

## 82. Structure of Hexaethylidenecyclohexane (Hexamethyl-[6]radialene) by X-ray Analysis

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(6. II. 75)

**Summary.** The crystal structure of the title compound (triclinic,  $a = 7.877$ ,  $b = 7.210$ ,  $c = 7.891$  Å,  $\alpha = 105.56$ ,  $\beta = 116.25$ ,  $\gamma = 79.84^\circ$ , space group  $P\bar{1}$ ,  $Z = 1$ ) has been determined by X-ray analysis. The molecule has effective  $S_6(3)$  symmetry, and the conformation of the six-membered ring is similar to that of cyclohexane.

Hexaethylidenecyclohexane (hexamethyl-[6]-radialene) was prepared several years ago and some of its properties have been described [1]. X-ray analysis revealed then [2] that the crystals had a monomolecular triclinic cell and suggested the likely molecular conformation, but the analysis was not carried past the preliminary stages. We have now taken up the problem again and report our results here.

**Crystal Data.** - Hexaethylidenecyclohexane,  $C_{18}H_{24}$ , M. W. 240.4, m.p.  $134^\circ$ , triclinic,  $a = 7.877$ ,  $b = 7.210$ ,  $c = 7.891$  Å,  $\alpha = 105.56$ ,  $\beta = 116.25$ ,  $\gamma = 79.84^\circ$ ,  $V = 386.3$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.033$ ,  $D_m = 1.00$ , space group  $P\bar{1}$  (from structure analysis). These data supersede those cited in the earlier report [1].

**Experimental.** - A small amount of material left over from the earlier investigation yielded colourless prisms elongated along [100] on sublimation at  $100^\circ$ . Crystals for X-ray analysis were sealed in thin-walled glass capillaries. Rough cell dimensions were obtained from rotation, Weissenberg and precession photographs, more accurate values by least-squares analysis of Bragg angles for 13 reflections in the range  $\theta = 9-12^\circ$ , measured with a Hilger-Watts Y290 diffractometer using  $MoK\alpha$  radiation ( $\lambda = 0.71069$  Å) monochromatized by reflection from graphite.

Intensity data were collected out to  $\theta = 25^\circ$  ( $\theta - 2\theta$  scan, 70 measurement steps of 1 second at  $0.01^\circ$  intervals, 17.5 second stationary background counts at beginning and end of each scan). Out of 1363 independent reflections measured, 1168 (86%) gave counts significantly ( $1\sigma$ ) above background. The remaining 195 reflections were regarded as unobserved but were included in the refinement if  $|F_o| > |F_c|$ .

**Structure Analysis and Refinement.** - The distribution of  $E$ -values indicated that the structure is centrosymmetric, space group  $P\bar{1}$ . The structure was solved by direct methods using 198 reflections with  $|E| > 1.4$  as input to program MULTAN [3]. As expected, the 'best' solution (highest figure of merit and lowest residual) was that with all signs positive, but an  $E$ -map based on the second best solution revealed the positions of all nine carbon atoms in the asymmetric unit.

The structure was refined by full-matrix least-squares analysis, the quantity minimized being  $\sum w (F_o - F_c)^2$  with  $w$  taken as the reciprocal of the variance of  $F_o$ , as estimated from counting statistics. With only carbon atoms included in the model structure, convergence was reached at  $R = 0.139$  (isotropic thermal parameters) and  $R = 0.101$  (anisotropic thermal parameters). At this stage a  $(F_o - F_c)$ -map showed

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peaks corresponding to all the hydrogen atoms in the molecule. With hydrogens included in the model structure convergence was reached at  $R = 0.045$  for the 1168 observed reflections. Scattering curves were taken from International Tables of X-ray Crystallography [4].

