The transition to the plastic phase is accompanied by the appearance of tumbling movements which lead to six different equiprobable orientations in one site for a molecule. That transition is coherent with the creation of six domains. Zielinski & Foulon (1987) showed that the transition can be interpreted according to Landau theory in terms of the order parameter. The transition is induced by the interaction between displacive and orientational modes belonging to the (k_4, τ^3) irreducible representation.

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Crystal Structure and Direction of the Polar Axis of (−)-(1*S*)-Pinonic Acid β-Oxime

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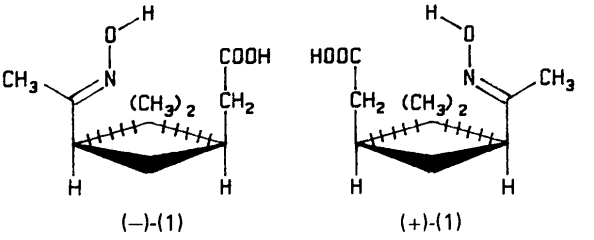
Abstract

(−)-(1*S*)-*cis*-3-(Hydroxyiminoethyl)-2,2-dimethylcyclobutylacetic acid, $C_{10}H_{17}NO_3$, $M_r = 199{\cdot}25$, monoclinic, $P2_1$, $a = 14{\cdot}632\ (8)$, $b = 12{\cdot}193\ (3)$, $c = 7{\cdot}103\ (2)$ Å, $\beta = 112{\cdot}54\ (3)°$, $V = 1170{\cdot}5\ (8)$ Å^3, $Z = 4$ (two independent molecules in the asymmetric unit), $D_x = 1{\cdot}130$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}69$ cm^{-1}, $F(000) = 432$, $T = 295$ K, $R = 0{\cdot}047$ for 1156 observed reflections [$I > 2{\cdot}5\sigma(I)$] and 257 parameters. Calculation suggests that the polarization of molecules of the (−)-enantiomer, oriented as in the crystal, is such that the positive end of the crystal's electric dipole is toward the + end of the *b* axis; conversely, for the (+)-enantiomer the polarization is in the opposite sense with the electrically positive end of the crystal dipole toward −*b*. This electrical polarization, due to the molecular orientation found from the crystal structure determination, is in the same direction as the polarization of the crystal produced by heating (the pyroelectric effect) as determined by the Kundt–Bürker powder test. Thus, as has been found in previous examples, the orientation along the polar axis of the electric dipole induced by heating is the same as the orientation of the polarization of the crystal deduced from the X-ray structure.

Introduction

The determination of the crystal structure of chiral (−)-(1*S*)-*cis*-3-(hydroxyiminoethyl)-2,2-dimethylcyclobutylacetic acid [(−)-pinonic acid β-oxime, (−)-(1)]



was carried out as part of an investigation of the utility of the Kundt–Bürker pyroelectric test for assigning the

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absolute directions of the polar axes of electrically polar crystals (Curtin & Paul, 1982, 1987). This study was undertaken because the previously reported absolute configuration and crystal morphology (Groth, 1910) of enantiomers of (1) provide a method for relating the absolute direction of the polar axis to the crystal structure without recourse to the Bijvoet method employing anomalous scattering. The chiral β-oximes, (+)-(1) and (−)-(1), m.p. 401 K, were of particular interest because they have the symmetry of the polar point group 2.

The direction of the polarization (see Burns, 1985) of the crystal is estimated from *AM*1 calculations (Dewar, Zoebisch, Healy & Stewart, 1985) using the orientations of the molecules determined by X-ray crystallography; this is compared to the direction of the pyroelectric effect found by the Kundt–Bürker powder method (see Lang, 1974).

