Crystal Structure of Spirodienone II

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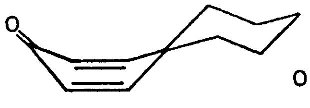
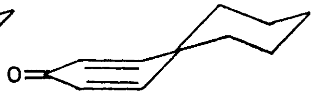
The crystal structure of the title compound has been determined by a three-dimensional X-ray analysis. The crystals are orthorhombic, with $a = 9{\cdot}781 \pm 0{\cdot}003$, $b = 9{\cdot}923 \pm 0{\cdot}003$, $c = 9{\cdot}428 \pm 0{\cdot}003$ Å, and $Z = 4$, in space group $P2_12_12_1$. The structure was solved from diffractometer data by the phase-addition and tangent refinement procedures and refined by full-matrix least-squares calculations to a final R of 0·055 for 878 independent observed reflections. The molecule consists of a cyclodienone ring and a cyclohexane ring, joined through a spiro-carbon atom: it contains an almost perfect mirror plane. The mean of the angles around the spiro-carbon atom is *ca.* 109·4°.

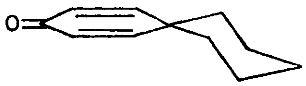
SPIRODIENONE II[1] has three possible conformations (I)—(III). In order to obtain detailed information on the molecular conformation and the configuration around the spiro-carbon atom, we have determined the structure of spirodienone II by means of a single-crystal X-ray analysis and shown it to correspond to (III).



(I)



(II)



(III)

EXPERIMENTAL

Samples were prepared by the method of ref. 1, and recrystallized from n-hexane as colourless prisms (m.p. 83·5—84·5°).

Crystal Data.—$C_{11}H_{14}O$, $M = 162{\cdot}2$. Orthorhombic, $a = 9{\cdot}781 \pm 0{\cdot}003$, $b = 9{\cdot}923 \pm 0{\cdot}003$, $c = 9{\cdot}428 \pm 0{\cdot}003$ Å, $U = 915$ Å^3, $D_m = 1{\cdot}165$ (by flotation), $Z = 4$, $D_c = 1{\cdot}177$, $F(000) = 352$. Space group $P2_12_12_1$ (D_2^4) from systematic absences: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 0{\cdot}785$ cm^{-1}.

Precession and Weissenberg photographs were taken with Cu-K_α radiation; the unit-cell dimensions were determined from the precession photographs and refined from the diffractometer data.

The three-dimensional intensity data were collected on a Hilger and Watts automatic four-circle diffractometer Y 290 controlled by a PDP 8 computer. Integrated intensities were measured for $\theta < 27{\cdot}5°$ by the θ—2θ scan technique with Mo-K_α radiation and a scintillation counter (with a Zirconium filter and pulse-height analyser). Each reflection was integrated in 80 steps of intervals of 0·01°. In this way 1231 independent reflections were recorded, of which 978 had counts more than one standard deviation of the total counts, after the two background readings had been subtracted. All the intensities were corrected for Lorentz and polarization factors, and the normalized structure factors $|E|$ as well as structure amplitudes $|F|$ were derived. No absorption corrections were applied since the specimen was considered to be sufficiently small (0·23 × 0·26 × 0·28 mm.).

Structure Analysis.—The structure was solved by the phase-addition procedure[2] for noncentrosymmetric space groups followed by tangent refinement. The normalized structure-factor magnitudes $|E|$ and the Σ_2 relationships were calculated with the use of a programme of Okada,[3] and 392 reflections with $|E| > 1{\cdot}00$ were used in subsequent calculations. Initially only terms with $|E_h| > 1{\cdot}5$ were used in the Σ_2-relationship. The origin and enantiomorph were defined by arbitrary choices of phase for the following reflections:

	E	ϕ	
1,2,0	3·87	$\phi = -\pi/2$	Fixes origin
0,7,10	2·86	$\pi/2$	
2,0,1	2·49	$-\pi/2$	
5,0,8	2·44	0	Fixes enantiomorph

