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Conformations of *trans,trans*-Cycloundecadienes: Molecular-Mechanics Calculations for Cycloundeca-1,4-, -1,5- and -1,6-dienes and X-ray Analysis of Conformationally Disordered (4*E*,8*E*)-Cycloundeca-4,8-dien-1-ylmethyl *p*-Toluenesulfonate at 292 and 160 K

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Abstract

Conformations for cycloundeca-1,4-, -1,5- and -1,6-dienes with *trans* double bonds have been derived by molecular-mechanics calculations. Low-energy conformations of the 1,5- and 1,6-dienes match conformations of the eleven-membered rings in various cytochalasans and dolabellane diterpenoids. (4*E*,8*E*)-Cycloundeca-4,8-dien-1-ylmethyl *p*-toluenesulfonate, $C_{19}H_{26}O_3S$, $M_r = 334{\cdot}5$, monoclinic, $P2_1/c$, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å. At 292 K, $a = 8{\cdot}457\ (2)$, $b = 11{\cdot}076\ (4)$, $c = 19{\cdot}552\ (7)$ Å, $\beta = 96{\cdot}65\ (6)°$, $V = 1819\ (1)$ Å^3, $D_x = 1{\cdot}22$ Mg m^{-3}, $\mu = 0{\cdot}19$ mm^{-1}, $R = 0{\cdot}087$ for 1638 reflections with $I > 2{\cdot}5\sigma(I)$. At 160 K, $a = 8{\cdot}347\ (3)$, $b = 10{\cdot}967\ (4)$, $c = 19{\cdot}408\ (9)$ Å, $\beta = 96{\cdot}03\ (9)°$, $V = 1767\ (1)$ Å^3, $D_x = 1{\cdot}26$ Mg m^{-3}, $\mu = 0{\cdot}20$ mm^{-1}, $R = 0{\cdot}049$ for 2921 reflections with $I > 2{\cdot}5\sigma(I)$. The eleven-membered ring is conformationally disordered in the crystal at 292 and 160 K. The X-ray results at the lower temperature are compared with the molecular-mechanics calculations for cycloundeca-1,5-diene and interpreted in terms of a conformational mixture in which the predominant species are derived from the two lowest-energy conformations of cycloundeca-1,5-diene. The C(sp^3)–C(sp^3)–C(sp^3) angles in the eleven-membered ring are larger than tetrahedral, 113·3–116·1 (3)°.

Introduction

Eleven-membered rings occur in a variety of natural products, *e.g.* the cytochalasans (Tamm, 1980), dolabellane diterpenoids (Matsuo, Kamio, Uohama, Yoshida, Connolly & Sim, 1988) and pyrrolizidine alkaloids (Robins, 1982). Among unsaturated compounds, examination of crystallographic results for several cytochalasans (Tsukuda & Koyama, 1972; Beno, Cox, Wells, Cole, Kirksey & Christoph, 1977; Neupert-Laves & Dobler, 1982) and dolabellane diterpenoids (Ireland, Faulkner, Finer & Clardy, 1976; Gonzalez, Martin, Norte, Perez, Weyler, Rafii & Clardy, 1983) with the cycloundeca-1,6-diene system or epoxide analogues reveals essentially a common conformation for the eleven-membered ring in these compounds. X-ray analyses have disclosed two conformations for the cycloundeca-1,5-diene ring in dimorphic crystals of humulene nitrosite (Khan, MacAlpine, Porte & Sim, 1983) and these conformations have also been found in several dolabellane diterpenoids (Matsuo, Uohama, Yoshida, Nakayama, Hayashi, Connolly & Sim, 1985; Huneck, Baxter, Cameron, Connolly, Harrison, Phillips, Rycroft & Sim, 1986; Connolly, Sim & Matsuo, 1987).

The conformations of cycloundecane and cycloundecene have been derived by systematic molecular-mechanics procedures with the White & Bovill (1977) force field (Russell, 1981). As an extension of that work, we have now generated the conformations of cycloundeca-1,4-, -1,5- and -1,6-dienes with *trans* double bonds and compared the results with the available X-ray data. An X-ray investigation of cycloundeca-4,8-dien-1-ylmethyl *p*-toluenesulfonate (1) was undertaken to examine the conformation of a lightly substituted cycloundeca-1,5-diene and to com-

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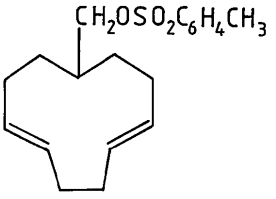
pare the results with those obtained for cycloundeca-1,5-diene by the force-field calculations.



(1)

Experimental

Compound (1) was synthesized from (4*E*,8*E*)-cycloundeca-4,8-diene-1-carboxylic acid (Haufe, 1983) by reduction with $LiAlH_4$ and subsequent tosylation.

