Structure Solution by Visual Packing and Optimization Techniques.
The Crystal and Molecular Structure of Spiro[5,5]undeca-1,4,7,10-tetraene-3,9-dione

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The structure of spiro[5,5]undeca-1,4,7,10-tetraene-3,9-dione, $C_{11}H_8O_2$, has been determined from three-dimensional X-ray counter data. The crystals have the space group $P\bar{1}$ with $a = 9\cdot080$ (4), $b = 13\cdot608$ (2), $c = 7\cdot493$ (3) Å, $\alpha = 91\cdot11$ (2), $\beta = 96\cdot91$ (4), $\gamma = 100\cdot50$ (2)° and four molecules per unit cell. The observed and calculated densities are $1\cdot26$ (1) and $1\cdot272$ g cm^{-3} respectively. 3180 independent reflections were collected by the θ–2θ scan method. The structure was solved independently by two methods. In one method a three-dimensional color television display system was used to search for the most likely packing arrangements in the unit cell. The other method involved an application of Boolean programming. Both methods arrived at the same model, which was refined by least-squares techniques to a conventional R index of $0\cdot048$ for the 1485 reflections having $I \geq 3\sigma_I$. The two independent molecules in the asymmetric unit are virtually identical and consist of two cyclodienone rings joined by a common spiro C atom. The average C–C bond length for bonds involving the spiro C atom is $1\cdot50$ (1) Å. The average bond angle around this atom is $109\cdot4°$.

Introduction

Spiro compounds are beginning to play a more prominent role in the theory of organic and biosynthetic reactions in that certain intermediates, often incapable of isolation, can assume the spiro type of bonding. Spiro configurations have been associated with carbenium ion, carbanion, free radical, and dipolar ionic intermediates (Newman, 1972), as well as specific reactions such as phenolic oxidation, Pschorr-type reactions, and photochemical reactions (Ward, 1973).

Several interesting natural products containing spiro C atoms have been isolated, *e.g.* athrotoxin (Daniels, Erdtman, Nishimura, Norin, Kierkegaard, & Pilotti, 1972; Pilotti, 1972). There are also several spiro-lactones which have been studied: Weber & Galantay

(1972), Mariezcurrena, Rasmussen, Lam & Wollenweber (1972).

Spiro compounds have also been of great interest in the development of the theory of spiroconjugation (Simmons & Fukunaga, 1967; Boschi, Dreiding & Heilbronner, 1970) as well as extending the theory of energy transfer between intramolecular chromophores (Keller, 1968; Hudson & Hedges, 1969).

Only a limited number of X-ray diffraction studies have been carried out on this type of compound. For this reason a study of spiro[5,5]undeca-1,4,7,10-tetraene-3,9-dione, originally prepared by Farges & Dreiding (1966), was undertaken. The molecule consists of two cyclodienone rings joined by a spiro C atom. A schematic representation of this molecule is shown in Fig. 1. The structure of this relatively simple symmetric compound, in which both rings are unsaturated, would be of help in understanding the interesting spectral and chemical properties of spiro compounds.

Because this compound has no internal degrees of freedom, it provided an excellent opportunity to use the visual display equipment in this laboratory as an aid in determining the structure based on crystal packing considerations. It also provided a test case for a direct method of determining phases by an application of Boolean programming that is currently under development. The two determinations were carried out in parallel and with the exceptions noted, independently of each other.
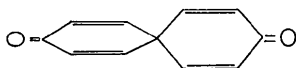

Fig. 1. Schematic representation of spirodienone.

Experimental

Samples of spiro[5,5]undeca-1,4,7,10-tetraene-3,9-dione, $C_{11}H_8O_2$, were provided by Dr Guy Farges. Large, transparent irregularly shaped plates were recrystallized from dioxane. The crystal used for intensity measurements was mounted in a thin-walled glass capillary (Meyer, 1973).

Cell data are summarized in Table 1. Cell dimensions were determined by least squares, minimizing the differences between the observed and calculated 2θ values for 23 reflections measured on a Datex-Syntex automated diffractometer. For these measurements and the subsequent intensity measurements, Mo $K\alpha$ radiation ($\lambda = 0.71069$Å), monochromatized by pyrolytic graphite, was used. The ambient temperature was 19 °C. The density was measured by flotation in an aqueous KI solution. The successful completion of the structure confirmed the choice of the centrosymmetric space group $P\bar{1}$, rather than $P1$. Because there are four molecules in the unit cell, there must be two independent molecules in the asymmetric unit.

