

The Crystal and Molecular Structure of 1,2-Diphenylcyclopentene, an Analogue of *cis*-Stilbene

BY J. BERNSTEIN

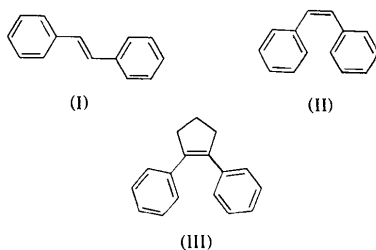
Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel

(Received 9 August 1974; accepted 12 September 1974)

1,2-Diphenylcyclopentene ( $C_{17}H_{16}$ ) is monoclinic, space group  $P2_1$ , with  $a=9.025$  (3),  $b=9.516$  (4),  $c=8.036$  (2) Å,  $\beta=112.4$  (5)°,  $Z=2$ . The structure was solved by direct methods from 1647 counter reflexions, and refined anisotropically to  $R=0.078$ . The angle between the normals to the two phenyl rings, whose disposition approximates  $C_2$  symmetry, is 62°. The pattern of deviations of atoms from the best plane in the cyclopentene ring is consistent with approximate  $C_s$  symmetry corresponding to the 'envelope' conformation, with a dihedral angle of 17.2°.

## Introduction

Stilbene has been the subject of a wide variety of studies, among them photochemical, spectroscopic and theoretical. One of the central points of interest is that of the difference in structure and properties of the *trans* (I) and *cis* (II) isomers. In the case of the isoelectronic analogue azobenzene, both isomers are solids at room temperature and structural information has been obtained from the respective crystal structures (Brown, 1966; Hampson & Robertson, 1941; Mostad & Rømming, 1971). However, (II) is a liquid at room temperature and its crystal structure has not been reported. A good model for (II) is 1,2-diphenylcyclopentene (III), since it cannot undergo thermal or photochemical *cis* → *trans* isomerism and is a solid at room temperature (m.p. 59–60°C). Hence the structure determination of this model compound was undertaken.



## Experimental

Crystals of the material grown from methanolic solutions are elongated along [010] and show the {010} and {101} forms. Lattice constants were obtained from a least-squares fit of 39  $2\theta$  values determined on a diffractometer ranging between 8° and 54° (Mo  $K\alpha_1$  and Mo  $K\alpha_2$ ). Preliminary Weissenberg and precession photographs had indicated monoclinic symmetry with systematic absences  $0k0$ ,  $k$  odd, compatible with space groups  $P2_1$  (No. 4) and  $P2_1/m$  (No. 11); the former was confirmed during the course of the study.

## Crystal data

$C_{17}H_{16}$ , F.W. 220.32. Monoclinic, space group  $P2_1$ ,  $a=9.025$  (3),  $b=9.516$  (4),  $c=8.036$  (2) Å,  $\beta=112.4$  (5)°;  $\rho_{calc}=1.15$  g cm<sup>-3</sup>,  $\rho_{meas}=1.12$  (flotation, aqueous KI),  $Z=2$ ,  $F(000)=236$ ,  $\mu=0.698$  cm<sup>-1</sup> (Mo  $K\alpha$ ).

A crystal of dimensions 0.52 × 0.16 × 0.30 mm measured perpendicular to the (100), (101) and (010) faces was mounted along **b** on an IBM 1800-controlled Siemens diffractometer. Two independent sets of  $I(hkl)$  were recorded for  $\sin \theta/\lambda \leq 0.66$  with Mo  $K\alpha$  radiation and balanced zirconium and yttrium filters.

Intensities were measured by an  $\omega/2\theta$  scan technique described by Ingartinger, Leiserowitz & Schmidt (1970). The procedure for the treatment of the data, including correction for absorption, is that given by Coppens, Leiserowitz & Rabinovich (1965). Averaging of the two sets of data yielded 1647 independent reflexions, of which 404 had intensities  $< 2\sigma$  of the mean value or  $2\sigma$  (mean) for equivalent reflexions and were treated as unobserved.