Colourless crystals, dimensions 0·15 × 0·15 × 0·30 mm. Enraf–Nonius diffractometer, Mo $K\alpha$ radiation. Cell dimensions from setting angles of 25 independent reflections with θ 8–17°. At 292 K, 2858 intensities surveyed in range 1·5–23·0°, h 0→9, k 0→12, $l\ \overline{21}$→21; scan width (0·90+0·25tanθ)°; max. counting time 120 s; 2495 independent reflections after deletion of systematic absences and averaging of equivalent reflections, 1638 reflections with $I > 2{\cdot}5\sigma(I)$, R_{int} = 0·034. At 160 K, 4413 intensities surveyed in range 1·5–27·0°, h 0→11, k 0→14, $l\ \overline{25}$→25; scan width (0·90 + 0·25tanθ)°, max. counting time 120 s; 3853 independent reflections after deletion of systematic absences and averaging of equivalent reflections, 2921 reflections with $I > 2{\cdot}5\sigma(I)$, $R_{int} = 0{\cdot}045$. Two reference reflections monitored periodically showed no significant variation in intensity. No absorption correction. Structure determined by direct phasing using *MITHRIL* (Gilmore, 1984).

At 292 K, after preliminary refinement, 16 H atoms were located in difference Fourier syntheses: those of the *p*-toluene group and those on C(1), C(2), C(3), C(11) and C(12) of the cycloundecadienylmethyl moiety. Full-matrix least-squares calculations on F with anisotropic thermal parameters for the C, S and O atoms and isotropic thermal parameters for the H atoms converged at $R = 0{\cdot}087$, $wR = 0{\cdot}089$ with unit weights, $\Delta\rho$ max. = 0·39 e Å^{-3}. The large thermal ellipsoids in the eleven-membered ring (see Fig. 1) and unrealistic geometry in the region of the C=C double bonds were indicative of conformational disorder. The larger residual peaks of the $\Delta\rho$ maps in the region of the C=C double bonds were included in some further calculations as alternative C-atom sites with occupation parameters set at 0·2; this gave $R = 0{\cdot}082$, $wR = 0{\cdot}079$, but the resulting geometry was still unsatisfactory.

At 160 K, the largest eleven peaks in the region occupied by the cycloundecadiene defined a ring with acceptable geometry and all the H atoms associated with those C atoms were located in difference electron-density distributions. Additional peaks in the electron-density difference maps represented atomic sites arising from minor amounts of other conformers with the $CH_2CH{=}CHCH_2$ systems rotated through 180° and could be allocated as alternative sites for C(4), C(5), C(7), C(8), C(9), C(10). These sites were incorporated in subsequent least-squares calculations with the sum of the occupations of the major and minor sites for an atom [C(4) and C(4′), *etc.*] constrained to unity. The minor sites were restricted to isotropic thermal parameters and several patterns of constraints were considered. In the first, C(4) occupation = C(5) occupation, C(8) occupation = C(9) occupation, and separate occupation parameters for C(4), C(7), C(8) and C(10) were included in the least-squares calculations with appropriate constraints on the H-atom occupations; in this case 344 parameters were adjusted and at convergence $R = 0{\cdot}0487$, $wR = 0{\cdot}0718$ with C(4) occupation = 0·727 (10), C(7) occupation = 0·698 (14), C(8) occupation = 0·811 (13) and C(10) occupation = 0·810 (14). In the second set of calculations, C(4) occupation = C(5) occupation and C(7) occupation = C(8) occupation = C(9) occupation = C(10) occupation; with these constraints there were 342 parameters and at convergence $R = 0{\cdot}0491$, $wR = 0{\cdot}0724$, with C(4) occupation = 0·729 (10), C(7) occupation = 0·770 (9). In the third set of calculations, we kept the occupation parameters of C(4), C(5), C(7), C(8), C(9), C(10) equal and this gave 341 parameters with $R = 0{\cdot}0492$, $wR = 0{\cdot}0725$, and C(4) occupation = 0·751 (7). In all three cases $w = 1/\sigma^2(|F|)$, final $\Delta\rho$ max. 0·38, min. −0·31 e Å^{-3}, $\Delta/\sigma < 0{\cdot}5$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Calculations were performed on a SEL 32/27 computer with the *GX* system of programs (Mallinson & Muir, 1985).*

For the molecular-mechanics calculations, the conformations of cycloundeca-1,4-, -1,5- and -1,6-dienes were generated from the conformations of cycloundecane and cycloundecene (Russell, 1981) by incorporating *trans* CH=CH groups in place of CH_2–CH_2 groups at sites with torsion angles exceeding 130° and the resultant geometries optimized by block-diagonal and full-matrix iterative Newton–Raphson procedures with the White & Bovill (1977) force field. The calculations were terminated when values of the first derivatives of energy with respect to the coordinates were less than 10^{-5} kJ mol^{-1} Å^{-1} and the results are shown in Tables 1–3 and Figs. 1–3.

*Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond lengths, bond angles and torsion angles for the 160 K measurements have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51765 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Torsion angles* (°) *and relative steric energies* (kJ mol^{-1}) *for conformations* I–VII *of cycloundeca-1,4-diene*

The angles are given in sequence around the ring, with the first and fourth rows corresponding to the double bonds.

