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(±)-3-Formyl-1-methyl-2-(2-phenylethyl)cyclohex-2-enecarboxylic Acid: an Investigation of Disorder

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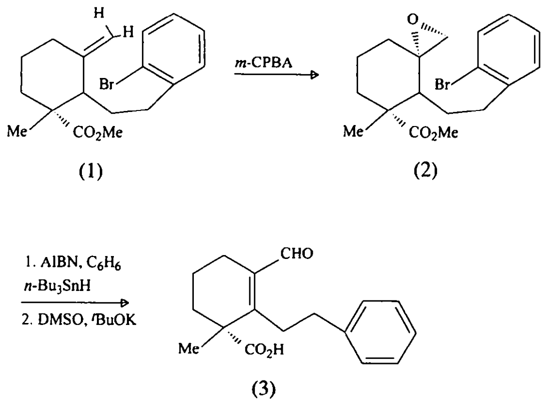
Abstract

The structure of the title compound, $C_{17}H_{20}O_3$, a substituted cyclohexene system, has been determined. The high degree of disorder in various substituent moieties results in two different orientations of the molecule in the crystal lattice which have unequal occupancy factors. Lattice-energy calculations based on van der Waals attractive and repulsive potentials clearly show minima at the observed disordered positions. The difference in occupancy factors between the two molecular orientations can be explained from the relative values of lattice energies.

Comment

The structure determination of the title compound (3) was not straightforward. The *E* map computed using the phases from the best set [ABSFOM = 0.700, PSIZERO = 0.702, RESID = 27.14, CFOM = 2.548 (*MULTAN*88; Debaerdemaeker *et al.*, 1988)] was too confusing to interpret. Only a small fragment of the molecule consisting of five C atoms of the cyclohexene ring (C1–C5) could be identified unambiguously. Successive weighted Fourier maps revealed three more positions (C7, C8, C9) and several low-weight peaks which could be explained by introducing two orientationally disordered molecules (*A* and *B*). Full-matrix least-squares refinement (on F^2) of the positional and isotropic displacement parameters of eight C atoms (C1–C5, C7–C9) common to both orientations *A* and *B* with occupancy factors of 1.0 while the disordered atoms were held fixed with occupancy values of 0.5 reduced the *R* value to 0.24. Further cycles of refinement were carried out in which the occupancy and isotropic displacement parameters of the atoms in the two disordered molecules were refined in alternate cycles, allowing the occupancy to vary while keeping the displacement parameters fixed. The refined occupancy factors of the two orientations (*A* and *B*) were close to 0.6 and 0.4, respectively. All H atoms, except the one on the disordered carboxy group, were placed at geometrically calculated positions and not refined. In the final cycles of least-squares refinement, all the non-H atoms were made anisotropic and the two disordered molecules were refined alternately keeping the occupancy factors of the two molecules *A* and *B* fixed at 0.6 and 0.4, respectively. Though the final *R* value of 0.1052 is apparently large, a consequence of the high degree of disorder prevailing in the structure, the difference map did not reveal any peaks of stereochemical significance at this stage (maximum/minimum peak heights = +0.31/−0.20 e Å^{-3}). This indicated that the gross structural features were correct. In the light of the approximation involved in the refinement of occupancies and the interaction between these and the displacement parameters, the observed values of temperature factors may not be very reliable.



The *ORTEP*II (Johnson, 1976) views (Fig. 1) show that the molecule consists of a tri-substituted cyclohexene system joined to a phenyl ring at the 2-position through an ethyl moiety. Apart from the cyclohexene ring disordered at positions C6*A* and C6*B*, all other non-rigid groups of the molecule are disordered about different directions probably as a result of the vibrational motions. The two molecular orientations *A* and *B* could arise from rotation about an axis perpendicular to the substituent moieties at C4, and libration about the axis joining C3 and the centroid of the terminal phenyl ring.

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Since the crystal structure is highly disordered, a detailed discussion of the geometrical parameters has not been undertaken. The cyclohexene rings in both the orientations adopt half-chair conformations with C6*A* and C6*B* displaced by 0.68 (3) and −0.69 (2) Å, respectively, from the basal planes through the remaining endocyclic atoms.

