Structure of 4,8-Dihydrodibenzo[*cd,gh*]pentalene

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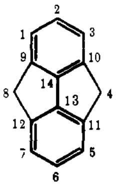
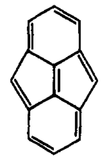
Abstract: The consideration of molecular models and the application of some empirical correlations between nmr coupling constants and various dihedral angles in the molecule suggests that the 4,8-dihydrodibenzo[*cd,gh*]pentalene (I) molecule is cup shaped. X-Ray studies, however, show that I is planar (within 0.02 Å) in the crystalline state with considerable bond length and angle deformations. The crystals are monoclinic with a = 5.588 (1), b = 5.095 (1), c = 17.693 (4) Å, β = 115°16′ (2′); the space group is $P2_1/c$ with two molecules in the unit cell occupying crystallographic centers of symmetry. The structure has been refined to an R factor of 0.053 on 438 observed reflections. The central C_{13}–C_{14} bond is 1.392 (8) Å, the C_4–C_{10} and C_4–C_{11} bonds are 1.578 (8) and 1.568 (9) Å, the C_9–C_{14}–C_{10} angle is 134.2 (6)°, and the C_1–C_9–C_8 and C_3–C_{10}–C_4 angles are 142.3 (5) and 141.5 (6)°. Empirical calculations based on this geometry indicate a strain energy of 65.6 kcal/mole. There is evidence from uv spectra that I is planar in solution as well as in the crystalline state. It appears to be a dangerous practice to apply nmr correlations when the molecule is considerably strained.

4,8-Dihydrodibenzo[*cd,gh*]pentalene (I) is a stable molecule which exhibits the dibenzo[*cd,gh*]pentalene (II) carbon skeleton.[4] Information concerning its geometry is of value for comparison with the theoretically important antiaromatic dibenzopentalene, since much of the strain energy in dibenzopentalene is already incorporated in dihydrodibenzopentalene. Several possibilities for the structure of dihydrodibenzopentalene are a planar molecule, a cup-shaped molecule, a twisted molecule, and a molecule with a ladder type of structure. Nonequivalence in the nmr spectrum (at a temperature of 39°) of the methylene protons has not been observed in dihydrodibenzopentalene or in any of its derivatives. Equivalence of these protons would be expected if the molecules were planar or if there were averaging of the environment of the protons with respect to the nmr time scale by rapid ring inversion or twisting.



I



II

A consideration of molecular models suggests that the most reasonable structure for dihydrodibenzopentalene is cup shaped. This conclusion is based on the assumption[5] that distortions of the strained framework would most likely be observed as distortions of bond angles rather than distortions of bond lengths. Such an assumption is usually valid. An idea of the strain incorporated in the molecule is afforded by considering that in dihydrodibenzopentalene a one carbon bridge connects carbon atoms which are 3.30 Å apart in fluorene[6]—a distance more than twice that of a carbon–carbon single bond, even were such bonds to be arranged linearly.

Nmr Studies. A number of correlations of spectral parameters with the geometry of molecules are available;[7–10] many of these are extensively employed in structural studies of strained molecules. Two of these, namely the dependences of nmr allylic and geminal coupling constants on the geometry of molecules, were examined to provide information on the geometry of dihydrodibenzopentalene. The coupling constant (J) between benzylic methylene hydrogen atoms and the hydrogen atom ortho to the methylene substituent has been found to depend on the intervening LCAO π bond order $P_{\mathrm{NN}'}$ and on the square of the cosine of the angle (ϕ) between the interhydrogen axis of the methylene group and the axis of the p orbital on the atom adjacent to the methylene group[10] (Figure 1). Equation 1 describes this relationship where K is a constant for a given molecule.

Dihydrodibenzopentalene exhibits an allylic coupling constant (J) of −0.7 Hz (sign inferred from other systems).[10] A ratio of this coupling constant to the allylic coupling constant (J') of fluorene[10] (−0.95) affords expression 2. For fluorene $\cos^2\phi$ is 1. Assuming that

$$J = KP_{\mathrm{NN}'}\cos^2\phi \qquad (1)$$

$$\frac{J}{J'} = \frac{KP_{\mathrm{NN}'}\cos^2\phi}{K'P'_{\mathrm{NN}'}\cos^2\phi} = \frac{-0.7}{-0.95} \qquad (2)$$

corresponding parameters K and $P_{\mathrm{NN}'}$ in fluorene and dihydrodibenzopentalene are insignificantly different affords eq 3 and 4. An angle ϕ of 36° corresponds to

$$\cos^2\phi = 0.801 \qquad (3)$$

$$\phi = 36° \qquad (4)$$

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[4] (a) For the synthesis of I and derivatives of II see B. M. Trost and P. L. Kinson, *J. Amer. Chem. Soc.*, **92**, 2591 (1970). (b) For an attempted synthesis of I see L. J. Altman and T. R. Erdman, *J. Org. Chem.*, **35**, 3237 (1970).

[5] G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

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[10] K. D. Bartle, D. W. Jones, and R. S. Mathews, *Rev. Pure Appl. Chem.*, **19**, 191 (1969).

