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STRUCTURAL PROPERTIES OF DICYCLOPENTENOBENZOCYCLOBUTENE, A SMALL RING TRIS-ANNELATED BENZENE

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Abstract—The synthesis of dicyclopententobenzocyclobutene from 1,1-dicyclopentenyl and dimethyl cyclobutene-1,2-dicarboxylate is described. Current theories regarding sterically induced aromatic bond alternation would predict that both the σ and π frameworks should show more double bond character exocyclic to the small fused rings. The structural parameters of dicyclopentenobenzocyclobutene have been determined by single crystal X-ray analysis. No significant bond alternation is observed in the central ring. The thermal ellipsoids for the cyclopentene rings show the non-benzylic methylene groups to be moving perpendicularly through the plane of the molecule while the adjacent benzylic methylenes compensate by lateral movement in the plane.

The fusion of a cycloalkene containing five or less carbons onto a benzene ring has been seen to significantly affect the chemical and physical properties of the aromatic portion of the molecule.[1] As the size of the ring fused to benzene is decreased, these effects become more pronounced. The various properties observed for small ring fused aromatic molecules are often rationalized in terms of a theory of double bond localization first put forth by Mills and Nixon in 1930.[2] These workers, as well as later ones, claimed that many of the properties of indan could be explained by the existence of a predominant Kekulé resonance contributor in which the double bonds of the benzene ring were oriented such that they were exocyclic to the 5-membered ring. In theory, such an effect should be dramatically amplified in systems where two or three such small rings are fused *meta* to one another around the benzene nucleus.

The triscycloalkenobenzenes where the fused rings contain from 5 to 8 carbons have been known for some time. An NMR study of these molecules has led to the conclusion that when one or more 5-membered rings or three 6-membered rings are fused to benzene, a considerable distortion of the ring current or magnetic anisotropy results.[3] A determination of the ionization potentials, UV spectra and charge-transfer spectra for a series of cycloalkenobenzenes, bicycloalkenobenzenes, and triscycloalkenobenzenes has aided in the investigation of the effect of strain on the π-electron sextet in the ground state as well as in higher energy states.[4]

We have recently prepared dicyclopentenobenzocyclobutene (**6**) which is the smallest tris-annelated benzene hydrocarbon yet known.[5] This paper reports on the details of its preparation, physical properties, and structure as determined by single crystal X-ray analysis.

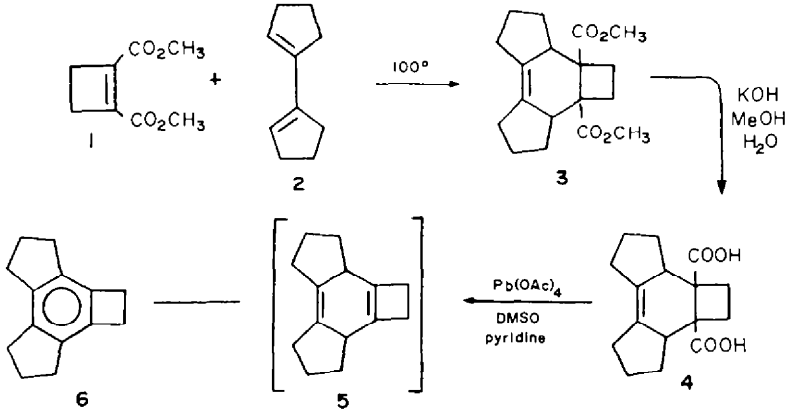
EXPERIMENTAL

1. *Synthesis*

The reaction of 1,1'-dicyclopentenyl[6] (**2**) with dimethylcyclobutene-1,2-dicarboxylate[7] (**1**) results in a 55% yield of the Diels–Alder adduct **3**. Although both ester functions in **3** are sterically hindered, they may be readily hydrolyzed by refluxing overnight with KOH in aqueous MeOH to afford the diacid **4**. Treatment of **4** with two equivalents of lead tetraacetate in dimethylsulfoxide containing four equivalents of pyridine results in the formation of the aromatic hydrocarbon **6**. The reaction is presumed to involve first a *bis*-decarboxylation to provide the intermediate diene **5**, which is then oxidized to **6** under the reaction conditions.

