BRÜNING, K.-H. (1963). Nicht veröffentlicht.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least Squares Program.* ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p.45. London: Pergamon Press.
DICKERSON, R. E. (1959). *Acta Cryst.* **12**, 610.
HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
HOFMANN, W. (1935). *Z. Kristallogr.* A, **92**, 161.
KANDLER, H. & PENN, W. (1965). *Änderungen im Programm ORFLS.* Deutsches Rechenzentrum, Darmstadt.
MACGILLAVRY, C. H., NIJVELD, H., DIERDORP, S. & KARSTEN, J. (1939). *Rec. Trav. chim. Pays-Bas*, **58**, 193.
MOH, G. H. & BERNDT, F. (1964). Neues *Jb. Miner. Mh.* (3), 94.
MOOTZ, D. & KUNZMANN, R. (1962). *Acta Cryst.* **15**, 913.
MOSBURG, S., ROSS, D.R., BETHKE, P.M. & TOULIN, P. (1961). *U. S. Geol. Surv. Profess. Papers* no. 444-C, 347.
OFTEDAL, I. (1928). *Z. physikal. Chem.* **134**, 301.
ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273
VOLYNSKI, I. S. & SEVRYUKOV, N. N. (1955). *J. gen. Chem. Moscow*, **25**, 2380.

Acta Cryst. (1967). **23**, 476

The Crystal Structure of *trans*-15,16-Diethyldihydropyrene

BY A. W. HANSON

Division of Pure Physics, National Research Council of Canada, Ottawa, Canada

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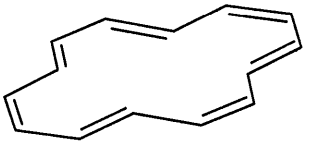
The crystal is monoclinic, $P2_1/c$. The cell constants at -160°C are $a=8{\cdot}276$, $b=11{\cdot}680$, $c=7{\cdot}345$ Å, $\beta=104{\cdot}7°$; $Z=2$, formula $C_{20}H_{20}$. The structure was deduced from a three-dimensional Patterson synthesis, and refined by block-diagonal least squares. The bond-length distribution in the peripheral 14-ring is characteristically aromatic. However, strain in the system is indicated by some departure from planarity of this ring, and by an abnormally long substituent bond.

Introduction

The title compound, $C_{20}H_{20}$ (I), can be regarded as a derivative of [14]annulene (II), the four 'internal' hydrogen atoms being replaced by a single n-hexane nucleus (III). (II) is aromatic (Sondheimer, 1964) and it is to be expected that aromatic character will be retained in the peripheral 14-ring of (I); in fact a ring current has been observed for the molecule (Boekelheide & Miyasaka, 1967). Several such compounds, bearing substituents within the cavities of their π-electron clouds, have been prepared by Professor Boekelheide and his associates (Phillips, Molyneux, Sturm & Boekelheide, 1967; Boekelheide & Phillips, 1963, 1967). The crystal structure of one of them, $C_{22}O_4H_{20}$ (IV), in which the internal substituent is somewhat smaller, has already been determined (Hanson, 1965). The present analysis was undertaken in order to confirm the aromatic character of the ring, and to observe the consequences of increasing the bulk of the internal substituent.



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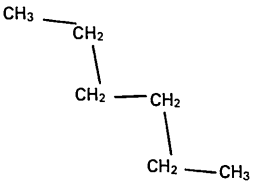

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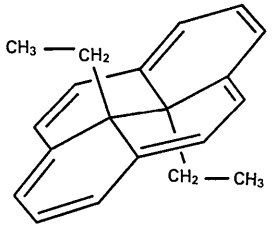
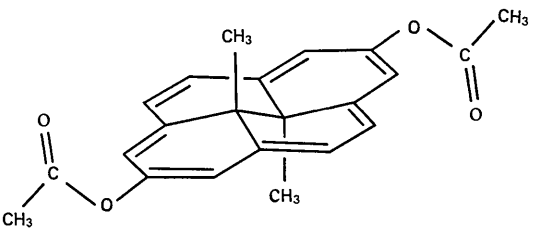


I



IV

Experimental

Crystal data at −160°C

Values in parentheses refer to measurements at room temperature.