Table 1. Crystal data

Estimated standard deviations are in parentheses.

$a = 9\cdot080$ (4) Å	$D_m = 1\cdot26$ (1) g cm^{-3}
$b = 13\cdot608$ (2)	$D_c = 1\cdot267$
$c = 7\cdot493$ (3)	M.W. 172·2
$\alpha = 91\cdot11$ (2)°	$Z = 4$
$\beta = 96\cdot91$ (4)	Systematic absences: none
$\gamma = 100\cdot50$ (2)	Space group $P\bar{1}$
$V = 902\cdot9$ Å^3	μ(Mo $K\alpha$ radiation) $= 0\cdot94$ cm^{-1}

The intensity data were collected by the θ–2θ scan method, the intensity scale being monitored by periodic measurement of a group of five standard reflections. Towards the end of the data collection the intensities of these check reflections started decreasing uniformly, indicating some crystal decomposition. Intensities of all reflections were corrected by a factor calculated from the weighted mean of the intensities of the check reflections. The maximum correction was 7%.

The intensities were also corrected for coincidence by the method of Sletten, Sletten & Jensen, (1969) ($\tau = 2\cdot19 \times 10^{-7}$ counts^{-1}). The small linear absorption coefficient indicated absorption effects could be neglected. 3180 independent reflections were measured out to a sin θ/λ of $0\cdot595$ or 25° in θ. The scan rate was 2° min^{-1}, while the scan range was 2°. Backgrounds were measured for half the scan time at each end of the scan range. The standard deviation of the intensities, σ_I, was defined in terms of the statistical variances of the counts as $\sigma_I^2 = \sigma_I^2(\text{count}) + K^2[S + B1 + B2]^2$ where S, $B1$, and $B2$ are the observed counts for the scan and two backgrounds respectively. $\sigma_I(\text{count})$ is the standard deviation derived purely from counting statistics. A value of $0\cdot03$ was used for K. 1485 reflections had $I \geq 3\sigma_I$ and were used in the analysis. Structure factors were calculated in the normal way assuming an ideally imperfect monochromator for the polarization correction.

Methods of solution

(a) Visual packing analysis

The phases of the intensity data were determined in a unique way termed 'visual packing analysis' (VPA). Only a brief description of the technique is given here with details described elsewhere (Hass, Willoughby, Morimoto, Cullen & Meyer, 1975). The general procedure implies a known or assumed molecular configuration from which atomic coordinates can be calculated using known bond distances and angles. These approximate coordinates were transformed into fractional coordinates assuming an arbitrary orientation in the unit cell and these, along with the atomic connectivities, and cell parameters were used as input to a Data General Nova minicomputer which drives a three-dimensional color television display designed by Syntex Analytical Instruments. The system is described elsewhere (Willoughby, Morimoto, Sparks & Meyer, 1974). This system allows the observer to visualize molecular models in and adjacent to the unit cell in three dimensions and to manipulate the contents of the asymmetric unit in order to determine the best possible packing arrangements of the molecules using criteria such as intermolecular distances and known packing principles (Kitaigorodskii, 1955).

The computer program could not accommodate simultaneous adjustment of the two, separate molecules in the asymmetric unit; therefore each molecule was manipulated separately on one of the two stereo channels available, then the images were superimposed and inspected visually. Intermolecular distances could also be calculated using an ancilliary program.

After a probable orientation was found it was first refined by using the potential energy packing program $PCK5$ (Williams, 1969), which minimizes the interatomic non-bonded repulsive potential. Potentials used for C–C, C–H, and H–H interactions were those most recently tabulated by Williams (1973a). The O–O and O–C potential parameters were $d_o = 3\cdot40$, $w_p = 1\cdot87$, while the O–H parameters were $d_o = 2\cdot90$, $w_p = 1\cdot56$ (Williams, 1973b). Use of the program $PCK6$ (Williams, 1972), which also considers attractive forces, proved to be unsatisfactory for this purpose since this program requires the molecule to be close to its correct position in order to reach convergence.

The coordinates obtained from the packing energy calculations were then further refined by block-diagonal least-squares techniques. The function minimized was $\sum w(F_o - F_c)^2$. In testing possible solutions all reflections were given equal weight, w. Hydrogen atoms were not included in these least-squares refinements, although they were included in the packing energy calculations.

