

The Crystal and Molecular Structure of a Novel Cage Compound, C₁₆H₁₄OCl₂

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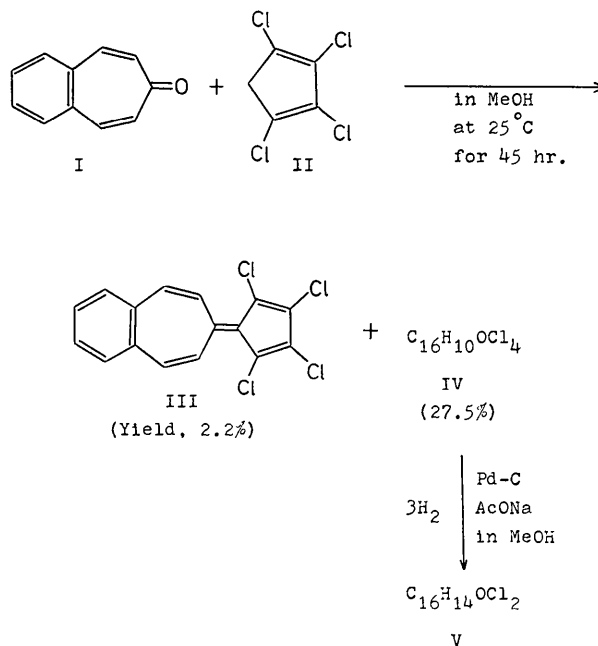
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The configuration of the molecule, C₁₆H₁₄OCl₂, prepared by the reaction of 4,5-benzotropone and 1,2,3,4-tetrachlorocyclopentadiene followed by catalytic hydrogenation has been determined by X-ray crystal analysis. Crystals are orthorhombic, with eight molecules in a unit cell of dimensions: $a=23.95$, $b=7.46$ and $c=15.16$ Å. The space group is *Pbca*. The intensities were recorded on Weissenberg photographs and measured visually. The structure was solved by the symbolic addition method. The final *R* value is 0.068. The result indicates that the molecule has a cage structure in which the reactant molecules are connected by three single bonds. The compound may then be called 3,6-dichloro-11,12-benzotetracyclo[5,3,2,0^{2,6},0^{3,8}]dodecan-9-one. The bond lengths and angles in this fused ring system are discussed in detail.

Introduction

As a part of their investigations of the non-benzenoid aromatic compounds, Kitahara and his co-workers have synthesized a sesquifulvalene derivative (III) by the reaction of 4,5-benzotropone (I) and 1,2,3,4-tetrachlorocyclopentadiene (II) (Kitahara, Murata & Katagiri, 1965). The structure of III has been confirmed by X-ray crystal analysis (Nishi, Sasada, Ashida & Kakedo, 1966). However, III is a minor product, and the major product of this reaction is IV. The compound (IV) is a colourless crystal (m.p. 185°C) and the elementary analysis has shown that IV is the 1:1 adduct of I and II, but its structure has remained unknown in spite of various chemical and spectroscopic investigations. In connection with the fact that reactions of 4,5-benzotropone (I) are generally different from those of monocyclic tropone derivatives, it is interesting, from the organic chemical point of view, to determine the structure of IV. The crystals used for the present work are of V, which is obtained by the catalytic hydrogenation of IV.

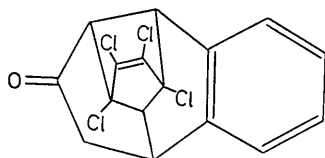
From the structure of V, the original product (IV) could be unambiguously assigned to



Experimental

Colourless hexagonal tabular crystals were obtained from an ethanol solution, with well-developed (001) faces. The unit-cell dimensions were determined from zero-layer Weissenberg photographs about the *a* and the *b* axes, calibration being made with superimposed aluminum powder lines.

Multiple-film equi-inclination Weissenberg photographs were taken at room temperature for the layer lines from 0 to 10 about the *a* axis and from 0 to 6 about *b*, using Cu *K*α radiation. The crystals used were square in cross-section with rectangular dimensions of 0.03 × 0.05 cm and 0.02 × 0.006 cm for the *a* and *b* axis



The preliminary report has already been published, in which a plausible reaction mechanism was proposed (Sasada, Shimanouchi, Murata, Tajiri & Kitahara, 1969).

rotation respectively. Intensities were estimated by visual comparison with a standard scale prepared from the same crystal; they ranged from 1 to 9372. Out of 2592 independent reflexions recorded, 1225 were too weak to be measured. Lorentz and polarization corrections were made in the usual way and corrections for spot-size variation in high-layer photographs by the method of Phillips (1954). The correction for absorption was neglected.

The data were put on to an absolute scale by means of a Wilson plot. Both the structure factor magnitudes, $|F_h|$, and the normalized structure factor magnitudes, $|E_h|$, were computed. For the space group *Pbca*,

$$E_h^2 = F_h^2 / \varepsilon \sum_{j=1}^N f_{jh}^2 \quad (1)$$

where $\varepsilon = 2$ for *Ok**l*, *h*0*l*, or *hk*0, $\varepsilon = 1$ otherwise, f_{jh} is the atomic scattering factor for the *j*th atom, and *N* is the number of atoms in the unit cell.

The statistical averages of $|E|$'s where $|E|$ values for unobserved reflexions were assigned to zero are shown in Table 1. The experimental values correspond to those for a crystal with a centre of symmetry.

Table 1. Statistical averages of $|E|$

	Experimental	Theoretical	
		Centro-symmetric	Noncentro-symmetric
$\langle E \rangle$	0.577	0.798	0.886
$\langle E^2 - 1 \rangle$	1.114	0.968	0.736
$\langle E ^2 \rangle$	0.912	1.000	1.000

Crystallographic and physical data

3,6-Dichloro-11,12-benzotetracyclo[5,3,2,0^{2,6},0^{3,8}]dodecan-9-one, C₁₆H₁₄OCl₂, m.p. 189–190°C. Orthorhombic, $a = 23.95 \pm 0.01$, $b = 7.460 \pm 0.003$, $c = 15.160 \pm 0.005$ Å. Absent spectra, *Ok**l* when *k* is odd, *h*0*l* when *l* is odd and *hk*0 when *h* is odd. Space group, *Pbca*. Eight molecules per unit cell. Volume of the unit cell, 2708.6 Å³. Density (by flotation), 1.447 g.cm⁻³; density (calculated), 1.437 g.cm⁻³. Linear absorption coefficient for Cu *K*α radiation, $\mu = 42.4$ cm⁻¹. Total number of electrons per unit cell, $F(000) = 1216$. λ_{\max} ($m\mu$) in ultraviolet absorption spectra:

In n-pentane; 254(2.31, sh); 261(2.52, sh); 263(2.53, sh); 267(2.65); 275(2.64); 288(1.54, sh); 299(1.54); 310(1.42); 319(1.24); 330(1.02, sh).

In methylene chloride; 233(2.69); 255(2.08, sh); 263(2.30, sh); 268(2.41); 276(2.38); 295(1.40); 305(1.32, sh); 316(1.03, sh), where the number in parentheses shows log ε and sh designates shoulder.

Structure determination

The phases were determined by the symbolic addition procedure (Karle & Karle, 1966). The *SGMA* system of programs (Ashida, 1967) was utilized to list the Σ_2 relationships for each reflexion and to calculate the

associated probabilities. In the initial stages of sign determination, only those reflexions with $|E| \geq 2.0$ were considered. Ten reflexions were chosen as a starting set for the phase determination; three were used to specify the origin as shown in Table 2, and phases of seven were obtained from strong Σ_1 relationships. Using the Σ_2 relationships signs of 72 reflexions were determined in the initial set. The procedure was then extended to 385 reflexions with $|E| \geq 1.5$ and phases for 319 were accepted as determined with the Σ_2 formula. The criterion was that more than two-thirds of the contributors to Σ_2 for a particular reflexion should indicate the same sign. Of the 319 phases, only three were subsequently shown to be incorrect. Not all the incorrectly determined phases had low $|E|$ values, but all these scarcely contributed to the Σ_2 formula. An *E* map computed with 319 terms is illustrated in Fig. 1.

Table 2. Starting set of reflexions for the application of Σ_2

<i>h</i>	<i>k</i>	<i>l</i>	$ E $	Sign
4	3	14	4.23	+
13	4	7	4.02	+
9	5	6	3.61	+
0	8	0	4.81	—
0	0	14	3.82	+
0	0	12	3.47	—
0	6	0	2.85	—
8	0	0	2.72	—
26	0	0	2.29	—
0	0	4	2.12	—

* To specify the origin.

An examination of the *E* map revealed two heavy peaks which could represent the chlorine atoms, and

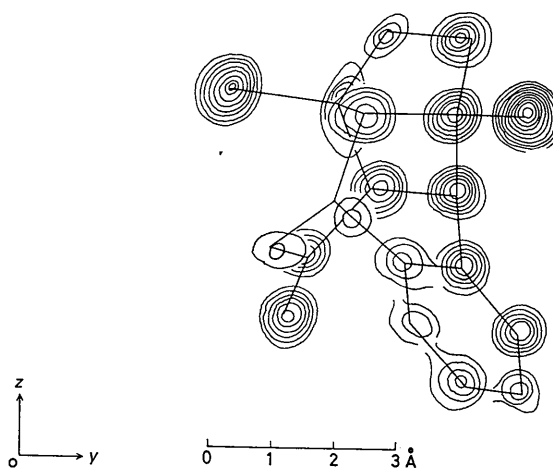


Fig. 1. Composite drawing of the three-dimensional *E* map using 319 phases directly determined. The contours are at equal intervals on an arbitrary scale. The intervals of the chlorine atoms are doubled. The final skeleton of the molecule is superimposed.

twenty-one peaks above the background. Of these, fifteen peaks could be assigned to light atoms by means of bond length and angle criteria. The other peaks were

excluded because they were all located too close to the chlorine atom peaks. The remaining two carbon atoms, C(1) and C(10), were found in a difference map synthesized at this stage.