Monoclinic
$a = 8{\cdot}276\ (8{\cdot}355) \pm 0{\cdot}004$ Å
$b = 11{\cdot}680\ (11{\cdot}812) \pm 0{\cdot}006$
$c = 7{\cdot}345\ (7{\cdot}460) \pm 0{\cdot}004$
$\beta = 104{\cdot}70\ (105{\cdot}50) \pm 0{\cdot}05°$
Assumed wavelengths: 1·54050 Å (Cu $K\alpha_1$); 1·54434 Å (Cu $K\alpha_2$)
$V = 686{\cdot}8\ (709{\cdot}4)$ Å^3
Formula $C_{20}H_{20}$ F.W. 260·4
$D_x = 1{\cdot}259\ (1{\cdot}219) \pm 0{\cdot}002$ g.cm^{-3}
$D_m = (1{\cdot}22) \pm 0{\cdot}01$ g.cm^{-3}
$Z = 2$
$\mu = 6{\cdot}4$ cm^{-1} (Cu $K\alpha$)
Space group $P2_1/c$ (from precession and Weissenberg photographs. Systematic absences: $h0l$ for l odd; $0k0$ for k odd.)
Molecular symmetry: centre.

The material supplied consisted of well-formed, deep green, opaque crystals. The invariable habit was the prism {011} modified by the pinacoid {100}. Occasionally the pinacoid {010} was present also. The specimen used was somewhat reduced by solvent action to a smooth solid of extreme dimensions 0·35 and 0·5 mm. The cell constants and relative intensities were measured on the General Electric XRD 5 spectrogoniometer and goniostat, using a scintillation counter. Copper $K\alpha$ radiation was used, and reasonable monochromatization was achieved by means of a $K\beta$ filter and a reverter (pulse-height analyser). The moving-crystal moving-counter technique was used (Furnas, 1957). Goniostat settings were precomputed, and set by hand. The specimen was maintained at the working temperature of about −160°C by immersion in a stream of cold gaseous nitrogen which was itself surrounded by an envelope of dry nitrogen at room temperature. As a precaution against thermal shocks the crystal was enclosed in a thin-walled fused-quartz tube. Of the 1539 accessible reflexions (those for which $2\theta \leq 165°$) significant counts were recorded for 1487. Absorption corrections were considered to be unnecessary, and were not made.

Structure determination

The crystal structure was readily deduced by inspection of the three-dimensional Patterson synthesis. It was refined by means of Fourier syntheses followed by block-diagonal least-squares analysis. At first Mair's (1963) least-squares program for the IBM 1620 computer was used. However, the 1620 computer became unavailable before completion of the project, and refinement was continued with a very similar program, written by the author in Fortran IV for use on the IBM System 360 computer. The quantity minimized is $\Sigma w(F_o - F_c)^2$. The program computes a 3×3 matrix for the position parameters and a 6×6 matrix (or 1×1 if the thermal motion is assumed to be isotropic) for the thermal parameters of each atom. The scale of observed structure amplitudes and the overall isotropic temperature factor are refined in a 2×2 matrix (Cruickshank, 1961). Schomaker's correction is applied to the shifts in the thermal parameters (Hodgson & Rollett, 1963). No convergence acceleration factors were applied. The weighting scheme used was $1/w = 1 + \{(I^{\frac{1}{2}} - 8)/13\}^2$ where I is the relative intensity, ranging from 1 to about 35,000.

The thermal motion was assumed to be isotropic for the hydrogen atoms (initially located from a difference synthesis) and anisotropic for the carbon atoms. The scattering factor curves of Freeman (1959) were used throughout.

During refinement some unacceptable discrepancies between F_o and F_c were observed. Very intense reflexions were found to have calculated structure factors considerably greater than the observed values, and a systematic extinction correction was applied in the manner described by Pinnock, Taylor & Lipson (1956). 93 reflexions were corrected; the greatest correction was about 80% of F_o, but exceeded 10% of F_o for only 17 reflexions. Of course, the weighting scheme used discriminates so strongly against the more intense reflexions that the correction can hardly affect the final parameters.