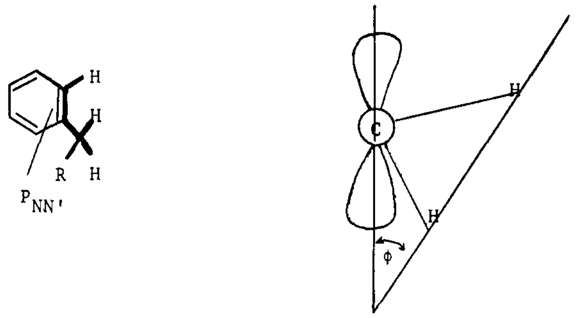

Figure 1. Dependence of an allylic coupling constant on bond order and ϕ.

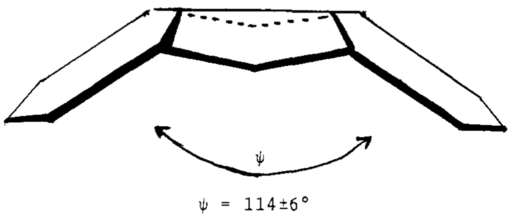

Figure 2. Potential nonplanar conformation of I.

an angle of 108° between the benzene rings of the cup-shaped dihydrodibenzopentalene molecule (see Figure 2).

The application of correlations of geminal coupling constants with geometry[7-9] to dihydrodibenzopentalene results in a prediction of its geometry in good agreement with that obtained from allylic coupling constants. An adjacent π system makes a contribution (ΔJ) to the geminal coupling constant of a methylene group. The dependence of ΔJ on the angle (θ) between the hydrogen–carbon axis in the methylene group and the axis of the p orbital on the adjacent carbon atom is given by the Barfield–Grant curve.[8] The Barfield–Grant curve has received experimental verification.[9]

The geminal coupling constant of the methylene hydrogen atoms in dihydrodibenzopentalene is not directly measurable due to the equivalence of these nuclei in the nmr. Its value, however, can be calculated from the corresponding H–D coupling constant (J_{HD} = 2.3 Hz) found in 4,8-dideuterio-4,8-dihydrodibenzo[*cd,gh*]pentalene by the relation $J_{HH'} = (\gamma_{HH'}/\gamma_{HD})J_{HD} = 6.55J_{HD}$. Employment of this relationship indicates that the geminal coupling constant (J) in dihydrodibenzopentalene is -15.0 Hz. The geminal coupling constant in fluorene is -22.3 Hz. The geometry of fluorene ($\theta = 30°$) is such that the maximum contribution (negative) from an adjacent π system is expected to be felt in this molecule. The magnitude of this contribution is -4.5 Hz per benzene ring. Application of the correction for the π systems of fluorene (2×-4.5 Hz = 9.0 Hz) indicates that in the absence of the π contribution, the geminal coupling constant of fluorene is expected to be -13.3 Hz. This value for the corrected coupling constant of fluorene (-13.3 Hz) is in good agreement with the geminal coupling constant of cyclopentane[9] (-15.0 Hz) since the former is expected to be slightly more positive due to the inductive effects of the benzene rings.

Assuming again that fluorene is a good model, the coupling constant of dihydrodibenzopentalene (-15.0 Hz) shows the effect of a π contribution of -1.7 or -0.85 Hz for each benzene ring. Reference to the Barfield–Grant curve indicates that the angle θ in dihydrodibenzopentalene is 65°. An angle θ of 65° corresponds to an angle of 120° between the benzene rings of the cup-shaped dihydrodibenzopentalene.

The excellent agreement obtained for the two independent approaches (114 ± 6°) using the existing correlations of spectral parameters with the geometry of molecules lends credence to the answers in spite of the many assumptions involved. In order to test the validity of the nmr approach, we determined the exact conformation by X-ray crystallography.

X-Ray Determination. The crystals grow as plates elongated somewhat along the b axis and with (001) the developed face of the plate. Crystal data were as follows: $C_{14}H_{10}$, M_w = 178.23, monoclinic, a = 5.588 (1), b = 5.095(1), c = 17.693(4) Å, β = 115°16′(2′), $V = 455.5 \times 10^{-24}$ cm^3, ρ_{measd} = 1.28 g cm^{-3}, Z = 2, ρ_{calcd} = 1.30 g cm^{-3}, $F(000)$ = 188, μ(Cu Kα) = 5.7 cm^{-1}. Space group $P2_1/c$. The site symmetry of the molecule is therefore $C_i(\bar{1})$.

Data Collection. A small (0.03 × 0.10 × 0.20 mm) plate of dihydrodibenzopentalene obtained by slow evaporation of an ethanol solution was used to collect the intensity data; the plate was elongated along the b axis. Cell data were obtained by a least-squares fit to the hand-centered settings for the four angles for ten reflections obtained on a Picker FACS-1 diffractometer (Cu Kα, λ = 1.54178 Å). The density of the crystal was measured by flotation in aqueous zinc chloride.

Intensity data were collected on the diffractometer (Cu Kα radiation) using a θ–2θ scan technique. The base width of the scan range was 2°, the scan rate was 1 deg/min with 10-sec stationary background counts being made at the two extremes of the scan. Pulse height analysis gave approximately monochromatic Cu Kα radiation. Initially, the two octants of data $\bar{h}\bar{k}l$ and $h\bar{k}\bar{l}$ were measured out to 2θ = 130°, and then the two octants $\bar{h}\bar{k}l$ and $\bar{h}\bar{k}\bar{l}$ were measured to the same limit. A few reflections in the last two octants of data were discarded because of a movement of the crystal. A standard reflection was measured after every group of 25 reflections. During the period of data collection the intensity of the standard fell more or less linearly to 90% of its original value and the data were corrected by assuming linear fall-off in intensity between the periodic measurements of the standard and by scaling to a normalized value for the intensity of the standard.