Experimental

Preparation of pinonic acid oxime (−)-(1)

Oxidation of (−)-α-pinene (Delepine, 1936) with potassium permanganate in the presence of ammonium sulfate gave (−)-*cis*-pinonic acid which, on treatment with hydroxylamine hydrochloride in the presence of potassium bicarbonate, afforded (−)-(1): m.p. 401 K; $[\alpha]_D^{20\cdot0^\circ C} = -20\cdot7^\circ$ (methanol, 0·705 g ml^{-1}), −42·4° (ether, 0·67 g ml^{-1}). Reported (Delepine, 1936) $[\alpha]_D^{20\cdot0^\circ C} = -47^\circ$ (ether, 0·8 g ml^{-1}).

Analysis. Calculated for $C_{10}H_{17}NO_3$: C, 60·28; H, 8·60; N, 7·03%. Found: C, 59·89; H, 8·60; N, 6·89%.

Crystal structure of (−)-(1)

Suitable crystals of (−)-(1) (0·45 × 0·20 × 0·10 mm) were obtained by slow evaporation of a methanol solution. Syntex $P2_1$ diffractometer; graphite-monochromated Mo $K\alpha$ radiation, cell parameters refined from diffractometer angles for 15 centered reflections ($24 < 2\theta < 26^\circ$). Intensity data collected by $\omega/2\theta$ scans for 2760 reflections with $3 < 2\theta < 53^\circ$ (h −18/18, k 0/15, l 0/8); three standard reflections monitored (±1%). Corrections for Lorentz and polarization effects were made, no corrections were made for absorption (minimum and maximum transmission factors 0·987 and 0·992), 2549 unique reflections ($R_{int} = 0\cdot018$), 1156 counted as observed with $I > 2\cdot5\sigma(I)$. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain & Woolfson, 1980). H atoms were located from a difference Fourier map, but due to the small number of reflections, the C–H hydrogens were fixed in their idealized positions with only their group thermal parameters being refined; hydroxyl hydrogens were clearly shown on the difference map and were included at these fixed positions with the same group thermal parameters. Full-matrix refinement, positional and anisotropic thermal parameters for all non-H atoms, group isotropic thermal parameters for the different type of hydrogens. Final $R = 0\cdot047$, 257 parameters, 1156 observations, $wR = 0\cdot51$, $S = 1\cdot665$, $w = 4\cdot14/[\sigma^2(F_o) + 0\cdot0004F_o^2]$, $(\Delta/\sigma)_{max} = 0\cdot001$, $\Delta\rho$ within 0·21 and −0·16 e Å^{-3}.

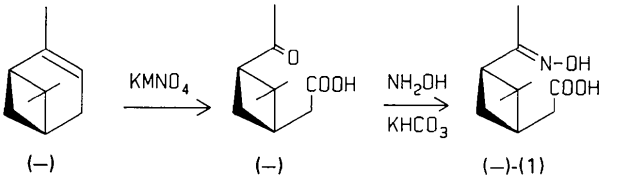
The *SHELX*76 (Sheldrick, 1976) program was used for full-matrix refinement. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are given in Table 1.*

Application of Kundt–Bürker pyroelectric test to single crystals of (−)-(1)

A single crystal of oxime (−)-(1) was heated on a microscope glass slide to 353 K for 5–10 min. The slide was removed from the hot plate and, after 3–5 s, the crystal was sprayed with a mixture of yellow flowers of sulfur, carmine and lycopodium powder dyed with methyl violet as described earlier (Patil, Curtin & Paul, 1985).

Results and discussion

Repetition of the previously reported synthesis (Delepine, 1936) of the chiral β-oxime (−)-(1) shown below established the absolute configuration of this compound since the absolute configuration of the starting (−)-pinene is known (Berson, Walia, Remanick, Suzuki, Reynolds-Warnhoff & Willmer, 1961; Delepine, 1936; Arcus & Bennett, 1955) and no change of configuration at the asymmetric centers is involved in these reactions.