Further discrepancies were found at the other end of the intensity scale, where it was found that for 11 weak reflexions, F_o considerably exceeded F_c. These discrepancies are believed to result from double reflexion, a phenomenon convincingly demonstrated in a subsequent examination. These 11 reflexions were omitted in the final stages of refinement. One other weak reflexion whose intensity appeared to have been underestimated (most probably because of an erroneous goniostat setting) was omitted also. The omitted reflexions are identified in Table 4. It was felt that their inclusion might adversely affect the final parameters, but that their omission could not. In the last cycle no parameter shift exceeded 0·2 e.s.d.'s. The final parameters are given in Tables 1 and 2. It will be observed that the isotropic temperature factors of the hydrogen atoms are small and mostly negative. This is the typical result of using an inappropriate scattering-factor curve for bonded hydrogen atoms.

Thermal motion analysis

The thermal motion of the system has been analysed in terms of rigid-body vibrations, using the method of Cruickshank (1956). Details are given in Table 3. The hypothesis of rigid-body behaviour is reasonably well supported; the e.s.d. of observed U_{ij}'s is 0·0009 Å^2, compared with the mean value of 0·0005 Å^2 indicated by the least-squares refinement. The modes of motion are physically reasonable; the axes of *least* translation

Table 1. *Final parameters (and e.s.d.'s) of carbon atoms*

$\pm(x,y,z;\ x,\frac{1}{2}-y,\frac{1}{2}+z)$

T.F. $=\exp\{-2\pi^2(U_{11}a^{*2}h^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+U_{22}b^{*2}k^2+2U_{23}b^*c^*kl+U_{33}c^{*2}l^2)\}$

	x ($\times 10^5$)	y ($\times 10^5$)	z ($\times 10^5$)	U_{11} (Å$^2\times 10^4$)	U_{12} (Å$^2\times 10^4$)	U_{13} (Å$^2\times 10^4$)	U_{22} (Å$^2\times 10^4$)	U_{23} (Å$^2\times 10^4$)	U_{33} (Å$^2\times 10^4$)	B_1 (Å^2)	B_2 (Å^2)	B_3 (Å^2)
C(1)	22249	3460	−1822	101	27	22	109	36	140	0·55	0·96	1·29
	14	11	18	5	5	4	6	5	6			
C(2)	35387	10139	8359	104	7	17	143	52	185	0.76	0·94	1·80
	16	12	19	5	5	5	6	5	6			
C(3)	35033	15013	25640	146	−18	−30	128	12	182	0·81	1·00	2·10
	17	11	19	6	5	5	6	5	6			
C(4)	21122	13948	33055	186	10	−4	130	−10	124	0·86	1·02	1·78
	17	11	18	6	5	5	6	5	6			
C(5)	7318	7439	23994	151	28	8	110	15	98	0·62	0·94	1·39
	16	11	18	6	5	4	6	5	6			
C(6)	8491	−71	7430	102	6	15	108	0	93	0·70	0·83	0·91
	14	10	17	5	4	5	6	4	5			
C(7)	−7389	6821	30014	178	43	36	133	12	111	0·82	0·91	1·61
	17	11	18	6	5	5	6	5	6			
C(8)	−21383	864	19828	130	37	56	160	45	154	0·83	0·92	1·68
	17	11	18	6	5	5	6	5	6			
C(9)	12538	−12579	15172	120	16	18	114	18	122	0·72	1·05	1·10
	16	11	18	5	5	4	5	5	6			
C(10)	29282	−14133	29668	127	26	10	161	45	162	0·73	1·28	1·65
	16	12	19	6	5	5	6	5	6			

