torsion angle (Tanaka, Iinuma & Mizuno, 1986). More detailed work on this subject is in progress.

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Structure and Absolute Configuration of (*E*)-(−)-2-Cyclododecenyl Camphanate

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Abstract. $C_{22}H_{34}O_4$, $M_r = 362 \cdot 51$, monoclinic, $P2_1$, $a = 7 \cdot 371$ (1), $b = 10 \cdot 571$ (1), $c = 13 \cdot 538$ (2) Å, $\beta = 90 \cdot 36$ (1)°, $V = 1054 \cdot 84$ Å^3, $Z = 2$, $D_x = 1 \cdot 141$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1 \cdot 5418$ Å, $\mu = 0 \cdot 577$ mm^{-1}, $F(000) = 396$, $T = 296$ K, $R = 0 \cdot 057$ for 1550 unique reflections with $I \geq \sigma(I)$. The crystal conformation of the 12-membered ring in the title compound and its absolute configuration (1*R*) have been determined. The ring adopts a conformation with a necessarily approximate twofold axis in the crystal but it appears to be highly flexible.

Introduction. As part of an ongoing study of the relation of the configuration and conformation of medium-ring 2-cycloalkenyl *p*-bromobenzoates with their chiroptical properties, we prepared a sample of (*E*)-2-cyclododecanol. Earlier studies by Ito, Kasai,

Ziffer & Silverton (1987) had shown that although the sign of the CD curve predicted for five-, six- and seven-membered 2-cycloalkenyl *p*-substituted benzoates is independent of the conformation of the cycloalkene ring, information on the conformations of eight- and nine-membered rings is required to reconcile the observed and predicted signs of the CD curves. The predictions are based on a theoretically based exciton model developed by Harada, Iwabuchi, Yokota, Uda & Nakanishi (1981). As (*E*)-2-cyclododecenol was resolved *via* its camphanate ester, a crystal-structure determination of the ester was carried out to establish its conformation and configuration. To our knowledge there has been no previous determination of the conformation of a 2-cyclododecene by crystallography although theoretical calculations were reported for (*Z*)-cyclododecene by Anet & Rawdah (1979). References to previous uses of camphanate derivatives for determining absolute configuration are given in our paper on the structure of a cycloundecene (Ito, Ziffer & Silverton, 1988).

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Experimental. Preparation of (1). Commercial cyclododecene was brominated with N-bromosuccinimide in carbon tetrachloride to yield a mixture of allylic bromides. The solution was filtered, the organic layer concentrated and the residue dissolved in THF. An aqueous solution of sodium bicarbonate was added and the solution refluxed for several hours. The THF layer was separated and concentrated to yield a mixture of (E) and (Z) alcohols. The (E) isomer was purified by converting the alcohols into 3,5-dinitrobenzoates by standard methods and fractional crystallization from heptane yielded the pure (E) isomer. The ester was hydrolyzed with potassium hydroxide in aqueous methanol to yield the (E) alcohol. The camphanate ester was prepared by reaction with 1·2 equivalents of (−)-camphanoyl chloride in dichloromethane containing an equivalent of 4-dimethylaminopyridine. The reaction mixture was treated with water, the methylene chloride solution was separated and concentrated. The diastereomeric esters were separated by fractional crystallization from hexane/ethyl acetate to yield one diastereomer as colorless needles, m.p. 364–366 K; $[\alpha]_D^{20.0°C} = -16·0°[\text{CHCl}_3, \ 2·6 \ \text{g dm}^{-3}]$. Analysis: calculated for $\text{C}_{22}\text{H}_{34}\text{O}_4$: C 72·93, H 9·39%; found: C 72·80, H 9·49%.

(1)
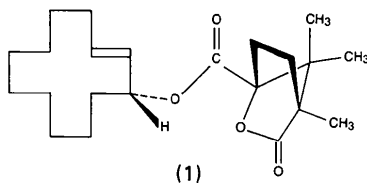
The crystal used for X-ray investigation was a needle cut to 0·53 × 0·13 × 0·15 mm. Lattice parameters were obtained by least-squares refinement using Bragg angles of 18 reflections with $20 < \theta < 25°$ measured with Cu $K\alpha$ X radiation at $\pm\theta$. The Friedel symmetry was $2/m$ and the sole systematic absence was $0k0$ for $k \neq 2n$. The only space group obeying the reflection conditions and suitable for an optically active compound is $P2_1$ with polar axis b. The intensity data were measured with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation and no significant changes were observed in the intensities of three standard reflections (20$\bar{5}$, 313, 14$\bar{5}$) measured every 4 h. Absorption ignored. There were 2267 unique reflections {maximum θ angle: 74°, $[(\sin\theta)/\lambda]_{max}$: 0·6238 Å^{-1}, extrema of h, k and l: 0,9; 0,13 and 16,−16 respectively; 717 with $I < \sigma(I)$}. The phase problem was solved by direct methods (Gilmore, 1983) and the initial partial stucture was expanded using weighted Fourier maps and refined by the programs of the XRAY72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The final cycles of full-matrix least-squares refinement employed the CRYLSQ component of XTAL (Stewart, Hall, Alden,