The atomic coordinates and isotropic temperature factors thus obtained were then refined by the block-diagonal matrix least-squares method. After four cycles of the refinement the discrepancy index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, was reduced to 0.140 for the observed reflexions. Subsequent refinements were performed by taking account of anisotropic temperature factors in the form: $\exp\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\}$, for all the non-hydrogen atoms. After three cycles the R value was 0.092. At this stage, all the hydrogen atoms were assumed to be at stereochemically reasonable positions. All the hydrogen atoms were then included in further least-squares refinements; the positions and individual isotropic temperature factor of the hydrogen atoms were allowed to shift. After three cycles no significant changes in parameters were observed and the R value was reduced to 0.068 for the observed reflexions. The atomic scattering factors used in the calculations were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and the temperature factors are given in

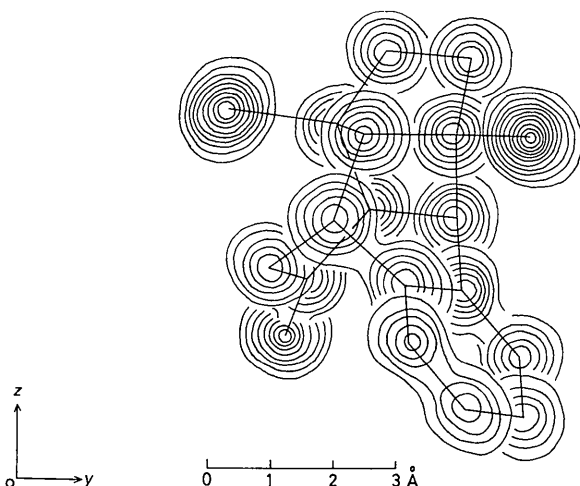


Fig. 2. Composite electron density diagram of sections parallel to (100). The contours of light atoms are at intervals of $1.0 \text{ e.}\text{\AA}^{-3}$, and those of chlorine atoms are at intervals of $2.0 \text{ e.}\text{\AA}^{-3}$, the lowest being $1.0 \text{ e.}\text{\AA}^{-3}$.

Table 3. Final atomic coordinates and temperature factors

The anisotropic temperature factors are expressed in the form of

$$\exp\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\}.$$

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	0.0583	0.4423	0.3890	0.00368	0.01856	0.00595	-0.00283	0.00022	0.00563
Cl(2)	0.1803	1.0826	0.3621	0.00203	0.02277	0.00501	-0.00231	-0.00033	-0.00493
O	0.0415	0.5653	0.1533	0.00244	0.03002	0.00496	-0.00564	0.00011	-0.00277
C(1)	0.1673	0.6711	0.2730	0.00169	0.01982	0.00610	0.00077	-0.00032	-0.00448
C(2)	0.1391	0.7281	0.3631	0.00220	0.01913	0.00430	0.00254	-0.00131	-0.00009
C(3)	0.0759	0.6744	0.3726	0.00213	0.01446	0.00514	-0.00098	0.00045	0.00324
C(4)	0.0537	0.7803	0.4497	0.00285	0.02133	0.00432	-0.00139	0.00161	0.00105
C(5)	0.0855	0.9600	0.4442	0.00284	0.02316	0.00326	-0.00070	0.00099	-0.00275
C(6)	0.1222	0.9268	0.3626	0.00204	0.01795	0.00334	0.00064	-0.00027	-0.00074
C(7)	0.0869	0.9309	0.2761	0.00155	0.01498	0.00365	0.00031	-0.00027	-0.00013
C(8)	0.0548	0.7446	0.2837	0.00144	0.01848	0.00391	-0.00034	-0.00001	0.00013
C(9)	0.0720	0.6116	0.2126	0.00212	0.01877	0.00410	-0.00405	0.00052	0.00108
C(10)	0.1306	0.5306	0.2239	0.00216	0.02091	0.00650	0.00031	0.00089	-0.00558
C(11)	0.1726	0.8190	0.2055	0.00172	0.01752	0.00512	-0.00151	0.00083	-0.00602
C(12)	0.1278	0.9384	0.1996	0.00151	0.01606	0.00404	-0.00131	-0.00044	-0.00168
C(13)	0.1243	1.0634	0.1302	0.00256	0.02136	0.00431	-0.00531	-0.00052	-0.00041
C(14)	0.1665	1.0684	0.0671	0.00361	0.03689	0.00354	-0.01164	0.00085	-0.00228
C(15)	0.2112	0.9506	0.0746	0.00322	0.03864	0.00548	-0.01239	0.00386	-0.01215
C(16)	0.2153	0.8276	0.1435	0.00221	0.02697	0.00724	-0.00398	0.00250	-0.01034
B									
H(1)	0.2060	0.6251	0.2892	5.1 \AA^2					
H(2)	0.1690	0.6831	0.4112	5.2					
H(3)	0.0093	0.7969	0.4452	4.1					
H(4)	0.0606	0.7171	0.5099	4.5					
H(5)	0.0593	1.0850	0.4348	4.4					
H(6)	0.1088	0.9899	0.4997	5.6					
H(7)	0.0591	1.0457	0.2686	3.8					
H(8)	0.0106	0.7615	0.2787	4.1					
H(9)	0.1480	0.4902	0.1605	5.8					
H(10)	0.1288	0.4002	0.2621	6.0					
H(11)	0.0878	1.1628	0.1252	4.6					
H(12)	0.1647	1.1725	0.0106	5.4					
H(13)	0.2443	0.9485	0.0254	6.2					
H(14)	0.2529	0.7409	0.1482	4.9					

Table 3, and their standard deviations in Table 4. The observed and calculated structure factors are listed in Table 5. The final three-dimensional electron density distribution calculated with signs based on these parameters is shown in Fig. 2. The final difference map showing the location of the fourteen hydrogen atoms is illustrated in Fig. 3.

The computations were done on a NEAC 2101 computer at the Institute for Protein Research of Osaka University with the programs written by T. Takano and Y. Nishi and on a HITAC 5020E computer in the University of Tokyo with the programs written by T. Ashida.

Results and discussion

Molecular geometry

The direct determination of the structure led to the unambiguous solution of the cage structure as shown in Fig. 4(a); this compound can be called 3,6-dichloro-11,12-benzotetracyclo[5,3,2,0^{2,6},0^{3,8}]dodecan-9-one, on which the atomic numbering is based. It is composed of a benzocycloheptenone ring combined with a cyclopentane ring by three single C-C bonds. The connection of the two rings results in formation of three six-membered rings and a five-membered ring. It is of in-

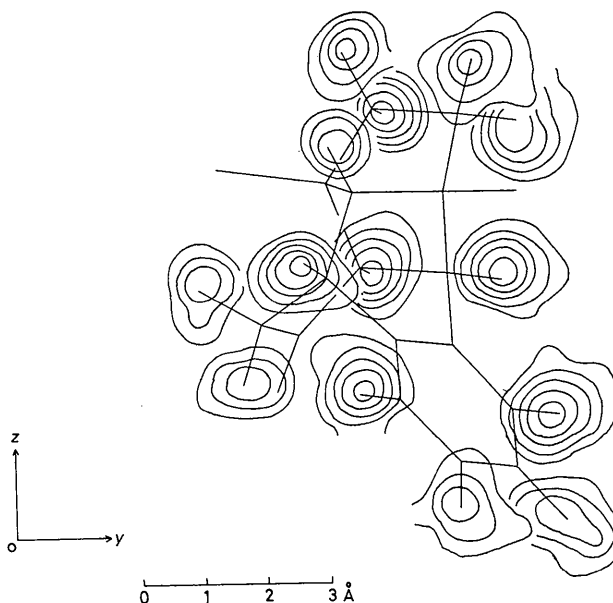


Fig. 3. Composite drawing of the three-dimensional difference map. The contours are at intervals of 0.1 e.Å⁻³, beginning with the 0.1 e.Å⁻³ contour.

Table 4. Estimated standard deviations

$\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ in Å, $\sigma(B)$ in Å².

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
Cl(1)	0.0018	0.0015	0.0016	0.00004	0.00028	0.00008	0.00020	0.00010	0.00028
Cl(2)	0.0014	0.0015	0.0014	0.00003	0.00029	0.00007	0.00017	0.00008	0.00027
O	0.0036	0.0041	0.0036	0.00009	0.00098	0.00020	0.00053	0.00022	0.00081
C(1)	0.0050	0.0052	0.0057	0.00011	0.00112	0.00033	0.00060	0.00031	0.00108
C(2)	0.0051	0.0053	0.0053	0.00011	0.00112	0.00027	0.00062	0.00032	0.00096
C(3)	0.0052	0.0048	0.0053	0.00011	0.00096	0.00028	0.00056	0.00032	0.00091
C(4)	0.0060	0.0056	0.0053	0.00014	0.00125	0.00028	0.00073	0.00034	0.00099
C(5)	0.0058	0.0057	0.0048	0.00014	0.00129	0.00025	0.00073	0.00030	0.00097
C(6)	0.0049	0.0050	0.0047	0.00010	0.00101	0.00022	0.00061	0.00027	0.00093
C(7)	0.0045	0.0046	0.0045	0.00009	0.00093	0.00022	0.00053	0.00024	0.00086
C(8)	0.0046	0.0050	0.0048	0.00009	0.00099	0.00024	0.00057	0.00027	0.00087
C(9)	0.0052	0.0050	0.0050	0.00011	0.00109	0.00024	0.00061	0.00030	0.00089
C(10)	0.0056	0.0055	0.0059	0.00012	0.00123	0.00034	0.00067	0.00035	0.00111
C(11)	0.0050	0.0049	0.0052	0.00010	0.00105	0.00028	0.00057	0.00030	0.00094
C(12)	0.0046	0.0048	0.0046	0.00009	0.00095	0.00024	0.00054	0.00025	0.00088
C(13)	0.0056	0.0055	0.0053	0.00012	0.00116	0.00026	0.00069	0.00030	0.00106
C(14)	0.0066	0.0069	0.0053	0.00017	0.00179	0.00026	0.00099	0.00035	0.00125
C(15)	0.0063	0.0072	0.0060	0.00016	0.00188	0.00033	0.00096	0.00039	0.00142
C(16)	0.0055	0.0061	0.0065	0.00013	0.00143	0.00038	0.00072	0.00037	0.00133
				$\sigma(B)$					
H(1)	0.053	0.055	0.056	1.5					
H(2)	0.054	0.056	0.056	1.5					
H(3)	0.050	0.054	0.051	1.4					
H(4)	0.053	0.055	0.054	1.4					
H(5)	0.051	0.054	0.051	1.4					
H(6)	0.057	0.060	0.059	1.6					
H(7)	0.050	0.050	0.050	1.3					
H(8)	0.050	0.054	0.052	1.4					
H(9)	0.055	0.060	0.058	1.7					
H(10)	0.057	0.057	0.060	1.7					
H(11)	0.051	0.053	0.055	1.5					
H(12)	0.056	0.057	0.058	1.6					
H(13)	0.064	0.061	0.056	1.6					
H(14)	0.057	0.058	0.052	1.4					