The 4,1,0 reflection (E 2·27) was added to this list with its two possible phases of 0, π and the sets were extended by the use of the equation:[2] $\phi_{h+k} \approx \phi_h + \phi_k$, only those phases being accepted whose variance did not exceed 0·5 radians. This yielded two sets of 76 phases which were extended and refined with the formula[2] $\tan \phi_h \approx \Sigma|E_{h-k}||E_k| \sin(\phi_{h-k} + \phi_k)/\Sigma|E_{h-k}||E_k| \cos(\phi_{h-k} + \phi_k)$ by means of a computer program written by Okada.[3] The set with $\phi_{4,0,1} = \pi$ gave 322 phases and led smoothly to an E map containing twelve distinctively strong peaks per asymmetric unit (peak heights ranging from 628—212, the next highest being 110), and they were readily shown to represent the whole molecule. The other option for $\phi_{4,1,0}$ gave a map containing nothing meaningful and its few strong peaks would not refine. The approximate co-ordinates of the molecule were refined isotropically by two cycles of full-matrix least squares to R 0·140, and anisotropically to R 0·104 using a CDC 3600 computer with the programme of Busing and Levy.[4] At this stage a difference-Fourier synthesis was calculated from which the positions of the 14 hydrogen atoms were found (Figure 1). Inclusion of the hydrogen atoms with constant temperature factor $B = 2{\cdot}0$ Å^2 in subsequent cycles of least-squares refinement reduced R to 0·055 for the 878 reflections whose intensities were less than twice the standard deviation of the total counts; the remainder were rejected. In this refinement an equal weight was applied to the 878 structure factors. No more appropriate weighting scheme could be found from an analysis of the ΔF values.

Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20273 (3 pp., 1

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[1] A. S. Dreiding, *Helv. Chim. Acta*, 1957, **40**, 1812.

[2] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[3] K. Okada, personal communication.

[4] W. L. Busing, K. O. Martin, and H. A. Levy, 1962, ORFLS, A Fortran Crystallographic Least-squares Program, Oak Ridge National Laboratory, Tennessee.

microfiche).* The atomic scattering factors used in all calculations were taken from ref. 5. A final three-dimensional difference Fourier map over one molecule of spirodienone II is shown in Figure 1. The positional and thermal parameters for the final structure are given in Tables 1 and 2. Bond distances and valency angles are given in Table 3, together with their standard deviations computed from the least-squares residuals. The molecular packing arrangement seen along the c axis is illustrated in Figure 2. All intermolecular distances were calculated,

TABLE 1

Final fractional atomic co-ordinates and anisotropic thermal parameters,* with estimated standard deviations in parentheses

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	0·3341(4)	0·1236(4)	1·0328(3)	0·0217(6)	0·0216(6)	0·0161(4)	−0·0031(5)	0·0085(5)	−0·0016(5)
C(1)	0·3923(5)	0·1318(4)	0·9184(5)	0·0150(6)	0·0106(4)	0·0153(6)	0·0004(5)	0·0034(6)	0·0007(5)
C(2)	0·3299(4)	0·0819(4)	0·7872(5)	0·0113(5)	0·0121(5)	0·0165(6)	−0·0017(4)	0·0022(5)	0·0016(5)
C(3)	0·3924(4)	0·0898(4)	0·6642(5)	0·0097(5)	0·0125(5)	0·0139(6)	−0·0009(4)	−0·0016(4)	0·0011(4)
C(4)	0·5327(4)	0·1492(4)	0·6430(4)	0·0104(4)	0·0106(4)	0·0100(4)	−0·0008(4)	0·0000(4)	0·0007(4)
C(5)	0·5930(4)	0·1979(4)	0·7805(4)	0·0114(5)	0·0111(4)	0·0123(5)	−0·0012(4)	−0·0009(5)	−0·0001(4)
C(6)	0·5315(5)	0·1892(4)	0·9047(4)	0·0137(5)	0·0108(4)	0·0119(5)	0·0000(4)	−0·0002(5)	−0·0011(4)
C(7)	0·5265(5)	0·2695(4)	0·5387(4)	0·0138(6)	0·0099(5)	0·0138(6)	0·0001(4)	0·0016(5)	0·0020(4)
C(8)	0·4915(5)	0·2271(5)	0·3871(5)	0·0173(7)	0·0139(6)	0·0126(6)	0·0003(6)	−0·0010(6)	0·0036(5)
C(9)	0·5886(6)	0·1207(5)	0·3324(5)	0·0180(8)	0·0179(7)	0·0111(5)	−0·0014(7)	0·0004(6)	−0·0011(5)
C(10)	0·5920(5)	−0·0003(5)	0·4293(5)	0·0158(6)	0·0133(5)	0·0134(6)	0·0020(5)	0·0008(5)	−0·0022(5)
C(11)	0·6306(4)	0·0411(4)	0·5805(5)	0·0120(5)	0·0115(5)	0·0133(6)	0·0014(4)	−0·0005(5)	0·0006(4)