The data were corrected for Lorentz and polarization effects, but the effects of absorption were neglected. The transmission coefficients were calculated to lie in the range 0.94–0.99. The threshold count was taken as 0.06 times the total background count or 50 counts, whichever was greater. Where two symmetry-equivalent reflections were measured, the intensities were averaged. Using these criteria, a total of 438 out of a possible 769 reflections were considered observed.

Structure Determination. The structure was determined by the symbolic addition procedure[11] with extensive use of the computer programs written by Fleischer, *et al.*[12] Two E maps were computed based on

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[11] J. Karle and I. L. Karle, *Acta Crystallogr.*, 21, 849 (1966).

[12] E. B. Fleischer, R. B. K. Dewar, and A. L. Stone, Abstracts of the American Crystallographic Association, Atlanta, Ga., Jan 1967.

Table I. Final Atomic Parameters and Estimated Standard Deviations in Fractions of the Unit Cell

	x	y	z
C_1	0.9350 (12)	0.4198 (12)	0.3303 (3)
C_2	0.7419 (12)	0.2256 (13)	0.3159 (3)
C_3	0.6480 (12)	0.1402 (12)	0.3746 (3)
C_4	0.7481 (12)	0.2460 (13)	0.5406 (3)
C_9	1.0464 (10)	0.5388 (10)	0.4079 (3)
C_{10}	0.7588 (10)	0.2555 (12)	0.4530 (3)
C_{14}	0.9438 (11)	0.4420 (12)	0.4606 (3)
H_1	0.974 (9)	0.462 (10)	0.290 (2)
H_2	0.637 (10)	0.148 (11)	0.259 (3)
H_3	0.514 (11)	0.008 (11)	0.355 (3)
H_{4a}	0.560 (13)	0.294 (12)	0.534 (3)
H_{4b}	0.805 (10)	0.061 (12)	0.568 (3)

Table II. Final Thermal Parameters and Estimated Standard Deviations[a]

	b_{11} ($\times 10^3$)	b_{22} ($\times 10^3$)	b_{33} ($\times 10^4$)	b_{12} ($\times 10^3$)	b_{13} ($\times 10^3$)	b_{23} ($\times 10^3$)
C_1	37 (3)	39 (3)	30 (3)	0 (5)	12 (1)	4 (2)
C_2	40 (3)	38 (3)	31 (2)	−6 (5)	9 (1)	−1 (2)
C_3	30 (3)	33 (3)	39 (3)	−14 (4)	9 (1)	0 (1)
C_4	32 (3)	29 (2)	35 (2)	−8 (5)	12 (1)	3 (2)
C_9	31 (3)	27 (3)	35 (3)	−5 (4)	12 (1)	2 (1)
C_{10}	31 (2)	27 (2)	35 (2)	0 (5)	11 (1)	2 (2)
C_{14}	35 (3)	30 (3)	33 (2)	−15 (4)	12 (1)	−2 (1)

	B_θ		B_θ		B_θ
H_1	3 (1)	H_3	4 (1)	H_{4b}	4 (1)
H_2	4 (1)	H_{4a}	6 (2)		

[a] The anisotropic thermal parameters are of the form exp $-[b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl]$ and isotropic of the form exp $-[B_\theta \sin^2 \theta/\lambda^2]$.

a different sign for one of the symbols. Each map showed a reasonable molecular structure, but only one had the molecule on a crystallographic center of symmetry. Full-matrix, least-squares refinement of the positional and isotropic thermal parameters for the carbon atoms obtained from this map reduced R to 0.116 and R_2 to 0.122.[13] Unit weights were applied to all the reflections and the quantity minimized was $\Sigma w \cdot ||F_o| - |F_c||^2$. Anisotropic thermal parameters for the carbon atoms were introduced into the model and full-matrix, least-squares refinement gave R of 0.098 and R_2 of 0.110. A difference map was calculated and five peaks in the range 0.2–0.3 e/Å^3 could clearly be identified as representing hydrogen atoms. There was one other peak of comparable height which could not be identified with any reasonable structural feature.

Inclusion of the five hydrogen atoms with isotropic thermal parameters in the model followed by further full-matrix least-squares refinement gave a final R factor of 0.053 and R_2 of 0.067 on all observed data. A final difference map was calculated at this stage and showed no peaks outside the range ±0.15 e/Å^3. The final positional and thermal parameters are given in Tables I and II. The bond lengths and angles calculated from these positions are listed in Table III. Some best planes in the molecule are given in Table IV, while some short intermolecular contacts are listed in Table V. A stereoscopic drawing of a single molecule viewed along the b axis is shown in Figure 3, while packing diagrams of the crystal are shown in Figures 4 and 5.

