

THE MOLECULAR STRUCTURE OF HEPTAPHENYL-TETRARADIALENE

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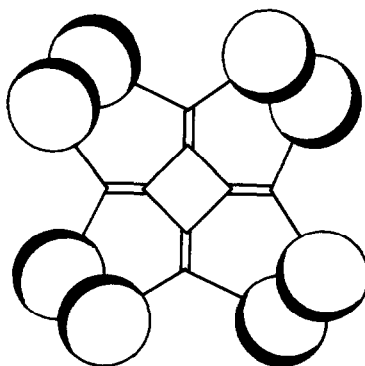
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Summary: It was found by X-ray structural study that the title radialene is puckered and its seven phenyl groups are not arranged regularly.

Tetraradialene (tetramethylenecyclobutane) has been of interest for its unique π -electron system and ring strain.^{1,2} We are interested in screw-shaped tetraradialenes such as A . When the eight wings of A are large enough to prevent flipping, A will become a screw-shaped molecule and hence chiral. When the wings are aromatic rings, electronic interactions through the wings will become possible, and then a new conjugated system can be obtained. In view of these interests, we studied the molecular structure of the title radialene (A).¹



A

As shown in Figure 1, the bond lengths in the four-membered ring are normal for the single bond between sp^2 hybridized carbons.³ The exo-methylene bond lengths are also normal, but a little longer than those of the corresponding bonds of octachlorotetraradialene.⁴

The quite large deviation of atoms C(1), C(2), C(3), and C(4) from the "4-atom" plane⁵ (Table 1) shows that the four-membered ring is puckered. The data in the Table also show non-planarity of the "8-atom" group.⁵ The puckered structure of the "4-atom" and "8-atom" groups can also be estimated by the torsion angles (Table 2). Two torsion angles of exo-exo bonds 5-1-2-6⁵ (-54.6°) and 6-2-3-7 (41.7°) are much larger than those of 7-3-4-8 (-18.1°) and 8-4-1-5 (27.7°). This is probably due to the less hindered circumstance around the hydrogen which is bonded to C(5).

atom	deviation (Å) from	
	"4-atom"	"8-atom"
C(1)	0.090	-0.066
C(2)	-0.090	0.014
C(3)	0.088	-0.116
C(4)	-0.088	0.161
C(5)	0.579	-0.518
C(6)	-0.699	0.535
C(7)	0.403	-0.470
C(8)	-0.290	0.460

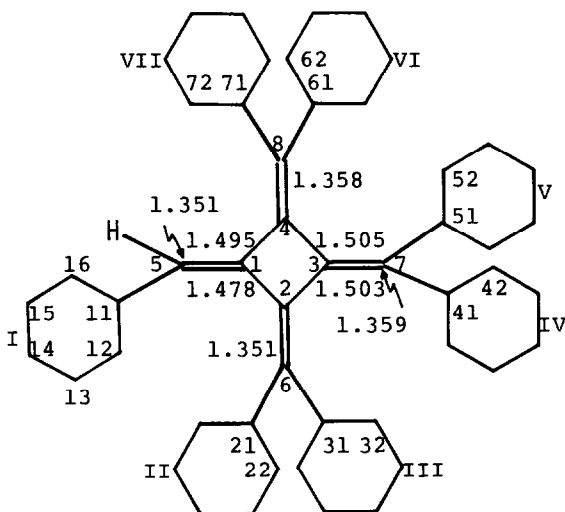


Figure 1. Numbering of atoms and bond lengths of \downarrow

ring-ring	angle($^\circ$)	exo-exo	angle($^\circ$)	ring-exo	angle($^\circ$)	ring-exo	angle($^\circ$)
4-1-2-3	-13.7	5-1-2-6	-54.6	5-1-2-3	149.6	7-3-4-1	160.4
1-2-3-4	13.6	6-2-3-7	41.7	4-1-2-6	142.1	2-3-4-8	168.1
2-3-4-1	-13.4	7-3-4-8	-18.1	6-2-3-4	-143.5	8-4-1-2	-167.6
3-4-1-2	13.7	8-4-1-5	27.7	1-2-3-7	-161.2	3-4-1-5	-151.0