Table 5 (cont.)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
18	34	-33	26	9	-9	5	17	-16	5	0	-1	9	19	21	11	27	-27	21	0	7	6	48	-49	2	27	-27			
19	11	-14	27	0	0	6	8	10	6	0	0	10	13	12	12	0	0	22	0	2	8	16	-15	3	20	0			
22	24	-27	K.L. = 3	5	5	7	14	-15	7	0	0	11	0	0	0	0	K.L. = 4	11	0	4	11	57	56	3	20	0			
24	23	-22	1	31	-29	8	8	-8	8	12	-15	12	21	18	14	10	10	0	30	30	12	0	-2	5	-3				
26	20	18	2	8	-9	9	0	1	9	11	10	13	26	-26	15	12	-11	1	10	12	14	0	0	6	0	0			
K.L. = 3	1	3	19	17	10	12	12	10	12	9	10	14	0	-1	16	10	-10	2	26	25	16	21	18	7	20	-17			
1	8	-8	4	18	33	11	19	-17	11	0	-3	15	16	13	17	0	3	3	28	26	18	22	-19	8	0	-3			
7	20	-17	5	19	-15	12	0	-1	12	14	-14	16	0	-2	18	0	-2	18	0	-2	8	4	20	16	-15	9	11	-11	
5	12	33	6	40	-39	13	0	-3	13	0	0	17	9	-8	19	-13	12	5	0	-1	22	0	-1	10	21	21			
4	8	-8	7	7	-6	14	C	-3	14	0	-3	18	0	-2	20	0	3	6	12	-13	24	0	3	11	0	6			
5	19	17	8	13	13	15	0	5	15	0	-5	19	10	-9	21	0	0	7	33	-34	K.L. = 5	3	12	17	-14	14			
6	29	29	9	35	31	16	0	0	16	10	10	20	8	-7	22	0	-4	8	12	-16	1	8	9	13	14	14			
7	0	0	10	17	16	17	0	-2	17	0	-4	21	9	10	23	0	3	9	8	12	2	34	35	14	12	12			
8	18	-18	11	9	8	18	0	-8	18	0	-3	22	0	-4	24	0	0	10	22	-20	3	30	-29	15	0	-4			
9	18	-17	12	0	-5	19	0	5	19	0	0	23	0	0	1	25	0	0	11	6	7	4	33	-32	16	8	5		
15	22	22	13	9	7	20	0	4	1	0	-6	24	0	2	K.L. = 4	7	12	10	-11	5	20	17	8	11	-15	17	0	-3	
11	21	-20	14	17	-16	21	0	4	2	0	1	25	0	-1	0	50	-49	13	11	-13	6	28	-28	18	21	-20			
12	0	-5	15	12	12	22	0	0	3	0	-3	26	0	2	1	19	18	14	0	2	7	0	1	19	0	4			
14	18	-18	16	12	11	23	0	-5	4	0	-7	27	0	1	2	40	-40	15	17	18	8	9	9	20	0	6			
14	11	-12	17	12	-13	24	0	1	5	0	-2	K.L. = 4	3	22	-22	16	0	7	0	0	10	8	-7	21	0	-5			
15	9	-7	18	15	14	K.L. = 3	10	6	0	0	-3	0	16	14	4	16	-13	17	0	0	10	8	-7	21	0	-5			
16	19	-19	19	11	-12	1	32	30	7	11	9	1	30	30	5	40	-40	18	0	5	11	20	18	23	0	-2			
17	14	13	20	10	-10	2	17	15	8	0	-3	2	39	42	6	27	27	19	0	-1	12	13	14	24	0	-3			
18	0	-9	21	0	0	3	9	-9	9	0	0	5	39	69	7	34	37	20	0	0	3	13	9	0	K.L. = 5	6			
19	10	10	22	0	0	4	54	-53	10	0	0	4	42	9	8	41	43	21	0	-5	14	0	-4	1	44	44			
20	0	0	23	0	-7	5	18	17	11	0	-2	5	55	55	0	44	-48	0	44	-48	K.L. = 4	12	15	0	1	45	12		
21	0	3	24	0	-3	6	16	-14	12	0	5	6	58	-57	10	28	29	0	8	6	16	10	-6	3	32	-33			
22	0	4	25	0	-2	7	12	-12	13	0	-3	7	8	-5	11	30	-32	1	12	11	17	0	4	4	18	16			
23	0	-4	26	0	-2	8	0	-2	14	0	3	8	14	-12	12	0	0	2	0	-2	18	12	13	5	0	-3			
24	0	10	27	0	-8	9	0	-50	15	0	-2	9	25	24	4	54	56	6	3	-7	19	11	-4	6	0	-4			
25	0	-2	K.L. = 3	6	10	0	0	-7	16	0	0	10	17	-18	14	10	-9	0	0	-2	20	0	-9	0	50	63			
26	0	-2	1	26	-29	11	0	4	K.L. = 3	16	11	10	-10	15	0	-4	5	12	-10	21	0	-1	8	23	23	0			
27	0	-4	2	0	0	12	11	12	1	0	0	12	17	-13	16	0	-1	6	0	-2	22	0	-4	9	54	60			
K.L. = 3	2	3	26	26	13	0	3	2	12	-12	13	38	-40	17	0	3	7	0	10	23	5	7	10	0	-2	2			
1	124	130	4	17	15	3	17	15	2	3	14	34	35	14	0	-15	-15	14	0	0	1	24	25	12	15	-17			
2	51	-48	5	48	-49	15	10	7	4	0	-1	15	9	7	19	0	1	9	0	-7	25	0	-3	12	12	-11			
3	5	3	6	15	14	16	0	1	5	10	9	16	9	7	20	0	-5	10	0	-5	K.L. = 5	2	13	9	-6	6			
4	49	-49	7	35	36	17	21	20	6	0	0	17	12	-13	21	12	-11	11	0	1	1	35	35	14	8	-8			
5	58	44	8	19	16	18	0	15	7	0	15	18	0	0	1	22	0	12	9	7	2	-15	15	8	6				
6	50	20	9	60	65	19	0	-2	8	0	-4	19	0	4	23	11	9	13	9	8	3	17	-21	11	-11	1			
7	69	-70	10	9	11	20	0	-7	9	0	1	20	8	5	24	0	0	14	0	1	4	25	-24	17	13	-14			
8	0	-1	11	51	-53	21	0	4	10	0	3	21	7	5	25	0	0	15	9	-10	5	17	15	18	0	2			
9	112	-112	12	20	-21	22	0	-4	11	10	11	22	9	-10	K.L. = 4	8	16	0	0	6	10	11	19	0	-4	4			
10	0	-2	13	0	-2	23	0	0	12	0	-2	0	22	-12	0	22	-12	17	0	0	3	39	-40	20	0	0			
11	18	-18	14	18	-18	K.L. = 3	11	13	0	0	0	24	0	-1	5	-10	18	0	0	8	5	-5	2	12	11	2			
12	16	14	15	27	27	1	21	21	14	0	-2	25	0	6	2	0	0	19	0	5	9	44	-42	22	0	1			
13	21	-20	16	15	-15	2	0	4	K.L. = 3	17	26	0	0	3	11	-10	K.L. = 4	13	10	17	-10	23	0	3	3				
14	0	3	17	0	0	3	12	-12	2	1	0	-1	27	29	4	0	-4	0	15	17	11	0	0	K.L. = 5	7	0			
15	18	17	18	0	-6	4	12	-12	2	10	-8	0	27	29	4	0	-2	1	0	-2	12	6	7	1	12	11			
16	11	-12	19	8	10	5	0	-5	3	0	0	1	13	13	6	0	6	2	12	-13	13	0	-11	3	27	-26			
18	0	-4	21	14	-14	7	0	-8	5	0	6	3	4	5	8	20	20	4	0	5	15	0	6	4	0	2			
19	8	-7	22	0	-3	8	0	-2	6	0	-2	4	4	5	9	12	-14	5	12	14	16	0	-1	5	16	17			
20	0	5	23	0	-6	9	0	0	7	0	0	5	12	-10	10	-12	6	6	23	-2	17	14	6	23	-2	2			
21	15	16	24	0	-5	10	0	-7	8	0	-1	6	0	5	11	12	14	7	0	5	16	0	-3	7	15	15			
22	10	10	25	11	13	11	0	0	9	0	0	7	0	0	12	0	-4	8	24	-21	19	0	-1	8	0	-1			
23	8	-6	26	8	7	12	0	2	K.L. = 3	18	8	16	-15	13	0	1	9	10	-10	20	10	8	9	0	1	1			
24	0	5	K.L. = 3	7	13	4	0	1	1	0	-8	9	0	1	14	10	8	10	0	-2	21	0	6	10	0	0			
25	26	-22	1	11	-11	14	0	0	2	0	2	10	12	11	15	15	11	-5	11	-5	22	0	-4	11	0	-4			
26	8	-7	2	0	4	15	0	4	3	0	0	11	0	-2	16	0	-3	12	0	4	23	0	-1	12	0	-2			
27	0	5	3	16	-16	16	0	-3	4	8	-11	12	0	0	17	0	-1	13	0	-6	24	0	-5	13	12	-12			
K.L. = 3	3	4	23	-21	17	0	-2	0	K.L. = 4	0	13	7	8	18	0	-4	14	11	-13	25	0	-3	14	0	-2	2			
1	29	26	5	2	0	17	0	0	0	5	2	14	18	-15	14	0	-5	15	0	-2	K.L. = 5	3	15	0	-2	1			
2	9	-6	6	0	0	19	0	-2	2	36	36	15	0	-5	20	0	4	16	0	7	1	35	-36	16	7	4			
3	38	-36	7	31	33	20	0	3	4	6	3	16	9	9	21	0	0	17	0	0	2	10	9	17	0	5			
4	42	41	8	9	6	21	0	-2	6	21	-21	17	0	-3	22	0	0	18	0	8	3	34	33	18	0	-2			
5	29	28	9	13	-11	22	0	0	8	23	21	18	10	8	23	0	-5	19	5	2	4	24	-25	19	9	-10			
6	41	40	10	11	-18	K.L. = 3	1																						