## Structure determination and refinement

The cell parameters and density indicated two molecules per cell which is compatible with a general position in  $P2_1$  but requires molecular site symmetry  $C_s$  in  $P2_1/m$ . Such a possibility exists for diphenylcyclopentene but seemed unlikely since it requires a butterfly arrangement of the two phenyl rings. Statistics of normalized structure factors ( $E$ ) support the assignment of the non-centrosymmetric space group  $P2_1$ .  $E$  statistics:

	Observed	Theoretical*	
		Noncentric	Centric
$\langle  E ^2 \rangle$	0.987	1.000	1.000
$\langle  E^2 - 1  \rangle$	0.689	0.736	0.968
$\langle  E  \rangle$	0.897	0.886	0.798

\* Karle, Dragonette &amp; Brenner (1965).

Table 1. Final positional and thermal parameters for non-hydrogen ( $\times 10^4$ ) and hydrogen ( $\times 10^3$ ) atoms

E.s.d.'s in parentheses are in units of the least significant digit. Hydrogen atoms are numbered according to the atom to which they are bonded. Anisotropic thermal parameters are in the form  $\exp[-2\pi^2 \sum_i \sum_j a_i a_j h_i h_j U^{ij}]$ ; isotropic,  $\exp[-8\pi^2 U \sin^2 \theta / \lambda^2]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>11</sup>	<i>U</i> <sup>22</sup>	<i>U</i> <sup>33</sup>	<i>U</i> <sup>12</sup>	<i>U</i> <sup>23</sup>	<i>U</i> <sup>13</sup>
C(1)	7362 (4)	2750 (0)	4955 (5)	449 (19)	537 (27)	478 (21)	47 (19)	-30 (21)	196 (17)
C(2)	7952 (6)	2806 (8)	6987 (6)	512 (26)	946 (50)	511 (26)	75 (29)	-70 (29)	188 (21)
C(3)	6616 (6)	2130 (9)	7417 (6)	632 (27)	1176 (54)	511 (27)	81 (35)	8 (37)	268 (22)
C(4)	5145 (6)	2127 (11)	5648 (6)	556 (28)	1373 (61)	633 (30)	-52 (44)	34 (42)	307 (25)
C(5)	5813 (4)	2387 (5)	4220 (5)	463 (20)	611 (30)	519 (23)	1 (22)	-18 (25)	235 (17)
C(6)	8487 (4)	3007 (4)	4048 (5)	405 (16)	560 (25)	469 (20)	36 (18)	21 (20)	118 (15)
C(7)	8487 (4)	2199 (6)	2622 (5)	462 (20)	619 (27)	574 (23)	0 (23)	-12 (24)	197 (17)
C(8)	9628 (5)	2367 (6)	1878 (6)	565 (22)	875 (33)	597 (26)	144 (27)	43 (29)	277 (20)
C(9)	10779 (5)	3387 (6)	2541 (7)	473 (21)	1014 (39)	709 (29)	19 (25)	195 (31)	268 (21)
C(10)	10791 (5)	4214 (6)	3929 (7)	529 (24)	847 (35)	828 (33)	-113 (26)	81 (31)	202 (24)
C(11)	9670 (5)	4034 (6)	4696 (6)	531 (24)	684 (30)	628 (27)	-50 (22)	-55 (24)	157 (21)
C(12)	4757 (4)	2296 (5)	2296 (5)	387 (16)	580 (24)	582 (21)	13 (19)	-4 (23)	235 (16)
C(13)	3793 (5)	1130 (5)	1638 (6)	557 (22)	694 (33)	700 (30)	-49 (24)	-11 (26)	227 (23)
C(14)	2775 (5)	1050 (7)	-154 (7)	582 (25)	785 (36)	797 (35)	-81 (26)	-172 (32)	212 (25)
C(15)	2694 (5)	2119 (7)	-1314 (6)	516 (21)	1022 (41)	571 (26)	76 (28)	-84 (32)	141 (20)
C(16)	3625 (5)	3296 (6)	-676 (6)	633 (25)	781 (35)	635 (30)	138 (27)	136 (30)	227 (25)
C(17)	4649 (5)	3386 (6)	1108 (6)	523 (21)	592 (29)	695 (30)	-33 (23)	-31 (27)	241 (22)

The structure was solved by direct methods with the aid of *MULTAN* (Main, Woolfson & Germain, 1971) which employs the multiresolution technique to the tangent formula. The 'residual' of the set of phases which corresponds to the correct solution was by far the lowest of the 64 possible sets, but the 'absolute figure of merit' for this set was lower than that for seven other sets. *R* for 1441 reflexions with an overall isotropic temperature factor was 0.26 Å<sup>2</sup> at this stage.