Table III. Bond Lengths (Ångströms) and Angles (Degrees) with Estimated Standard Deviations

C_1–C_2	1.405 (9)	C_1–H_1	0.85 (5)
C_1–C_9	1.382 (9)	C_2–H_2	1.01 (7)
C_2–C_3	1.418 (9)	C_3–H_3	0.95 (6)
C_3–C_{10}	1.384 (9)	C_4–H_{4a}	1.04 (7)
C_4–C_{10}	1.578 (8)	C_4–H_{4b}	1.05 (6)
C_4–C_{11}	1.568 (9)		
C_{10}–C_{14}	1.367 (9)		
C_9–C_{14}	1.378 (8)		
C_{13}–C_{14}	1.392 (8)		
C_2–C_1–C_9	118.3 (4)	C_2–C_1–H_1	118 (4)
C_1–C_2–C_3	125.4 (4)	C_9–C_1–H_1	123 (4)
C_2–C_3–C_{10}	117.1 (6)	C_1–C_2–H_2	122 (3)
C_3–C_{10}–C_4	141.5 (6)	C_3–C_2–H_2	112 (3)
C_3–C_{10}–C_{14}	113.0 (4)	C_2–C_3–H_3	115 (3)
C_4–C_{10}–C_{14}	105.5 (4)	C_{10}–C_3–H_3	128 (3)
C_{10}–C_4–C_{11}	102.9 (5)	C_{10}–C_4–H_{4a}	110 (4)
C_1–C_9–C_8	142.3 (5)	C_{10}–C_4–H_{4b}	111 (3)
C_1–C_9–C_{14}	112.0 (5)	C_{11}–C_4–H_{4a}	111 (4)
C_8–C_9–C_{14}	105.7 (4)	C_{11}–C_4–H_{4b}	111 (3)
C_9–C_{14}–C_{10}	134.2 (6)	H_{4a}–C_4–H_{4b}	111 (5)
C_9–C_{14}–C_{13}	112.7 (4)		
C_{10}–C_{14}–C_{13}	113.2 (3)		

Table IV. Details of Some Best Planes in the Molecule[a]

	A	B	C	D	E
C_1	*−0.007*	*−0.001*	*−0.001*	*−0.007*	
C_2	*−0.005*	*−0.003*	*−0.003*	*−0.007*	
C_3	*0.011*	*0.005*	*0.005*	*0.009*	
C_4	*−0.015*	−0.030	−0.030	*−0.012*	*−0.009*
C_5	*0.007*				
C_6	*0.005*				
C_7	*−0.011*				
C_8	*0.015*	0.022	0.021	0.022	
C_9	*−0.003*	*0.001*	*0.002*	*0.001*	
C_{10}	*0.004*	*−0.004*	*−0.003*	*0.005*	*0.004*
C_{11}	*0.003*				*0.008*
C_{12}	*−0.004*				
C_{13}	*−0.005*	−0.011	−0.009		*−0.006*
C_{14}	*0.005*	*0.002*	0.003	*0.008*	*0.001*
χ^2	21.3	1.3	1.2	9.7	4.8
P	0.025	>0.5	∼0.5	∼0.05	0.10

[a] The distances (Å) of atoms included in the plane calculations are shown in italic type.

Table V. Some Important Intermolecular Contacts (Ångströms)[a]

H_2–H_5^{I}	2.82	H_3–H_{8a}^{IV}	2.66
H_2–C_6^{II}	2.91	H_3–H_{8b}^{IV}	2.69
H_2–H_6^{II}	2.92	H_{4a}–H_{8b}^{IV}	2.75
H_3–H_6^{II}	2.58	C_2–H_{8b}^{V}	2.88
H_{4a}–C_8^{III}	2.87	C_3–H_{8b}^{V}	2.96
H_{4a}–H_{8a}^{III}	2.37		

[a] I corresponds to $x, \frac{1}{2} - y, -\frac{1}{2} + z$; II corresponds to $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; III corresponds to $-1 + x, y, z$; IV corresponds to $-1 + x, -1 + y, z$; V corresponds to $x, -1 + y, z$.

There remains the possibility that some of the anomalous bond lengths (Table III) are artifacts of a structural disorder or of some uncorrected thermal motion. If the short central (C_{13}–C_{14}) bond resulted from statistical disorder of two structures each with these two atoms, respectively, above and below the plane of the ring, one would expect the thermal parameter of C_{14} to be elongated in a direction normal to the plane of the molecule. For the real length of the C_{13}–C_{14} bond to be 1.50 Å, the nucleus of the atom C_{13} would have to lie

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paper A7, p 20; R. B. K. Dewar, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1968.

(13) $R = \Sigma||F_{obsd}| - |F_{calcd}||/\Sigma|F_{obsd}|$ and $R_2 = [\Sigma w||F_{obsd}| - |F_{calcd}||^2/\Sigma w|F_{obsd}|^2]^{1/2}$.

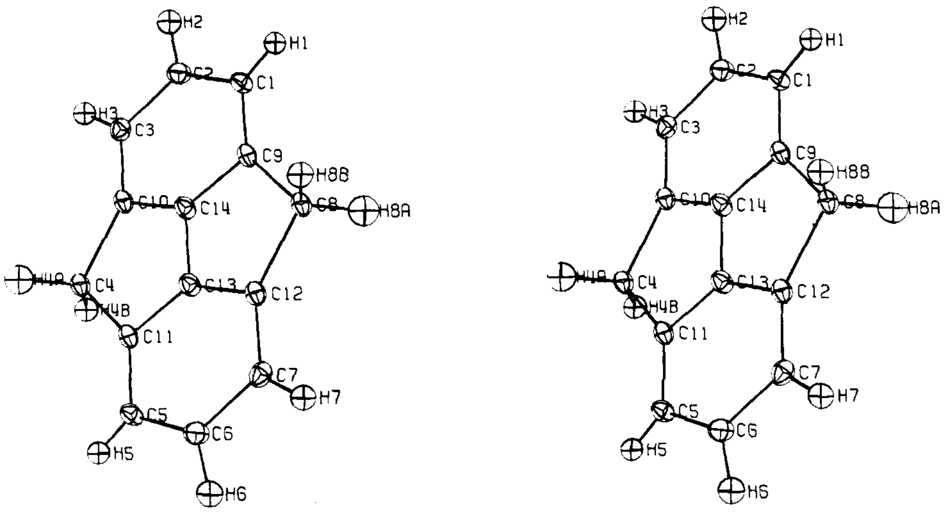

Figure 3. Stereoscopic view of a single molecule showing the anisotropic thermal ellipsoids.