Table 1. *Positional coordinates ( $\times 10^4$ ) for carbon atoms*

Atom	x	y	z
C(1)	-1361(2)	1572(2)	-0717(2)
C(2)	-0963(2)	1157(2)	1184(2)
C(3)	0920(2)	0109(2)	2083(2)
C(4)	-1955(3)	3344(3)	-1057(3)
C(5)	-2272(4)	4046(4)	-2806(3)
C(6)	-2182(3)	1553(2)	2003(3)
C(7)	-4167(3)	2445(4)	1235(4)
C(8)	2174(3)	0656(3)	3903(2)
C(9)	2034(4)	2392(3)	5396(3)

*Vibration tensor components (in  $\text{\AA}^2 \times 10^4$ ) for carbon atoms*

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	417(9)	474(9)	417(9)	060(7)	182(7)	115(7)
C(2)	487(9)	382(8)	404(9)	024(7)	200(7)	075(7)
C(3)	473(9)	444(9)	392(9)	018(7)	193(7)	128(7)
C(4)	806(11)	520(10)	508(10)	121(8)	279(9)	167(8)
C(5)	826(16)	641(13)	657(13)	173(12)	382(13)	307(11)
C(6)	595(11)	486(10)	466(10)	041(8)	270(9)	080(8)
C(7)	583(12)	671(14)	730(15)	094(10)	365(11)	094(11)
C(8)	522(11)	561(10)	453(10)	011(8)	174(8)	138(8)
C(9)	789(18)	623(12)	457(11)	-101(11)	206(11)	044(9)

*Positional coordinates ( $\times 10^3$ ) and isotropic vibration parameters ( $\text{\AA}^2 \times 10^4$ ) for hydrogen atoms*

Atom	x	y	z	U
H(4)	-213(3)	435(3)	001(3)	543(49)
H(6)	-178(2)	118(2)	319(3)	522(45)
H(8)	337(3)	-011(3)	431(3)	574(48)
H(51)	-368(4)	405(4)	-372(4)	1156(87)
H(52)	-165(3)	323(3)	-356(3)	852(70)
H(53)	-184(4)	537(4)	-241(4)	1127(99)
H(71)	-467(4)	239(4)	-014(4)	994(80)
H(72)	-500(4)	178(4)	147(3)	994(77)
H(73)	-420(3)	384(4)	186(4)	1027(83)
H(91)	102(4)	336(3)	486(3)	895(72)
H(92)	325(4)	299(4)	608(4)	1090(82)
H(93)	175(3)	205(3)	637(4)	928(77)

Standard deviations are given in brackets.

**Results.** - Final atomic coordinates are listed in Table 1, together with vibration tensor components for carbon atoms and isotropic  $U$ -values (mean-square vibration amplitudes) for the hydrogens. Bond lengths and angles are given in Table 2, torsion angles in Table 3.

**Discussion.** - The dimensions given in Tables 1 and 2 show that the hexamethyl-[6]-radialene molecule has effective  $S_6(\bar{3})$  symmetry in the crystal, although only a centre of symmetry is required by the space group. The 12 inner atoms, the six atoms of the ring with the six atoms directly bonded to them, deviate slightly but

Table 2. Bond lengths (Å) and angles (degrees)

C(1)-C(4)	1.337(3)	C(4)-H(4)	1.00(2)
C(2)-C(6)	1.332(3)	C(6)-H(6)	0.95(2)
C(3)-C(8)	1.332(2)	C(8)-H(8)	0.97(2)
C(1)-C(2)	1.493(3)	C(5)-H(51)	1.02(3)
C(2)-C(3)	1.495(2)	C(5)-H(52)	0.95(3)
C(3)-C(1*)	1.495(2)	C(5)-H(53)	0.99(3)
C(4)-C(5)	1.499(4)	C(7)-H(71)	0.97(3)
C(6)-C(7)	1.497(3)	C(7)-H(72)	0.98(3)
C(8)-C(9)	1.497(3)	C(7)-H(73)	1.00(3)
		C(9)-H(91)	0.98(2)
		C(9)-H(92)	0.98(3)
		C(9)-H(93)	0.99(3)
C(2)-C(1)-C(3*)	114.1(1)	C(4)-C(5)-H(51)	109.7(21)
C(1)-C(2)-C(3)	114.2(2)	C(4)-C(5)-H(52)	113.9(16)
C(2)-C(3)-C(1*)	114.1(1)	C(4)-C(5)-H(53)	109.9(19)
C(1)-C(4)-C(5)	127.9(2)	H(51)-C(5)-H(52)	104.8(21)
C(2)-C(6)-C(7)	128.1(2)	H(51)-C(5)-H(53)	109.6(22)
C(3)-C(8)-C(9)	128.3(2)	H(52)-C(5)-H(53)	108.7(27)
C(2)-C(1)-C(4)	120.9(2)	C(6)-C(7)-H(71)	111.8(17)
C(3)-C(2)-C(6)	121.0(2)	C(6)-C(7)-H(72)	110.2(14)
C(1*)-C(3)-C(8)	121.4(2)	C(6)-C(7)-H(73)	110.4(13)
C(3*)-C(1)-C(4)	124.9(2)	H(71)-C(7)-H(72)	109.7(22)
C(1)-C(2)-C(6)	124.7(2)	H(71)-C(7)-H(73)	106.2(22)
C(2)-C(3)-C(8)	124.3(2)	H(72)-C(7)-H(73)	109.4(25)
C(5)-C(4)-H(4)	115.3(13)	C(8)-C(9)-H(91)	113.6(13)
C(7)-C(6)-H(6)	114.8(12)	C(8)-C(9)-H(92)	109.2(17)
C(9)-C(8)-H(8)	114.7(10)	C(8)-C(9)-H(93)	111.7(13)
C(1)-C(4)-H(4)	116.7(12)	H(91)-C(9)-H(92)	109.1(22)
C(2)-C(6)-H(6)	117.0(12)	H(91)-C(9)-H(93)	105.5(24)
C(3)-C(8)-H(8)	116.9(10)	H(92)-C(9)-H(93)	107.4(23)