Table 1. *Positional* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\times 10^3)$ *for the* C *and* O *atoms*

The equivalent U values are as given by Fischer & Tillmans (1988) with e.s.d.'s after Schomaker & Marsh (1983). Origin fixed by holding mean y constant.

	x	y	z	$U_{eq}(\text{Å}^2)$
O1	4379 (4)	3227 (6)	7393 (2)	66 (1)
C1	5853 (7)	3233 (10)	6667 (4)	73 (2)
C2	4996 (8)	3490 (10)	5686 (4)	81 (2)
C3	5178 (10)	2757 (11)	4918 (4)	86 (2)
C4	4574 (10)	3028 (11)	3876 (4)	114 (3)
C5	5981 (14)	2811 (14)	3147 (5)	162 (4)
C6	7901 (15)	3398 (13)	3392 (6)	140 (3)
C7	7816 (13)	4779 (12)	3311 (5)	126 (3)
C8	9570 (12)	5422 (12)	3706 (7)	134 (3)
C9	10182 (10)	5092 (12)	4731 (6)	122 (3)
C10	8783 (10)	5314 (11)	5503 (6)	115 (3)
C11	8870 (9)	4363 (15)	6362 (6)	131 (4)
C12	7188 (8)	4272 (11)	6982 (5)	93 (2)
C1'	3049 (5)	2684 (8)	8892 (3)	45 (1)
C2'	1120 (6)	2788 (9)	8485 (4)	61 (1)
C3'	92 (6)	3254 (9)	9401 (4)	62 (1)
C4'	1594 (6)	3386 (8)	10206 (3)	48 (1)
O5'	1877 (5)	1354 (7)	11083 (3)	75 (1)
C5'	2128 (6)	2037 (9)	10392 (3)	51 (1)
O6'	3022 (4)	1622 (7)	9574 (2)	48 (1)
C7'	3244 (5)	3826 (8)	9596 (3)	45 (1)
C8'	3031 (8)	5121 (9)	9132 (4)	63 (2)
C9'	5031 (7)	3800 (9)	10197 (4)	61 (1)
C10'	1092 (10)	4123 (10)	11121 (5)	80 (2)
O11'	5835 (5)	1771 (8)	8307 (2)	80 (1)
C11'	4585 (6)	2467 (8)	8179 (3)	51 (1)

Olthof-Hazekamp & Doherty, 1985). The function minimized was $\sum[w(|F_o| - |F_c|)]^2$ with $w = 1/\sigma$ and σ calculated following Peterson & Levy (1957). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

All C and O atoms were successfully identified from bond lengths and thermal parameters and indications were found for all expected H atoms. The configuration of the camphanate corresponded to the absolute configuration of (−)-camphanic acid which is unambiguously known from its synthesis from (+)-camphor (Gerlach, 1968). Refinement was continued with anisotropic thermal parameters of the form $\exp(-2\pi^2\sum_i\sum_j U_{ij}h_ih_ja_i^*a_j^*)$ for the C and O atoms and isotropic parameters for the H atoms to a final R factor of 0·057 ($R_w = 0·057$). Some problems were encountered during refinement especially with atoms of the 12-membered ring, notably C4 through C9 and their associated H atoms. All C atoms of the ring have large and very anisotropic thermal parameters and it is possible that the implied harmonic motion is not really appropriate. The positional parameters of C5–C9 showed evidence of oscillation and the positions of H atoms attached to C3 through C11 were not very satisfactory. A damping factor of 0·5 was applied in the final refinement and the positional parameters of the H atoms attached to C3 through C11 were set to calculated values. The thermal parameters for H atoms were held at values derived from their attachments. Even so, the largest ratio of parameter shift to

Table 2. *Bond lengths (Å) and bond angles (°) for the complete molecule and torsion angles (°) in the 12-membered ring*