Block-diagonal least-squares refinement was carried out with all carbon atoms in one block and refinement on coordinates and individual isotropic temperature factors (three cycles). The molecule was then divided into three blocks corresponding to the three rings, and hydrogen atom coordinates, calculated on the basis of chemically expected positions, were included in the next three cycles with individual isotropic temperature factors. For the same three cycles carbon atoms were assigned anisotropic temperature factors. Five reflex-

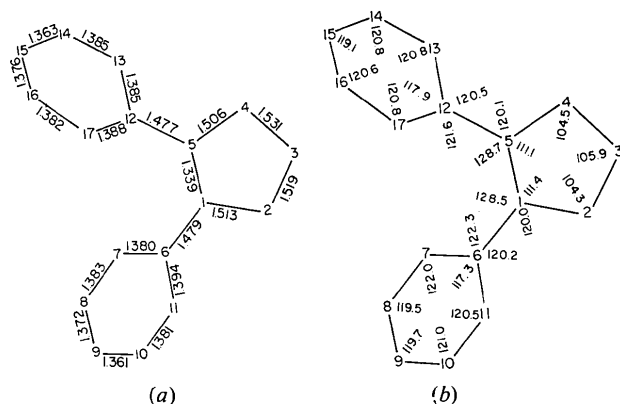


Fig. 1. Molecular dimensions for 1,2-diphenylcyclopentene. (a) Bond lengths (Å); average e.s.d.'s: for bonds involving C(2), C(3), C(4) 0.009 Å, others 0.007 Å. (b) Bond angles (°); average e.s.d.'s: for angles at C(2), C(3), C(4) 0.5°, others 0.4°.

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>iso</sup>
H(C2)	809 (5)	384 (8)	733 (7)	59 (20)
H'(C2)	896 (4)	232 (5)	757 (5)	28 (11)
H(C3)	639 (5)	268 (6)	834 (7)	64 (17)
H'(C3)	697 (6)	108 (7)	784 (8)	86 (23)
H(C4)	436 (7)	292 (7)	557 (8)	70 (19)
H'(C4)	457 (7)	135 (7)	555 (8)	56 (22)
H(C7)	772 (3)	149 (4)	224 (4)	15 (10)
H(C8)	959 (5)	176 (5)	89 (6)	44 (14)
H(C9)	1159 (5)	342 (5)	204 (5)	51 (14)
H(C10)	1169 (5)	496 (6)	442 (6)	60 (16)
H(C11)	962 (5)	465 (5)	562 (6)	41 (14)
H(C13)	384 (5)	40 (6)	261 (6)	61 (17)
H(C14)	208 (5)	16 (6)	-55 (6)	52 (16)
H(C15)	197 (4)	207 (5)	-256 (5)	43 (12)
H(C16)	359 (5)	401 (5)	-145 (6)	42 (14)
H(C17)	526 (4)	417 (5)	152 (5)	22 (11)

ions which exhibited effects of secondary extinction were removed from the next three cycles. The final *R* was 0.078 (observed only) and 0.083 (including unobserved). In the final cycle 217 parameters were refined and 82 of them had shifts which were larger than the corresponding standard deviation. However, the electron density in the difference map calculated at this stage showed that it did not exceed 0.12 e Å<sup>-3</sup>.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Computer programs used, in addition to *MULTAN*, were locally modified versions of *ORFLS* (Busing, Martin & Levy, 1963), *FORDAP* (Zalkin, 1962) and *ORTEP* (Johnson, 1965).

Final positional parameters and temperature factors are given in Table 1, observed and calculated structure factors in Table 2.

## Discussion

Bond distances and angles involving only carbon atoms are shown in Fig. 1; those with hydrogen are given in

Table 2. *Observed and calculated structure factors*

The three columns list respectively  $l$ ,  $10kF_o$ ,  $10F_c$ .  $U$  signifies reflexions for which  $F_o \leq 2.50(F_c)$ . Asterisks indicate reflexions not included in least-squares refinement owing to extinction.