PMR spectra were obtained on a Varian Associates T-60 or XL-100 spectrometer and chemical shifts are reported in ppm downfield from TMS. IR spectra were obtained on a Beckman IR-4250 spectrometer. UV spectra were obtained on a Cary 14 spectrometer. All m.p. are uncorrected.

Dimethyl tetracyclo[10.2.0.0^{2,6}.0^{7,11}]*tetradec*-6,7-*ene*-1,10-*dicarboxylate* (**3**). In a heavy wall glass tube were placed 6.90 g (0.052 mol) of **2**,[6] 8.40 g (0.050 mol) of **1**,[7] and 25 mg of hydroquinone. The tube was sealed and heated in an oil bath at 100° for 16 hr. The tube was then cooled and opened, and the crude product was recrystallized from hexane at −10° to provide 8.40 g (55%) of **3**, m.p. 72–75°: NMR (CCl_4) δ 3.62 (s, 6H,



CO_2CH_3) and 2.8–1.2 ppm (overlapping m, 18H); IR (KBr) 3000, 2960, 2880, 1740, 1450, 1327, 1190 and 1112 cm^{-1}.

Tetracyclo[10.2.0.0^{2,6}.0^{7,11}]*tetradec - 6,7 - ene - 1,10 - dicarboxylic acid* (**4**). To a soln of 8.24 g (0.027 mol) of **3** in 45 ml MeOH was added a soln of 10 g (0.178 mol) of KOH in 8 ml water. The mixture was refluxed for 60 hr, poured into 200 ml water and acidified with conc. HCl. The aqueous soln was extracted with ether and the extracts were dried over Na_2SO_4. Filtration, removal of solvent, and drying under vacuum provided 7.33 g (95%) of **4**: NMR (DMSO-d_6) δ 11.8 (broad s, 2H, COOH) and 3.0–1.2 ppm (overlapping m, 18H); IR (KBr) 3500–2800 (b), 1710, 1690, 1420 and 1280 cm^{-1}.

Dicyclopentenobenzocyclobutene (**6**). To a soln of 7.13 g (0.026 mol) of **4** and 8.93 g (0.113 mol) of freshly distilled pyridine in 90 ml dry DMSO under N_2 was added 32.3 g (0.062 mol) of 85% lead tetraacetate. An exothermic reaction was observed with considerable gas evolution. The temp. was maintained at 35° with ice bath cooling. After stirring 21 hr, the mixture was poured into 400 ml water and extracted five times with ether. The ether soln was dried over K_2CO_3, filtered, and the solvent removed on the steam bath by distillation through a vigreux column. The residue was chromatographed on silica gel eluting with hexane to afford 231 mg of white crystals, m.p. 80–84°. Sublimation of this material at 50° (0.02 mm) followed by recrystallization from EtOH provided X-ray quality crystals of **6**, m.p. 90–91°: NMR (CCl_4) δ 3.04 (s, 4H), 2.69 (two coincidental triplets, 8H, $\underline{J}$ = 7 Hz) and 2.01 ppm (quintet, 4H, $\underline{J}$ = 7 Hz); IR (KBr) 2985, 2967, 2930, 1458, 1434, and 1244 cm^{-1}; UV λ_{max} (isooctane) 278 (ϵ 278), 275 (ϵ 326), 268 (ϵ 402), 265 (ϵ 382) and 260 mμ (ϵ 346). (Found: C, 90.98; H, 8.73. Calc. for $C_{14}H_{16}$: C, 91.25; H, 8.75%).