Table 2. *Final parameters (and e.s.d.'s) of hydrogen atoms*

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	B (Å^2)
H(2)	4495	1147	261	−0·31
	24	16	26	0·32
H(3)	4431	1974	3203	−0·02
	25	17	28	0·34
H(4)	2100	1787	4412	−0·14
	25	17	28	0·28
H(7)	−781	1048	4150	−0·62
	22	16	25	0·30
H(8)	−3105	−23	2515	0·01
	26	17	29	0·35
H(9a)	326	−1524	2047	−0·34
	24	17	27	0·32
H(9b)	1238	−1776	462	−0·57
	22	16	25	0·31
H(10a)	2998	−923	4080	−0·34
	24	17	27	0·32
H(10b)	3882	−1260	2431	−0·07
	25	17	28	0·35
H(10c)	3060	−2217	3348	0·13
	25	18	29	0·36

and of *greatest* libration lie quite close to the normal to the mean plane of the 14-ring. Appropriate bond-length corrections have been made by the method of Busing & Levy (1964), assuming all atoms to ride on the centre of symmetry. The corrections are very small and could safely have been ignored.

Assessment of results

The agreement between observed and calculated structure amplitudes (Table 4) is such that there can be no doubt of the essential correctness of the proposed structure. The agreement residual ($R=\Sigma\ ||F_o|-|F_c||/\Sigma\ |F_o|$) is 0·048, for observed reflexions only.

A three-dimensional difference synthesis reveals no unexpected features. Peaks reasonably attributable to bonding electrons occur at the mid-points of most of the carbon–carbon bonds, and for the longer bonds, these are as high as 0·4 e.Å^{-3}. Elsewhere the residual electron density stays between the limits $\pm$0·2 e.Å^{-3}.

Table 3. *Rigid-body thermal parameters*

$$T=\begin{pmatrix}108 & 17 & -8\\ & 99 & 14\\ & & 99\end{pmatrix}\times 10^{-4}\ \text{Å}^2 \qquad L=\begin{pmatrix}22 & -2 & 4\\ & 33 & -13\\ & & 19\end{pmatrix}\times 10^{-1}\ (^\circ)^2$$

$$\sigma(T)=\begin{pmatrix}4 & 3 & 3\\ & 5 & 3\\ & & 4\end{pmatrix}\times 10^{-4}\ \text{Å}^2 \qquad \sigma(L)=\begin{pmatrix}3 & 2 & 2\\ & 3 & 2\\ & & 3\end{pmatrix}\times 10^{-1}\ (^\circ)^2$$

Principal axes of T

Eigenvalue	Direction cosines ($\times 10^3$)			Comment
0·0122 Å^2	737	659	148	18° from normal to mean plane of 14-ring
0·0110	468	−343	−814	
0·0075	486	−670	562	