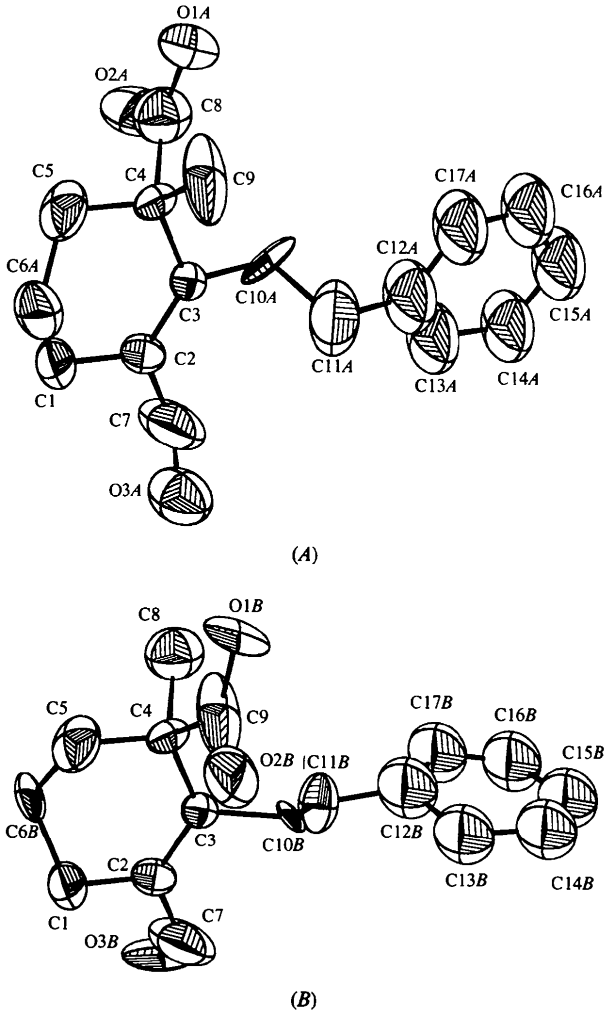

Fig. 1. *ORTEP*II (Johnson, 1976) views (50% probability level) of the two molecular orientations *A* and *B* with the atom-labelling scheme. H atoms are omitted for clarity.

To supplement the crystallographic observation of orientational disorder between two molecular conformations with different occupancy factors, we decided to carry out lattice-energy calculations for *A* and *B* in which the orientations of the molecules were allowed to vary independently with the corresponding change in the potential energy. The calculations were performed using the program *WMIN* (Busing, 1981). The energy was calculated by a pairwise van der Waals attractive and repulsive potential given below:

$$E = \sum_{i}^{\text{one cell}} \sum_{i \neq j}^{\text{all cells}} (-A_iA_j/r_{ij}^6) + \sum_{i}^{\text{one cell}} \sum_{i \neq j}^{\text{all cells}} (D_{ij}/r_{ij}^{12}).$$

The non-bonded interaction parameters used for lattice-energy calculations (A_i and D_i) were taken from Mirsky (1978). Contributions arising from the Coulombic interaction energy were not included. In all calculations, the molecules were treated as rigid bodies and all the symmetry-related molecules were allowed to rotate together so as to preserve the space-group symmetry. The energy E was calculated by rotating