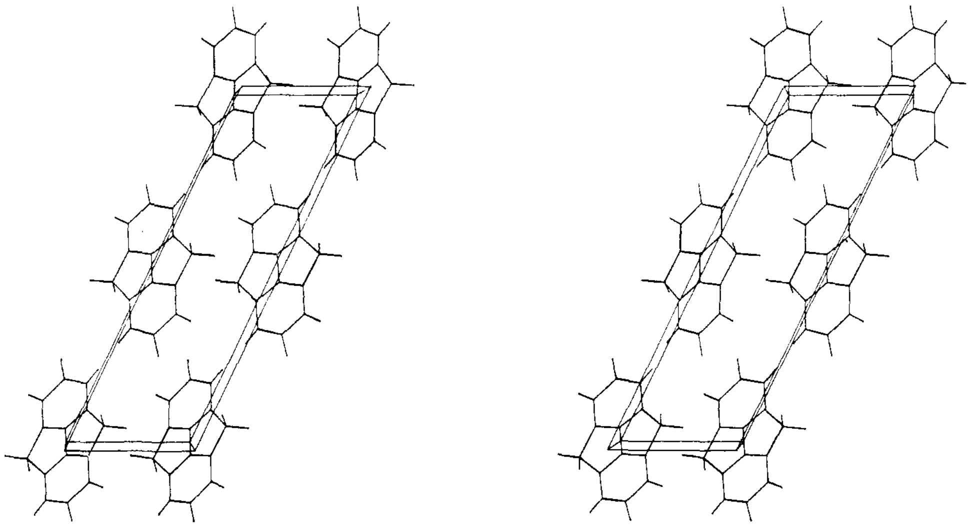

Figure 4. Stereoscopic view of the contents of one unit cell looking along the *b* direction.

0.26 Å above the plane of the ring. Neither the refined thermal parameters nor the final difference map are compatible with disorder of this magnitude. While the maximum rms displacement (0.234 Å) for C_{13} is in a direction almost perpendicular to the plane of the ring (Figure 3), the displacement of atom C_9 in the same direction lies in the range 0.16–0.20 Å, and the displacement for C_1 in almost the same direction is also 0.234 Å. For the ellipsoid of C_{13} to represent substantial disorder of the atom position, a much greater displacement relative to the other atoms would be anticipated and some features >0.2 e/Å^3 would be expected near C_{13} on the final difference map. An approximate upper limit to the extent of possible disorder can be estimated by assuming that the difference (0.07 Å) between the displacements of atoms C_{13} and C_9 in the direction perpendicular to the ring is due to disorder of C_{13}. If the standard deviations are taken into account, this difference might be as great as 0.10 Å. In that case the real C_{13}–C_{14} length would be 1.405 Å and the $C_9C_{14}C_{10}$ angle would be 133.5°. In the discussion section, the values resulting directly from the refinement have been used.

Furthermore, it is unlikely that the observed difference in the C_1–C_9 and C_3–C_{10} lengths on the one hand and the C_1–C_2 and C_2–C_3 lengths on the other hand is due to thermal motion. For thermal motion to be responsible for an artificial shortening of the C_1–C_9 and C_3–C_{10} lengths in the refined model would require an oscillation of the molecule about the C_4–C_8 axis. There is no evidence in the form of large thermal parameters for the atoms C_1, C_2, and C_3 for such a molecular motion. As a test of whether some of the unusual molecular dimensions (Table III) arose as a result of the crystal decomposition, we refined our model with the data measured from the octants $\bar{h}\bar{k}l$ and $h\bar{k}\bar{l}$, these being the two octants measured at the beginning of the data collection. Of the 36 positional parameters that resulted from this refinement, 27 agreed within the estimated standard deviations and the remaining nine agreed within 1.5 times the standard deviations. It does not appear, therefore, that the results are artefacts arising from decomposition of the crystal.

The atomic scattering curve for carbon was that given by Cromer and Mann,[14] while that for hydrogen

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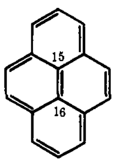
[14] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

was calculated by Stewart, *et al.*[15] The final values of h, k, l, $|F_{\mathrm{obsd}}|$, and F_{calcd} are deposited.[16]

Discussion

The X-ray structure reveals the deep abnormalities created by introducing such a large amount of strain. The molecules lie on centers of symmetry at 0,0,0 and 0,$^1/_2$,$^1/_2$. Most surprisingly, the carbon skeleton deviates from planarity by less than 0.02 Å (Table IV); the best planes through the five- and six-membered rings are within 0°40′ of each other. To accommodate planarity large deviations of *both bond angles and bond lengths* occur. The C_{11}–C_{13}–C_{12} angle has opened to an unprecedented 134.2(6)° compared to 122.5 and 118.9° for the comparable angles in fluorene[17] and biphenyl,[18] respectively. The C_8–C_9 bond length of 1.574(9) Å appears to be the longest known for a sp^2–sp^3 single bond; a value of 1.567(8) Å for such a bond has been observed for 1,2,4,5-tetra-*tert*-butylbenzene.[19] Among sp^3–sp^3 single bonds many long ones (up to 1.63 Å) are known (*e.g.*, central bond of hexamethylbicyclo[2.2.0]-hexa-2,5-diene[20] is 1.629(10) Å and of bicyclo[2.1.0]-pentane[21] is 1.622 (16) Å) although in many of these cases the unusual length is associated with repulsive interactions.