Table 5 (cont.)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC			
21*	0	-2	14*	0	1	13*	0	0	14*	0	6	19*	0	-5	2*	0	-1	7*	0	9			
K,L=	5	10	15*	0	0	14*	0	2	15	13	-12	K,L=	6	9	3*	0	1	7	13	-13			
1	9	5	K,L=	5	14	15	21	21	16*	0	0	16	-17	4*	0	0	8*	0	3	1*	0	-4	
2	12	-13	1*	0	1	16*	0	5	17*	0	0	1*	0	1	5	12	11	9*	0	-7	2*	0	-4
3	9	-4	2	9	10	17*	0	5	18*	0	-8	2	0	0	6*	0	2	10*	0	1	3*	0	0
4	26	-27	3*	0	0	18	11	-11	19	9	10	3*	-2	7*	0	3	K,L=	7	6	4*	0	3	
5	9	10	4	22	20	19	12	-8	20*	0	4	4*	0	6	8*	0	1	11*	0	1	5*	0	4
6	14	-13	5*	0	0	20*	0	2	21*	0	3	5*	0	-5	9*	0	0	2*	0	6	6*	0	4
7*	0	-3	6*	0	2	21*	0	1	22*	0	2	6*	0	0	K,L=	6	14	3*	0	10	7	5	-6
8*	0	-7	7*	0	4	22*	0	6	K,L=	6	6	7*	0	5	0	12	-14	4*	0	6	8	13	-9
9	25	-24	8*	0	0	23	0	-14	9	9	-8	8*	1	1*	0	5	5*	0	3	9*	0	0	
10	10	9	9*	0	1	K,L=	6	3	1	25	25	9*	0	-8	2*	0	2	6	17	14	K,L=	8	2
11	9	14	10*	0	5	0	17	17	2	9	7	10*	0	3	3*	0	-3	7	6	8	0*	0	4
12	10	12	11*	0	-6	1*	0	-2	3*	0	-5	11*	0	-3	4*	0	7	8*	0	2	1*	0	-6
13*	0	0	12	10	-13	2	21	-24	4	9	7	12*	0	0	5*	0	-2	9*	0	-2	2*	0	-6
14*	0	0	K,L=	5	15	1*	0	4	5	20	-19	13	15	13	6*	0	-6	10	7	-6	10	7	-10
15*	0	-6	1*	0	3	4	10	9	6	20	-19	14*	0	-6	7*	0	13	K,L=	7	7	4*	0	-7
16*	0	3	2*	0	6	5	10	6	7	13	16	15*	0	-2	8	8	1	1*	0	1	5	20	-16
17*	0	0	3*	9	-9	6	17	-14	8*	0	-2	16*	0	-6	K,L=	7	0	2*	0	5	6*	0	6
18*	0	5	K,L=	5	16	7*	0	4	9*	0	-2	17*	0	1	2	17	14	3	11	-15	7	7	-8
19*	0	-4	1*	0	-5	8	14	-13	10*	0	-1	18*	0	3	4	33	-33	4	13	10	6	6	5
20*	0	-3	2	7	-7	9	9	6	11*	0	-3	K,L=	6	10	6	12	-10	5	18	14	9	17	16
K,L=	5	11	K,L=	6	0	10	13	-16	12*	0	4	0	9	9	8	7	-5	6	10	9	K,L=	8	3
1	9	-13	0	12	-71	11*	0	1	13*	0	0	1	19	-18	10*	0	-9	7*	0	2	0	17	13
2*	0	-6	2	19	-19	12	12	-12	14	13	14	2*	0	9	K,L=	7	1	8*	0	0	1*	0	5
3	25	24	4	19	17	13*	0	-3	15	11	-9	3*	0	-9	1*	0	-4	9*	0	-2	2*	0	4
4*	0	-5	6*	0	5	14*	0	5	16	8	-8	4*	0	-4	2	19	20	10*	0	-2	3*	0	-4
5*	0	-10	8	21	9	15*	0	-6	17*	0	5	5*	0	-2	3*	0	-7	K,L=	7	8	4*	0	-4
6*	0	-3	10	13	12	16*	0	1	18*	0	5	6	23	20	4	21	-21	5	14	-13	6	9	-7
7*	0	1	12	12	11	17*	0	-6	19	10	8	7	11	-11	5	12	12	2*	0	-2	6	9	7
8*	0	-6	14	14	10	18	11	10	20*	0	3	8*	0	-4	6	15	-14	3*	0	2	7	12	10
9*	0	6	16	23	-25	19*	0	-1	21*	0	-4	9*	0	4	7*	0	1	4*	0	-1	8*	0	-1
10	13	15	18*	0	-1	20	9	10	K,L=	6	7	10*	0	1	8	6	-5	5*	0	-1	9*	0	4
11	15	-16	20*	0	5	21*	0	1	0*	0	1	11*	0	4	9*	0	0	4*	0	2	K,L=	8	4
12*	0	2	22	12	-12	22*	0	-1	1*	0	-2	12*	0	5	10*	0	-3	7*	0	1	0	32	28
13*	0	0	K,L=	6	1	K,L=	6	4	2	13	-16	13*	0	3	K,L=	7	2	8*	0	-2	1*	0	-5
14*	0	-1	0	23	23	0	42	45	3*	0	1	14	16	-18	1*	0	6	9	8	11	2	14	11
15*	0	4	1	8	-8	1	11	13	4	2	-13	15	8	-7	2	6	-9	6	16	6	3*	0	-6
16*	0	3	2	15	13	2	11	-14	5*	0	0	16*	0	1	3*	0	7	K,L=	7	9	4*	0	0
17*	0	-3	3	31	-32	3	10	-7	6	9	9	K,L=	6	11	4	13	17	1	18	-14	5*	0	-1
18*	0	-5	4*	0	2	4	14	-16	7	9	-5	5*	0	2	2*	0	2	7	6	10	-10	1*	0
19	8	11	5	24	8	10	18	8	8	12	12	1*	0	2	6*	0	4	3*	0	-10	7*	0	-4
K,L=	5	12	6	21	-17	6	33	34	9*	0	-3	2	13	12	7*	0	-2	4*	0	-7	6	15	-16
1	24	23	7	12	-11	7	9	8	10	12	10	3*	0	4	8	8	-11	5*	0	4	9*	0	-5
2*	0	5	8	21	-19	8	13	-12	11*	0	0	4*	0	0	9*	0	0	6*	0	0	K,L=	8	5
3*	0	6	9*	0	0	9	9	-7	12*	0	3	5*	0	-3	10*	0	0	7*	8	7	0	13	-11
4*	0	-8	10*	0	-1	10	12	-10	13*	0	4	6*	0	-4	K,L=	7	3	8*	0	-2	1*	0	4
5	19	-19	11	11	12	11*	0	-2	14*	0	0	7	11	-8	1*	0	4	9	7	10	1*	0	7
6	18	17	12	9	7	12*	0	-3	15*	0	7	8	10	-7	2*	0	-7	10	7	-9	3*	0	3
7	10	-10	13	10	6	13	12	8	16*	0	0	9*	0	3	3	10	13	K,L=	7	10	4*	0	1
8*	0	-2	14*	0	2	14	23	-24	17*	0	2	10	13	-12	4	20	-22	1*	0	0	5*	0	1
9*	0	-3	15	14	12	15*	0	-1	18*	0	0	11*	0	5	5	18	-16	6	19	-10	6	19	-10
10	10	-10	16*	0	0	16	15	19	19	8	-8	12*	0	-1	6*	0	-2	3*	0	2	7	7	7
11	10	-10	17*	0	6	17*	0	-5	20*	0	-7	13*	0	0	7*	0	0	4*	0	0	8*	0	3
12*	0	3	18	9	8	18	10	10	K,L=	6	8	14*	0	0	8*	0	3	5*	0	0	9*	0	-1
13*	0	5	19*	0	-2	19*	0	3	0	25	-24	15*	0	1	9*	0	0	6	18	-15	K,L=	8	6
14*	0	0	20*	0	-3	20	4	-10	1	14	-14	K,L=	6	12	10*	0	2	1*	0	2	3*	0	3
15*	0	7	21*	0	-1	21*	0	-2	2*	0	2	0	21	20	K,L=	7	4	8*	0	2	1	12	12
16*	0	-3	22*	0	-3	22*	0	4	3	14	16	1*	0	11	1*	0	0	9*	0	1	2*	0	2
17*	0	2	23*	0	-2	K,L=	6	5	4*	0	7	2*	0	6	2*	0	3	10	8	9	3*	0	9
K,L=	5	13	K,L=	6	2	0	18	17	5	22	22	3*	0	-1	3*	0	-1	K,L=	7	11	4*	0	0
1	10	11	0	9	8	1	10	9	6	12	-10	4*	0	-9	4*	0	0	1	11	-9	5*	0	4
2	8	-9	1	32	-35	2	8	8	7*	0	-4	5*	0	-7	5*	0	3	2*	0	-2	6*	0	-2
3*	0	-3	2	15	15	3	24	23	8	12	12	6*	0	-2	6	10	-9	3*	0	7	7	13	13
4	14	13	3*	0	-1	4*	0	-6	9*	0	2	7*	0	0	7	6	-6	4*	0	-6	8*	0	-6
5*	0	3	4*	0	-2	5	24	20	10*	0	0	8*	0	4	8	10	12	5*	0	-3	9*	0	-2
6	12	11	5	9	7	6	11	-11	11*	0	-4	9*	0	-3	9	7	-7	6	9	-9	K,L=	8	7
7*	0	-6	6	18	-17	7	11	11	12*	0	0	10*	0	-5	10	11	11	7	9	8	0*	0	0
8*	0	-3	7	29	-29	8*	0	-6	13*	0	-4	11*	0	7	K,L=	7	5	K,L=	8	0	1*	0	-7
9*	0	-6	8*	0	0	9	9	1	14	12	14	12*	0	-5	1	12	11	0	53	-49	2*	0	-4
10*	0	0	9	21	19	10*	0	2	15*	0	1	13*	0	-1	2*	0	2	2*	0	-3	3*	0	5
11*	0	1	10	9	6	11	14	-14	16	11	-13	K,L=	6	13	3*	0	11	4	12	13	4*	0	-4
12*	0	-7	11	9	7	12*	0	-1	17*	0	-3	0*	0	0	4	22	24	6*	0	3	5	11	10
13*	0	-3	12*	0	-7	13	12	-13	18*	0	-3	1*	0	-1	5	10	-10	8	14	14	6*	0	0