The measured optical rotation of (−)-(1) agreed with the previously reported value (Delepine, 1936). The crystal structure of (−)-(1) is shown in Fig. 1. Groth (1910) had reported the morphology of (+)-(1) crystals prepared by A. von Baeyer (1894). Our crystals showed similar morphology when the difference in absolute configuration is taken into account as is indicated by drawings of crystals of (+)-(1) and (−)-(1) (Fig. 2) calculated from the unit-cell constants from X-ray crystallography. [The axial ratios obtained from

* A table of anisotropic thermal parmeters and a list of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51717 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters and equivalent isotropic thermal parameters for non-*H *atoms and positional and isotropic thermal parameters for* H *atoms of* (−)-*cis-pinonic acid oxime*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}(Å^2)
Molecule I				
C(1)	0·9973 (4)	0·2036†	0·2167 (8)	0·0516
C(2)	1·0369 (4)	0·1593 (5)	0·0584 (7)	0·0457
C(3)	1·1245 (4)	0·1121 (6)	0·2421 (8)	0·0474
C(4)	1·0596 (4)	0·1181 (6)	0·3677 (8)	0·0617
C(5)	0·8861 (4)	0·2090 (6)	0·1665 (8)	0·0551
C(6)	0·8598 (4)	0·2602 (6)	0·3318 (8)	0·0546
C(7)	0·9711 (4)	0·0697 (6)	−0·0784 (8)	0·0631
C(8)	1·0601 (4)	0·2461 (6)	−0·0716 (9)	0·0716
C(9)	1·2315 (4)	0·0108 (6)	0·0822 (8)	0·0616
C(10)	1·1751 (3)	0·0103 (6)	0·2229 (8)	0·0474
N	1·1708 (3)	−0·0727 (5)	0·3305 (6)	0·0500
O(1)	0·8952 (3)	0·3604 (5)	0·3799 (6)	0·0676
O(2)	0·8140 (3)	0·2145 (5)	0·4158 (7)	0·0875
O(3)	1·2247 (3)	−0·1643 (4)	0·3054 (6)	0·0676
H(1)	1·0031	0·2802	0·2506	0·101
H(3)	1·1886	0·1462	0·2914	0·101
H(41)	1·0930	0·1447	0·5044	0·077
H(42)	1·0252	0·0514	0·3703	0·077
H(51)	0·8602	0·1357	0·1438	0·077
H(52)	0·8558	0·2513	0·0443	0·077
H(71)	0·9569	0·0155	0·0045	0·132
H(72)	1·0048	0·0358	−0·1555	0·132
H(73)	0·9104	0·1017	−0·1700	0·132
H(81)	1·1014	0·3019	0·0152	0·132
H(82)	0·9996	0·2785	−0·1631	0·132
H(83)	1·0941	0·2126	−0·1487	0·132
H(91)	1·2245	0·0812	0·0174	0·132
H(92)	1·2054	−0·0450	−0·0198	0·132
H(93)	1·3003	−0·0034	0·1601	0·132
H(O1)	0·8792	0·3810	0·4686	0·092
H(O3)	1·2222	−0·2122	0·3863	0·092
Molecule II				
C(1)	0·4249 (4)	0·4337 (6)	0·2992 (8)	0·0627
C(2)	0·3965 (4)	0·4847 (6)	0·4671 (9)	0·0574
C(3)	0·3101 (4)	0·4006 (6)	0·4064 (8)	0·0570
C(4)	0·3646 (5)	0·3307 (6)	0·3035 (9)	0·0675
C(5)	0·5321 (4)	0·4138 (6)	0·3244 (9)	0·0684
C(6)	0·5882 (4)	0·5126 (6)	0·3052 (9)	0·0624
C(7)	0·4715 (4)	0·4618 (7)	0·6812 (9)	0·0919
C(8)	0·3655 (5)	0·6040 (6)	0·437 (1)	0·1157
C(9)	0·2162 (5)	0·4219 (7)	0·6468 (10)	0·0852
C(10)	0·2794 (4)	0·3534 (6)	0·5672 (8)	0·0581
N	0·3090 (3)	0·2578 (5)	0·6331 (7)	0·0551
O(1)	0·5896 (3)	0·5916 (5)	0·4335 (7)	0·0881
O(2)	0·6305 (3)	0·5202 (5)	0·1924 (7)	0·0972
O(3)	0·2775 (3)	0·2197 (5)	0·7842 (6)	0·0753
H(1)	0·4131	0·4770	0·1794	0·101
H(3)	0·2429	0·4225	0·3309	0·101
H(41)	0·4029	0·2718	0·3859	0·077
H(42)	0·3234	0·3031	0·1716	0·077
H(51)	0·5317	0·3620	0·2223	0·077
H(52)	0·5666	0·3829	0·4573	0·077
H(71)	0·4890	0·3855	0·6934	0·132
H(72)	0·4431	0·4800	0·7787	0·132
H(73)	0·5296	0·5055	0·7066	0·132
H(81)	0·3183	0·6147	0·3005	0·132
H(82)	0·4225	0·6492	0·4599	0·132
H(83)	0·3360	0·6237	0·5320	0·132
H(91)	0·2021	0·4911	0·5768	0·132
H(92)	0·2509	0·4343	0·7902	0·132
H(93)	0·1553	0·3841	0·6240	0·132
H(O1)	0·6121	0·6393	0·3919	0·092
H(O3)	0·3160	0·1776	0·8378	0·092