\*) Related by centre of symmetry.

Table 3. Torsion angles (in degrees)

C(3*)-C(1)-C(2)-C(3)	46.2	C(2)-C(1)-C(4)-C(5)	174.8
C(1)-C(2)-C(3)-C(1*)	-46.2	C(3)-C(2)-C(6)-C(7)	-174.8
C(2)-C(3)-C(1*)-C(2*)	46.2	C(1*)-C(3)-C(8)-C(9)	174.0
C(3*)-C(1)-C(4)-C(5)	-1.2	C(4)-C(1)-C(2)-C(6)	53.8
C(1)-C(2)-C(6)-C(7)	1.0	C(6)-C(2)-C(3)-C(8)	-54.0
C(2)-C(3)-C(8)-C(9)	-1.8	C(8)-C(3)-C(1*)-C(4*)	53.8
C(2*)-C(3*)-C(1)-C(4)	130.0	C(3)-C(2)-C(1)-C(4)	-130.1
C(3*)-C(1)-C(2)-C(6)	-129.8	C(1*)-C(3)-C(2)-C(6)	130.0
C(1)-C(2)-C(3)-C(8)	129.8	C(2*)-C(1*)-C(3)-C(8)	-130.0

\*) Related by centre of symmetry.

significantly from  $D_{3d}(\bar{3}m)$  symmetry, as indicated by the comparison between the two sets of bond angles C(2)-C(1)-C(4), etc. (121.1°) and C(3\*)-C(1)-C(4), etc. (124.6°). A stereo-view of the molecule is shown in the Figure.

The geometry of the six-membered ring is similar to that of cyclohexane. The bonds are a little shorter (1.494 Å compared with 1.536 Å [5]) and the angles are a little greater (114.1° compared with 111.4°). Thus the changes brought about by

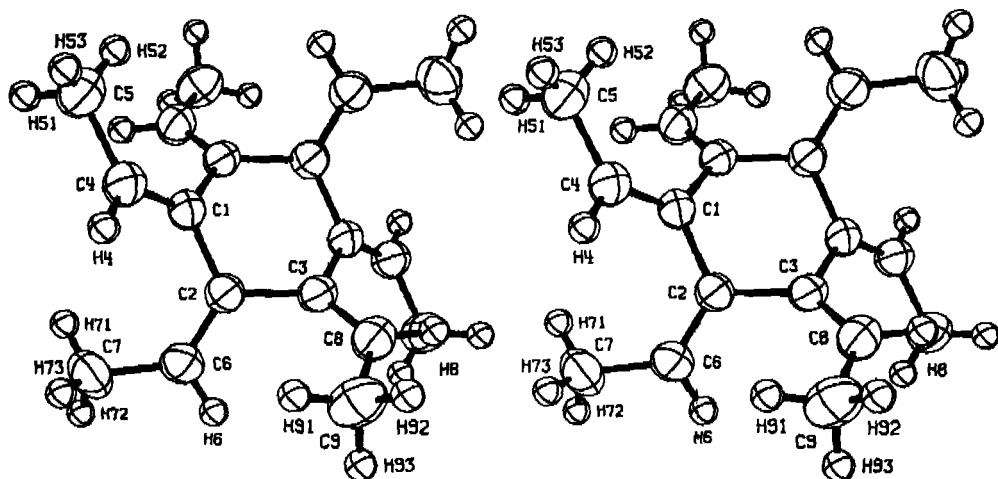


Fig. Stereoscopic view of the hexamethyl-[6]radialene molecule, showing atom numbering system