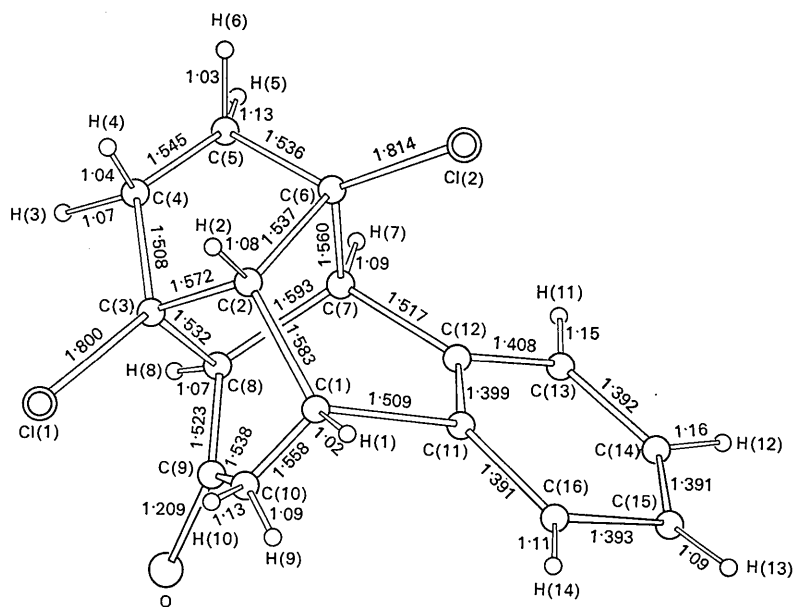
Table 6. Bond lengths and their e.s.d.'s

	Distance	e.s.d.		Distance	e.s.d.
C(1)—C(2)	1.583 Å	0.008 Å	C(11)—C(16)	1.391 Å	0.008 Å
C(2)—C(3)	1.572	0.007	C(9)—O	1.209	0.007
C(3)—C(4)	1.508	0.008	Cl(1)—C(3)	1.800	0.006
C(4)—C(5)	1.545	0.008	Cl(2)—C(6)	1.814	0.005
C(5)—C(6)	1.536	0.008	C(1)—H(1)	1.02	0.06
C(6)—C(7)	1.560	0.007	C(2)—H(2)	1.08	0.06
C(7)—C(8)	1.593	0.007	C(

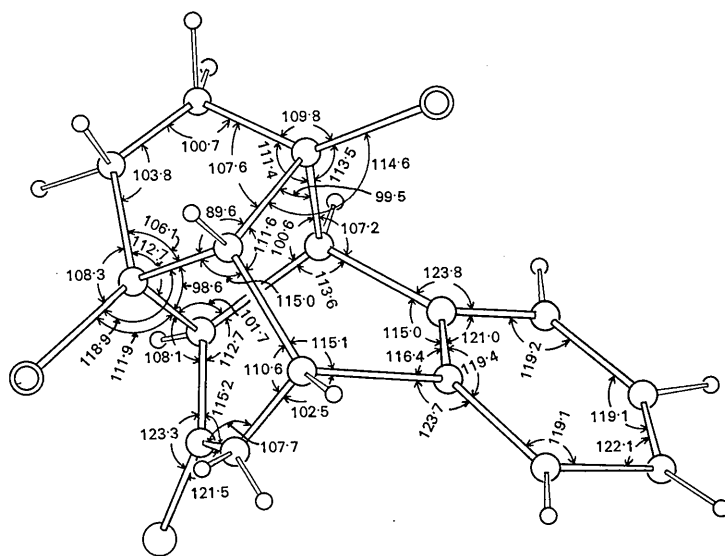
Bastiansen & Fernholt, 1958; Kimura & Kubo, 1960) and that found for crystalline benzene by X-ray diffraction ($1.392 \pm 0.004 \text{ \AA}$) by Cox, Cruickshank & Smith (1958).

There is surprisingly wide variation in the single C-C bond lengths, ranging from 1.508 to 1.593 \AA . Judging from the precision of the parameters described above, this variation does not appear to result from the errors of the reflexion data. The average length, 1.552 \AA , of the ten C-C bonds is significantly greater than the value

of $1.533 \pm 0.003 \text{ \AA}$, which is generally accepted as the normal length for $C(sp^3)-C(sp^3)$ (Bartell, 1959). Similar results have already been reported in some cage molecules (Ammon & Jensen, 1967; Alden, Kraut & Traylor, 1968). This lengthening might be expected in view of the departure from ideal tetrahedral hybridization caused by geometrical factors and the large number of non-bonded interactions. Recent elaborate investigations by Alden, Kraut & Traylor (1968) have supported the suggestion by Dewar & Schmeising (1959) that bond



(a)



(b)

Fig. 4. (a) Bond lengths (\AA). (b) Bond angles ($^\circ$).

lengths of C—C single bonds depend on the percentage *s* character in the hybrid atomic orbitals composing the bond.

Among C(*sp*³)-C(*sp*³) bond lengths, C(7)-C(8) (1.593 Å) and C(1)-C(2) (1.583 Å) are quite long. The former appears to be the longest so far reported. It is worth noticing that for these bonds each relevant atom has two non-hydrogen substituents, a conformation of which furnishes the conditions for non-bonded eclipsed interaction as shown in Fig. 5(a) and (c). The difference

in the bond lengths is consistent with that in the projected angles.

However, the polycyclic nature of the structure makes justification of all bond length variations impossible for the time being. A comparison of the projected angles between substituents for each of the bonds in question provides little help in explaining the differences. For example, the distances of C(3)-C(8) and C(6)-C(7) are different while the projected angles are similar as shown in Fig. 6(c) and (d). However, it is interesting

Table 7. Bond angles and their e.s.d.'s

	Angle	e.s.d.		Angle	e.s.d.
O—C(9)—C(8)	123.3°	0.5°	C(14)—C(15)—H(13)	121.0°	3.0°
O—C(9)—C(10)	121.5	0.5	C(15)—C(14)—C(13)	119.1	0.6
C(8)—C(9)—C(10)	115.2	0.4	C(15)—C(14)—H(12)	121.0	3.0
C(9)—C(8)—C(7)	112.7	0.4	C(13)—C(14)—H(12)	120.0	3.0
C(9)—C(8)—C(3)	108.1	0.4	C(12)—C(13)—C(14)	119.2	0.5
C(9)—C(8)—H(8)	107.0	3.0	C(12)—C(13)—H(11)	121.0	3.0
C(7)—C(8)—C(3)	101.7	0.4	C(14)—C(13)—H(11)	119.0	3.0
C(7)—C(8)—H(8)	112.0	3.0	Cl(1)—C(3)—C(8)	111.9	0.4
C(3)—C(8)—H(8)	115.0	3.0	Cl(1)—C(3)—C(2)	118.9	0.4
C(8)—C(7)—C(12)	113.6	0.4	Cl(1)—C(3)—C(4)	108.3	0.4
C(8)—C(7)—C(6)	100.6	0.4	C(8)—C(3)—C(2)	98.6	0.4
C(8)—C(7)—H(7)	113.0	3.0	C(8)—C(3)—C(4)	112.7	0.4
C(12)—C(7)—C(6)	107.2	0.4	C(2)—C(3)—C(4)	106.1	0.4
C(12)—C(7)—H(7)	107.0	3.0	C(1)—C(2)—C(3)	115.0	0.4
C(6)—C(7)—H(7)	116.0	3.0	C(1)—C(2)—C(6)	111.6	0.4
C(7)—C(12)—C(11)	115.0	0.4	C(1)—C(2)—H(2)	103.0	3.0
C(7)—C(12)—C(13)	123.8	0.4	C(3)—C(2)—C(6)	89.6	0.4
C(11)—C(12)—C(13)	121.0	0.5	C(3)—C(2)—H(2)	120.0	3.0
C(12)—C(11)—C(1)	116.4	0.5	C(6)—C(2)—H(2)	119.0	3.0
C(12)—C(11)—C(16)	119.4	0.5	Cl(2)—C(6)—C(7)	113.5	0.3
C(1)—C(11)—C(16)	123.7	0.5	Cl(2)—C(6)—C(2)	114.6	0.4
C(11)—C(1)—C(10)	102.5	0.4	Cl(2)—C(6)—C(5)	109.8	0.4
C(11)—C(1)—C(2)	115.1	0.5	C(7)—C(6)—C(2)	99.5	0.4
C(11)—C(1)—H(1)	109.0	3.0	C(7)—C(6)—C(5)	111.4	0.4
C(10)—C(1)—C(2)	110.6	0.5	C(2)—C(6)—C(5)	107.6	0.4
C(10)—C(1)—H(1)	114.0	3.0	C(6)—C(5)—C(4)	100.7	0.4
C(2)—C(1)—H(1)	106.0	3.0	C(6)—C(5)—H(5)	110.0	3.0
C(9)—C(10)—C(1)	107.7	0.5	C(6)—C(5)—H(6)	112.0	3.0
C(9)—C(10)—H(9)	111.0	3.0	C(4)—C(5)—H(5)	117.0	3.0
C(9)—C(10)—H(10)	111.0	3.0	C(4)—C(5)—H(6)	114.0	3.0
C(1)—C(10)—H(9)	113.0	3.0	H(5)—C(5)—H(6)	103.0	4.0
C(1)—C(10)—H(10)	111.0	3.0	C(3)—C(4)—C(5)	103.8	0.5
H(9)—C(10)—H(10)	103.0	4.0	C(3)—C(4)—H(3)	111.0	3.0
C(11)—C(16)—C(15)	119.1	0.6	C(3)—C(4)—H(4)	113.0	3.0
C(11)—C(16)—H(14)	122.0	3.0	C(5)—C(4)—H(3)	113.0	3.0
C(15)—C(16)—H(14)	119.0	3.0	C(5)—C(4)—H(4)	111.0	3.0
C(16)—C(15)—C(14)	122.1	0.7	H(3)—C(4)—H(4)	105.0	4.0
C(16)—C(15)—H(13)	117.0	3.0			

Table 8. Comparison of the geometry in cyclic ketones

	Androsterone*	Present compound	Cyclohexane-1,4-dione†
C=O (Å)	1.189	1.209	1.220 1.223
C—C (Å)	1.517 1.520	1.523 1.538	1.496 1.504 1.505 1.512
C—CO—C (deg)	107.8	115.2	117.3 117.5

* High & Kraut (1966).