	I	II	III	IV	V	VI	VII
	−169	−169	−164	−165	−161	−167	−167
	58	83	66	85	84	58	81
	58	−93	66	−95	−79	52	−90
	−169	165	−164	165	168	−166	161
	114	−68	119	−122	−123	110	−75
	−50	−49	−37	27	82	−65	−58
	105	132	−65	69	−66	142	156
	−171	−159	174	−175	−70	−70	−67
	105	100	−65	101	155	−79	−71
	−50	−50	−37	−40	−66	70	74
	114	112	119	113	101	84	78
ΔE	0·0	6·4	8·4	9·4	9·8	10·7	12·2

Table 2. *Torsion angles* (°) *and relative steric energies* (kJ mol^{-1}) *for conformations* I–VII *of cycloundeca-1,5-diene*

	I	II	III	IV	V	VI	VII
	−177	171	172	−174	172	176	−173
	104	−110	−95	111	−117	−34	51
	−56	46	56	−43	30	−46	39
	100	−94	−95	−52	61	115	−105
	−171	172	172	172	−170	−170	169
	78	−103	−79	−110	86	75	−104
	64	78	−79	74	66	63	68
	−151	−146	68	−144	−150	−138	−139
	100	71	68	106	64	111	59
	−57	43	−79	−49	36	−50	40
	119	−127	−79	119	−129	−90	44
ΔE	0·0	3·1	6·6	7·7	12·2	16·2	17·6

Table 3. *Torsion angles* (°) *and relative steric energies* (kJ mol^{-1}) *for conformations* I–V *of cycloundeca-1,6-diene*

	I	II	III	IV	V
	179	178	178	174	173
	−116	−37	−44	−115	−53
	70	−65	−68	81	−66
	−74	80	68	−37	48
	114	−107	63	−87	83
	−178	178	−179	176	−174
	85	−114	107	−132	137
	64	78	−75	47	−41
	−111	−100	110	60	−53
	73	78	−64	−81	100
	−111	−120	−89	−62	−125
ΔE	0·0	5·6	10·2	13·3	20·3

Discussion

The molecular structures derived from the X-ray results at 292 and 160 K are illustrated by *ORTEP* diagrams (Johnson, 1965) in Figs. 4 and 5. The atomic coordinates and molecular dimensions from the 160 K analysis are listed in Tables 4 and 5.

In order to establish which conformations of cycloundeca-1,5-diene contribute to the disordered crystal structure of compound (1), various possible sequences of atomic sites were compared with the molecular-mechanics results shown in Table 2. Conformation I corresponds to sequence C(1,2,3,-4′,5′,6′,7′,8′,9′,10′,11), conformation II to C(1,2,3,-4,5,6,7,8,9,10,11), conformation IV to C(1,2,3,4,5,-6,7′,8′,9′,10′,11), and conformation V to C(1,2,3,-4′,5′,6,7,8,9,10,11). Conformation III could not be fitted to the X-ray results and conformations VI and VII could only be matched at the cost of unacceptable distortions from ideal geometry, *e.g.* bond angles

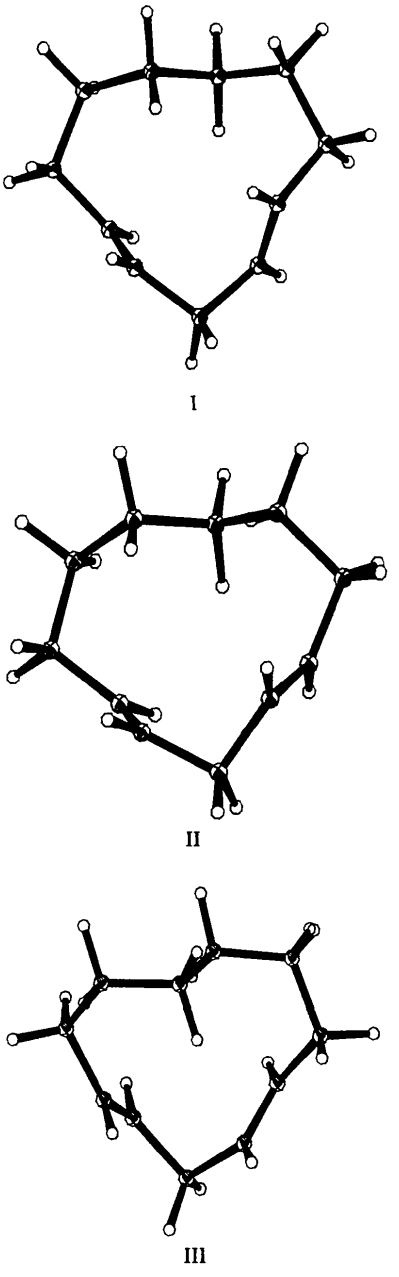


Fig. 1. Conformations I, II and III of cycloundeca-1,4-diene.