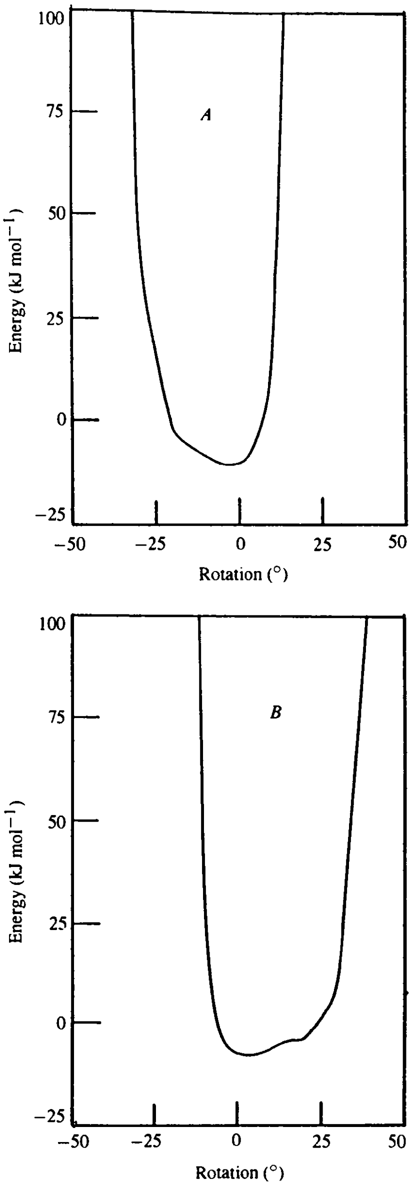

Fig. 2. Graphs showing packing energy (kJ mol^{-1}) *versus* rotation (°) for each of the molecular orientations.

the molecule about the C3···C12*A* axis (in the case of *A*) and C3···C12*B* axis (in the case of *B*) at intervals of 5° over a range of 180°. The energies computed for the X-ray-determined positions of *A* and *B*, −10.3 and −7.8 kJ mol^{-1}, respectively, are in agreement with the corresponding lattice-energy minima of −10.4 and −8.0 kJ mol^{-1}, respectively (Fig. 2). From the relative values of lattice energies for the two molecules, one may conclude that molecule *A* has a higher probability of occurrence in the crystal lattice than that of *B*. This explains the observed difference in occupancy factors between the two molecular orientations, *A* having the higher value of 0.6.

Experimental

A diastereoisomeric mixture of epoxyesters (2), was prepared from the racemic olefinic ester (1) by reaction with *m*-CPBA (Frinjuelli, Germani, Pizzo & Savelli, 1989). (2) was then treated with tri-*n*-butyltin hydride (1.3 mol. equiv.) in the presence of a catalytic amount of azo-isobutyronitrile (AIBN) in boiling benzene containing *tert*-butanol (1 mol. equiv.) for 10 h and followed by usual workup (Pal, Mukhopadhyaya & Ghatak, 1994). This afforded a thick gummy product which on reaction with potassium *tert*-butoxide in dry DMSO gave the title acid, (3). Recrystallization was from an ethyl acetate–petroleum mixture.

Crystal data

$C_{17}H_{20}O_3$
$M_r = 272.32$
Monoclinic
$P2_1/a$
$a = 10.598\,(2)$ Å
$b = 9.184\,(2)$ Å
$c = 16.683\,(3)$ Å
$\beta = 108.39\,(2)°$
$V = 1540.9\,(5)$ Å^3
$Z = 4$
$D_x = 1.17$ Mg m^{-3}
$D_m = 1.16$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 30–50°$
$\mu = 0.64$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
0.8 × 0.6 × 0.3 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: none
1524 measured reflections
1390 independent reflections
787 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.0131$
$\theta_{\rm max} = 70°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 10$
$l = -20 \rightarrow 19$
3 standard reflections monitored every 100 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.1052$
$wR(F^2) = 0.4178$
$S = 1.197$

$(\Delta/\sigma)_{\rm max} = 0.153$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: none

