported in Tables 3-6.

The six C-C bonds of the whole propane bridge ($\bar{\sigma} 0.007 \text{ \AA}$), are not different according to the χ^2 test, at a significance level $\alpha 0.25$. The mean values are 1.510 for uncorrected and 1.517 \AA for libration-corrected distances. These values are significantly shorter than the standard tetrahedral bond length, which is not surprising keeping in mind the sp^2-sp^3 character of the C(1)-C(15) bond and

range of intermolecular distances is normal. There are only three C...H contacts (2.89 , 2.86 , and 2.81 \AA) shorter than the sum of van der Waals radii ($r_O 1.7$ and $r_H 1.2 \text{ \AA}$ ³⁴), but the hydrogen atom positional uncertainties make these shortenings scarcely significant.

A plotter output of the packing of molecules in the crystal is shown in Figure 4.

The final column in Tables 3-6 refers to the calculated geometry of the isolated molecule. The assumed C-C bond length in the ring (1.397 \AA) is in good agreement

³⁴ L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960.

TABLE 7
Experimental and calculated electronic spectra

Experimental				Calc. (Pariser-Parr-Pople)							
				Planar geometry				Exptl. geometry			
				$\beta^0 - 2.5$		$\beta^0 - 2.32$		$\beta^0 - 2.5$		$\beta^0 - 2.32$	
λ/nm	E/eV	ϵ_{max}	f_{osc}	E/eV	f_{osc}	E/eV	f_{osc}	E/eV	f_{osc}	E/eV	f_{osc}
513	2.416	230	0.005	3.416	0.247	3.257	0.219	1.957	0.0005	1.80	0.0004
506	2.450	300	0.005	3.570	0.006	3.328	0.0047	2.286	0.0001	2.129	0
498	2.489	385	0.005	4.480	0	4.240	0	4.286	1.176	4.085	0.002
492	2.520	440	0.005	5.053	0	4.733	0	4.360	0.003	4.144	1.127
486	2.551	435	0.005	5.061	0.008	4.770	0.006	4.597	0	4.326	0
480	2.583	410	0.005	5.327	0	5.077	0	4.849	3.899	4.676	3.691
374	3.314	6560	0.163	5.485	3.227	5.237	3.063				
362	3.424	6620	0.163	5.931	0.284	5.616	0.279				
322	3.850	23,100	0.18			5.820	0.0041				
303	4.091	165,000	1.193								

with the mean experimental value (1.395 uncorrected, 1.401 Å libration-corrected). However bond distances

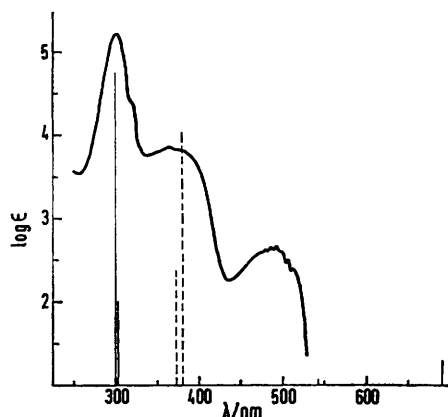


FIGURE 5 Experimental and theoretical electronic spectra, calculated from experimental geometry (solid line), and from assumed planar geometry (dotted line). Experimental spectrum determined for iso-octane solution. Calculated energies and intensities of electronic transitions are shown for the planar (dotted lines) and non-planar (full lines) geometry. The theoretical value for ϵ was evaluated by means of the formula $f = 2 \cdot 10^{-5} \epsilon_{\text{max}}$. (G. Favini and A. Gamba, *Gazzetta*, 1966, **96**, 391)

involved in the propane bridge are predicted 0.02 Å too short or too long. The agreement for bond angles is excellent.

The loss of π electron delocalization energy from the planar to the experimental geometry has been calculated as 20.8 kcal mol⁻¹. This seems a reasonable price to pay for the relief of steric strain.

The u.v. spectrum of the compound has been measured for an iso-octane solution. The position and intensity of the various peaks are in agreement with those already published.²

As a test of the ability of spectral information to predict the conformation of the annulene ring the experimental position and intensity of absorption bands were compared with the values calculated in the PPP approximation of MO theory. The calculations were performed for the experimental and the assumed planar geometry with different values of β^0 . Theoretical and experimental results are collected in Table 7. It appears that the results are not strongly dependent on the assumed value of β^0 in a reasonable range. The transition energy and oscillator strength are very much dependent on the geometry and the agreement with the experiment is better for the experimental geometry, as can be seen from Figure 5.

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