C(8)–C(9)–C(10′) 155° (conformation VI) and C(8′)–C(9′)–C(10) 149° (conformation VII), and were also excluded from further consideration. The differences between the X-ray and force-field torsion angles are 1–28, mean 8·5°, for conformation I, 1–10, mean 4·5°, for conformation II, 2–16, mean 6·8°, for conformation IV, and 0–18, mean 8·0°, for conformation V. Conformation II is the predominant species in the crystal. The minor species, conformations I, IV, V are derived from II by rotation of both double bonds (I) or one double bond (IV, V) through *ca* 180°. The interconversion of these conformations in solution follows the mechanism for the racemization of medium-ring *trans* cycloalkenes (Newton & Whitham, 1979) and *trans* lactones (Brown, Chaloner & Martens, 1981). The rotation of double bonds through the rings in unsaturated cyclic hydrocarbons has been studied by force-field calculations and NMR spectroscopy (Anet & Rawdah, 1978) and is expected to be a facile process for an eleven-membered ring in the liquid phase at normal temperatures (Shirahama, Osawa & Matsumoto, 1980).

If we represent the population of conformations I, II *etc.* by *P*(I), *P*(II) *etc.*, and the occupation of atomic sites C(1), C(2) *etc.* by *O*(1), *O*(2) *etc.*, then

$$P(\mathrm{II}) + P(\mathrm{IV}) = O(4) = O(5)$$

$$P(\mathrm{II}) + P(\mathrm{V}) = O(7) = O(8) = O(9) = O(10)$$

$$P(\mathrm{I}) + P(\mathrm{V}) = O(4') = O(5')$$

$$P(\mathrm{I}) + P(\mathrm{IV}) = O(7') = O(8') = O(9') = O(10')$$

$$P(\mathrm{I}) + P(\mathrm{II}) + P(\mathrm{IV}) + P(\mathrm{V}) = 1.$$

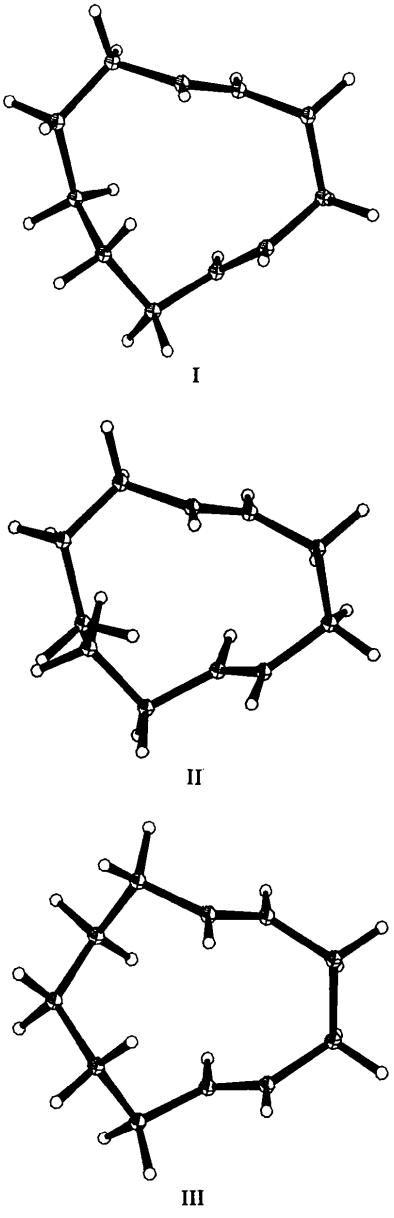


Fig. 2. Conformations I, II and III of cycloundeca-1,5-diene.

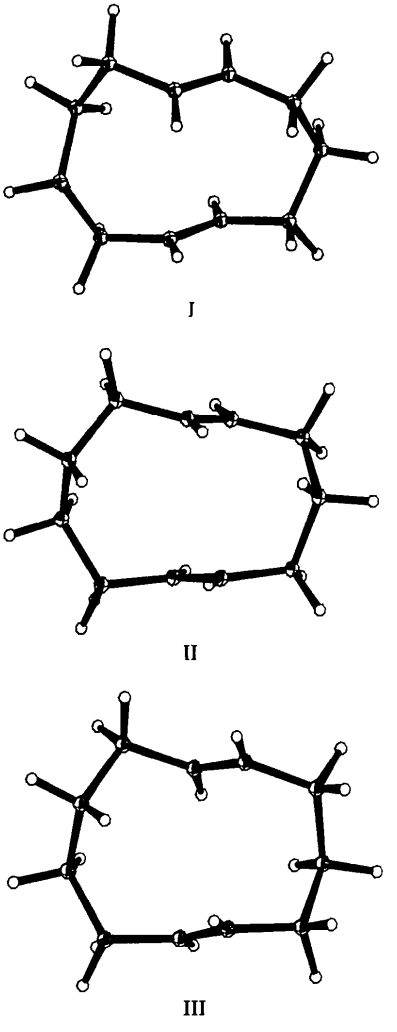


Fig. 3. Conformations I, II and III of cycloundeca-1,6-diene.