The seven phenyl rings are not arranged regularly as can be deduced by the data shown in Table 3 and the following data of the angle between the adjoining phenyl rings; Ph(I)-Ph(II) 43.9°, Ph(II)-Ph(III) 66.3°, Ph(III)-Ph(IV) 8.3°, Ph(IV)-Ph(V) 59.5°, Ph(V)-Ph(VI) 25.1°, Ph(VI)-Ph(VII) 73.2°. An ORTEP stereoscopic view of $\frac{1}{\lambda}$ is shown in Figure 2. The phenyl rings which are arranged most parallel to each other are Ph(III) and Ph(IV). The next ones are Ph(V) and Ph(VI). Therefore, the three single NMR signals of 10H integral each of $\frac{1}{\lambda}$ can be assigned as follows: the most shielded signal (δ 6.78) is due to Ph(III) and Ph(IV), the next one (δ 6.87) is due to Ph(V) and Ph(VI), and the most less shielded one (δ 6.92) is due to Ph(I) and Ph(II). Study of molecular models of $\frac{1}{\lambda}$ shows the absence of any additional space for insertion of the 8th Ph group. This agrees with the formation of 1,3-bis(diphenylvinylidene)-2,2,4,4-tetraphenylcyclobutane instead of the octaphenyl-substituted tetradialene by photochemical dimerization of tetraphenylbutatriene,⁷ even though octachlorotetradialene is easily obtained by thermal dimerization of tetrachlorobutatriene.⁸

Table 3. Torsion angles showing rotation of phenyl rings

	angle(°)
12-11-5-1	-20.1
22-21-6-2	144.5
32-31-6-2	69.6
42-41-7-3	-145.7
52-51-7-3	45.0
62-61-8-4	-144.2
72-71-8-4	56.6

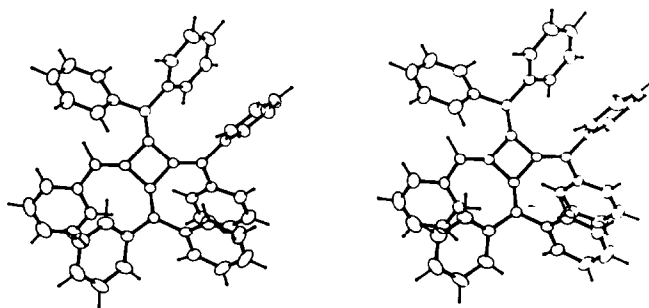


Figure 2. ORTEP Stereoscopic view of $\frac{1}{\lambda}$

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3. Crystals of λ are triclinic; space group $P\bar{1}$; $a=12.176(3)$, $b=14.039(4)$, $c=12.090(3)\text{\AA}$; $\alpha=102.66(2)$, $\beta=116.44(1)$, $\gamma=85.12(1)^\circ$; $Z=2$; $M=636.84$; $\rho_c=1.171\text{ g cm}^{-3}$. Lattice dimensions were determined using a Picker FACS-I automatic diffractometer and $\text{MoK}\alpha_1$ ($\lambda=0.70926\text{\AA}$) radiation. Intensity data were measured using $\text{MoK}\alpha$ radiation ($2\theta_{\text{max}}=50^\circ$) yielding 6403 total data, and based on $I > 2\sigma(I)$, 2717 observed data. The final R value was 0.056. The final difference electron density map showed densities ranging from 0.46 to $-0.42\text{ e}^- \text{\AA}^{-3}$. Tables of the atomic coordinates, bond distances, bond angles, thermal parameters, all with standard deviation (11pp) are available or request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. A copy of the structure factor table (24pp) is deposited with the British Library, Lending Division.
4. F. P. van Remoortere and F. P. Boer, *J. Am. Chem. Soc.*, 92, 3355 (1970).
5. The "4-atom" and "8-atom" are least-squares planes which calculated for the four-atoms C(1)-C(4) and the eight atoms C(1)-C(8), respectively.
6. Angle 5-1-2-6, for example, is defined as that between the two planes formed by three carbons each C(5)-C(1)-C(2) and C(1)-C(2)-C(6).
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