* In the form: $T = \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

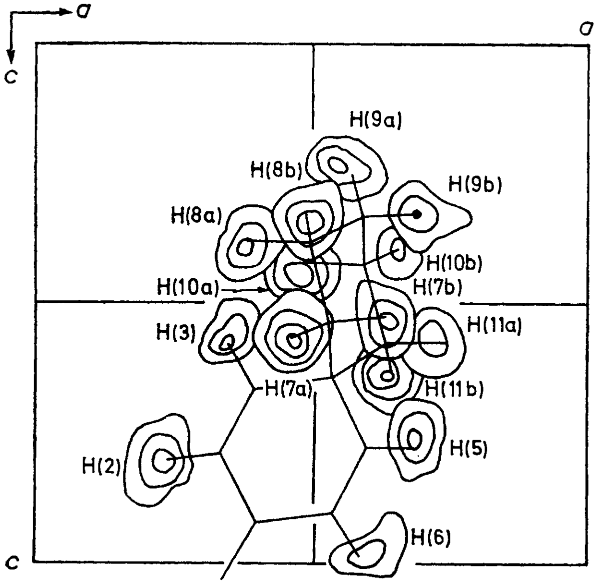

FIGURE 1 The difference electron-density map showing the hydrogen atoms. Contours are drawn on an arbitrary scale

TABLE 2

Final fractional hydrogen atom co-ordinates with their standard deviations in parentheses, and isotropic temperature factors

Atom	x	y	z	B
H(2)	0·236(4)	0·041(3)	0·801(4)	2·000
H(3)	0·349(4)	0·051(4)	0·579(4)	2·000
H(5)	0·691(3)	0·252(3)	0·775(4)	2·000
H(6)	0·583(3)	0·228(3)	0·991(4)	2·000
H(7a)	0·460(4)	0·335(4)	0·575(4)	2·000
H(7b)	0·632(4)	0·320(3)	0·534(4)	2·000
H(8a)	0·379(4)	0·200(3)	0·385(4)	2·000
H(8b)	0·487(4)	0·317(3)	0·327(3)	2·000
H(9a)	0·572(4)	0·097(4)	0·245(4)	2·000
H(9b)	0·693(4)	0·161(4)	0·330(4)	2·000
H(10a)	0·479(4)	−0·053(3)	0·433(4)	2·000
H(10b)	0·650(4)	−0·073(3)	0·396(4)	2·000
H(11a)	0·735(4)	0·075(3)	0·580(4)	2·000
H(11b)	0·637(4)	−0·035(4)	0·643(4)	2·000

TABLE 3

Interatomic distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Bond distances

O–C(1)	1·222(6)	C(4)–C(11)	1·554(6)
C(1)–C(2)	1·465(7)	C(5)–C(6)	1·319(6)
C(1)–C(6)	1·481(7)	C(7)–C(8)	1·528(6)
C(2)–C(3)	1·313(6)	C(8)–C(9)	1·511(7)
C(3)–C(4)	1·506(6)	C(9)–C(10)	1·509(7)
C(4)–C(5)	1·503(6)	C(10)–C(11)	1·531(7)
C(4)–C(7)	1·547(5)		