In terms of this model, the occupation of sites C(7) and C(10) should not differ from the occupation of sites C(8), C(9). In the most general least-squares calculations with the X-ray data (see *Experimental*), we allowed these occupations to differ and obtained $O(7) = 0{\cdot}698\ (14)$, $O(8) = O(9) = 0{\cdot}811\ (13)$, $O(10) = 0{\cdot}810\ (14)$. Clearly, $O(10)$ is identical with $O(8)$, $O(9)$, but $O(7)$ may differ from $O(8)$, $O(9)$, $O(10)$; if there is a genuine difference small amounts of other higher-energy conformations must contribute, though neither VI nor VII lead to a difference between $O(7)$ and $O(10)$. When $O(7)$ was constrained to be equal to $O(8)$, $O(9)$, $O(10)$, the X-ray least-squares refinement converged to values of R, wR very close to those

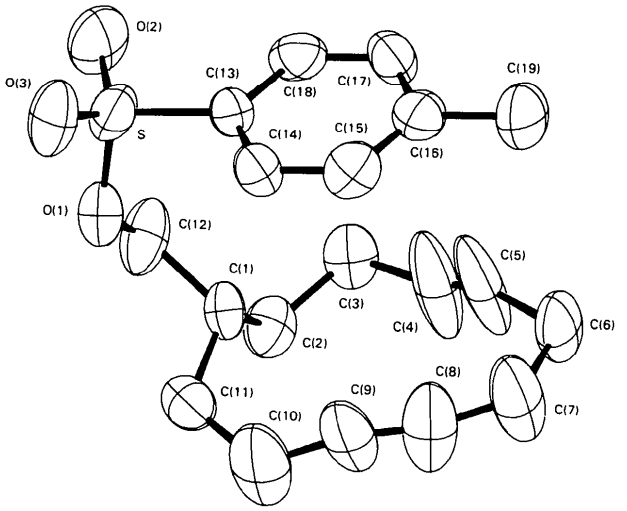


Fig. 4. Molecular structure and atomic numbering at 292 K. The thermal ellipsoids of the C, O and S atoms are drawn at the 50% probability level.

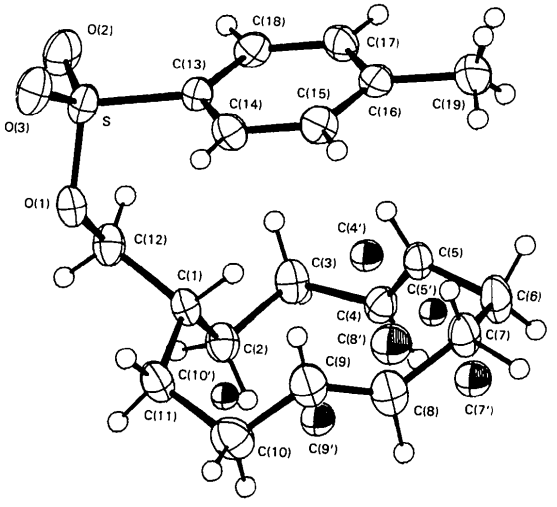


Fig. 5. Molecular structure and atomic numbering at 160 K. The thermal ellipsoids of the C, O and S atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0·1 Å.

Table 4. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for compound* (1) *at* 160 K

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
C(1)	−0·3414 (3)	0·2718 (2)	0·3032 (1)	0·027
C(2)	−0·4758 (3)	0·1847 (3)	0·3199 (1)	0·031
C(3)	−0·4158 (4)	0·0732 (3)	0·3630 (1)	0·033
C(4)	−0·3975 (6)	0·1129 (3)	0·4388 (2)	0·031
C(5)	−0·2635 (5)	0·1449 (3)	0·4746 (2)	0·029
C(6)	−0·2647 (5)	0·2043 (3)	0·5441 (2)	0·044
C(7)	−0·2340 (7)	0·3462 (3)	0·5362 (2)	0·045
C(8)	−0·3429 (7)	0·3948 (3)	0·4801 (2)	0·033
C(9)	−0·3129 (7)	0·4449 (3)	0·4218 (2)	0·035
C(10)	−0·4343 (7)	0·4697 (4)	0·3624 (2)	0·040
C(11)	−0·3966 (4)	0·4056 (3)	0·2955 (1)	0·035
C(12)	−0·2766 (4)	0·2274 (3)	0·2377 (1)	0·033
C(13)	0·0855 (3)	0·2384 (2)	0·3149 (1)	0·026
C(14)	0·1076 (3)	0·3442 (2)	0·3537 (1)	0·029
C(15)	0·1489 (3)	0·3352 (3)	0·4243 (1)	0·032
C(16)	0·1683 (3)	0·2225 (2)	0·4569 (1)	0·029
C(17)	0·1453 (3)	0·1175 (2)	0·4163 (1)	0·031
C(18)	0·1040 (3)	0·1248 (2)	0·3458 (1)	0·029
C(19)	0·2097 (5)	0·2131 (4)	0·5340 (2)	0·043
O(1)	−0·1436 (2)	0·3044 (2)	0·2193 (1)	0·031
O(2)	0·0322 (3)	0·1337 (2)	0·1945 (1)	0·042
O(3)	0·1226 (3)	0·3478 (2)	0·1985 (1)	0·043
S	0·03257 (8)	0·25191 (6)	0·22520 (3)	0·030
C*X*(4)	−0·3078 (14)	0·1013 (8)	0·4273 (5)	0·024 (3)
C*X*(5)	−0·3785 (12)	0·1302 (8)	0·4829 (6)	0·023 (3)
C*X*(7)	−0·3384 (15)	0·3321 (9)	0·5399 (5)	0·019 (3)
C*X*(8)	−0·251 (2)	0·389 (1)	0·482 (1)	0·045 (4)
C*X*(9)	−0·393 (2)	0·427 (1)	0·426 (1)	0·033 (4)
C*X*(10)	−0·3429 (19)	0·4798 (11)	0·3588 (6)	0·026 (3)

obtained in the less-constrained calculations and we incline to the view that the results of the calculation with the minimum number of independent variables should be accepted.