The solution which proved to be correct gave the minimum packing energy of all models tested. The

average shift of an atomic parameter, φ, is defined by Zugenmaier & Sarko (1972) as:

$$\varphi = \left(\sum_{i=1}^{N} \Delta_i^2 / 3N \right)^{1/2} .$$

N is the number of atoms in the molecule and Δ_i is the difference between corresponding atomic positions before and after the packing calculation. The value of φ for the correct solution was 0·25 Å, comparing models before and after the packing energy refinement. The shift of the spiro C atom in molecule 1 was 0·30 Å, while the shift of the same atom in molecule 2 was 0·09 Å. The conventional R value ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) was 0·421 after the packing calculation step. This converged to 0·153 after least-squares refinement assuming isotropic temperature factors.

Attempts to bypass the packing energy refinement and use only block-diagonal least-squares techniques failed. However, when full-matrix least-squares refinement of the six rigid-body parameters per molecule was employed, convergence did occur. An overall isotropic temperature factor for each molecule was assumed in this case.

On the basis of these results it is apparent that VPA is a valuable tool for obtaining starting models either for packing energy calculations or conventional least-squares techniques. The VPA method assists in avoiding false minima which can be a common occurrence with 'blind' packing energy minimizations.

To our knowledge, we report here the first instance where energy packing refinement has been used to determine a crystal structure containing two molecules in the asymmetric unit. The operator was adjusting up to 12 independent parameters with success, but not without difficulty. When the asymmetric unit contains a molecule or even a fraction of a molecule, internal rotations in the case of non-rigid molecules could be generated as a result of current programming efforts and followed visually to produce trial models.

(b) Boolean programming

The structure was also solved by a method which involves casting the phase problem in terms of a classical binary integer linear programming problem. This approach, which is described in more detail elsewhere (Klunk & Meyer, 1974), is otherwise known as Boolean programming. It can be formulated by constructing an objective function and inequality constraints as follows:

Maximize $\bar{C}\bar{X}$

subject to: $\bar{A}\bar{X} - \bar{b} \geq \bar{0}$

where all $\bar{X}$ are zero or one in value. The X variables, which represent the phases of a centrosymmetric crystal structure, take on these values as the phase angles of their respective reflections are assigned a value of 180° or 0°.

The inequality constraints are of two types. The first type constrains the amount of electron density at a point in the unit cell to be non-negative. The second

type places a near-zero upper bound on electron density at points in the unit cell which correspond to pronounced valleys in Patterson space. Constraints of this second type are constructed, then, at places where no atoms are likely to appear. The terms, A and b, are generated as functions of the normalized structure factors and the particular space group. The C terms, or objective function coefficients, can be biased in favor of the contribution to electron density due to each term in the Fourier summation at known atomic positions. As this was the first trial of the Boolean programming approach it was found necessary to include the bias of a known atomic position in the objective function coefficients. Without *a priori* information, these coefficients may be set to unity.

The structure was solved with the 170 highest E values and 160 non-negativity and upper-bound constraints in *ca.* 80 s on a Control Data Corporation 6600 computer. The signs which this method generated were used successfully to locate 23 of the 26 non-hydrogen atoms in the asymmetric unit. The remaining three atoms were found in a difference Fourier synthesis. The structure was refined by full-matrix least-squares methods, assuming isotropic temperature factors and unit weights to a conventional R index of 0·164. At this point the structure was virtually identical with that found by VPA at a similar stage of refinement.

Refinement of the structure

Once the correct solution had been obtained, several cycles of block-diagonal least-squares refinement were made using a weighting factor of $1/\sigma_F^2$. Initially isotropic temperature factors were used followed by refinement assuming anisotropic thermal parameters. The H atom positions were taken from a difference Fourier synthesis. These positions agreed well with calculated positions. The H atoms were refined assuming isotropic thermal motion.

The final refinement cycles were carried out by full-matrix least-squares methods. Because of computer-memory limitations, the whole asymmetric unit could not be refined at once. This necessitated the refinement of each molecule, including H atoms, separately, then in the final cycle only the non-hydrogen atoms of both molecules were refined. After this final cycle, the shifts on all but two parameters were well below one standard deviation. Since these two parameters had shift/error ratios of only slightly over 1·0, further refinement seemed unwarranted.*

The final conventional R index was 0·048, while the weighted R_w index $[(\sum w ||F_o| - |F_c||^2 / \sum w F_o^2)^{1/2}]$ was 0·047. A structure factor calculation using all the reflections, including those with $I < 3\sigma_I$ gave a conventional R of 0·118 (0·095 when reflections with $I = 0$ were