Analysis by vpc (8 ft × 0.25 in 10% Carbowax 20 M on Chromsorb W 60/80 mesh at 180°) of an earlier run showed a second volatile peak at longer retention time than **3**. This material was isolated by preparative vpc and tentatively identified as **5**, the dihydroprecursor to **6**: *m/e* 186.

2. *Crystallography*

A clear, lozenge-shaped crystal of approximate dimensions 0.30 × 0.35 × 0.60 mm was mounted on the tip of a glass capillary in a random orientation with respect to the phi axis of the diffractometer. Space group determination and data collection were carried out at ambient room temp. (~23°C) on an Enraf-Nonius CAD-4 diffractometer using MoK_α radiation (MoK_α = 0.71073 Å) monochromatized with a dense graphite crystal set at a 5.8° take-off angle. Preliminary measurements showed the crystal symmetry to be 2/m, and from the systematic absences noted during a rapid, limited data collection the space group was shown to be either of the monoclinic space groups C2/c or Cc. Accurate centering of 15 reflections having $2\theta > 20°$ led to a least squares determination of unit cell parameters and an orientation matrix, which were subsequently used for data collection. Precise lattice constants were derived from a least squares refinement of 24 reflections having $2\theta > 30°$, the results of which may be found in Table 1, along with other facts pertaining to the data collection. Data were collected using the $\theta - 2\theta$ scan technique, with the variable scan rate determined by the following scheme, based on a 5° min^{-1} prescan:

(1) Reflections having less than 70 net counts were classified as unobserved ($I_{net} = I_{Tot} - 2\Sigma I_{BG}$).

(2) Reflections having $70 \leq I_{net} < 3000$ counts were re-measured at a new speed estimated to yield $I_{net} \approx 3000$, with a maximum allowable scan time of 10 min.

(3) Reflections having $I_{net} \geq 3000$ were accepted without additional scanning.

As a check of electronic reliability and crystal stability, two standards were measured every 30 reflections. Both standards had decayed to 40% of their initial intensities at the conclusion of data collection, indicating a serious crystal decomposition. Additionally, a third reflection was monitored every 50 reflections to initiate automatic recentering and redetermination of the orientation matrix if any angle changed by more than 0.08°. No re-centering occurred throughout the data collection.

A total of 1482 independent reflections were collected, comprising the quadrant of reciprocal space where each of h and k is non-negative, and l assumes all values. The data were collected from 4.0° to 45° 2θ. A total of 833 reflections having $I > 3\sigma(I)$ were classified as "observed", with the remaining 649 being termed "less-thans". Standard deviations in the intensities, $\sigma(I)$,

Table 1.

Crystal Data:

$C_{14}H_{16}$

Monoclinic, C2/c

a = 17.516 (2), b = 5.466 (1), c = 23.431 (5) Å

β = 110.75 (2)°

Volume = 2097 Å^3

Z = 8 ρ = 1.17 g cm^{-3}

Data collection information:

Enraf-Nonius CAD-4 diffractometer

MoK_α radiation (graphite monochromatized, $2\theta_m$ = 12.13°)

Crystal to source = 216 mm

Crystal to detector = 173 mm

θ-2θ scan method, bisecting position

Scan range = 1.90 + 0.70 tan θ (θ = calculated peak center)

Backgrounds collected at 25% of range further out on either end of scan

Width of variable aperture 5.20 + 2.11 tan θ mm

Pulse-height analyzer set to obtain 95% of MoK_α peak

Data collection range: 4.0° < 2θ < 45°

Scan speeds: 0.2 to 5.0 degrees per minute

were estimated as $\sigma(I)^2 = I_{Tot} + 2\Sigma I_{BG} + 0.02I_{net}$ Lorentz and polarization factors were applied in converting the intensities to structure amplitudes, $|F_0|$. No absorption correction was made; the monochromator crystal was assumed to be ideally imperfect. A decay correction was made based on analysis of the standards. The decay was linear with time, regardless of exposure hours—a fact which was discovered from a gap during which the X-rays were off due to an electrical storm. The assumption was made, however, that the decay was a function of exposure hours in order to facilitate calculations. Two separate decay curves were calculated (pre-storm and post-storm), and quadratic corrections were applied of the form:

$$K_{pre} = 1 - 0.0285\chi + 0.0034\chi^2$$

$$K_{post} = 1 - 0.0121\chi + 0.0000\chi^2$$

where χ = exposure hours. The maximum value of χ was 52.5 hr. Standard deviations in the structure amplitudes, $\sigma(|F_0|)$, were estimated as $\sigma(|F_0|) = \sigma(I)/(2Lp|F_0|)$.