There is no unique solution to the set of relationships between the conformational populations and atomic site occupations. From the least-squares analysis with the fewest independent variables, *i.e.* that in which we set $O(4) = O(5) = O(7) = O(9) = O(10)$, we have $P(\mathrm{II}) + P(\mathrm{IV}) = 0{\cdot}751\ (7)$ and $P(\mathrm{II}) + P(\mathrm{V}) = 0{\cdot}751\ (7)$, giving the following limits to the solutions:

$$P(\mathrm{I}) = 0{\cdot}249\ (7) \rightarrow 0{\cdot}000\ (7)$$
$$P(\mathrm{II}) = 0{\cdot}751\ (7) \rightarrow 0{\cdot}502\ (14)$$
$$P(\mathrm{IV}) = 0 \rightarrow 0{\cdot}249$$
$$P(\mathrm{V}) = 0 \rightarrow 0{\cdot}249.$$

From the least-squares analysis in which we set $O(4) = O(5)$, $O(7) = O(8) = O(9) = O(10)$, $O(4) \neq O(7)$, we have $P(\mathrm{II}) + P(\mathrm{IV}) = 0{\cdot}729\ (10)$, $P(\mathrm{II}) + P(\mathrm{V}) = 0{\cdot}770\ (9)$, giving the following limits to the solutions:

$$P(\mathrm{I}) = 0{\cdot}230\ (9) \rightarrow 0{\cdot}000\ (9)$$
$$P(\mathrm{II}) = 0{\cdot}729\ (10) \rightarrow 0{\cdot}499\ (10)$$
$$P(\mathrm{IV}) = 0 \rightarrow 0{\cdot}230$$
$$P(\mathrm{V}) = 0{\cdot}041\ (19) \rightarrow 0{\cdot}271\ (19).$$

Table 5. *Interatomic distances* (Å) *and angles* (°) *for compound* (1)

C(1)–C(2)	1·534 (4)	C(1)–C(11)	1·540 (4)
C(1)–C(12)	1·514 (4)	C(2)–C(3)	1·536 (4)
C(3)–C(4)	1·525 (5)	C(4)–C(5)	1·301 (7)
C(5)–C(6)	1·499 (5)	C(6)–C(7)	1·587 (5)
C(7)–C(8)	1·445 (7)	C(8)–C(9)	1·306 (6)
C(9)–C(10)	1·478 (7)	C(10)–C(11)	1·537 (5)
C(12)–O(1)	1·468 (4)	C(13)–C(14)	1·385 (4)
C(13)–C(18)	1·383 (4)	C(13)–S	1·757 (3)
C(14)–C(15)	1·381 (4)	C(15)–C(16)	1·390 (4)
C(16)–C(17)	1·397 (4)	C(16)–C(19)	1·503 (5)
C(17)–C(18)	1·377 (4)	O(1)–S	1·572 (2)
O(2)–S	1·427 (3)	O(3)–S	1·422 (3)

C(2)–C(1)–C(11)	113·3 (3)	C(2)–C(1)–C(12)	108·1 (3)
C(11)–C(1)–C(12)	110·8 (3)	C(1)–C(2)–C(3)	114·0 (3)
C(2)–C(3)–C(4)	107·0 (3)	C(3)–C(4)–C(5)	125·8 (4)
C(4)–C(5)–C(6)	120·7 (4)	C(5)–C(6)–C(7)	108·9 (3)
C(6)–C(7)–C(8)	109·8 (4)	C(7)–C(8)–C(9)	130·2 (6)
C(8)–C(9)–C(10)	125·1 (6)	C(9)–C(10)–C(11)	112·9 (4)
C(1)–C(11)–C(10)	116·1 (3)	C(1)–C(12)–O(1)	111·4 (3)
C(14)–C(13)–C(18)	121·1 (3)	C(14)–C(13)–S	118·2 (2)
C(18)–C(13)–S	120·7 (2)	C(13)–C(14)–C(15)	118·9 (3)
C(14)–C(15)–C(16)	121·4 (3)	C(15)–C(16)–C(17)	118·2 (3)
C(15)–C(16)–C(19)	121·1 (3)	C(17)–C(16)–C(19)	120·6 (3)
C(16)–C(17)–C(18)	121·2 (3)	C(13)–C(18)–C(17)	119·2 (3)
C(12)–O(1)–S	119·8 (2)	C(13)–S–O(1)	103·8 (2)
C(13)–S–O(2)	109·0 (2)	C(13)–S–O(3)	109·6 (2)
O(1)–S–O(2)	110·0 (2)	O(1)–S–O(3)	103·3 (2)
O(2)–S–O(3)	119·9 (2)		