$l$	$10kF_o$	$10F_c$
000	10000	10000
010	10000	10000
020	10000	10000
030	10000	10000
040	10000	10000
050	10000	10000
060	10000	10000
070	10000	10000
080	10000	10000
090	10000	10000
100	10000	10000
110	10000	10000
120	10000	10000
130	10000	10000
140	10000	10000
150	10000	10000
160	10000	10000
170	10000	10000
180	10000	10000
190	10000	10000
200	10000	10000
210	10000	10000
220	10000	10000
230	10000	10000
240	10000	10000
250	10000	10000
260	10000	10000
270	10000	10000
280	10000	10000
290	10000	10000
300	10000	10000
310	10000	10000
320	10000	10000
330	10000	10000
340	10000	10000
350	10000	10000
360	10000	10000
370	10000	10000
380	10000	10000
390	10000	10000
400	10000	10000
410	10000	10000
420	10000	10000
430	10000	10000
440	10000	10000
450	10000	10000
460	10000	10000
470	10000	10000
480	10000	10000
490	10000	10000
500	10000	10000
510	10000	10000
520	10000	10000
530	10000	10000
540	10000	10000
550	10000	10000
560	10000	10000
570	10000	10000
580	10000	10000
590	10000	10000
600	10000	10000
610	10000	10000
620	10000	10000
630	10000	10000
640	10000	10000
650	10000	10000
660	10000	10000
670	10000	10000
680	10000	10000
690	10000	10000
700	10000	10000
710	10000	10000
720	10000	10000
730	10000	10000
740	10000	10000
750	10000	10000
760	10000	10000
770	10000	10000
780	10000	10000
790	10000	10000
800	10000	10000
810	10000	10000
820	10000	10000
830	10000	10000
840	10000	10000
850	10000	10000
860	10000	10000
870	10000	10000
880	10000	10000
890	10000	10000
900	10000	10000
910	10000	10000
920	10000	10000
930	10000	10000
940	10000	10000
950	10000	10000
960	10000	10000
970	10000	10000
980	10000	10000
990	10000	10000

Table 3. For the cyclopentene ring all bond lengths and angles agree within two e.s.d.'s with the results obtained from electron diffraction (Davis & Muecke, 1970).

Table 3. *Bond distances involving hydrogen atoms* (Å)

The e.s.d. (in parentheses) is in the units of the least significant digit given for the corresponding distance.

C(2)–H(C2)	1.02 (6)	C(9)–H(C9)	0.96 (5)
C(2)–H'(C2)	0.97 (4)	C(10)–H(C10)	1.04 (5)
C(3)–H(C3)	1.00 (6)	C(11)–H(C11)	0.96 (5)
C(3)–H'(C3)	1.06 (7)	C(13)–H(C13)	0.93 (5)
C(4)–H(C4)	1.02 (7)	C(14)–H(C14)	1.02 (5)
C(4)–H'(C4)	0.87 (7)	C(15)–H(C15)	0.96 (5)
C(7)–H(C7)	0.93 (4)	C(16)–H(C16)	0.92 (5)
C(8)–H(C8)	0.97 (5)	C(17)–H(C17)	0.92 (4)

The average C–C length in the two phenyl rings is 1.378 Å [ring C(6)–C(11)] and 1.380 Å [ring C(12)–C(17)] with corresponding scatters  $\{i.e. [\sum_n (\bar{r} - r_i)^2]^{1/2} / (n-1)\}$  of 0.011 and 0.009 Å respectively. The aromatic distance is shorter than the normally accepted value (1.398 Å) for benzene (Kennard *et al.*, 1972) but is similar to that observed in *cis*-azobenzene, a series of

*trans* azo compounds (Mostad & Rømming, 1971), and *trans*-stilbene (Finder, Newton & Allinger, 1974). The low observed value might be attributed to failure to correct for rigid-body motion; however, the validity of a rigid-body analysis by the method of Schomaker & Trueblood (1968) is questionable if  $R$  is greater than 0.07 (Pawley, 1970). Moreover, for *cis*-azobenzene the short average aromatic C–C distance is that obtained after correction for librational effects. This shortening, especially of bonds between carbons in the *meta* and *para* positions, is very often observed in compounds containing unsubstituted phenyl rings (Kennard *et al.*, 1972), and it has been suggested (Hirshfeld, 1974) that the effect may be due to internal vibrations. Comparison of accurate studies of a number of compounds at room and low temperature would test this hypothesis.