The unique feature of dihydrodibenzopentalene is the severe compression to 1.392(8) Å of the C_{13}–C_{14} bond (compare corresponding bonds in fluorene,[17] 1.482(30) Å; biphenyl,[18] 1.507 (32) Å; and 2,13-benzofluoranthene,[22] 1.49(3) Å). This bond is even shorter than the C_{15}–C_{16} bond of pyrene(III)[23] (1.417(7) Å). Many correlations of bond length with π bond order exist.[24] Such correlations suggest the importance of the valence bond structure depicted for pyrene in III to accommodate the bond length shortening to that of almost an aromatic double bond. Utilizing similar reasoning would imply the importance of diradical structures such as IV for I. However, the chemical properties are not in accord with such an expectation nor does the ultraviolet spectrum (*vide infra*) reflect a substantial increase in overlap compared to fluorene. Such a finding implies that correlations between bond length and π bond order may be fortuitous and clearly must be viewed with suspicion. *A priori*, no fundamental reason exists for such a correlation. In the present instance, each benzene ring has a complete set of filled molecular orbitals. Bringing these two completely occupied sets of orbitals into close proximity does not lead to increased delocalization.



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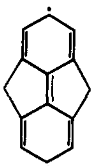

IV

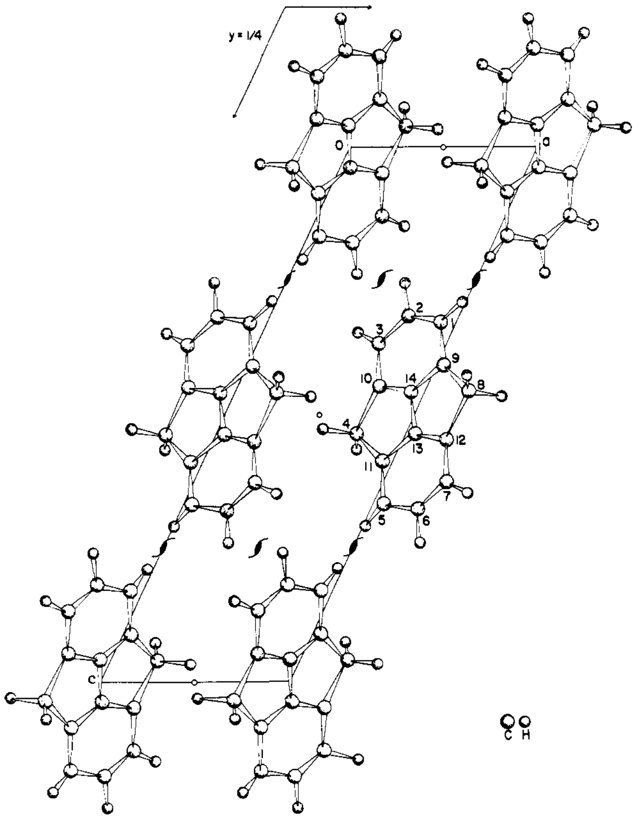

Figure 5. Packing diagram showing the molecule whose coordinates are given in Table I with atom numbers.

From Dauben's potential function[25] [$V_S = 0.5A\alpha^2$; A, the bond angle deformation constant (0.026 kcal/mole deg^2) and α the bond angle deformation] for the estimation of the strain energy (V_S) of molecules, dihydrodibenzopentalene is predicted to have a strain energy of 49.6 kcal/mole. This function, however, being based on the assumption that angular distortions account for the strain in molecules, does not take bond length distortions into account.

A somewhat more detailed although empirical approach to the calculation of strain in molecules has been developed by Westheimer.[26] In this approach, the total strain energy (E_{TS}) is the sum of the bond length strain (E_{BLS}), the bond angle strain (E_{BAS}), the torsional strain, and the nonbonded interaction strain. In the present case the latter two terms are zero, and only the bond length strain and the bond angle strain contribute. Equations 5 and 6 are used to calculate

$$E_{BLS} = k/2(\Delta r)^2 \quad (5)$$

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(15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(16) This table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(17) D. M. Burns and J. Iball, *Proc. Roy. Soc., Ser. A*, **227**, 200 (1955).

(18) J. Trotter, *Acta Crystallogr.*, **14**, 1135 (1961); G. B. Robertson, *Nature (London)*, **191**, 593 (1961); **192**, 1026 (1961); A. Hargreaves and S. Hasan Rizvi, *Acta Crystallogr.*, **15**, 365 (1962).

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(20) M. J. Cardillo and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 2399 (1970).

(21) R. K. Bohn and Y.-H. Tai, *ibid.*, **92**, 6447 (1970).

(22) H. W. Ehrlich and C. A. Beevers, *Acta Crystallogr.*, **9**, 602 (1956).

(23) A. Camerman and J. Trotter, *ibid.*, **18**, 636 (1965).

(24) For recent examples, see W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, **89**, 1438 (1967); D. H. Lo and M. A. Whitehead, *Can. J. Chem.*, **46**, 2027 (1968); N. Trinajstić, *Tetrahedron Lett.*, 1529 (1968).