† The y coordinate of C(1) of molecule I was fixed to define the origin along the twofold screw axis.

X-ray data (a:b:c = 1·2000:1:0·5825) agree well with the values reported by Groth (1910) (1·1805:1:0·5833).]

Groth (1910) had reported a correlation of the absolute direction of the polar b axis with the crystal morphology for the oxime (+)-(1); the flat end of the crystal is at the crystallographically positive end of the polar b axis and the pointed end toward $-b$. Conversely, for the (−)-oxime (−)-(1), the pointed end of the crystal is at the crystallographically positive end of the b axis and the flat end toward $-b$ (Fig. 2). As mentioned in the *Experimental* section, we found that application of a pyroelectric test using the Kundt–Bürker powder method to a heated crystal showed the blue positively charged particles attracted to the flat end of (−)-(1) and the negatively charged orange-red particles to the pointed end (Fig. 2). It follows that for (−)-(1), the $+b$ end of the polar axis becomes electrically positive on heating and the $-b$ end electrically negative. In apparent disagreement with this result, Groth (1910) had reported the pointed end of the (+)-crystal becoming the electrically negative end of the b axis when the crystal was heated and the flat end electrically positive.

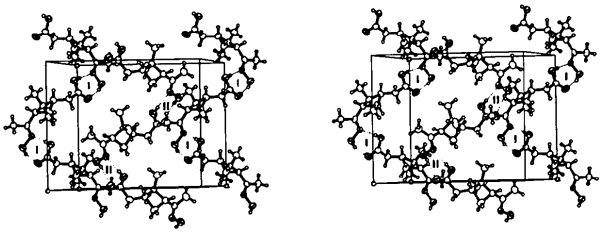


Fig. 1. Packing of pinonic acid oxime (−)-(1) showing the hydrogen-bonded chains of molecules of type I and chains of type II molecules running in the direction of the polar b axis.