Solution and refinement

The structure was solved by use of the multiple-entry tangent formula program MULTAN.[8] The E-map based on the starting phase set giving the highest absolute figure-of-merit (1.14) contained all 14 carbons of the molecule, with only two spurious peaks. Full-matrix least squares refinement of the carbon atoms with isotropic temperature factors and separate scale factors for the two data blocks converged at R = 12%. Conversion to anisotropic temperature factors was accomplished, and after several cycles of refinement the R value had only dropped 1%. At this point ideal hydrogen positions were calculated and entered into the refinement with isotropic temperature factors. The R value dropped to around 6%, at which time it was noted that four of the hydrogens had very high temperature factors, namely those four attached to C7 and C12, the two "flaps" of the cyclopentene "envelopes". Analysis of the thermal motion of the cyclopentene carbons indicated a possible disorder in the C7 and C12 positions, so an attempt was made to refine two separate, half-population atoms at each site. No appreciable difference in R value or ring parameters was noted following this procedure, even though the separate atoms did refine to different locations, one on each side of the planes of the cyclopentene rings, as would be expected with a disordered "flap". Since nothing seemed to be gained by this procedure, the two original, full-population atoms were resorted to.

In the final cycle of full-matrix least squares, 1221 contributing reflections were used (833 "observed" + 388 "less-thans" for which $|F_c| > |F_0|$). The 192 parameters varied were the two separate scale factors, all positional parameters, carbon anisotropic thermal parameters, and hydrogen isotropic temperature factors. The final agreement factors were:

$$R = (\Sigma||F_0| - |F_c||)/\Sigma|F_0| = 0.046$$

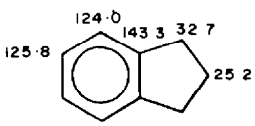
and

$$R_w = [(\Sigma w||F_0| - |F_c||^2)/\Sigma w|F_0|^2|]^{1/2} = 0.054$$

where the weights, w, were $\sigma(|F_0|)^{-2}$. Final shifts in all parameters were less than 0.15σ. The error-of-fit was 2.23 for 1221 observations and 192 variables. The atomic scattering factors for carbon were computed from numerical Hartree–Fock wave functions;[9] those for hydrogen of Stewart, Davidson and Simpson[10] were used. The XRAY72 system of programs of Stewart[11] was used. Final positional and thermal parameters are given in Tables 2 and 3. The estimated standard deviations were computed from the inverse matrix of the final full-matrix least squares cycle.

DISCUSSION

The ^{13}C NMR chemical shifts of the aromatic carbons of **6** and several related molecules are summarized in Table 4. Peak assignments for **6** are made by comparison with the values assigned to indan and benzocyclobutene by Günther *et al.*[12] For these two model compounds it will be noted that as the size of the fused ring decreases from 5 carbons to 4, the chemical shift of the bridgehead carbon moves to lower field while the chemical shift of the *ortho* carbon moves upfield. For compound **6**, the aromatic carbon which is contained in a 5-membered ring and ortho to the 4-membered ring should be the one which appears at highest field (δ 135.7). The two remaining peaks (δ 138.9 and δ 139.4) are too close to differentiate.