The disposition of the phenyl rings about C(1)–C(6) and C(5)–C(12) (dihedral angles with respect to the cyclopentene of 43.8° and –47.5° respectively) is consistent with approximate  $C_2$  symmetry with the two-fold axis bisecting C(1)–C(5) and passing through C(3). This conformation has been favoured in theoretical studies (Bromberg & Muszkat, 1972; Warshel, 1974a, and references therein) over that in which the phenyl

rings are related by a mirror plane, which would lead to an unacceptably short  $H(C7) \cdots H(C17)$  distance, and is found in *cis*-azobenzene (Mostad & Rømming, 1971) and about the double bonds in 1,2,3,4-tetra-phenylcyclopentadiene (Evrard, Piret, Germain & Van Meerssche, 1971). The dihedral angle between the best planes of the two phenyl rings is  $62^\circ$  compared to  $57.5^\circ$  in *cis*-azobenzene (Mostad & Rømming, 1971),  $65.0^\circ$  and  $72.5^\circ$  between the phenyl rings at positions 1,2 and 3,4 respectively in 1,2,3,4-tetra-phenylcyclopentadiene (Evrard *et al.*, 1971), and that calculated by Warshel (1974*b*),  $46.1^\circ$ .

In the cyclopentene ring the temperature factors on the methylene carbons are rather high with direction of maximum displacement corresponding closely to  $U^{22}$  nearly perpendicular to the ring. This feature is often observed in cyclopentane systems (Carrell, Gallen & Glusker, 1973; Margulis, Dalton & Kwiram, 1973) and is attributed to pseudorotation (*i.e.* an alternation in the puckering arrangement around the ring); the presence of the double bond in this case lowers the degree of torsional freedom in the ring resulting in a reduction of the possible vertical displacement of C(2), C(3), C(4) from the plane of the ring resulting from an alteration in conformation of these three atoms.

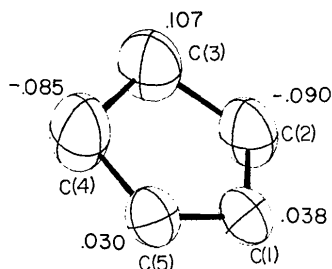


Fig. 2. View of the cyclopentene ring with thermal ellipsoids and distances (Å) of each atom from best plane of the ring.

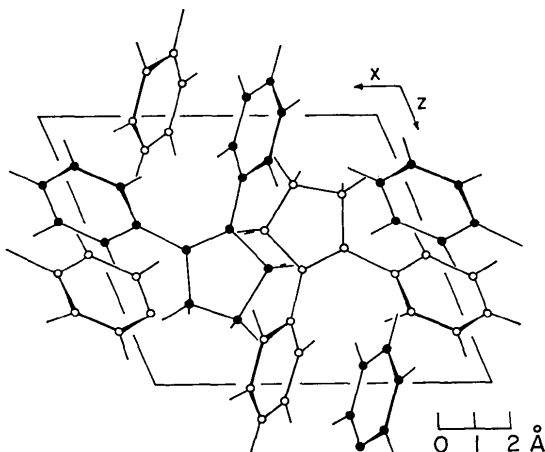


Fig. 3. View of the structure down the *b* axis.

The thermal ellipsoids in the cyclopentene ring are shown in Fig. 2 with the deviations from the best plane of all five atoms, the pattern of which is consistent with the envelope ( $C_s$ ) conformation. The alternative conformation of the ring with  $C_s$  symmetry, which may be approximately obtained by equal and opposite displacements from the ring of C(2), C(3) and C(4) from those shown in Fig. 2, leads to positions 0.2–0.3 Å apart. Disorder of this type has been observed and successfully refined in a number of cyclopentane derivatives (Margulis *et al.*, 1973; Mallikarjunan, Chacko & Zand, 1972) where the distance between equivalent positions of disordered atoms is about 0.6 Å. The distance found in the present case is well beyond the resolution of the structure and renders a least-squares refinement of such a disordered model of doubtful value. Furthermore, a separation of atomic positions of this magnitude is not properly accounted for by the ellipsoidal approximation for temperature factors, which probably leads to an *R* higher than that expected based on the quality of the data.