† Groth & Hassel (1964).

that the sum of the lengths of the four bonds around C(3) is approximately equal to that around C(6).

The lengths of the two bonds with C(sp³)-C(sp²) [C(7)-C(12), 1.517 Å, and C(1)-C(11), 1.509 Å] are con-

sistent with those reported for bonds of this type, 1.506-1.516 Å (*Tables of Interatomic Distances*, 1965), and 1.505 ± 0.003 Å (Bartell & Bonham, 1960). If the difference between the two is of some significance, it

Table 9. *Some least-squares planes*

		Plane									
	I	II	III	IV	V	VI					
<i>l</i>	-0.4924	-0.3711	-0.3873	-0.0873	-0.7198	0.7446					
<i>m</i>	-0.6698	-0.7409	-0.7477	-0.0291	0.3753	-0.4683					
<i>n</i>	-0.5558	0.5597	0.5394	-0.9958	-0.5840	-0.4757					
<i>p</i>	7.872	2.199	2.341	5.930	2.720	3.681					
Deviations of atoms (Å)											
C(11)	0.012	O	0.007	C(8)	0.000	C(2)	0.000	C(3)	0.001	C(3)	-0.008
C(12)	-0.005	C(8)	0.005	C(9)	0.000	C(3)	0.000	C(4)	-0.001	C(6)	0.008
C(13)	-0.004	C(9)	-0.017	C(10)	0.000	C(6)	0.000	C(5)	0.001	C(7)	-0.011
C(14)	0.005	C(10)	0.005	O	0.057*	C(4)	-1.140*	C(6)	-0.001	C(8)	0.011
C(15)	0.002	C(1)	-0.681*	C(1)	-0.723*	C(5)	-1.162*	C(2)	-0.854*	C(2)	1.000*
C(16)	-0.011	C(7)	-1.376*	C(7)	-1.400*	C(7)	1.379*	C(7)	1.384*	C(4)	-1.330*
				C(8)	1.371*	C(8)	1.371*	C(8)	1.349*	C(5)	-1.350*
C(1)	0.246*										
C(7)	-0.131*										
H(11)	-0.03*										
H(12)	-0.02*										
H(13)	0.04*										
H(14)	-0.06*										

The equations of the planes are expressed in the form $lx + my + nz + p = 0$.

* Asterisks indicate atoms not included in the plane calculations.

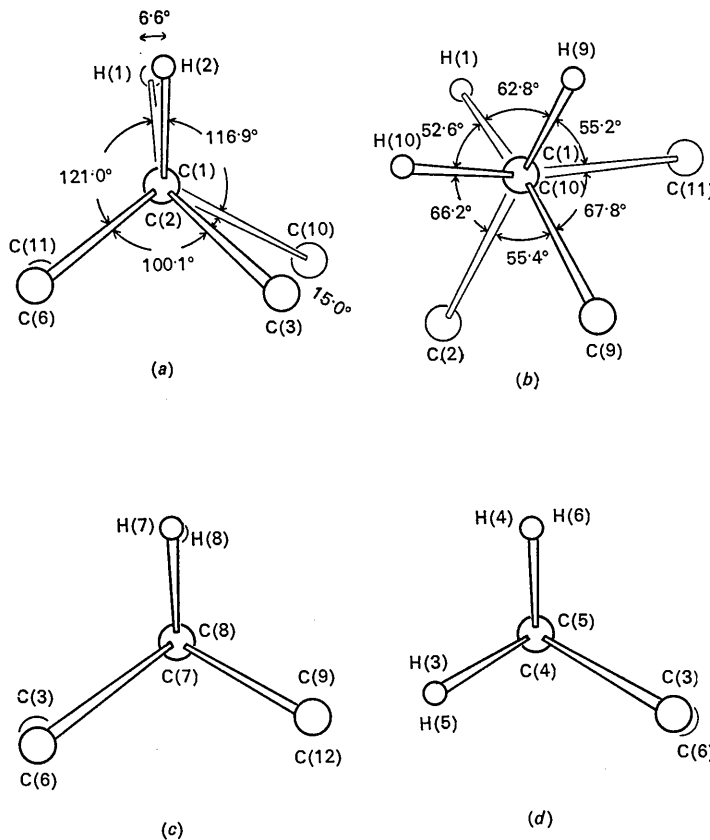


Fig. 5. Conformations about the bonds C(1)-C(2), C(1)-C(10), C(7)-C(8) and C(4)-C(5).

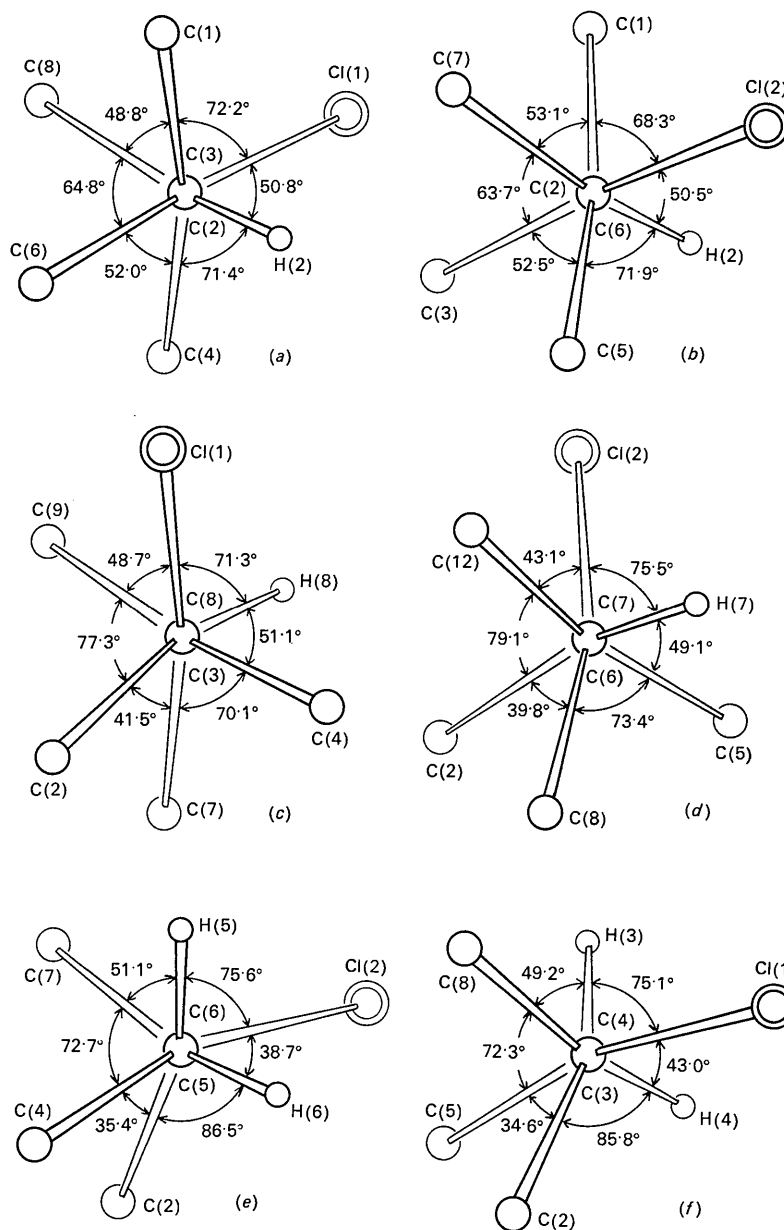


Fig. 6. Conformations about the bonds C(2)-C(3), C(2)-C(6), C(3)-C(8), C(6)-C(7), C(5)-C(6) and C(3)-C(4).

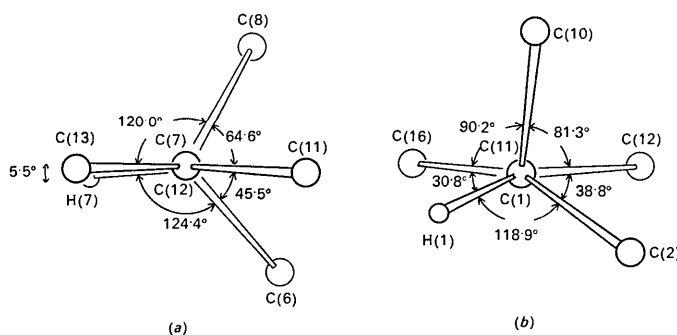


Fig. 7. Conformations about the bonds C(7)-C(12) and C(1)-C(11).

may be reasonably explained by different projected angles along the bonds as shown in Fig. 7(a) and (b). The other distances of the same type, C(8)–C(9) and C(9)–C(10), are somewhat longer than usual probably because of the polycyclic ring strain.