O1	C1	1·470 (6)	O1	C11'	1·341 (7)
C1	C2	1·493 (7)	C1	C12	1·533 (12)
C2	C3	1·304 (11)	C3	C4	1·505 (8)
C4	C5	1·454 (11)	C5	C6	1·579 (15)
C6	C7	1·466 (18)	C7	C8	1·553 (14)
C8	C9	1·498 (12)	C9	C10	1·491 (10)
C10	C11	1·538 (15)	C11	C12	1·505 (9)
O6'	C1'	1·454 (9)	O6'	C5'	1·365 (6)
C1'	C2'	1·526 (6)	C1'	C7'	1·545 (10)
C1'	C11'	1·510 (6)	C2'	C3'	1·538 (7)
C3'	C4'	1·554 (6)	C4'	C5'	1·501 (12)
C4'	C7'	1·546 (6)	C4'	C10'	1·511 (9)
O5'	C5'	1·197 (8)	C7'	C8'	1·513 (11)
C7'	C9'	1·544 (6)	O11'	C11'	1·191 (8)

C1	O1	C11'	116·9 (6)	O1	C1	C2	106·6 (5)
O1	C1	C12	107·1 (6)	C2	C1	C12	112·6 (7)
C1	C2	C3	123·8 (8)	C2	C3	C4	127·1 (9)
C3	C4	C5	113·4 (6)	C4	C5	C6	116·0 (7)
C5	C6	C7	109·8 (9)	C6	C7	C8	112·0 (8)
C7	C8	C9	117·5 (8)	C8	C9	C10	114·0 (7)
C9	C10	C11	113·6 (8)	C10	C11	C12	115·6 (8)
C1	C12	C11	114·9 (7)	C1'	O6'	C5'	106·0 (6)
O6'	C1'	C2'	105·6 (4)	O6'	C1'	C7'	102·3 (3)
O6'	C1'	C11'	107·6 (5)	C2'	C1'	C7'	104·5 (5)
C2'	C1'	C11'	118·8 (3)	C7'	C1'	C11'	116·5 (5)
C1'	C2'	C3'	101·2 (3)	C2'	C3'	C4'	104·0 (3)
C3'	C4'	C5'	102·5 (5)	C3'	C4'	C7'	102·3 (3)
C3'	C4'	C10'	116·4 (4)	C5'	C4'	C7'	99·7 (4)
C5'	C4'	C10'	114·7 (4)	C7'	C4'	C10'	118·7 (6)
O6'	C5'	C4'	107·2 (5)	O6'	C5'	O5'	121·2 (7)
C4'	C5'	O5'	131·5 (5)	C1'	C7'	C4'	91·4 (4)
C1'	C7'	C8'	116·2 (4)	C1'	C7'	C9'	112·8 (5)
C4'	C7'	C8'	114·4 (5)	C4'	C7'	C9'	112·6 (3)
C8'	C7'	C9'	108·7 (5)	O1	C11'	C1'	109·5 (6)
O1	C11'	O11'	124·7 (6)	C1'	C11'	O11'	125·7 (5)

C1	C2	C3	C4	−171·3 (7)	C2	C3	C4	C5	+130·2 (10)
C3	C4	C5	C6	−47·7 (14)	C4	C5	C6	C7	−70·3 (11)
C5	C6	C7	C8	+170·7 (6)	C6	C7	C8	C9	−53·6 (11)
C7	C8	C9	C10	−55·8 (14)	C8	C9	C10	C11	+146·9 (10)
C9	C10	C11	C12	−161·4 (9)	C10	C11	C12	C1	+93·7 (12)
C11	C12	C1	C2	−67·3 (10)	C12	C1	C2	C3	+118·4 (9)

standard deviation was 0·2 at the conclusion of the refinement (goodness-of-fit: 1·707). Atomic parameters for the C and O atoms are given in Table 1 and molecular dimensions in Table 2.* At the conclusion of the refinement, the extrema in a difference map were ±0·21 e Å⁻³ and neither was close to a C or O atom but there were some smaller densities near atoms of the 12-membered ring.

Discussion. The absolute configuration shown in Fig. 1 corresponds to *R*(C1); the known configurations are *S*(C1') and *R*(C4'). These configurations are indicated by their chiral angles [the torsion angle for the vectors