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* At the suggestion of a referee, who feared the refinement may not have reached convergence, an additional cycle was done. After this costly calculation, the maximum shift/error ratio was 0·4 and the shifts in the parameters were insignificant.

excluded). R_w was 0·065. The error in an observation of unit weight $\{[\sum w||F_o|-|F_c||^2/(N_o-N_v)]^{1/2}\}$ was 1·50. N_o is·the number of observations, N_v the number of variables. A final difference Fourier synthesis showed a maximum electron density of 0·22 e Å^{-3}. This peak was 1·64 Å from C(5). It did not coincide with any feature of the molecule and was not considered of any physical significance. All other peaks in this final difference synthesis had electron densities less than 0·17 e Å^{-3}

The data were examined by the method of Housty & Clastre (1957). No evidence of secondary extinction was found and no correction for this effect was made. No correction for anomalous dispersion was applied. Scattering factors were from *International Tables for X-ray Crystallography* (1974).

The final positional and thermal parameters are given in Table 2.* Calculations were carried out on

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31233 (23 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH 1 1 NZ, England. The structure-factor table includes all 3180 reflections.
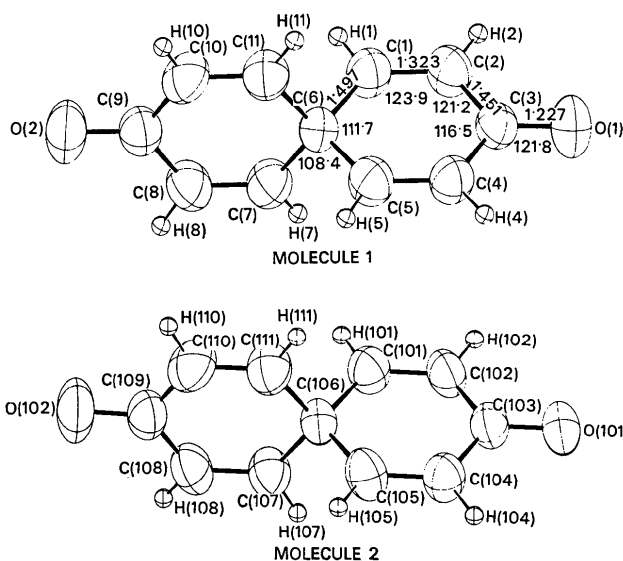

Fig. 2. *ORTEP* drawing of the two independent molecules. Thermal ellipsoids are drawn for 50 % probability except for H atoms which are not drawn to scale. Also shown on molecule 1 are the averaged values for chemically equivalent bond lengths and angles in both molecules.

Table 2. *Fractional coordinates and thermal motion parameters derived from the least-squares refinement*