replacing the six tetrahedral carbon atoms of the cyclohexane ring by trigonal atoms are not very great. In particular, the ring is still strongly puckered with torsion angles of  $\pm 46.2^\circ$  (compared with  $54.9^\circ$  in cyclohexane), in contrast to models constructed with standard units with  $120^\circ$  bond angles. The C=C double bond distance is normal (1.334 Å) and the outer C-C bonds are only slightly longer than the inner ones (1.498 Å compared with 1.494 Å).

The distances given in Table 2 (and cited above) are uncorrected for thermal motion effects. The rigid-body approximation [6] reproduces the observed vibration tensors only tolerably well (Table 4), but attempts to improve the agreement by introducing some relatively simple types of internal motion [7] did not lead to significant improvement in the overall agreement. The results of the rigid-body

Table 4. Analysis of atomic vibration tensor in terms of rigid-body motion. Tensor components (standard deviations  $\times 10^4$  in brackets) and eigenvectors are referred to an orthogonal, molecular coordinate system (X, Y, Z) related to the crystal system (x, y, z) by the transformation shown.

			(Å) <sup>2</sup>	l	m	n	
T (Å <sup>2</sup> )	=	$\begin{bmatrix} 0.0375(13) & 0.0000(11) & 0.0011(13) \\ & 0.0389(13) & 0.0005(13) \\ & & 0.0480(19) \end{bmatrix}$	0.0482	-0.0980	-0.0197	0.9950	
			0.0389	-0.0507	0.9986	0.0148	
			0.0374	-0.9939	-0.0490	-0.0989	
			(rad) <sup>2</sup>				(deg) <sup>2</sup>
L (rad <sup>2</sup> )	=	$\begin{bmatrix} 0.0025(3) & 0.0011(2) & -0.0002(2) \\ & 0.0025(3) & 0.0008(2) \\ & & 0.0022(2) \end{bmatrix}$	0.0037	-0.6091	0.5624	0.5592	12.1
			0.0024	-0.7351	-0.1358	-0.6642	7.9
			0.0010	-0.2976	-0.8156	0.4962	3.3

$$\langle (\Delta U_{ij})^2 \rangle^{1/2} = 0.0035 \text{ Å}^2$$

$$\langle \sigma^2(U_{ij}) \rangle^{1/2} = 0.0011 \text{ Å}^2$$

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 7.8770 & 1.2723 & -3.4895 \\ & 7.0968 & -1.5253 \\ & & 6.9112 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

analysis suggest that the translational tensor is roughly isotropic, the librational tensor less so, but the mean-square librational amplitudes are not very great for a molecular crystal of this type. The corrections for the bond-length shortening effect of libration would vary from 0.002–0.005 Å (to be added to the values given in Table 1). Bond-angle corrections are mostly less than 0.1°.

With allowance for librational corrections, the inner bonds are 1.497 Å, the outer ones 1.501 Å, the double bonds 1.337 Å. Thus the outer bonds become almost equal in length to the C(sp<sup>2</sup>)-C(sp<sup>3</sup>) bonds in propene (1.506 Å) [8] whereas the inner ones are definitely longer than the C(sp<sup>2</sup>)-C(sp<sup>2</sup>) bonds in butadiene (1.465 Å) [9]. A better comparison would be with *cis,trans*-3,4-dimethylhexa-2,4-diene, for which an electron-diffraction study [10] gives C=C, 1.360 (10) Å, C-C, 1.462 (20) Å, C-CH<sub>3</sub>, 1.530 (10) Å with a torsion angle of 114° about the central bond.

With six ethylidene substituents attached to the ring the molecule is severely 'overcrowded'. Distances between pairs of non-bonded carbon atoms are shown in Table 5; those of the same chemical type are virtually equal, in keeping with the effective S<sub>6</sub> symmetry of the molecule, and those of the same connectivity type (e.g. 1, 4) do not vary by more than a few percent, in accord with the suggestion [11] that non-bonded carbon atoms can be regarded as sterically equivalent.