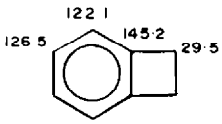


Table 2. Carbon fractional coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^3$)

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	8513(2)	5869(5)	4272(1)	50(2)	45(2)	47(2)	7(2)	17(1)	0(1)
C2	8978(2)	7897(6)	4705(1)	70(2)	48(2)	57(2)	5(2)	20(2)	- 9(2)
C3	9670(2)	7518(6)	4431(2)	55(2)	47(2)	61(2)	- 6(2)	13(2)	- 5(2)
C4	9123(2)	5540(5)	4032(1)	41(2)	43(2)	49(2)	0)2)	11(2)	2(1)
C5	9056(2)	3817(5)	3578(1)	42(2)	44(2)	48(2)	5(2)	15(1)	2(1)
C6	9619(2)	3143(7)	3242(2)	57(3)	68(3)	65(2)	2(2)	27(2)	- 8(2)
C7	9180(3)	1027(9)	2822(2)	78(3)	85(3)	81(3)	-10(2)	41(2)	-27(2)
C8	8358(2)	606(7)	2897(2)	64(3)	54(2)	59(2)	- 4(2)	16(2)	-12(2)
C9	8339(2)	2411(5)	3381(1)	45(2)	43(2)	45(2)	5(2)	12(1)	0(1)
C10	7731(2)	2736(5)	3623(1)	39(2)	44(2)	49(2)	- 1(2)	8(1)	8(1)
C11	6928(2)	1370(7)	3466(2)	51(2)	59(3)	75(2)	- 7(2)	18(2)	8(2)
C12	6562(3)	2294(11)	3924(3)	66(3)	134(5)	134(4)	-34(3)	53(3)	-39(3)
C13	7046(2)	4522(8)	4248(2)	64(3)	71(3)	80(3)	10(2)	38(2)	12(2)
C14	7799(2)	4507(6)	4076(1)	40(2)	52(2)	54(2)	8(2)	17(1)	11(2)

The chemical shift differences observed by Günther, as well as those which we observe for bis-[1a] and tris-annelated benzenes, are all consistent with a rehybridization argument put forth by Streitweiser in which he claims that for the bridgehead carbons of strained benzocycloalkenes "the atomic orbitals used to construct the strained ring have higher p-character. Hence, the remaining orbital has higher s-character. The *ortho*-carbon is thus bound to an orbital of higher electronegativity."[13] Application of this theory to dicyclopentenobenzocyclobutene (**6**) would result in the situation illustrated in Fig. 1, where the bridging bonds (C1–C4, C5–C9, and C10–C14) should have higher p-character and thus be longer than the adjacent bonds (C1–C14, C4–C5, and C9–C10) which are higher in s-character. This argument differs from the Mills–Nixon proposal in that it involves only the σ-framework of the benzene ring while earlier localization theories concentrated on the π-framework. Nevertheless, both theories predict bond alternation such that the shorter benzene bonds should be exocyclic to the small fused rings.[14]

Table 3. Fractional coordinates ($\times 10^3$) and isotropic temperature factors ($\times 10^2$) for the hydrogen atoms

Atom	X	Y	Z	U
H2A	872(2)	953(6)	464(1)	7(1)
H2B	915(2)	746(5)	519(1)	8(1)
H3A	977(2)	893(5)	422(1)	6(1)
H3B	1023(2)	698(5)	473(1)	6(1)
H6A	968(2)	454(7)	296(2)	11(1)
H6B	1015(2)	273(6)	351(1)	8(1)
H7A	915(2)	130(7)	242(2)	11(1)
H7B	953(3)	- 48(10)	294(2)	17(2)
H8A	790(2)	90(5)	251(1)	7(1)
H8B	829(2)	-108(7)	302(1)	9(1)
H11A	654(2)	164(6)	300(1)	10(1)
H11B	701(2)	- 42(7)	349(1)	9(1)
H12A	605(3)	235(8)	381(2)	12(2)
H12B	677(5)	97(14)	442(4)	35(4)
H13A	675(2)	599(7)	413(2)	10(1)
H13B	720(2)	445(6)	471(1)	8(1)