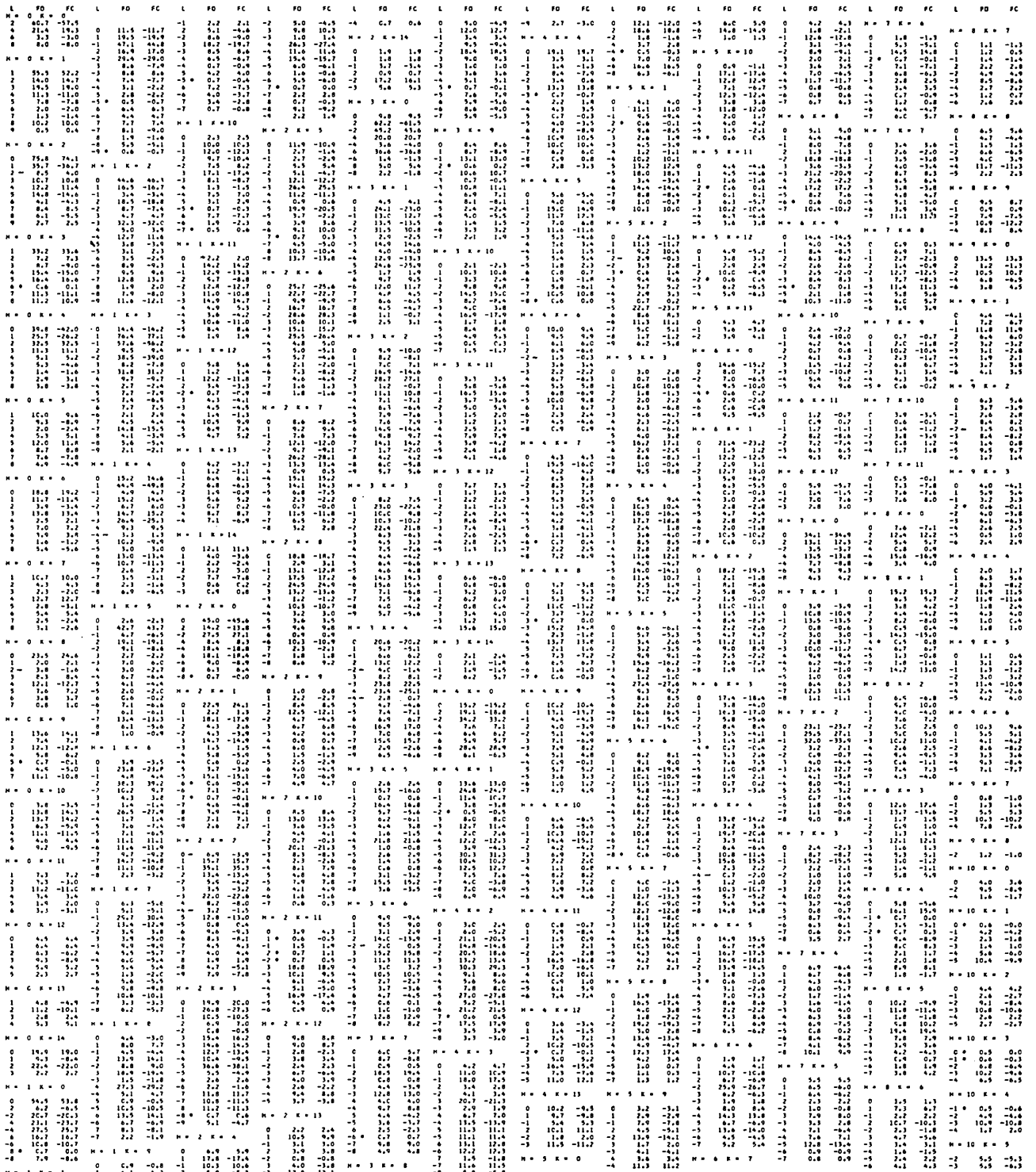
Principal axes of L

Eigenvalue	Direction cosines ($\times 10^3$)			
4·2 (°)^2	190	−832	522	5° from normal to mean plane of 14-ring
2·2	953	283	104	
1·0	234	−478	−847	

The reference coordinate system is orthogonal, with $x||\mathbf{a}$; $y||\mathbf{b}$; $z||\mathbf{c}^*$.

Table 4. *Observed and calculated structure factors*

An asterisk indicates an unobserved reflexion, for which the threshold value of F_o is listed. A dash indicates an observed reflexion omitted from least-squares analysis.



It is known that the e.s.d.'s derived from the normal equations of least-squares refinement are likely to be underestimated if correct weights are not assigned to the observed structure amplitudes. Comparison of the mean coordinate e.s.d. with the less precise but more objective value given by the approximate formula of Cruickshank (1960) $[\sigma(x)=(R/S)(N/8P)^{\frac{1}{2}}]$ indicates that the nominal values should be increased by 20%. This correction has been applied to all the e.s.d.'s given in Tables 1 and 2. The mean e.s.d. for coordinates of carbon atoms is 0·0014 Å.

The criterion of equality of chemically equivalent bonds (Table 5) is very well satisfied for this structure and it appears therefore that the coordinate e.s.d.'s are realistic.

Table 5(*a*). *Bond lengths*

	Uncorrected	Corrected	Mean
C(1)–C(2)	1·392	1·393	1·394
C(4)–C(5)	1·393	1·394	
C(2)–C(3)	1·398	1·399	1·399
C(3)–C(4)	1·398	1·399	
C(5)–C(7)	1·398	1·399	1·400
C(8)–C(1′)	1·400	1·401	
C(7)–C(8)	1·395	1·396	1·396
C(1)–C(6)	1·523	1·524	1·524
C(5)–C(6)	1·523	1·524	
C(6)–C(6′)	1·545	1·546	1·546
C(6)–C(9)	1·573	1·574	1·574
C(9)–C(10)	1·529	1·530	1·530

E.s.d. is 0·002 Å for all but C(6)–C(6′), for which the value is 0·003 Å.
Range of C–H distances is 0·94–1·00 Å, with mean e.s.d. 0·02 Å.