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51502 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

connecting the substituents ordered in chemical priority, given the symbol χ by Ito *et al.* (1987)]: +65 (3), −69·9 (3) and +71·0 (3)° at C1, C1' and C4', respectively. Most bond lengths are similar to those reported in the literature and apparent deviations can probably be attributed to effects of the high and anisotropic thermal parameters as can the relatively high *R* factor and large e.s.d.'s of the ring atoms. In contrast with the recent study of a similar 11-membered ring by Ito *et al.* (1988) where only one atom had highly anisotropic temperature factors, there is apparently highly anisotropic thermal motion for C5 through C11 and, correspondingly, there is a larger number of unusual bond lengths. This observation is in accord with the established classification of organic rings by V. Prelog and H. C. Brown (Brown, Fletcher & Johannesen, 1951) as modified by Eliel (1962) where the boundary between 'medium' and 'large' rings is assigned between 11- and 12-membered rings on a basis of heat of combustion data. Large rings have properties, such as lack of rigidity, similar to long-chain compounds. Given that the atoms concerned have no close non-bonded contacts, as shown in Fig. 2, it is not surprising that the difference between the two types of ring seems evident in the solid state. The ring conformation adopted possesses an approximate twofold axis through the centers of the C1—C12 and
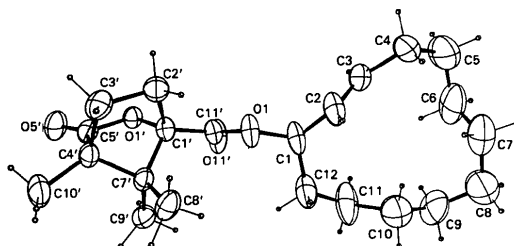

Fig. 1. *ORTEP* (Johnson, 1965) drawing showing crystal conformation. The thermal ellipsoids are drawn at 37% probability.
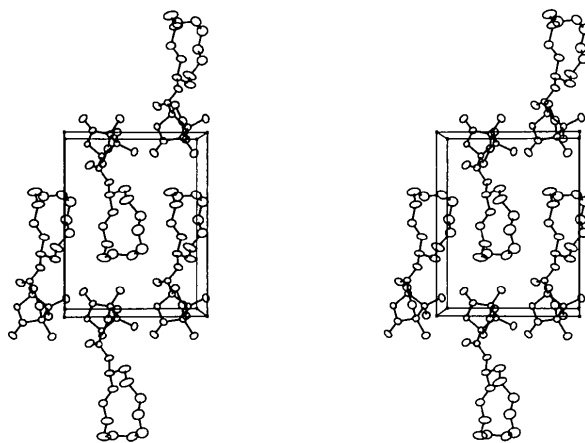

Fig. 2. *ORTEP* (Johnson, 1965) drawing showing crystal packing. The projection is down **b** and the **c** axis is horizontal.

C6—C7 bonds, although this axis cannot be exact since C2—C3 is a double bond and C10—C11 is single.

Molecular-mechanics calculations performed on cyclododecene rings with *XICAMM* (a program resembling standard main-frame programs with modifications to allow it to run on an IBM PC-AT desk computer; Bruger, 1986) supported the indications of flexibility in that several different conformational minima of similar energy were found. These conformers had torsion angles similar to the measured values for the bonds from C1 through C5 and also retained the near planarity of C5 through C8 but had different *gauche* conformations in the rest of the ring. An exhaustive search for all possible conformational energy minima seems beyond the scope of this paper. A model based on the observed crystal conformation changed somewhat after molecular-mechanics refinement in that the torsion angles of the C1—C2 and C3—C4 bonds became less nearly equal at 166 and 89°, respectively. The changes might be attributed to the omission of the camphanate moiety from the calculations but, since there are no close contacts between the ring and camphanate atoms in the crystal, intermolecular packing forces may also be important and may also make the choice of the crystal conformation from among the possible conformers. There could be a dynamic equilibrium among two or more conformations in the less restrictive environment of the solutions used for CD measurements. The conformation of the present (E)-cyclododecene is quite different from that calculated for the (Z) isomer by Anet & Rawdah (1979) which closely resembles the cyclododecane conformation described by Dunitz & Shearer (1960).

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Structure of a 1-Oxa-6,6aλ⁴-dithia-2,5-diazapentalene

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Abstract. 5-Oxa-2,5aλ⁴,6-trithia-4,7-diazacyclohexa[*cd*]pentalene, $C_5H_4N_2OS_3$ (2), $M_r = 204.3$, triclinic, $P\bar{1}$, $a = 8.158$ (3), $b = 8.892$ (2), $c = 11.517$ (4) Å, $\alpha = 68.11$ (2), $\beta = 88.91$ (3), $\gamma = 80.20$ (2)°, $V = 763.0$ (4) Å³, $Z = 4$ (two crystallographically independent molecules), $D_x = 1.78$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.54178$ Å, $\mu = 8.33$ mm⁻¹, $F(000) = 416$, room temperature, $R = 0.051$ for 1773 observed reflections with $|F_o| > 3\sigma(|F_o|)$. On comparing the structure of (2) with those of related heteropentalenes, the gross molecular structure remains virtually unperturbed. However, the replacement of one of the O atoms in the fused