The conformation of the six-membered ring [C(1)–C(2)–C(3)–C(8)–C(9)–C(10)] can be described as distorted twist or skew boat (Ammon & Jensen, 1967) as shown in Fig. 8(a). The strain in this polycyclic ring seems to have some effect on the stereochemistry of the keto group. Table 8 compares the bond lengths and angles found in the present molecule with those found in the unconjugated five-membered ring ketone (androsterone) (High & Kraut, 1966) and in the six-membered ring ketone (cyclohexane-1,4-dione) (Groth & Hassel, 1964). Both the C=O bond length and the C–CO–C angle in the present compound are intermediate between those in the other two. It is thus confirmed that decreasing the C–CO–C angle would make the orbitals forming the C=O bond assume a somewhat greater *s* character and would shorten the bond. The conclusion that C(9) does not have exactly *sp*² hybridization is consistent with the observation that the O atom lies 0.057 Å out of the plane through C(8), C(9) and C(10) (plane III in Table 9). However, the effect is slight; if a plane is fitted to all four atoms (plane II in Table 9), the largest atom-to-plane distance is 0.017 Å.

The infrared absorption spectrum shows the ketone band at 1728 cm⁻¹ (KBr), which is also a value intermediate between those of the five-membered and the six-membered ring ketones. In cases such as the present molecule where such strain is operative, it is difficult to determine the ring size from the infrared spectrum. Schleyer & Nicholas (1961) found that the frequency of the carbonyl stretching band in unconjugated ketones increases with diminishing C–CO–C angle. The frequency can be calculated, by their equation (Schleyer & Nicholas, 1961) using the observed C–CO–C angle in the present molecule, to be 1722 cm⁻¹, which is surprisingly close to the observed value (1728 cm⁻¹).

The C–Cl bond lengths are 1.800 and 1.814 Å. Only a few accurate C–Cl bond distances have been reported for saturated aliphatic compounds. However, the present values are between those observed in 3,4,5-trichlorotetracyclo[4,4,0,0^{3,9},0^{4,8}]decan-2-one (Schwarzenbach, 1968) and those in 2,3-bis-(*cis*-4-chloro-1-methylcyclohexyl)-*trans*-2-butene (Mootz, 1968), and are reasonable in view of the deviations of the bond angles of attached carbon atoms from the tetrahedral value.

The average of the fourteen C–H bonds, 1.09 Å, corresponds with the usual value.

The cage structure contains three six-membered rings with different conformations. The conformation of the ring [C(1)–C(2)–C(6)–C(7)–C(12)–C(11)] is twist half-boat, that of [C(1)–C(2)–C(3)–C(8)–C(9)–C(10)] is twist boat and that of [C(3)–C(4)–C(5)–C(6)–C(7)–C(8)] is boat, which composes a norbornane skeleton with the C(2) bridge, as shown in Fig. 8(a), (b) and (c)

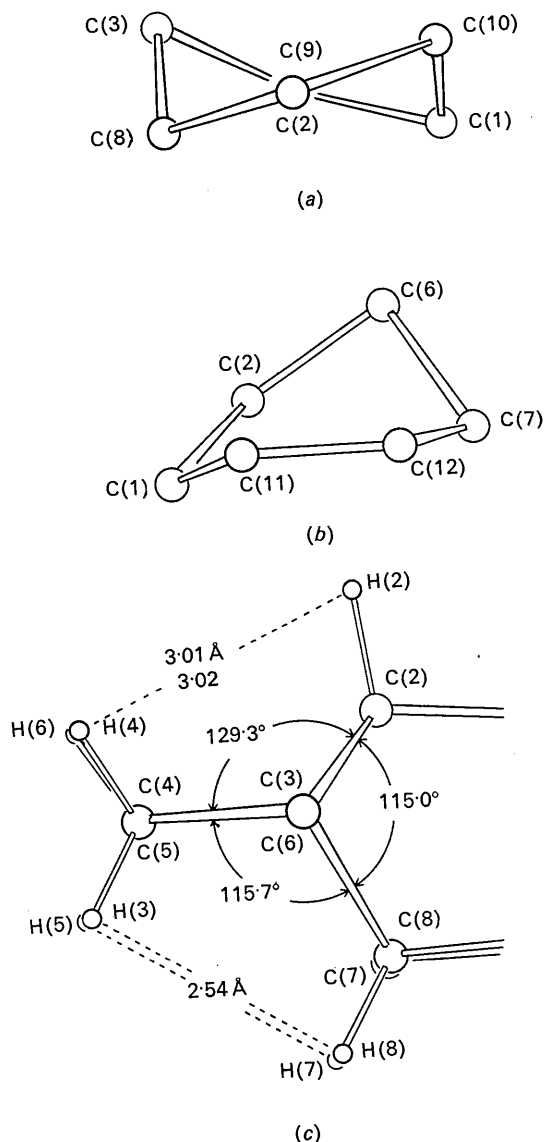


Fig. 8. Three six-membered rings of the molecule, viewed along the lines C(2)···C(9) in (a), C(15)···C(11) in (b) and C(3)···C(6) in (c).

respectively. The constraints imposed by the C(1)–C(2) bond cause large deviations from the tetrahedral value for the bond angles in the five-membered ring [C(2)–C(3)–C(8)–C(7)–C(6)]. The largest deviation occurs in the C(3)–C(2)–C(6) angle which is 89.6° and the smallest value among the corresponding angles in the norbornane skeletons so far reported (Alden, Kraut & Traylor, 1968; Norment, 1965; Cesur & Grant, 1965; Macdonald & Trotter, 1965). This can be compared with the values observed in the four-membered rings (Margulis, 1965; Greenberg & Post, 1968; Bock, 1968; Adman & Margulis, 1968). Because of this small value of the C(3)–C(2)–C(6) angle, the non-bonded C(3)···C(6) distance is 2.190 Å as shown in Fig. 9. The long

C(2)–C(3) length, 1.572 Å, is probably the result of non-bonded intramolecular C···C repulsion as suggested for cyclobutane rings (Margulis, 1965; Adman & Margulis, 1968; Bock, 1968; Greenberg & Post, 1968). Moreover, the large fluctuations of the bond angles from 98.6 to 118.9° and from 99.5 to 114.6° are observed around C(3) and C(6) respectively. The feature that C(2) is attracted by C(1) can be clearly seen in Fig. 8(c). The dihedral angle between planes through C(2), C(3) and C(6) and through C(3), C(6), C(7) and C(8) is 115.0°, which is considerably smaller than that between planes through C(2), C(3) and C(6) and through C(3), C(4), C(5) and C(6), 129.3°. The intramolecular H···H distances are also tabulated in Table 10.

Table 10. Intramolecular H···H distances

H(6)···H(2)	3.02 Å
H(4)···H(2)	3.01
H(11)···H(7)	2.44
H(14)···H(1)	2.56
H(5)···H(7)	2.54
H(3)···H(8)	2.54

The equations of the important least-squares planes and the displacements of atoms from the planes are given in Table 9. The phenyl ring is essentially planar, 0.012 Å being the largest deviation, while the atoms C(1) and C(7) are displaced 0.246 Å above and 0.131 Å below this plane respectively, as shown in Fig. 10(a). The dihedral angle between the planes through atoms C(1), C(11) and C(12) and through C(11), C(12) and C(7) is 14.5° as shown in Fig. 10(b), suggesting a considerable strain. The C(11)–C(12) distance, 1.399 Å, is not different from the average of the other five aroma-

tic C–C distances. It is interesting that such strain does not cause a deviation from planarity or variation in the bond lengths of the aromatic ring. Upon examining the aromatic ring more closely, there seems to be an approximate mirror plane through C(12) and C(15) perpendicular to the ring. None of these three pairs shows differences greater than 0.009 Å in their C–C bond lengths. Similarly there are two pairs of related C–C angles among which there are no differences greater than 0.2°.

The seven-membered ring [C(1)–C(10)–C(9)–C(8)–C(7)–C(12)–C(11)] is forced to take twist boat conformation. The dihedral angle between the phenyl ring, plane I, and the carbonyl plane, plane II, is 68.4° (Fig. 11) and the non-bonded distances, C(9)···C(11) and C(9)···C(12), are 2.866 and 2.787 Å respectively (Fig. 9). Judging from these structural features, some *trans*-annular π -electron interaction between the benzene ring and the carbonyl group may be assumed. The ultraviolet absorption spectra of this compound were measured in *n*-pentane and methylene chloride as shown in Fig. 12. Besides the absorption of cycloalkenobenzene chromophore at *ca.* 270 $m\mu$ and of saturated ketone at *ca.* 300 $m\mu$, a new absorption band at 233 $m\mu$ ($\log \epsilon = 2.69$) is exhibited in methylene chloride solution. It can be presumed that this band would shift to shorter wave-lengths than 230 $m\mu$ in non-polar *n*-pentane solution. Such solvent dependence is appropriate for $\pi \rightarrow \pi^*$ transition. The long wave-length $n \rightarrow \pi^*$ absorption at *ca.* 300 $m\mu$ does not exhibit the high extinction coefficient characteristic of many other ketones with a neighbouring olefinic or phenyl group. The similar behaviour of the spectra in γ, δ -unsaturated

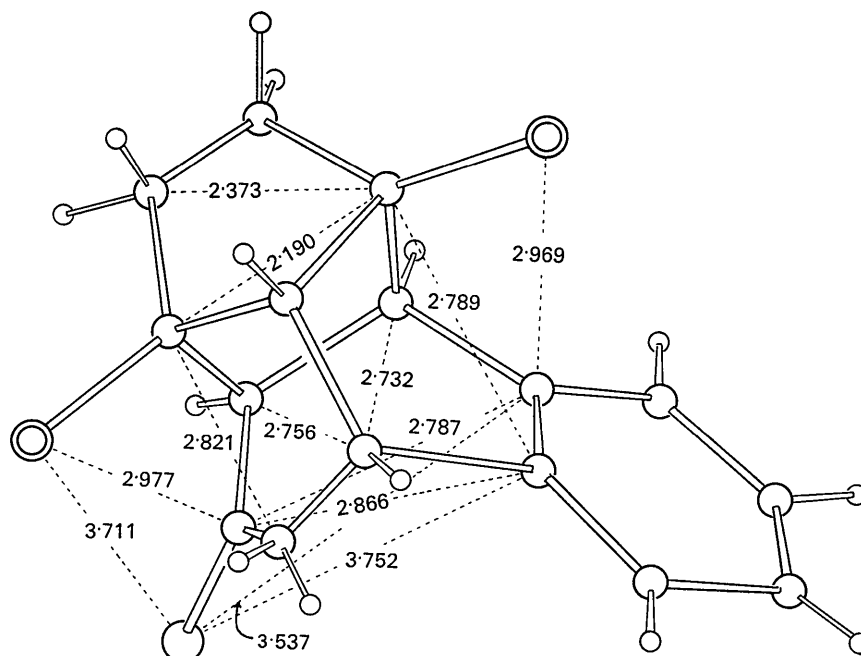


Fig. 9. Some non-bonded intramolecular distances (Å).

ketones has already been reported and the change of characteristic ultraviolet spectra by interactions between non-adjacent chromophores is of considerable theoretical interest (Winstein, de Vries & Orloski, 1961).