Table 5(*b*). *Bond angles*

		Mean
C(6) –C(1)–C(2)	118·8°	118·9°
C(4) –C(5)–C(6)	119·0	
C(1) –C(2)–C(3)	121·5	121·4
C(3) –C(4)–C(5)	121·3	
C(6) –C(1)–C(8′)	117·3	117·4
C(6) –C(5)–C(7)	117·4	
C(1) –C(6)–C(6′)	109·3	109·2
C(5) –C(6)–C(6′)	109·1	
C(4) –C(5)–C(7)	123·5	123·6
C(2) –C(1)–C(8)	123·8	
C(5) –C(7)–C(8)	121·8	121·6
C(7) –C(8)–C(1′)	121·5	
C(1) –C(6)–C(9)	107·3	107·3
C(5) –C(6)–C(9)	107·3	
C(2) –C(3)–C(4)	121·8	121·8
C(1) –C(6)–C(5)	114·0	114·0
C(6′)–C(6)–C(9)	109·7	109·7
C(6) –C(9)–C(10)	115·7	115·7

The mean e.s.d. of angles is 0·1°.

Discussion

The geometry of the molecule is illustrated in Fig. 1 and Table 5. The bond lengths in the peripheral ring all lie in the range 1·393–1·401 Å, thus unequivocally confirming the aromatic character of the ring. However, there are appreciable distortions from the ideal molecular form, as illustrated in Fig. 1. Comparison with the corresponding distortions in the dimethyl derivative (IV) supports the hypothesis that the bulkier internal substituent impinges more drastically on the π-electron system of the ring. One measure of the dis-