Table 5. Non-bonded C...C distances (in Å)

Type	1, 3-distances	Type	1, 4-distances
C(1)-C(8*)	2.463-2.464	C(1)-C(1*)	2.918-2.919
C(1)-C(3)	2.510-2.512	C(1)-C(7)	3.102-3.113
C(1)-C(6)	2.503-2.512	C(4)-C(6)	3.103-3.122
C(1)-C(5)	2.545-2.551		1, 5-distances
		C(4)-C(7)	3.245-3.262

The strain is also manifested in small (~0.01 Å) but significant out-of-plane deviations of the ring atoms. This is seen in the differences between corresponding pairs of *syn* torsion angles about the ring bonds (Table 3). The outer torsion angles are 7.6–7.8° larger than the inner ones, thus increasing the outer 1,4-distances at the expense of the inner ones. The twist angles round the ring bonds are, as a consequence, slightly smaller than the torsion angles (50° instead of 54°). Note that even if the six-membered ring were planar, the 1,4-distances in the ring would only increase to 2.99 Å; they would still be slightly shorter than the other two types of 1,4-distance.

The molecular packing shows no specially noteworthy features. With due allowance for the non-planarity of the hexamethyl-[6]-radialene molecule, its crystal structure can be regarded as a somewhat distorted version of the structures of hexamethylbenzene [12] or hexaethylbenzene [13].

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### 83. Nucleoside und Nucleotide. Teil 8. Synthese von Dinucleotiden mit Thymidin und 1-(2'-Desoxy- $\beta$ -D-ribofuranosyl)-2(1H)-pyridon als Bausteinen<sup>1)</sup>

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*Summary.* In order to investigate the stability of 1-(2'-deoxy- $\beta$ -D-ribofuranosyl)-2(1H)-pyridone ( $II_a$ , 3) under the conditions of oligonucleotide synthesis, the dinucleoside monophosphates (MeOTr) $II_a$ -T<sub>d</sub> (9) and  $II_a$ -T<sub>d</sub> (11), and the dinucleotides  $II_a$ -T<sub>d</sub>p (15) and p $II_a$ -T<sub>d</sub> (19) were prepared, using various procedures. The N-glycosidic bond between the deoxyribose and the 2(1H)-pyridone proved to be much more labile than the one in the naturally occurring nucleosides. It was partially cleaved in condensation reactions with TPS or MS, but no cleavage was observed when DCC was used. Similarly, the glycosidic linkage was attacked by hot 80% acetic acid, the usual reagent for the removal of a *p*-methoxytrityl group in thymidine oligonucleotides. Milder treatment with acetic acid/pyridine 7:3 at 100° removed this protecting group and left the N-glycoside intact. The compounds prepared were characterized by paper and thin layer chromatography as well as by enzymatic degradation.

**1. Einleitung.** – Im Rahmen unserer Untersuchungen von Nucleotidderivaten mit 2(1H)-Pyridon als Base haben wir verschiedene Dinucleosid-monophosphate und Dinucleotide hergestellt, die als Bausteine Thymidin (1) und 1-(2'-Desoxy- $\beta$ -D-ribofuranosyl)-2(1H)-pyridon ( $II_a$ , 3)<sup>2)</sup> [2] enthalten. Diese Arbeiten sollten Aufschluss vor allem darüber geben, wie sich dieses modifizierte Nucleosid (3) unter den Bedingungen der Oligonucleotid-Synthese (Einführung/Abspaltung von Schutzgruppen, Kondensationen, Phosphorylierungsreaktionen) verhält.

Zur Synthese von Dinucleosid-monophosphaten haben sich drei Methoden bewährt: (a) Kondensation eines Nucleosids mit einem Nucleosid-5'-phosphat [3]; (b) Kondensation eines Nucleosid-3'-phosphats mit einem Nucleosid [4]; und (c) Kondensation *via* die Triestermethode durch Umsatz eines Nucleosid-3'-( $\beta$ -cyanoäthylphosphats) mit einem Nucleosid [5]. Bei allen drei Verfahren müssen die Kom-

<sup>1)</sup> Teil 7, siehe [1].

<sup>2)</sup> Bzgl. Abkürzungen siehe [2].