Crystal structure

The molecular arrangement in the crystal is depicted in Fig. 13, and the closest intermolecular approaches are given in Table 11. There are no abnormally short intermolecular distances between the non-hydrogen atoms; the shortest C...C contact is 3.478 Å. The two short C...H contacts, 2.58 and 2.63 Å, are observed; the relevant hydrogen atom H(14) (*F*) is nearly above the centre of the bond C(14)–C(15) in the benzene ring of the molecule *A*. The shortest H...H contact is 2.43 Å, which is approximately the sum of the accepted van der Waals radii. The packing appears to be fairly efficient, but there are no intermolecular contacts so close that they should give rise to appreciable distortions of the molecule, and thus the major distortions which do exist must be ascribed to intramolecular effects.

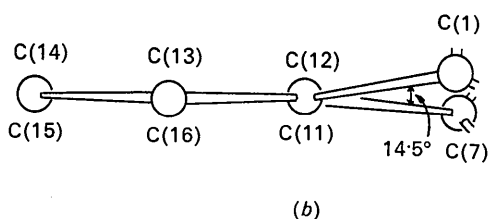
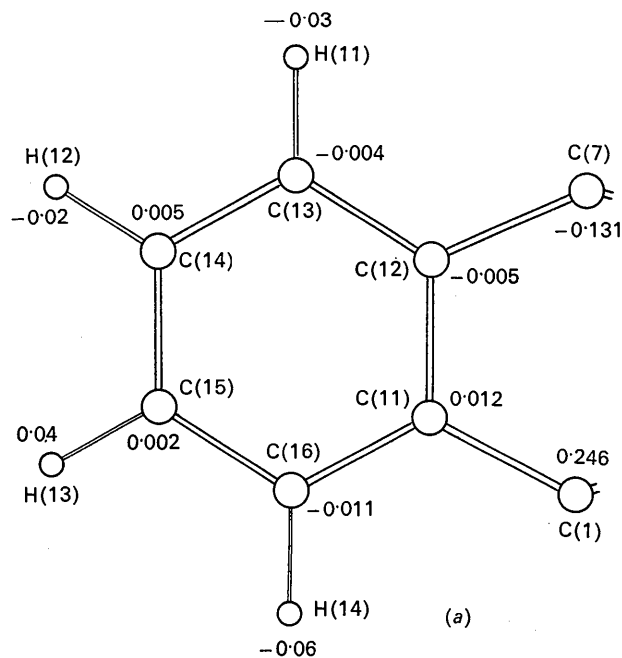


Fig. 10. (a) The deviations (Å) of the atoms from the least-squares plane through atoms C(11)–C(16). (b) Conformations about the bond C(11)–C(12).

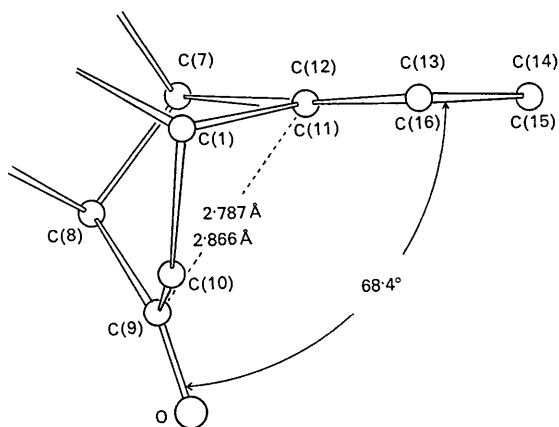


Fig. 11. The seven-membered ring, viewed along the bond C(11)–C(12).

Table 11. Shortest intermolecular distances

Cl(2) (<i>A</i>) ... Cl(1) (<i>B</i>)	3.989 Å
Cl(1) (<i>A</i>) ... C(14) (<i>C</i>)	3.743
O (<i>A</i>) ... Cl(1) (<i>D</i>)	3.745
C(4) (<i>A</i>) ... O (<i>C</i>)	3.308
C(15) (<i>A</i>) ... C(16) (<i>F</i>)	3.478
H(5) (<i>A</i>) ... Cl(1) (<i>B</i>)	2.75
Cl(2) (<i>A</i>) ... H(1) (<i>F</i>)	2.96
H(7) (<i>A</i>) ... O (<i>D</i>)	2.69
C(15) (<i>A</i>) ... H(14) (<i>F</i>)	2.58
C(14) (<i>A</i>) ... H(14) (<i>F</i>)	2.63
H(8) (<i>A</i>) ... H(7) (<i>E</i>)	2.43

Positions of molecules are: *A* at (*x*, *y*, *z*), *B* at (*x*, 1+*y*, *z*), *C* at (*x*, $\frac{1}{2}$ −*y*, $\frac{1}{2}$ +*z*), *D* at (\bar{x} , $\frac{1}{2}$ +*y*, $\frac{1}{2}$ −*z*), *E* at (\bar{x} , $-\frac{1}{2}$ +*y*, $\frac{1}{2}$ −*z*) and *F* at ($\frac{1}{2}$ −*x*, $\frac{1}{2}$ +*y*, *z*). They are also indicated in Fig. 13.

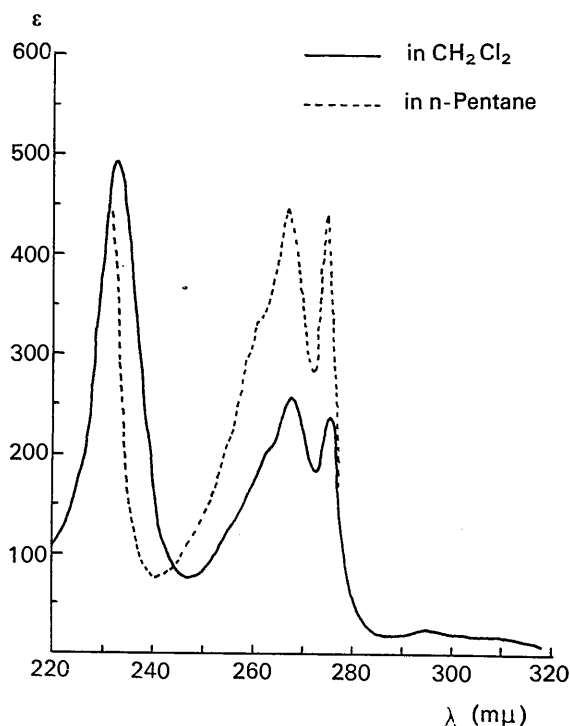


Fig. 12. Ultraviolet absorption spectra.

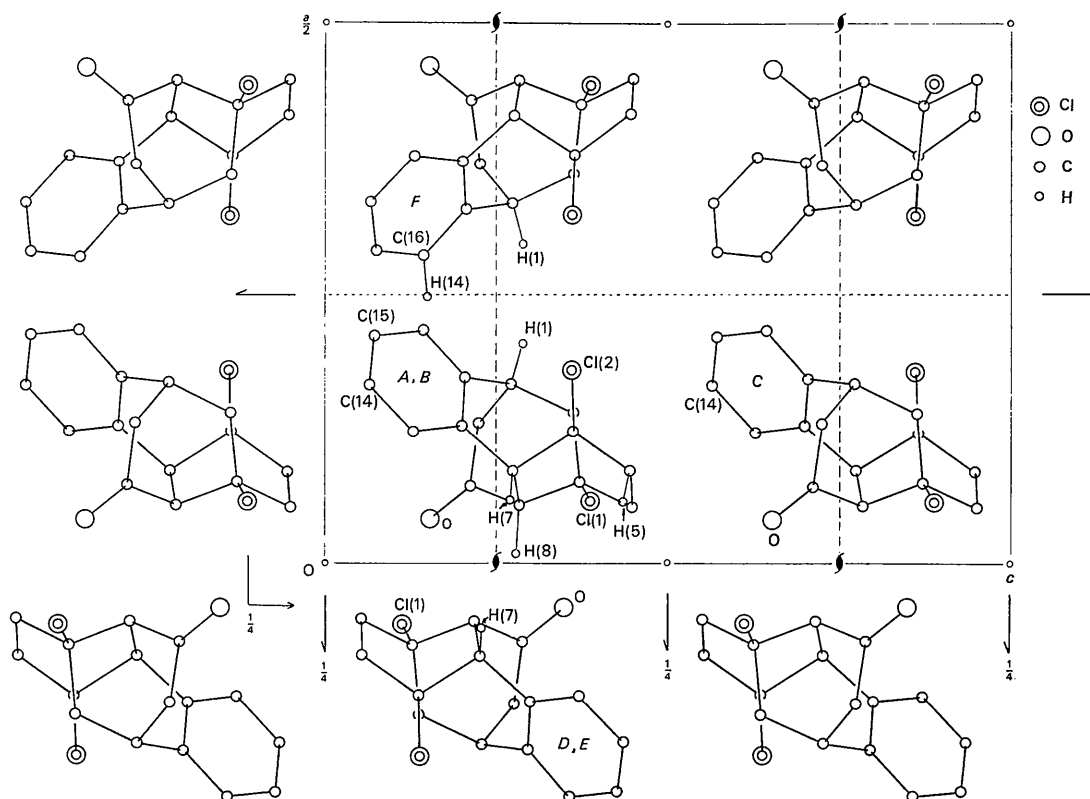


Fig. 13. The crystal structure projected along the b axis.

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