The 'puckering' of the cyclopentene ring [*e.g.*, the dihedral angle between planes C(1)–C(2)–C(4)–C(5) and C(2)–C(3)–C(4)],  $17.2^\circ$ , is somewhat less than that found by electron diffraction,  $28.8^\circ$  (Davis & Muecke, 1970), far infrared spectroscopic measurements,  $23.3^\circ$  (Laane & Lord, 1967),  $22.1^\circ$  (Ueda & Shimanouchi, 1967), or microwave spectroscopy,  $22.3^\circ$  (Rathjens, 1962) and exceeds that calculated theoretically by Dashevskii, Naumov & Zaripov (1970),  $14^\circ$ . All these authors estimate the barrier to inversion to be of the order of 0.6–0.7 kcal mole<sup>-1</sup>, which is consistent with the possible existence of the disorder described above.

Torsion angles in the cyclopentene ring are compared with those calculated by Warshel (1974*b*) and those observed in 1,2-cyclopentenophenanthrene (Entwistle & Iball, 1961) in Table 4. The agreement between the two cyclopentene derivatives is quite good; the differences in sign in the first two angles are not significant since these signs merely designate whether C(3) is above or below the plane of the other four atoms in the ring.

Table 4. Torsion angles in the cyclopentene ring ( $^\circ$ )

For the four atoms listed, say C(1)–C(2)–C(3)–C(4), the torsion angle is positive for a clockwise rotation about C(2)–C(3) when viewed along the direction C(2) to C(3).

	This work	1,2-Cyclo- pentenophen- anthrene*	Warshel (1974 <i>b</i> )
C(1)–C(2)–C(3)–C(4)	–16.7	21	–12.2
C(2)–C(3)–C(4)–C(5)	16.3	–19	7.7
C(1)–C(5)–C(4)–C(3)	–9.9	–9	0.3
C(2)–C(1)–C(5)–C(4)	–0.8	4	–8.8
C(3)–C(2)–C(1)–C(5)	11.2	16	13.1
C(6)–C(1)–C(5)–C(12)	–7.5	–5	–13.6

\* Entwistle & Iball (1961).

The angles C(1)–C(5)–C(12) and C(5)–C(1)–C(6) are larger and the internal angles at C(1) and C(5) smaller

than those expected for strict  $sp^2$  hybridization at these atoms [Fig. 1(b)]. A similar trend is observed in 1,2,3,4-tetraphenylcyclopentadiene (Evrard *et al.*, 1971), and probably results primarily from constraints on the atoms at the vertices due to their presence in the five-membered ring as well as to a possible contribution from steric factors between the two phenyl rings. Electron diffraction (Davis & Muecke, 1970) gave an angle of  $111.0^\circ$ , nearly identical with that found here. The two 'short' intramolecular distances are C(6)···C(12) (3.19 Å) and C(7)···C(17) (3.40 Å). Analogous distances in *cis*-azobenzene are significantly shorter (2.79 and 3.35 Å) undoubtedly due to the shorter double bond in the bridge, but also suggesting that the role of steric factors is secondary in the present case. Additional evidence comes from the results of the theoretical calculations by Warshel (1974*b*), in which the conformation of the molecule is determined by a minimization of the energy with respect to all coordinates, and the corresponding distances are 3.17 Å and 3.01 Å, suggesting that the contribution to the strain energy from the C(7)···C(17) contact in this structure is probably quite small.

The torsion angle C(6)–C(1)–C(5)–C(12) of  $-7.5^\circ$  agrees favourably with that found in *cis*-azobenzene  $8^\circ$  (Mostad & Rømming, 1971) as well as with that of the theoretically calculated values of Warshel (1974*a, b*) for *cis*-stilbene ( $-9^\circ$ ) but less so with Warshel's value for 1,2-diphenylcyclopentene ( $-13.6^\circ$ ).

The packing is shown in Fig. 3. There are no unusually short intermolecular distances (Table 5) and the packing appears to be due to only van der Waals forces.