(*b*) Valency angles

O–C(1)–C(2)	121·8(4)	C(5)–C(4)–C(11)	107·9(3)
O–C(1)–C(6)	122·0(4)	C(7)–C(4)–C(11)	108·3(3)
C(2)–C(1)–C(6)	116·0(4)	C(4)–C(5)–C(6)	124·4(4)
C(1)–C(2)–C(3)	122·0(4)	C(1)–C(6)–C(5)	121·4(4)
C(2)–C(3)–C(4)	124·3(4)	C(4)–C(7)–C(8)	113·0(3)
C(3)–C(4)–C(5)	111·6(3)	C(7)–C(8)–C(9)	111·7(4)
C(3)–C(4)–C(7)	110·5(3)	C(8)–C(9)–C(10)	111·2(4)
C(3)–C(4)–C(11)	109·9(3)	C(9)–C(10)–C(11)	110·7(4)
C(5)–C(4)–C(7)	108·3(3)	C(4)–C(11)–C(10)	112·7(3)

(*c*) Dihedral angles

C(2)–C(3) → C(4)–C(7)	−120·3
C(2)–C(3) → C(4)–C(11)	119·9
C(6)–C(5) → C(4)–C(7)	122·3
C(6)–C(5) → C(4)–C(11)	−120·5
C(5)–C(4) → C(7)–C(8)	169·4
C(5)–C(4) → C(11)–C(10)	−170·9
C(3)–C(4) → C(7)–C(8)	−67·9
C(3)–C(4) → C(11)–C(10)	67·0
C(4)–C(7) → C(8)–C(9)	−54·9
C(4)–C(11) → C(10)–C(9)	56·9
C(7)–C(8) → C(9)–C(10)	55·7
C(11)–C(10) → C(9)–C(8)	−56·5

(*d*) C–H bond distances

C(2)–H(2)	1·00(4)	C(8)–H(8b)	1·05(3)
C(3)–H(3)	0·97(4)	C(9)–H(9a)	0·86(4)
C(5)–H(5)	1·10(3)	C(9)–H(9b)	1·10(4)
C(6)–H(6)	1·03(4)	C(10)–H(10a)	1·21(4)
C(7)–H(7a)	0·97(4)	C(10)–H(10b)	0·97(3)
C(7)–H(7b)	1·15(4)	C(11)–H(11a)	1·08(4)
C(8)–H(8a)	1·12(4)	C(11)–H(11b)	0·97(4)

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[5] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, pp. 201—207.

and the most significant contacts ($\leqslant 3{\cdot}60$ Å) are given in Table 4. The mean estimated standard deviations are about 0·006 Å for bond distances and about 0·4° for angles.