In this and subsequent tables estimated standard deviations for the least significant figure are in parentheses. The Debye–Waller factor is defined as $T=\exp[-2\pi^2\sum_i\sum_j a_i^* a_j^* h_i h_j U_{ij}]$. The values for U have been multiplied by 10^4. For the H atoms, isotropic B's are defined by $\exp[-B(\sin^2\theta)/\lambda^2]$. These have been multiplied by 10.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·7904 (4)	0·0294 (2)	0·1312 (5)	813 (31)	605 (27)	548 (25)	199 (23)	146 (23)	78 (20)
C(2)	0·8368 (4)	−0·0578 (2)	0·1409 (5)	841 (31)	605 (27)	552 (25)	191 (23)	141 (23)	−63 (20)
C(3)	0·8376 (4)	−0·1135 (2)	0·3035 (5)	518 (23)	496 (27)	681 (27)	95 (17)	41 (20)	−14 (20)
C(4)	0·7913 (4)	−0·0679 (2)	0·4590 (5)	816 (31)	587 (27)	561 (25)	188 (23)	159 (20)	72 (20)
C(5)	0·7459 (4)	0·0197 (2)	0·4502 (5)	878 (31)	596 (27)	604 (27)	202 (23)	213 (23)	−20 (20)
C(6)	0·7373 (4)	0·0794 (2)	0·2866 (5)	575 (23)	437 (18)	602 (25)	114 (17)	101 (20)	14 (20)
C(7)	0·5786 (4)	0·0911 (2)	0·2331 (5)	627 (27)	507 (27)	871 (30)	32 (17)	79 (23)	−32 (20)
C(8)	0·5312 (5)	0·1768 (2)	0·2211 (5)	527 (27)	655 (27)	949 (33)	160 (23)	49 (23)	12 (25)
C(9)	0·6373 (5)	0·2721 (2)	0·2605 (5)	751 (31)	576 (27)	571 (25)	211 (23)	126 (23)	42 (20)
C(10)	0·7920 (5)	0·2644 (2)	0·3137 (5)	691 (31)	467 (27)	836 (30)	−27 (17)	35 (23)	−34 (20)
C(11)	0·8414 (4)	0·1790 (2)	0·3266 (5)	559 (23)	583 (27)	770 (27)	75 (17)	−4 (20)	−8 (20)
O(1)	0·8754 (2)	−0·1956 (1)	0·3116 (2)	1006 (23)	556 (18)	854 (19)	314 (17)	42 (16)	−40 (15)
O(2)	0·5957 (2)	0·3529 (1)	0·2499 (4)	1130 (23)	590 (18)	1034 (22)	367 (17)	134 (20)	104 (15)
C(101)	0·2662 (4)	0·4767 (2)	0·0510 (5)	793 (31)	557 (27)	565 (27)	154 (23)	101 (23)	61 (25)
C(102)	0·2335 (4)	0·3775 (2)	0·0451 (5)	841 (31)	478 (27)	593 (30)	155 (23)	117 (23)	−58 (25)
C(103)	0·2056 (4)	0·3207 (2)	0·2005 (5)	609 (27)	452 (27)	733 (30)	131 (17)	77 (23)	15 (25)
C(104)	0·2133 (4)	0·3770 (2)	0·3724 (5)	807 (27)	545 (27)	573 (27)	118 (17)	83 (20)	50 (20)
C(105)	0·2457 (5)	0·4766 (2)	0·3787 (5)	835 (31)	560 (27)	583 (30)	155 (23)	−7 (23)	−78 (25)
C(106)	0·2750 (4)	0·5391 (1)	0·2223 (5)	545 (23)	403 (18)	625 (25)	88 (17)	−3 (20)	0 (20)
C(107)	0·1570 (5)	0·6034 (2)	0·1934 (5)	555 (27)	546 (27)	868 (33)	97 (23)	−5 (23)	−21 (25)
C(108)	0·1872 (5)	0·7022 (2)	0·1972 (5)	841 (31)	541 (27)	807 (30)	276 (23)	102 (23)	56 (20)
C(109)	0·3398 (5)	0·7580 (2)	0·2281 (5)	1007 (39)	479 (27)	614 (27)	41 (23)	213 (26)	−37 (20)
C(110)	0·4587 (5)	0·6992 (2)	0·2595 (5)	652 (31)	721 (27)	948 (36)	−122 (23)	47 (26)	−43 (25)
C(111)	0·4302 (4)	0·6009 (2)	0·2587 (5)	578 (27)	609 (27)	955 (33)	92 (23)	−18 (23)	12 (25)
O(101)	0·1754 (2)	0·2292 (1)	0·1951 (4)	1043 (23)	428 (18)	965 (22)	139 (11)	244 (16)	−4 (15)
O(102)	0·3681 (4)	0·8497 (1)	0·2259 (4)	1700 (31)	429 (18)	987 (25)	−7 (17)	320 (20)	−48 (15)

	x	y	z	B		x	y	z	B
H(1)	0·793 (3)	0 067 (2)	0·027 (4)	50 (8)	H(101)	0·283 (3)	0·513 (2)	−0·058 (4)	45 (8)
H(2)	0·873 (3)	−0·085 (2)	0·042 (4)	64 (10)	H(102)	0·232 (3)	0·343 (2)	−0·066 (4)	46 (8)
H(4)	0·795 (3)	−0·106 (2)	0·566 (4)	52 (9)	H(104)	0·191 (3)	0·337 (2)	0·480 (4)	52 (8)
H(5)	0·712 (3)	0·043 (2)	0'546 (4)	55 (9)	H(105)	0·253 (3)	0·511 (2)	0·490 (4)	58 (10)
H(7)	0·520 (4)	0·036 (2)	0·208 (4)	72 (12)	H(107)	0·052 (3)	0·568 (2)	0·181 (4)	44 (8)
H(8)	0·422 (4)	0·178 (2)	0·190 (4)	76 (11)	H(108)	0·122 (3)	0·740 (2)	0·169 (4)	61 (9)
H(10)	0·856 (3)	0·314 (2)	0·340 (4)	46 (10)	H(110)	0·563 (4)	0·729 (2)	0·273 (5)	73 (12)
H(11)	0·947 (3)	0·177 (2)	0·372 (3)	42 (8)	H(111)	0·512 (3)	0·565 (2)	0·284 (4)	64 (10)

both the IBM 360/65 computer at Texas A&M University and the CDC 6600 computer at Brookhaven National Laboratory.*