Table 5. Intermolecular distances (Å)

Distances not greater than the following are given: H···H, 2.4 Å, H···C, 3.0 Å, C···C, 3.6 Å.

		Symmetry operation		
C(1)·····H(C10)	2.77	$2-x$	$y-\frac{1}{2}$	$1-z$
C(2)·····H(C10)	3.00	$2-x$	$y-\frac{1}{2}$	$1-z$
C(9)·····H(C14)	2.99	$1-x$	$\frac{1}{2}+y$	$-z$
C(12)·····H(C9)	2.99	$x-1$	$y$	$z$
C(14)·····H(16)	3.00	$1-x$	$y-\frac{1}{2}$	$-z$
C(16)·····H(C3)	2.95	$x$	$y$	$z-1$
C(3)·····C(8)	3.59	$x$	$y$	$1+z$
H(C2)·····H(C13)	2.31	$1-x$	$\frac{1}{2}+y$	$1-z$

It is a pleasure to acknowledge the computing assistance of Dr D. Rabinovich and Mrs Z. Shaked of the Weizmann Institute and the gift of the crystals by Professor E. Fischer of the same Institute.

## References

- BROMBERG, A. & MUSZKAT, K. A. (1972). *Tetrahedron Lett.* **28**, 1265–1274.
- BROWN, C. J. (1966). *Acta Cryst.* **21**, 146–152.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1963). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- CARRELL, H. L., GALLEN, B. & GLUSKER, J. P. (1973). *Acta Cryst.* **B29**, 2580–2585.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- DASHEVSKII, V. G., NAUMOV, V. A. & ZARIPOV, N. M. (1970). *Strukt. Khim.* **11**, 687–692.
- DAVIS, M. I. & MUECKE, T. W. (1970). *J. Phys. Chem.* **74**, 1104–1108.
- ENTWISTLE, R. F. & IBALL, J. (1961). *Z. Kristallogr.* **116**, 251–262.
- EVARD, G., PIRET, P., GERMAIN, G. & VAN MEERSSCHE, M. (1971). *Acta Cryst.* **B27**, 661–666.
- FINDER, C. J., NEWTON, M. G. & ALLINGER, N. L. (1974). *Acta Cryst.* **B30**, 411–415.
- HAMPSON, G. C. & ROBERTSON, J. M. (1941). *J. Chem. Soc.* pp. 409–413.
- HIRSHFELD, F. L. (1974). Private communication.
- INGARTINGER, H., LEISEROWITZ, L. & SCHMIDT, G. M. J. (1971). *J. Chem. Soc. (B)*, pp. 497–504.
- International Tables for X-ray Crystallography* (1968). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KARLE, I. L., DRAGONETTE, K. S. & BRENNER, S. A. (1965). *Acta Cryst.* **19**, 713–716.
- KENNARD, O., WATSON, D. G., ALLEN, F. H., ISAACS, N. W., MOTHERWELL, W. D. S., PETTERSON, R. C. & TOWN, W. G. (1972). *Molecular Structure and Dimensions*, Vol. A1. Utrecht: Oosthoek, Scheltema and Holkema.
- LAANE, J. & LORD, R. C. (1967). *J. Chem. Phys.* **47**, 4941–4945.
- MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures*.
- MALLIKARJUNAN, M., CHACKO, K. K. & ZAND, R. (1972). *J. Cryst. Mol. Struct.* **2**, 53–66.
- MARGULIS, T. N., DALTON, L. R. & KWIRAM, A. L. (1973). *Nature Phys. Sci.* **242**, 82–83.
- MOSTAD, A. & RØMMING, C. (1971). *Acta Chem. Scand.* **25**, 3561–3568.
- PAWLEY, G. S. (1970). *Acta Cryst.* **A26**, 289–292.
- RATHJENS, G. W. (1962). *J. Chem. Phys.* **36**, 2404–2406.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- UEDA, T. & SHIMANOCHI, T. (1967). *J. Chem. Phys.* **47**, 5018–5030.
- WARSHEL, A. (1974*a*) *J. Chem. Phys.* In the press.
- WARSHEL, A. (1974*b*). Private communication.
- ZALKIN, A. L. (1962). *FORDAP, a Fourier Synthesis Program*. Lawrence Radiation Laboratories, Livermore, California.