(25) H. J. Dauben and A. G. Osborne, Abstracts of the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., 1956, p 370.

(26) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 12.

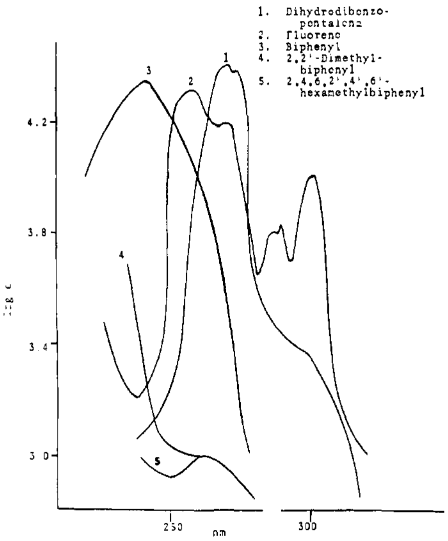

Figure 6. Uv spectra of dihydrodibenzopentalene, fluorene, biphenyl, dimethylbiphenyl, and hexamethylbiphenyl.

$$E_{\mathrm{BAS}} = A/2\alpha^2 \tag{6}$$

these components of the strain energy, where k is the bond force constant, Δr the change in length of the bond from its equilibrium value, A the bond angle deformation constant, and α the bond angle deformation. The bond force constant depends on the nature of the bond being considered, and can be calculated by an empirical equation developed by Dewar and Schmeising[27] for this purpose. Table VI contains the equilibrium values of the bond lengths and the bond force constants used in the calculation of the bond length deformation strain energy. The bond angle deformation constant depends on the hybridization of the central carbon atom. The parameters used in this study are shown in Table VII. These calculations predict a bond length strain of 14.1 kcal/mole and a bond angle strain of 51.6 kcal/mole for a total strain energy of 65.6 kcal/mole (see Table VIII for individual contributions). Schleyer[5] suggests, however, that these calculations may overestimate the contribution to the strain of large angular deformations. The value of 65.6 kcal/mole, therefore, may be viewed as an upper limit for the strain energy of dihydrodibenzopentalene.

Table VI. Bond Lengths and Force Constants

Bond hybridization type	Bond length, r_e, Å	Bond force constant, k, mdyn/Å
$sp^2{=}sp^2$ (aromatic)	1.396	8.7486
sp^2–sp^2	1.476	6.2826
sp^2–sp^3	1.501	5.5933

Table VII. Bond Angle Deformation Parameters

Angle	Hybridization of central atom	Equilibrium value, deg	$A/2$, kcal/mole deg^2
CCC	sp^2	120	0.0275
CCC	sp^3	112	0.0172
CCH	sp^2	120	0.0193
CCH	sp^3	109	0.0121

Table VIII. Individual Strain Contributions

Bond or angle	Strain energy	Bond or angle	Strain energy
1–2	0.161	3–10–14	0.776
3–10	0.364	3–10–4	6.619
10–14	0.333	4–10–14	2.862
10–4	2.143	10–4–11	0.601
13–14	3.189	10–14–9	2.783
1–2–3	0.402	10–14–13	0.696
2–3–10	0.067		

The finding that dihydrodibenzopentalene is planar in the solid state indicates that it might also be planar in solution, contrary to earlier expectations based on molecular models and the correlations of nmr allylic and geminal coupling constants. The ultraviolet spectrum of dihydrodibenzopentalene suggests that it is essentially planar in solution also. Figure 6 shows the ultraviolet spectra of dihydrodibenzopentalene, fluorene, biphenyl,[28] 2,2'-dimethylbiphenyl,[28] and 2,4,6,2',4',6'-hexamethylbiphenyl.[28] Studies[27,28] indicate that the transition observed for these molecules in the region 250–270 nm is associated with both benzene rings and reflects the coplanarity of these rings in the magnitude of the molar extinction coefficient. The absorption of dihydrodibenzopentalene (267 nm, log ϵ 4.31) relative to that of fluorene (262 nm, log ϵ 4.27, and 264 nm, log ϵ 4.27), a planar molecule, suggests that dihydrodibenzopentalene is planar also. The shift in the absorption of dihydrodibenzopentalene to slightly longer wavelength is associated with a slightly increased interaction between the two benzene rings facilitated by the short bond relative to fluorene. In striking contrast to the magnitude of the extinction coefficients of dihydrodibenzopentalene and fluorene, the magnitude of the extinction coefficients of 2,2'-dimethylbiphenyl and 2,4,6,2',4',6'-hexamethylbiphenyl, for which coplanarity of the benzene rings is sterically prohibited, is only 1×10^3. The conclusion that dihydrodibenzopentalene is planar in solution has the extremely important consequence that dibenzopentalene, itself, and other derivatives are expected to exhibit planarity.

The discrepancy concerning the geometry of dihydrodibenzopentalene between the conclusions based on uv data and those based on nmr spectral parameters arises in the assumptions involved in the latter approach. The assumption that the strain energy of the molecule would be observed exclusively as bond angle deformations is seen to be invalid in the present case, and suggests that caution should be used in applying the correlations of nmr coupling constants to other strained systems. The decrease in the magnitude of the allylic and geminal coupling constants of dihydrodibenzopentalene relative to fluorene arises through the decreased interaction of the methylene with the benzene rings associated with the increased length of these bonds relative to fluorene.