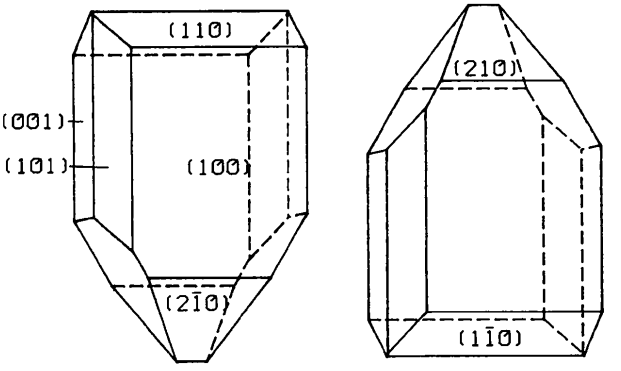


Fig. 2. Drawings of (+)-(1) (left) and (−)-(1) (right) crystals calculated from the cell constants. The b and c axes lie in the plane of the page, with b pointing toward the top of the page and c from right to left so that the major faces are {100}. Note that in each crystal the (001) and (101) faces at the left are slanting upward from the page while the pair of opposite faces generated by the twofold axis parallel to b are slanting inward. In each case the faces which cut the polar b axis have no parallel counterparts at the opposite end of the crystal. The plus end of the electric dipole is in the $-b$ direction (toward the pointed end) of the (+)-crystal and in the $+b$ direction (again toward the pointed end) of the (−)-crystal.

Molecular and crystal structure

The atom-numbering scheme is shown in Fig. 3. The bond lengths and angles, of the two independent molecules, I and II, are recorded in Tables 2 and 3 respectively. The torsional angles in the cyclobutane ring are given in Table 4(*a*). The cyclobutane ring is puckered with C(2)–C(1)–C(4)/C(2)–C(3)–C(4) dihedral angles of 30·8 and 27·7° in molecules I and II respectively. The corresponding value in (±)-*cis*-pinonic acid is reported to be 29·8° (Vanderhoff, Thompson & Lalancette, 1986). The crystal structure consists of zigzag chains of symmetry-related molecules running along the *b* axis (Fig. 1). The chains themselves are held together by pairs of strong intermolecular hydrogen bonds between the N–OH-oxime and CO_2H-carboxyl groups (Table 5). The association of adjacent symmetry-independent chains may be stabilized by C–H···O interactions involving the carbonyl O atoms* [see Desiraju (1987) and Sarma & Desiraju (1987, and references therein)].

The formation of eight-membered hydrogen-bonded rings involving the carboxyl group of one molecule and the oxime group of the next is a key structural feature responsible to a large degree for the polarity of the crystal structure described in this paper, since it leads to chains with pronounced polarity along the crystal's polar *b* axis. A principal hydrogen-bonding pattern shown by crystalline oximes uncomplicated by the presence of other functional groups is the eight-membered hydrogen-bonded dimer (Bertolasi, Gilli & Veronese, 1982) analogous to the dimers characteristic of many carboxylic acids (Leiserowitz, 1976). There seem to have been no other X-ray determinations of relatively simple structures whose molecules contain only carboxyl and oxime functional groups. An investigation of other such compounds would be of interest.

*It was pointed out by a referee that C–H···O interactions between the adjacent symmetry-independent chains may account for the presence of two symmetry-independent molecules in the structure. Thus in Fig. 1 it can be seen that there are such contacts between O2 of molecule I and methyl groups of molecule II. Similarly, O2 of molecule II makes a short contact of 3·30 Å to C9 of molecule I and other C–H···O contacts may provide further stabilization.

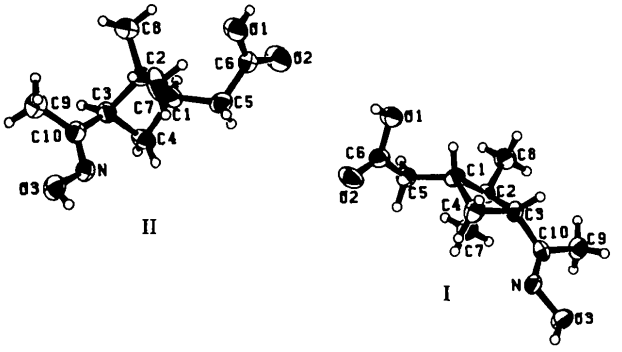


Fig. 3. The two independent molecules of oxime (−)-(1) as they exist in an idealized crystal. The *a* and *b* axes are in the plane of the page with *a* to the right and *b* up. The atom numbering is shown.