Results and discussion

Fig. 2 shows the two independent molecules in the asymmetric unit. There are no significant structural differences between the two. Table 3 lists the bond lengths and angles, while Table 4 gives the averaged values for equivalent bonds. Table 5 lists the deviations from the least-squares planes for each of the rings. They are quite planar with a maximum deviation of 0·02 Å from the least-squares plane. The cyclodienone rings in each molecule are virtually perpendicular, the interplanar angles being 89·8° and 90·0°. Thus the molecule has essentially D_{2d} symmetry in agreement

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* Programs used at BNL included, *JIMDAP* (version of the Zalkin Fourier summation program), *ECSORTH* (sorting and averaging of data), *MULTAN* [phasing program of Germain, Main & Woolfson (1971)], *LINUS* [modified version of the Busing Martin & Levy (1962) *ORFLS* least-squares program], and *ORTEP* [thermal ellipsoid plot program of Johnson (1965)]. Besides those already mentioned, programs used at Texas A & M included *LSLAT* (least-squares cell-parameter refinement), *BDLR4* (block-diagonal least-squares program), *FAME* (modified version of Dewar's program for Wilson statistics and calculation of *E*'s), *FOURIER* (another version of the Zalkin program modified by Robinson & Dellaca), *NUCLS* (another version of *ORFLS*, modified by Ibers & Doedens, used for the group refinement procedures), *RBANG* (program of S. F. Watkins to calculate group coordinates), *HOW* (molecular geometry program), *ORFFE* [function and error program written by Busing, Martin & Levy (1964) as modified by Brown, Johnson & Thiessen], *PERFACT* (program by Frenz for analyzing structure factors and weighting schemes), and *LIST* by Snyder for listing the structure factors. Several other local data handling programs were used as well as the autoindexing and least-squares cell parameter and refinement programs written by Sparks (1974) for the NOVA computer. Data collection programs used were those written by Stanford (unpublished) for the Varian 620 i.

with the assumptions and calculations made by Boschi, Dreiding & Heilbronner (1970).

The average C–C bond length for bonds involving the spiro C atom is 1·497 (11) Å. This agrees well with the length of 1·504 (2) Å found for the sp^3-sp^2 bonds in the similar compound, spirodienone II (Koyama & Irie, 1972), which has a cyclodienone ring and a cyclohexane ring joined by a spiro C atom. The bond length found in the present work is significantly shorter than the length of 1·527 (3) Å found in bis-(2,2'-biphenylene)methane (Schenk, 1972).

The spiro C atom is definitely tetrahedral with an average bond angle of 109·5 (17)°. However the angles between atoms in the same ring [e.g. C(1)–C(6)–C(5), C(7)–C(6)–C(11)] are significantly larger, averaging 111·7 (3)°, than the inter-ring angles, which average 108·4 (8)°. A similar effect can be noted in spirodienone II and can probably be attributed to ring strain. Other bond lengths and angles appear to be normal.

Table 3. *Bond lengths and angles*

Molecule 1

C(1)—C(2)	1·330 (6) Å	C(2)—C(1)—C(6)	123·6 (4)°
C(1)—C(6)	1·508 (6)	C(1)—C(2)—C(3)	122·0 (4)
C(2)—C(3)	1·448 (6)	C(2)—C(3)—C(4)	116·9 (4)
C(3)—C(4)	1·451 (6)	C(2)—C(3)—O(1)	122·3 (4)
C(3)—O(1)	1·227 (5)	C(4)—C(3)—O(1)	120·8 (4)
C(4)—C(5)	1·330 (6)	C(3)—C(4)—C(5)	121·3 (4)
C(5)—C(6)	1·487 (6)	C(4)—C(5)—C(6)	124·8 (4)
C(6)—C(7)	1·486 (5)	C(1)—C(6)—C(5)	111·4 (4)
C(6)—C(11)	1·507 (6)	C(1)—C(6)—C(7)	108·5 (3)
C(7)—C(8)	1·317 (6)	C(1)—C(6)—C(11)	107·1 (3)
C(8)—C(9)	1·469 (6)	C(5)—C(6)—C(7)	109·6 (3)
C(9)—C(10)	1·437 (6)	C(5)—C(6)—C(11)	108·5 (3)
C(9)—O(2)	1·227 (5)	C(7)—C(6)—C(11)	111·8 (4)
C(10)–C(11)	1·320 (6)	C(6)—C(7)—C(8)	125·4 (4)
		C(7)—C(8)—C(9)	120·8 (4)
		C(8)—C(9)—C(10)	115·7 (4)
		C(8)—C(9)—O(2)	121·9 (4)
		C(10)–C(9)—O(2)	122·4 (4)
		C(9)—C(10)–C(11)	124·3 (4)
		C(6)—C(11)–C(10)	122·0 (3)