Experimental Section

4,8-Dihydrodibenzo[*cd,gh*]pentalene and 4,8-dideuteriodibenzopentalene were prepared as previously described.[4] Nmr studies

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[27] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, 11, 96 (1960).

[28] M. T. O'Shaugnessy and W. H. Rodebush, *J. Amer. Chem. Soc.*, **62**, 2906 (1940).

performed on a Varian HA-100 nmr spectrometer fitted with a variable temperature probe were determined as a solution in carbon tetrachloride utilizing tetramethylsilane as an internal lock signal. Crystallographic computations were carried out on the IBM 360-75 at the University of Illinois. Computer programs used included NRC-2A (written by F. R. Ahmed), UCLA-LS (written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood), ALF (Ames Laboratory Fourier Program), and ORTEP (written by C. K. Johnson).

Acknowledgment. We wish to express our thanks to the Petroleum Research Fund, administered by the American Chemical Society, Grant No. 2994-A1 (B. M. T. and P. L. K.), and to the General Medical Sciences Institute of the National Institutes of Health, Grant No. GM12470 (C. A. M. and I. C. P.), for their generous support.

The X-Ray Structures of 7-Aminofurazano[3,4-*d*]pyrimidine and 7-Amino-1,2,5-thiadiazolo[3,4-*d*]pyrimidine

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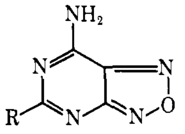
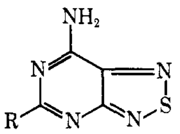
Princeton, New Jersey 08540. *Received January 20, 1971*

Abstract: X-Ray crystallographic analyses of 7-aminofurazano[3,4-*d*]pyrimidine (I, R = H) and 7-amino-1,2,5-thiadiazolo[3,4-*d*]pyrimidine (II, R = H) are reported, and the results correlated with both the chemical and biological activities of these adenine isosters. In particular, the remarkable reactivity of I and its derivatives toward nucleophilic displacement of the 7-amino grouping and toward photoreduction is discussed in the light of the bonding parameters determined by the X-ray analyses.

Continuing investigation of the novel heterocyclic system I (*e.g.*, 7-aminofurazano[3,4-*d*]pyrimidine, R = H) reveals a number of unusual physical and chemical properties of this fused pyrimidine. Like the 7-amino-1,2,5-thiadiazolo[3,4-*d*]pyrimidines (II)[1] and reminiscent of the isoelectronic 4-aminopteridines (III), the 7-aminofurazano[3,4-*d*]pyrimidines (hereafter referred to as 7-aminoFZP) undergo nucleophilic displacement of the 7-amino group. Unlike these related systems, however, the various representatives of I undergo such displacement with *extreme* facility, as illustrated by the following conversion.[2] This same conversion, when carried out on 7-amino-1,2,5-thiadiazolo[3,4-*d*]pyrimidine (II, R = H), requires 4.5 hr at 90°;[1] analogous amino group exchange in the pteridine series is a well-known reaction requiring even more vigorous conditions.[3] Also unexpected is the ready photoaddition of various solvents to the 6,7 bond of I (R = C_6H_5) described in an earlier communication[5] and summarized below. This reaction has no reported analog in systems II, III, or IV.



I



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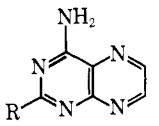

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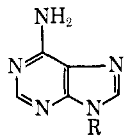

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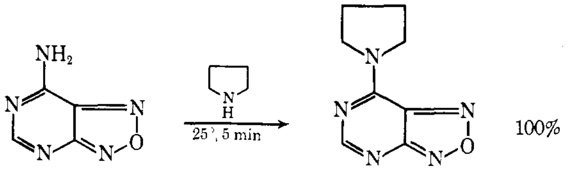

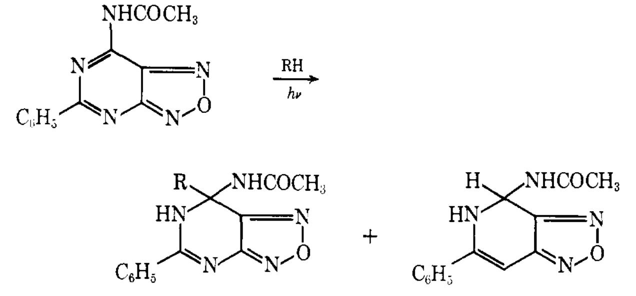

R = CH_2OH, $CH(CH_3)OH$, $C(CH_3)_2OH$, $CH_2C(CH_3)_2$, $CHOCH_2CH_2OCH_2$

That the uv spectra of the thiadiazolopyrimidines II resemble closely those of the corresponding pteridines III has been demonstrated by Shealy, Clayton, and Montgomery[6] who inferred from this similarity a matching resemblance in π-electronic structure between systems II and III. The uv spectra of the furazanopyrimidines I are characterized by three absorptions of nearly equal intensity (log ε = 3–4) occurring in the regions 210–240, 250–290, and 330–380 nm, fitting remarkably well the pattern described by Shealy and coworkers[6] for II and III. This similarity suggests that the isoelec-

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(1) Y. F. Shealy and C. A. O'Dell, *J. Org. Chem.*, **29**, 2135 (1964).

(2) E. C. Taylor, Y. Maki, and B. E. Evans, unpublished results.

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(4) R. C. Elderfield and A. C. Mehta, *Heterocycl. Compounds*, **9**, 64 (1967).

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