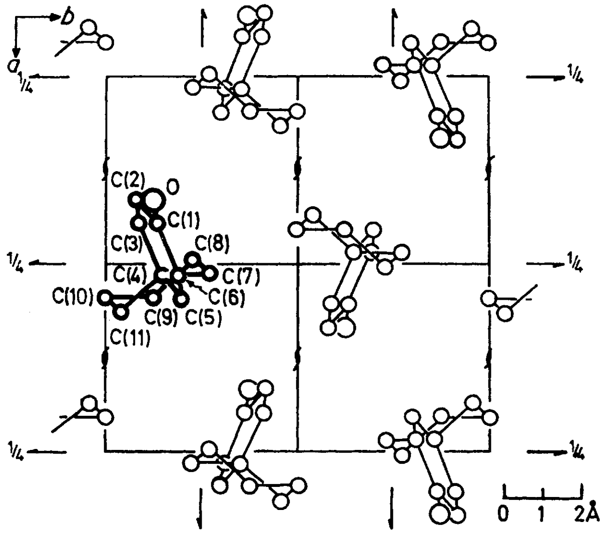

FIGURE 2 The view of the structure looking down *c*

DISCUSSION

The configuration of the molecule is illustrated[6] in Figure 3 where each atom is represented as an ellipsoid in conformity with the thermal parameters listed in Tables 1 and 2. The molecule consists of the cyclodienone ring and the cyclohexane ring, which are joined through a spiro-carbon atom. The planarity of the cyclodienone ring has been confirmed by calculating the least-squares plane through the atoms O, C(1)—(6) and the displacements of atoms from this plane are shown in Table 5. The cyclohexane ring has the normal chair conformation, and the groups of atoms C(3), C(4), C(5), C(7), and C(11) is tetrahedral. The mean of the angles around the spiro-carbon atom C(4) is *ca.* 109·4°.[7] The values for the C=C and C=O bond distances (1·313, 1·319, and 1·222 Å) in the cyclodienone ring are quite normal, but all the angles suggested the presence of considerable strain in the ring. The mean angle in the cyclohexane ring is *ca.* 111·3°.[8] The mean C–C bond (1·530 Å) in the cyclohexane ring is also considered normal, but the two mean C–C distances in the cyclodienone ring are considerably different from each other, 1·473 and 1·540 Å. The C_{sp^2}–C_{sp^2} single-bond distance of 1·473 Å is typical for conjugation. The values of 1·540 Å for C_{sp^3}–C_{sp^3} bonds is more strange and this may be due to spiro-carbon atom strains. The shortest contact is 3·306 Å between O and C(3^{I}) in the neighbouring molecule; other intermolecular contacts ($\leqslant 3{\cdot}60$ Å) are given in Table 4.

TABLE 4

Intermolecular distances ($<3{\cdot}60$ Å)

O · · · C(2^{I})	3·534	O · · · C(5^{II})	3·433
O · · · C(3^{I})	3·306	O · · · C(6^{II})	3·542

The Roman numerals as superscripts refer to the equivalent positions relative to the reference molecule at x, y, z:

I $\frac{1}{2} - x, -y, \frac{1}{2} + z$ II $-\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$

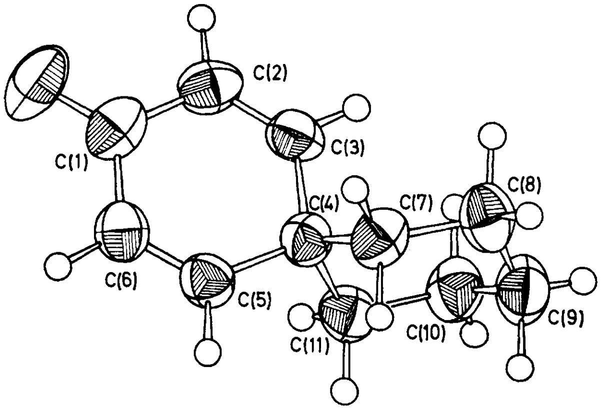

FIGURE 3 A diagram of the spirodienone II molecule

TABLE 5

Equations of best least-squares planes * and, in square brackets, displacements of the atoms (Å) from these planes †

Plane (a): O, C(1)—(6) $-0{\cdot}4045X + 0{\cdot}9017Y - 0{\cdot}1523Z = -1{\cdot}7000$
[C(7) 1·25, C(11) −1·26]

Plane (b): C(7), C(8), C(10), C(11) $0{\cdot}8854X + 0{\cdot}3355Y - 0{\cdot}3215Z = 3{\cdot}8319$
[C(4) −0·67, C(9) 0·66]

* X, Y, and Z are orthogonal co-ordinates in Å. † The atoms defining the planes were all 0·00 Å from them.

All other approaches correspond to normal van der Waals interactions.

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[7] O. Ermer and J. D. Dunitz, *Helv. Chim. Acta*, 1969, **52**, 1861.

[8] J. B. Lambert, R. E. Carhart, P. W. R. Corfield, and J. H. Enemark, *Chem. Comm.*, 1968, 999.