Intramolecular bond distances and angles for dicyclopentenobenzocyclobutene (**6**) are given in Table 5 and 6, according to the atom numbering scheme of Fig. 2. Considering the estimated bond length standard deviations, it may be concluded that there is no significant double bond alternation in the central ring of **6**. In fact, the bond lengths of the benzene ring are essentially identical with the accepted dimensions of benzene itself (1.39 Å). A similar observation was made for tricyclopentenobenzene (**7**), where the bonds endocyclic to the

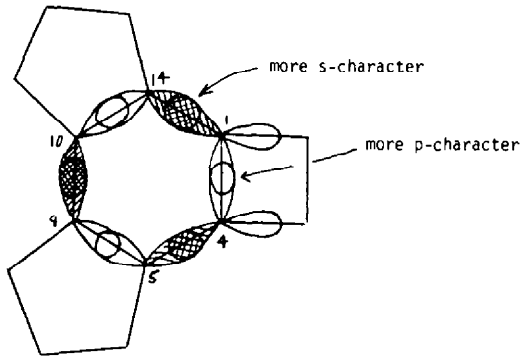
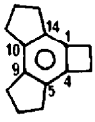
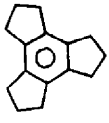
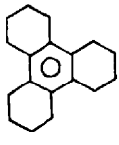
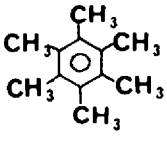
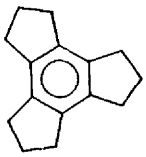


Fig. 1.

Table 4. Aromatic ^{13}C NMR of some tris-annelated benzenes. ^{13}C chemical shifts

	C-1/4	C-5/14	C-9/10
	138.9/139.4	135.7	138.9/139.4
	137.5		
	132.5		
	131.9		

fused rings (average length = 1.392 ± 0.016 Å) are essentially equal in length to those exocyclic to the fused rings (average length = 1.375 ± 0.014 Å).[15]



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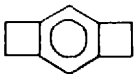

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In the case of benzo[1,2:4,5]-dicyclobutene (**8**), the bridging bonds (C1–C2 and C4–C5) are found to be 1.36 Å while the remaining bonds in the 6-membered ring equal 1.39 Å.[16] Again the esd's for this determination allow for little distinction between these measured values.

With regard to bond angles, tricyclopentenobenzene shows the central ring to be very regular, with internal angles equal to *ca.* 120° as would be expected for a symmetrical, planar system.[15] On the other hand, the para-bis-annelated molecule **8** shows significant angular distortion, with the bridgehead internal angles expanded to 126° and the remaining angles at C3 and C6 compressed to 106°.[16] Dicyclopentenobenzocyclobutene (**6**) shows intermediate behavior, with slight angular expansions at C1, C4, C9 and C10 and small angular compressions at C5 and C14. It should be noted that the results of determinations for **7** and **8** are highly questionable since film methods were used, hydrogens were not located or refined, and in the case of **8** the crystals examined were admittedly of "poor quality".

When the additional constraint of potential antiaromaticity is imposed on the 4-membered ring as in biphenylene (**9**), significant bond alternation does result. For this molecule a very accurate X-ray analysis indicates lengthening of the bridging bonds accompanied by a shortening of those benzene bonds exocyclic to the small

Table 5. Intramolecular bond distances (Å)

C1-C2	1.53(1)	C2-H2A	0.99(3)
C1-C4	1.39(1)	C2-H2B	1.09(3)
C1-C14	1.39(1)	C3-H3A	0.97(3)
C2-C3	1.57(1)	C3-H3B	1.02(3)
C3-C4	1.52(1)	C6-H6A	1.05(4)
C4-C5	1.39(1)	C6-H6B	0.94(3)
C5-C6	1.51(1)	C7-H7A	0.95(4)
C5-C9	1.40(1)	C7-H7B	1.01(5)
C6-C7	1.54(1)	C8-H8A	1.00(3)
C7-C8	1.53(1)	C8-H8B	0.99(4)
C8-C9	1.51(1)	C11-H11A	1.08(3)
C9-C10	1.38(1)	C11-H11B	0.99(4)
C10-C11	1.52(1)	C12-H12A	0.85(5)
C10-C14	1.41(1)	C12-H12B	1.31(9)
C11-C12	1.52(1)	C13-H13A	0.95(4)
C12-C13	1.52(1)	C13-H13B	1.02(3)
C13-C14	1.51(1)		