Table 2. *Bond lengths* (Å) *for* (−)-*pinonic acid oxime*

All C–H hydrogens were fixed geometrically at 0·96 Å.

	Molecule I	Molecule II
C(1)–C(2)	1·547 (7)	1·536 (8)
C(2)–C(3)	1·548 (7)	1·556 (7)
C(1)–C(4)	1·523 (7)	1·541 (8)
C(3)–C(4)	1·534 (7)	1·530 (9)
C(1)–C(5)	1·527 (7)	1·529 (8)
C(5)–C(6)	1·504 (7)	1·493 (8)
C(2)–C(7)	1·532 (7)	1·522 (8)
C(2)–C(8)	1·526 (7)	1·514 (9)
C(3)–C(10)	1·478 (8)	1·494 (8)
C(9)–C(10)	1·521 (7)	1·508 (8)
C(10)–N	1·284 (6)	1·269 (7)
C(6)–O(1)	1·320 (7)	1·321 (7)
C(6)–O(2)	1·192 (6)	1·188 (6)
N–O(3)	1·417 (5)	1·400 (6)
O(1)–H(O1)	0·79	0·78
O(3)–H(O3)	0·83	0·75

Table 3. *Bond angles* (°) *for* (−)-*cis-pinonic acid oxime*

All C–H hydrogens were fixed in their ideal positions with group thermal parameters. The hydroxyl hydrogens were located from the difference Fourier map, refined for a few cycles and kept fixed in the final cycles of least-squares refinement.

	Molecule I	Molecule II
C(2)–C(1)–C(4)	89·0 (4)	89·3 (4)
C(2)–C(1)–C(5)	120·5 (4)	122·9 (5)
C(4)–C(1)–C(5)	119·4 (4)	116·0 (5)
C(1)–C(2)–C(3)	86·4 (4)	87·1 (4)
C(1)–C(2)–C(7)	113·0 (4)	113·3 (5)
C(1)–C(2)–C(8)	115·5 (4)	115·9 (5)
C(3)–C(2)–C(7)	112·7 (4)	110·7 (5)
C(3)–C(2)–C(8)	117·6 (4)	115·3 (5)
C(7)–C(2)–C(8)	110·0 (4)	112·3 (6)
C(2)–C(3)–C(4)	88·6 (4)	89·0 (4)
C(2)–C(3)–C(10)	121·1 (4)	119·6 (5)
C(4)–C(3)–C(10)	122·5 (5)	121·0 (5)
C(1)–C(4)–C(3)	87·7 (4)	87·9 (4)
C(1)–C(5)–C(6)	113·8 (4)	115·9 (5)
C(5)–C(6)–O(1)	113·2 (5)	112·8 (5)
C(5)–C(6)–O(2)	123·9 (6)	124·8 (6)
O(1)–C(6)–O(2)	122·8 (5)	122·3 (6)
C(3)–C(10)–N	118·3 (5)	118·8 (6)
C(3)–C(10)–N	117·8 (4)	118·3 (5)
C(9)–C(10)–N	123·8 (5)	122·9 (6)
C(10)–N–O(3)	112·9 (4)	114·9 (5)
C(6)–O(1)–H(O1)	107	100
N–O(3)–H(O3)	107	102

Table 4. *Angles* (°) *in* (−)-*pinonic acid oxime*

(*a*) Relevant torsional angles

	Molecule I	Molecule II
C(1)–C(2)–C(3)–C(4)	21·3 (4)	19·4 (4)
C(2)–C(3)–C(4)–C(1)	−21·6 (4)	−19·3 (4)
C(3)–C(4)–C(1)–C(2)	21·6 (4)	19·5 (4)
C(4)–C(1)–C(2)–C(3)	−21·5 (4)	−19·2 (4)

(*b*) Angle between planes in the four-membered ring

Planes	Molecule I	Molecule II
C(2)–C(1)–C(4) C(2)–C(3)–C(4)	30·8	27·7

Note for (*b*): the value for this angle between these two planes in (±)-*cis*-pinonic acid is 29·8° (Vanderhoff, Thompson & Lalancette, 1986).