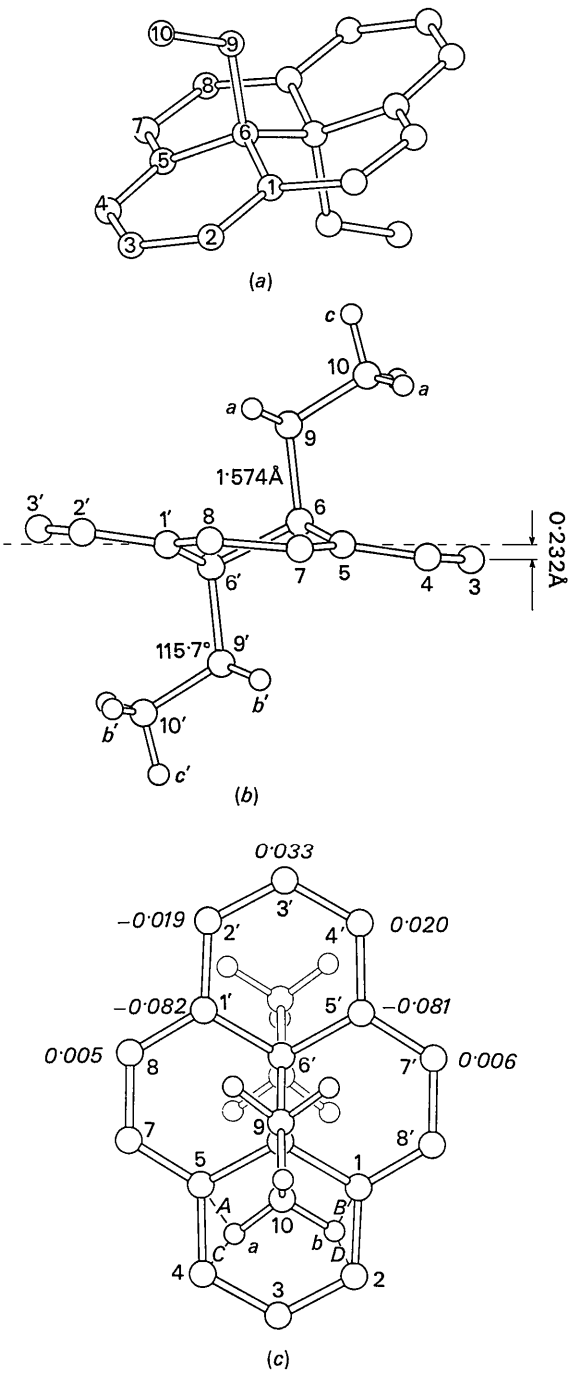


Fig. 1. (*a*) The carbon skeleton of the molecule. (*b*) The molecule viewed parallel to C(7)–C(8′). (*c*) The molecule viewed normal to the mean plane of the 14-ring (equation $0{\cdot}2585x - 0{\cdot}8509y + 0{\cdot}4573z = 0$; coordinate system specified as in Table 3). The italicized quantities are the distances (Å) of some atoms from this plane. The distances of H(10a) and H(10b) from the nearest carbon atoms of the 14-ring are $A = 2{\cdot}77$, $B = 2{\cdot}78$, $C = 2{\cdot}82$, $D = 2{\cdot}89$ Å.

tortion from planarity of the ring is the distance of C(3) from the plane containing the four carbon atoms bonded to the internal substituent. This distance (0·232 Å) is nearly twice as great as the corresponding distance (0·117 Å) found in (IV). Also, the length of the bond C(6)–C(9) (1·574 Å) is significantly greater than the corresponding distance (1·564 Å) in (IV). Furthermore, the angle C(6)–C(9)–C(10) (115·7°) is much greater than the tetrahedral angle (109·5°). The effect of these distortions is to increase the distance of the two nearer methyl hydrogen atoms [H(10a) and H(10b)] from the carbon skeleton of (and presumably from the π-electron cloud of) the 14-ring. This effect could be reinforced by increasing the angles C(9)–C(10)–H(10a) and C(9)–C(10)–H(10b) from the tetrahedral value. In fact these angles are found to be 111·1° and 112·2°, respectively. However, the e.s.d. for these angles is 1·2°, so that the observed increase is of doubtful significance. The distances of these hydrogen atoms from the nearest carbon atoms of the 14-ring are shown in Fig. 1(*c*). Considering the distortions required to achieve them, they are probably close to the minimum possible for such structures.

The van der Waals contacts between adjacent molecules are normal. The shortest intermolecular distance is 3·29 Å, between C(7) and the atom related to it by the centre of symmetry at $0,0,\frac{1}{2}$.

The problem was suggested by, and the specimen material was supplied by, Professor V. Boekelheide. Programs used in the analysis, but not identified in the text, are those of Dr F. R. Ahmed, Dr S. R. Hall, Dr J. A. Bevan, and Mrs M. E. Pippy. The assistance of these people, and the continued encouragement of Dr W. H. Barnes, are gratefully acknowledged.

References

BOEKELHEIDE, V. & MIYASAKA, T. (1967). *J. Amer. Chem. Soc.* **89**, 1709.
BOEKELHEIDE, V. & PHILLIPS, J. B. (1963). *J. Amer. Chem. Soc.* **85**, 1545.
BOEKELHEIDE, V. & PHILLIPS, J. B. (1967). *J. Amer. Chem. Soc.* **89**, 1695.
BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
CRUICKSHANK, D. W. J. (1960). *Acta Cryst.* **13**, 774.
CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. London: Pergamon Press.
FREEMAN, A. J. (1959). *Acta Cryst.* **12**, 261.
FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. Milwaukee: General Electric Company.
HANSON, A. W. (1965). *Acta Cryst.* **18**, 599.
HODGSON, L. T. & ROLLETT, J. S. (1963). *Acta Cryst.* **16**, 329.
MAIR, G. A. (1963). Private communication.
PHILLIPS, J. B., MOLYNEUX, R. J., STURM, E. & BOEKELHEIDE, V. (1967). *J. Amer. Chem. Soc.* **89**, 1704.
PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1956). *Acta Cryst.* **9**, 173.
SONDHEIMER, F. (1964). *Proc. Chem. Soc.* p. 397.