Table 6. Intramolecular bond angles (Å)

(For hydrogens, only the range of angles involved is given)			
C4-C1-C2	93.3(1)	C7-C8-C9	105.0(3)
C14-C1-C2	144.6(3)	C8-C9-C10	128.0(3)
C14-C1-C4	122.1(3)	C8-C9-C5	110.5(3)
C1-C2-C3	86.5(3)	C5-C9-C10	121.5(3)
C2-C3-C4	86.3(3)	C9-C10-C11	128.3(3)
C3-C4-C5	144.2(3)	C9-C10-C14	121.6(3)
C3-C4-C1	93.8(2)	C11-C10-C14	110.1(3)
C1-C4-C5	122.0(3)	C10-C11-C12	104.6(3)
C4-C5-C6	132.0(3)	C11-C12-C13	108.6(5)
C4-C5-C9	116.4(3)	C12-C13-C14	104.3(4)
C6-C5-C9	111.6(3)	C13-C14-C10	110.9(3)
C5-C6-C7	104.3(3)	C13-C14-C1	132.8(3)
C6-C7-C8	108.5(4)	C10-C14-C1	116.3(3)
C2-H	107-116(2)	C8-H	107-113(2)
C3-H	106-117(2)	C11-H	104-114(2)
C6-H	106-113(2)	C12-H	94-118(5)
C7-H	102-115(4)	C13-H	104-113(3)

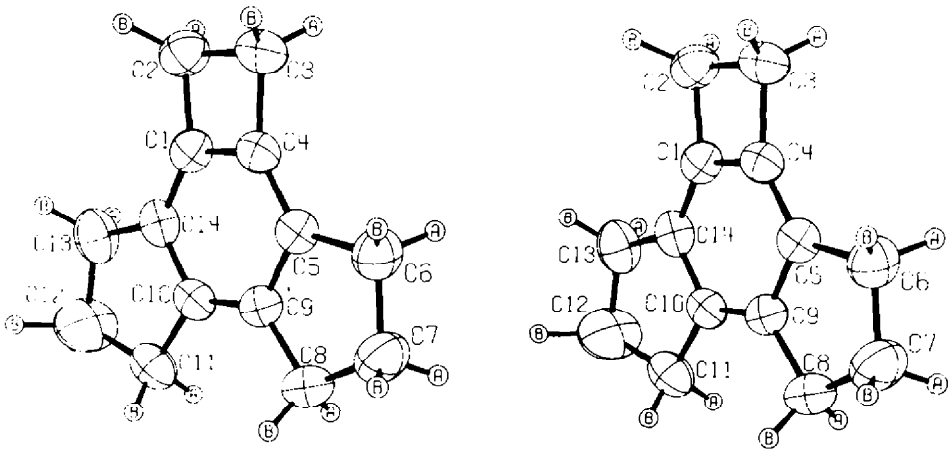
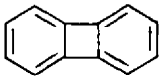
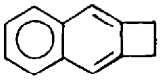


Fig. 2. Stereoscopic atom labelling scheme; 50% equiprobability ellipsoids.

ring.[17] Bond angle distortions are also in line with observations for compounds **6** and **8**.