Table 3 (*cont.*)

Molecule 2

C(101)–C(102)	1·327 (6) Å	C(102)–C(101)–C(106)	122·6 (4)°
C(101)–C(106)	1·511 (6)	C(101)–C(102)–C(103)	122·9 (4)
C(102)–C(103)	1·432 (6)	C(102)–C(103)–C(104)	117·2 (4)
C(103)–C(104)	1·474 (6)	C(102)–C(103)–O(101)	123·0 (4)
C(103)–O(101)	1·225 (5)	C(104)–C(103)–O(101)	119·8 (4)
C(104)–C(105)	1·331 (6)	C(103)–C(104)–C(105)	120·0 (4)
C(105)–C(106)	1·483 (6)	C(104)–C(105)–C(106)	125·1 (4)
C(106)–C(107)	1·501 (6)	C(101)–C(106)–C(105)	112·1 (3)
C(106)–C(111)	1·495 (6)	C(101)–C(106)–C(107)	107·5 (3)
C(107)–C(108)	1·321 (6)	C(101)–C(106)–C(111)	108·0 (3)
C(108)–C(109)	1·443 (6)	C(105)–C(106)–C(107)	108·8 (4)
C(109)–C(110)	1·457 (7)	C(105)–C(106)–C(111)	108·9 (3)
C(109)–O(102)	1·227 (5)	C(107)–C(106)–C(111)	111·5 (3)
C(110)–C(111)	1·315 (6)	C(106)–C(107)–C(108)	124·1 (4)
		C(107)–C(108)–C(109)	122·1 (5)
		C(108)–C(109)–C(110)	116·1 (4)
		C(108)–C(109)–O(102)	122·1 (5)
		C(110)–C(109)–O(102)	121·8 (4)
		C(109)–C(110)–C(111)	122·5 (4)
		C(106)–C(111)–C(101)	123·7 (4)

Table 4. *Averaged bond lengths and angles*

Root-mean-square standard deviations are in parentheses. C_s refers to spiro C atom. C_k refers to C atom bonded to O.

C_s–C	1·497 (11) Å
C_s=C	1·323 (6)
C_k=C	1·451 (15)
C_k–O	1·227 (1)
C –H	0·94 (5)
C –C_s–C (overall)	109·5 (17)°
C –C_s–C (intra-ring)	111·7 (3)
C –C_s–C (inter-ring)	108·4 (8)
C_s–C =C	123·9 (11)
C_k–C =C	121·2 (22)
C –C_k–C	116·5 (7)
C –C_k–O	121·8 (10)
C_s–C –H	115·6 (13)
C =C –H	119·7 (32)
C_k–C –H	118·3 (23)

The packing in the unit cell is shown in Fig. 3. The two independent molecules are arranged so that there is a near twofold screw axis along y relating the two. Table 6 lists the intermolecular contacts shorter than 3·7 Å. With the exception of the C(11)–O(101) distance of 3·26 Å, none of these is considered to be unusually short. This one exception is not sufficiently short to be considered a hydrogen bond. The C(11)–H(11)–O(101) angle is 125°.

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Table 6. *Intermolecular contacts less than* 3·7 Å

Symmetyr operations

(a)	$1+x,$	$y,$	z		(e)	$1-x,$	$1-y,$	z
(b)	$1-x, 1-y, 1-z$				(f)	$1-x,$	$-y, 1-z$	
(c)	$1-x,$	$-y,$	$-z$		(g)	$x, -1+y,$		z
(d)	$x,$	$y,$	z		(h)	$-1+x,$	$1+y,$	z

C(11)—O(101)^a	3·26 Å		C(7)—O(102)^g	3·48 Å
C(5)—O(102)^b	3·35		C(104)-O(1)^f	3·51
C(2)—O(101)^c	3·38		C(102)-O(1)^c	3·53
C(8)—O(101)^d	3·42		C(102)-O(2)^d	3·53
C(101)-O(2)^e	3·44		C(108)-O(1)^h	3·56
C(4)—O(101)^f	3·45		C(8)—O(102)^e	3·60
C(103)-O(2)^d	3·46		C(7)—O(102)^e	3·62
C(1)—O(102)^e	3·47		C(10)—C(108)^b	3·66