C(11)–C(1)–C(2)–C(3)	−150·1 (4)	C(2)–C(1)–C(11)–C(10)	69·7 (4)
C(12)–C(1)–C(2)–C(3)	86·7 (3)	C(2)–C(1)–C(12)–O(1)	−178·4 (3)
C(12)–C(1)–C(11)–C(10)	−168·6 (4)	C(11)–C(1)–C(12)–O(1)	57·0 (3)
C(1)–C(2)–C(3)–C(4)	83·8 (3)	C(2)–C(3)–C(4)–C(5)	−98·8 (5)
C(3)–C(4)–C(5)–C(6)	168·4 (7)	C(4)–C(5)–C(6)–C(7)	−103·3 (5)
C(5)–C(6)–C(7)–C(8)	50·7 (4)	C(6)–C(7)–C(8)–C(9)	−116·8 (7)
C(7)–C(8)–C(9)–C(10)	167·5 (8)	C(8)–C(9)–C(10)–C(11)	−121·2 (6)
C(9)–C(10)–C(11)–C(1)	43·9 (4)	C(1)–C(12)–O(1)–S	111·0 (3)
C(18)–C(13)–C(14)–C(15)	0·0 (3)	C(14)–C(13)–C(18)–C(17)	0·0 (3)
S–C(13)–C(14)–C(15)	179·8 (4)	C(14)–C(13)–S–O(1)	−68·8 (3)
C(14)–C(13)–S–O(2)	174·1 (3)	C(14)–C(13)–S–O(3)	41·0 (3)
S–C(13)–C(18)–C(17)	−179·9 (4)	C(18)–C(13)–S–O(1)	111·0 (3)
C(18)–C(13)–S–O(2)	−6·1 (3)	C(18)–C(13)–S–O(3)	−139·2 (3)
C(13)–C(14)–C(15)–C(16)	−0·1 (3)	C(14)–C(15)–C(16)–C(17)	0·2 (3)
C(14)–C(15)–C(16)–C(19)	−178·7 (5)	C(15)–C(16)–C(17)–C(18)	−0·2 (3)
C(19)–C(16)–C(17)–C(18)	178·6 (5)	C(16)–C(17)–C(18)–C(13)	0·2 (3)
C(12)–O(1)–S–C(13)	−69·8 (2)	C(12)–O(1)–S–O(2)	46·7 (2)
C(12)–O(1)–S–O(3)	175·7 (3)		

From the least-squares analysis in which we set $O(4) = O(5)$, $O(8) = O(9)$, $O(7) \neq O(8)$, $O(10) \neq O(8)$, we calculated a mean value for $O(7)$, $O(8)$, $O(9)$, $O(10)$ and obtained $P(\mathrm{II}) + P(\mathrm{IV}) = 0{\cdot}727\ (10)$, $P(\mathrm{II}) + P(\mathrm{V}) = 0{\cdot}783\ (7)$, giving the following limits to the solutions:

$$P(\mathrm{I}) = 0{\cdot}217\ (7) \rightarrow 0{\cdot}000\ (7)$$
$$P(\mathrm{II}) = 0{\cdot}727\ (10) \rightarrow 0{\cdot}510\ (10)$$
$$P(\mathrm{IV}) = 0 \rightarrow 0{\cdot}230$$
$$P(\mathrm{V}) = 0{\cdot}056\ (17) \rightarrow 0{\cdot}273\ (17).$$

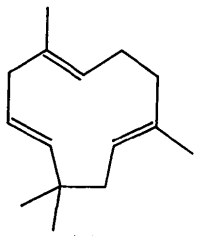
Though we cannot distinguish between the various solutions on the basis of the X-ray results, in view of the higher energies calculated for conformations IV and V it is likely that conformations I and II are predominant. On the basis of the steric energies listed in Table 2, (*E*,*E*)-cycloundeca-1,5-diene in the gas phase at 292 K should contain 73·6% I, 20·2% II, 2·4% III, 3·1% IV, 0·5% V, 0·1% VI and less than 0·1% of higher-energy forms. If these results can be extrapolated to cycloundeca-1,5-diene derivatives in solution at room temperature and subsequently to the crystals obtained from solution, conformations I and II are expected to be readily available in solids. Indeed, in the earlier X-ray studies of humulene nitrosite (MacAlpine, Porte & Sim, 1982; Khan, MacAlpine, Porte & Sim, 1983) and several dolabellane diterpenoids (Matsuo, Uohama, Yoshida, Nakayama, Hayashi, Connolly & Sim, 1985; Huneck, Baxter, Cameron, Connolly, Harrison, Phillips, Rycroft & Sim, 1986; Connolly, Sim & Matsuo, 1987), no indication was found of any conformation other than I and II. We conclude that the most likely solution for the conformational populations in the crystal structure of (1) involves very small (possibly zero) values for $P(\mathrm{IV})$ and $P(\mathrm{V})$, with $P(\mathrm{I}) \sim 0{\cdot}25$, $P(\mathrm{II}) \sim 0{\cdot}75$.