Calculation of the dipole moments of the independent molecules of (−)-(1)

The ready electrostatic contamination of the surfaces at the ends of the polar axis of a polar crystal makes

Table 5. *Intermolecular hydrogen-bonding parameters (Å and °) for (−)-cis-pinonic acid oxime*

	Molecule I	Molecule II
N···O(1)	2·711 (6)[i]	2·659 (8)[ii]
N···H(O1)	1·92	1·90
N···H(O1)–O(1)	175	164
C(10)–N···H(O1)	143	143
O(2)···O(3)	2·700 (7)[iii]	2·754 (8)[iv]
O(2)···H(O3)	1·90	2·11
O(2)···H(O3)–O(3)	160	144
C(6)–O(2)···H(O3)	121	117

Symmetry elements: (i) $2-x, -\frac{1}{2}+y, 1-z$; (ii) $1-x, -\frac{1}{2}+y, 1-z$; (iii) $2-x, \frac{1}{2}+y, 1-z$; (iv) $1-x, \frac{1}{2}+y, 1-z$.

impossible the direct measurement of the surface charges of such a crystal at constant temperature (Lang, 1974). However, the magnitude and sign of the dipole was estimated by calculation with *AM*1 (Dewar *et al.*, 1985) of the vector sum of the molecular dipole moments of the molecules in the unit cell assuming the geometry found in the crystal structure determination. The results are summarized in Table 6 for the two independent molecules. The molecular moment of molecule I was found to be 2·357 debye making an angle of 47° with the polar *b* axis; the component along the *b* axis is therefore 1·603 debye as shown in Table 6. Corresponding values for molecule II are also given in Table 6. As can be seen, components of both molecular moments have the same sign along the polar *b* axis indicating that in the oxime (−)-(1), the (+) end of the *b* axis is electrically positive and the (−) end electrically negative.*

Concluding remarks

If it is assumed, as has been shown in other examples (Pennington, Chakraborty, Paul & Curtin, 1988), that the direction of the crystal dipole induced by heating such organic crystals is the same as that estimated from the internal structure of the crystal then the direction of our calculated dipole moment is in agreement with our determination of the direction of the pyroelectric effect induced by heating.† Because of the unavailability of the details of the earlier experiments (reported by Groth, 1910) we have no explanation for the disagreement between their reported results and ours.

Table 6. *Summaries of dipole moment data for molecules* I *and* II *of pinonic acid oxime*

(*a*) Dipole moment calculations

Molecule	Dipole moment (debye)	Angle with polar *b* axis (°)	Component along polar axis (debye)
I	2·357	47	1·603
II	1·696	45	1·190

(*b*) Vector addition of dipole moments for molecules I and II starting from simple acetoxime and acetic acid molecules

Molecule and starting molecule	Dipole moment (debye)	Angle with *b* axis (°)	Component along *b* axis (debye)	Sum (debye)
I Acetoxime	1·000	20	0·940	1·649
Acetic acid	1·509	62	0·709	
II Acetoxime	1·254	18	1·194	1·095
Acetic acid	1·464	94	−0·099	

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* Although these calculations have not taken into account intermolecular interactions of neighboring molecules in the crystal, the well-defined choice with the components of the two independent dipoles oriented in the same direction along the polar *b* axis makes it seem unlikely that the sign of the electric vector is incorrect although the magnitude is unreliable.

† Careful measurements have recently been reported of the change of the pyroelectric coefficient with temperature of some polar disubstituted benzenes (Giermanska, Nowak & Sworakowski, 1985; Asaji, Taya & Nakamura, 1987; Weiss & Fleck, 1987; Fleck & Weiss, 1987, and references cited therein). This work has not been concerned with correlation of the absolute direction of the polar axis with crystal morphology, however.

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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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