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Table 5. *Deviations from least-squares planes* (Å) *of atoms in cyclodienone rings*

	Molecule 1				Molecule 2		
	Ring 1		Ring 2		Ring 3		Ring 4
C(1)	0·005	C(6)	−0·002	C(101)	0·004	C(106)	−0·019
C(2)	−0·022	C(7)	−0·000	C(102)	−0·001	C(107)	−0·001
C(3)	−0·001	C(8)	0·003	C(103)	0·002	C(108)	0·017
C(4)	0·022	C(9)	−0·002	C(104)	0·001	C(109)	0·007
C(5)	0·003	C(10)	0·003	C(105)	0·003	C(110)	0·008
C(6)	0·016	C(11)	0·000	C(106)	−0·006	C(111)	0·008
O(1)	−0·023	O(2)	−0·001	O(101)	−0·003	O(102)	−0·019

Plane 1 [C(1)–C(6), O(1)]	$7·67X+3·97Y+1·21Z=6·34$
Plane 2 [C(6)–C(11), O(2)]	$-2·52X-0·32Y+7·39Z=0·24$
Plane 3 [C(101)–C(106), O(101)]	$8·91X-2·92Y+0·55Z=1·00$
Plane 4 [C(106)–C(111), O(102)]	$-1·74X+0·44Y+7·46Z=1·44$

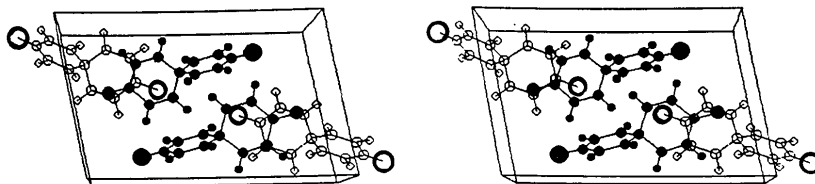Note: All planes are unweighted. X, Y, Z are in triclinic fractional coordinates.

Fig. 3. Stereo view of the packing in the unit cell. View is down c^* axis, b axis is horizontal. Molecule 1 has open circles, molecule 2 filled circles.

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The Synthesis and Molecular Structure of a Cage Dimer of 7-t-Butoxynorbornadiene

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The cage dimer, 13,14-di-t-butoxyheptacyclo[5,5,1,1^{4,10},0^{2,6},0^{3,11},0^{5,9},0^{8,12}]tetradecane is obtained as one of the products in the thermal reaction of 7-t-butoxynorbornadiene with iron pentacarbonyl. The preparation, purification and spectral data of the compound are described. Crystals of the dimer are triclinic, space group $P\bar{1}$. The cell dimensions are $a = 6\cdot282$ (1), $b = 11\cdot159$ (2), $c = 14\cdot219$ (3) Å, $\alpha = 106\cdot49$ (2)°, $\beta = 92\cdot66$ (2)° and $\gamma = 97\cdot17$ (2)°. The structure was determined by direct methods and refined with least-squares calculations using 3220 data. The final R value is 0·081. Both the distances of like bonds and the values of corresponding bond angles are closely similar. The longest bond distances 1·568 (4) Å are the four ethano bridges of the norbornane systems. All other bond distances in the cage are between 1·526 and 1·544 Å. The results on the cage dimer are generally in good agreement with the electron diffraction results of Dallinga & Toneman [*Rec. Trav. Chim. Pays-Bas* (1968), **87,** 795–804]. The major difference is a change in the flap angle, which, however, does not change the conformation of the five-membered rings of the norbonane skeleton.

Introduction

The reaction of norbornadiene (1) with iron carbonyls has been extensively studied (Bird, 1962, 1967). Of particular interest is a saturated dimeric species [(2) $C_{14}H_{16}$] formed in the photochemical reaction of (1) with iron pentacarbonyl (Lemal & Shim, 1961) and in

the thermal reaction of (1) with diiron enneacarbonyl (Bird, Colinese, Cookson, Hudec & Williams, 1961). Structures (2a) and (2b) have been suggested for this saturated dimer. More recently, indirect chemical evidence has been forwarded which supports structure (2a) [rather than (2b)] for this dimer (Acton, Roth, Katz, Frank, Maier & Paul, 1972). However, to our knowledge, no direct method (X-ray crystallography, electron or neutron diffraction) has been applied to verify this structural assignment.