Although conformational interconversions can occur in solids (Sim, 1987), it is likely that rotation of the bulky rigid $CH_2CH{=}CHCH_2$ groups in (1) can only occur in solution and the conformational mixture in the crystal probably does not vary with temperature.

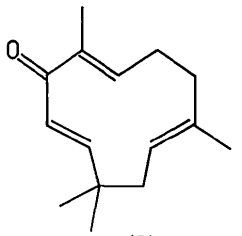
The preponderance of conformation II rather than I in the crystal of (1) can be ascribed to crystal packing and/or the effect of the substituent at C(1). An earlier molecular-mechanics study of the highly substituted 1,4,4,8,8,9-hexamethylcycloundeca-1,5-diene with the White & Bovill (1977) force field gave conformation II marginally lower in energy than I by 1·4 kJ mol^{-1}, whereas conformations IV and VI were 15·1 and 18·4 kJ mol^{-1}, respectively, above II (Khan, MacAlpine, Porte & Sim, 1983). The conformations of the eleven-membered rings in (3*S*,4*S*,7*S*,8*S*,10*R*)-3,4;7,8-diepoxy-10,18-dihydroxydolabellane, (*E*)-(3*S*,4*S*,10*R*)-10,18-diacetoxy-3,4-epoxydolabell-7-ene, (3*S*,4*S*,7*S*,-8*S*)-18-acetoxy-3,4;7,8-diepoxydolabellane, (*E*,*E*)-(6*R*,12*R*)-6-acetoxy-12,16-dihydroxydolabella-3,7-diene, (*E*,*E*)-(6*R*,12*R*)-6-(*p*-bromobenzoyloxy)-12-hydroxy-dolabella-3,7-diene and (3*S*,4*S*,6*R*)-6-acetoxy-3,4-epoxy-3,4-dihydroodontoschismenol were compared with the molecular-mechanics calculations for cycloundeca-1,5-diene and the first four found to adopt conformation II and the final two conformation I (Huneck, Baxter, Cameron, Connolly, Harrison, Phillips, Rycroft & Sim, 1986). Conformation II of cycloundeca-1,5-diene has also been observed in crystals of dinitrohumulene, nitronitratohumulene, and the needle form of humulene nitrosite (MacAlpine, Porte & Sim, 1982) and conformation I in the platelet form of humulene nitrosite (Khan, MacAlpine, Porte & Sim, 1983). The observation of both conformations I and II in crystal structures of derivatives of cycloundeca-1,5-diene is not unexpected in view of the small energy difference, 3·1 kJ mol^{-1}, between these conformations. The analogous energy difference for cycloundeca-1,6-diene is larger, 5·6 kJ mol^{-1} (Table 3),

and examination of torsion angles shows that only the lowest-energy conformation I of this ring system is observed in the crystal structures of cytochalasin D (Tsukuda & Koyama, 1972), cytochalasin H (Beno, Cox, Wells, Cole, Kirksey & Christoph, 1977), 17,18-di-*O*-acetylaspochalasin (Neupert-Laves & Dobler, 1982), 10-acetoxy-18-hydroxydolabella-2,7-diene (Ireland, Faulkner, Finer & Clardy, 1976) and 10,18-dihydroxy-7,8-epoxydolabell-2-ene (Gonzalez, Martin, Norte, Perez, Weyler, Rafii & Clardy, 1983).

Inspection of the molecular-mechanics results in Table 1 suggests that a *trans* double bond could be introduced at bond 8–9, *i.e.* the eighth row of torsion angles, in several of the conformations of cycloundeca-1,4-diene to yield possible conformations for cycloundeca-1,4,8-triene. Similarly, inspection of Table 2 suggests that a *trans* double bond could be introduced at bond 8–9 in several conformations of cycloundeca-1,5-diene to yield possible conformations for cycloundeca-1,5,8-triene, which is merely an alternatively numbered cycloundeca-1,4,8-triene [see formula (2)]. The sesquiterpenes humulene (2) and zerumbone (3) provide examples of substituted



(2)



(3)

cycloundeca-1,4,8-trienes (or cycloundeca-1,5,8-trienes). Three derivatives of humulene have been characterized by X-ray diffraction (McPhail & Sim, 1966; Cradwick, Cradwick & Sim, 1973; Murray-Rust & Murray-Rust, 1977) and all exhibit a common conformation that corresponds to conformation 1,4-II and 1,5-II. A zerumbone derivative has been examined (Russell, Sim & White, 1982) and this exhibits a conformation that corresponds to conformation 1,4-I and 1,5-I. Previous molecular-mechanics treatments of humulene were based on molecular models (Shirahama, Osawa & Matsumoto, 1980) or X-ray results (Russell, Sim & White, 1982) with rotation of the planes of the double bonds. The results presented here indicate that the conformational properties of humulene could be deduced directly by systematic molecular-mechanics calculations without recourse to additional information. The *CC, CT, TC,* and *TT* humulene conformations described by Shirahama, Osawa & Matsumoto (1980) correspond to conformations 1,5-I, 1,5-II, 1,5-IV and 1,5-V of Table 2.

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