9



10

The cyclobutene fragment of **6** compares well with the analogous portion of naphtho[b]cyclobutene (**10**).[18] The bond lengths and internal angles of the small ring are virtually the same, with the exception of the shared bond, which is found to be longer in the naphthalene derivative (1.407 Å). This result is to be expected from a simple analysis of the resonance contributors to **10**. In both cases (**6** and **10**), however, the internal cyclobutene bond lengths are substantially greater than the value of 1.33 Å determined by gas phase electron diffraction for the double bond of cyclobutene.[19]

Analysis of the cyclopentene rings of **6** is more difficult since each seems to be disordered. The disorder would appear to be a dynamic thermal one rather than a simple static type, as evidenced by the thermal ellipsoid shapes of C11, C13, C8 and to a lesser extent C6. As the "flaps" of the cyclopentene "envelopes" (C7 and C12) shift from one side of the benzene plane to the other, the adjacent carbons move laterally out of the way as the "flap" passes through the plane. Since only a single atom was refined at each position, the effects of the liberation of thermal disorder are manifested in a shortening of the bonds to C7 and C12, caused by the positioning of the equiprobability ellipsoid center inside the density arc.[20] Analyses of bond distances and ellipsoid shapes indicate a more pronounced disorder in the C12 ring. This is also confirmed by a planarity analysis of the molecule. The out-of-plane distances for all C atoms are given in Table 7, based on the best least squares plane through the six benzenoid atoms.

In conclusion, it appears that dicyclopentenobenzocy-

Table 7. Distances out of benzene plane (Å)*

**C1	0.002	C8	0.012
C2	0.004	**C9	0.000
C3	0.004	**C10	0.005
**C4	0.003	C11	0.022
**C5	-0.004	C12	0.185
C6	-0.024	C13	-0.032
C7	0.034	**C14	-0.006

*The standard deviation from the plane of the six atoms defining the plane is 0.004 Å.

**Atoms defining the plane.

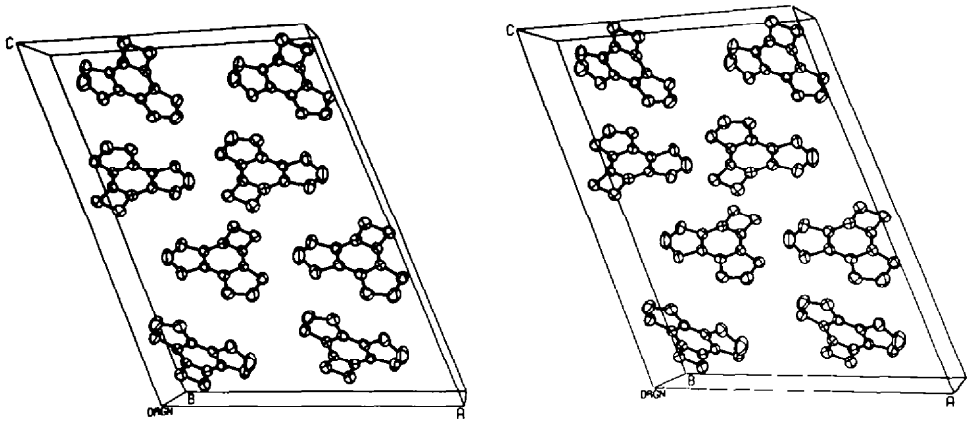


Fig. 3. Contents of the unit cell as viewed down the *b*-axis.

clobutene (**6**) does not exhibit any significant bond alternation in the central ring; although at room temperature the effects of thermal disorder and crystal decay might prevent an accurate enough determination to reveal such an effect. Earlier arguments for bond alternation based on π-framework effects as elaborated by Mills and Nixon, as well as σ-framework distortions based on benzenoid carbon rehybridizations are therefore unsubstantiated. Low temperature X-ray determinations of the structures of **6**, **7** and **8** would presumably result in more accurate data (lower esd's) which would allow definite limits to be set upon the actual geometric distortions imposed by the fusion of a 4- or 5-membered ring to the benzene nucleus.

A stereoscopic packing diagram of **6** is shown in Fig. 3. No unusually close intermolecular contacts were noted.

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