787 reflections
229 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.2634P)^2 + 0.68P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.8359 (12)	0.3884 (11)	0.4328 (6)	0.079 (3)
C2	0.7960 (10)	0.3823 (8)	0.3374 (6)	0.058 (3)
C3	0.7750 (8)	0.2546 (10)	0.2959 (4)	0.048 (2)
C4	0.7965 (9)	0.1118 (9)	0.3407 (6)	0.052 (2)
C5	0.8486 (13)	0.1245 (13)	0.4376 (8)	0.095 (4)
C6*A*†	0.794 (2)	0.257 (2)	0.469 (1)	0.126 (7)
C6*B*	0.923 (2)	0.256 (2)	0.468 (1)	0.085 (7)
C7	0.791 (2)	0.523 (2)	0.294 (1)	0.153 (7)
C8	0.896 (3)	0.018 (3)	0.317 (2)	0.113 (8)
C9	0.678 (2)	0.019 (1)	0.314 (1)	0.160 (8)
C10*A*	0.761 (1)	0.241 (1)	0.201 (1)	0.084 (5)
C10*B*	0.696 (1)	0.254 (1)	0.202 (1)	0.043 (3)
C11*A*	0.622 (2)	0.285 (3)	0.151 (1)	0.152 (10)
C11*B*	0.776 (2)	0.293 (2)	0.143 (1)	0.088 (7)
C12*A*	0.614 (3)	0.273 (2)	0.058 (1)	0.157 (4)
C12*B*	0.700 (3)	0.250 (4)	0.051 (2)	0.151 (5)
C13*A*	0.644 (3)	0.382 (3)	0.010 (1)	0.157 (4)
C13*B*	0.563 (3)	0.277 (4)	0.014 (2)	0.151 (5)
C14*A*	0.608 (3)	0.372 (3)	−0.079 (1)	0.157 (4)
C14*B*	0.490 (4)	0.254 (4)	−0.071 (2)	0.151 (5)
C15*A*	0.562 (3)	0.244 (2)	−0.120 (1)	0.157 (4)
C15*B*	0.567 (3)	0.255 (4)	−0.124 (2)	0.151 (5)
C16*A*	0.563 (3)	0.130 (3)	−0.068 (1)	0.157 (4)
C16*B*	0.703 (3)	0.247 (4)	−0.089 (2)	0.151 (5)
C17*A*	0.579 (3)	0.143 (3)	0.015 (1)	0.157 (4)
C17*B*	0.765 (4)	0.237 (3)	−0.006 (2)	0.151 (5)
O1*A*	0.859 (3)	−0.115 (3)	0.303 (2)	0.099 (8)
O2*A*	1.006 (3)	0.064 (2)	0.322 (2)	0.144 (12)
O3*A*	0.698 (3)	0.595 (2)	0.299 (2)	0.131 (8)
O1*B*	0.688 (1)	−0.117 (1)	0.301 (1)	0.083 (5)
O2*B*	0.579 (3)	0.073 (3)	0.319 (2)	0.147 (10)
O3*B*	0.881 (2)	0.604 (2)	0.296 (2)	0.109 (8)

† Site occupancy of atoms labelled *A* = 0.60, *B* = 0.40.

Table 2. *Selected geometric parameters (Å, °)*

C1—C2	1.51 (2)	C12*A*—C17*A*	1.38 (3)
C2—C3	1.34 (2)	C12*A*—C13*A*	1.38 (3)
C2—C7	1.48 (3)	C13*A*—C14*A*	1.41 (3)
C3—C4	1.49 (2)	C14*A*—C15*A*	1.37 (3)
C4—C5	1.54 (2)	C15*A*—C16*A*	1.36 (3)
C6*A*—C1	1.48 (5)	C16*A*—C17*A*	1.34 (3)
C6*A*—C5	1.51 (5)	C6*B*—C5	1.45 (3)
C8—O2*A*	1.23 (2)	C6*B*—C1	1.53 (3)
C8—O1*A*	1.28 (2)	C10*B*—C11*B*	1.53 (2)
C8—C4	1.50 (3)	C10*B*—C3	1.53 (1)
C7—O3*A*	1.22 (2)	C11*B*—C12*B*	1.54 (2)
C7—O3*B*	1.21 (2)	C12*B*—C17*B*	1.35 (3)
C9—O2*B*	1.19 (2)	C12*B*—C13*B*	1.41 (3)
C9—O1*B*	1.27 (2)	C13*B*—C14*B*	1.40 (3)
C9—C4	1.46 (2)	C14*B*—C15*B*	1.38 (3)
C10*A*—C11*A*	1.50 (2)	C15*B*—C16*B*	1.38 (3)
C10*A*—C3	1.54 (2)	C16*B*—C17*B*	1.35 (3)
C11*A*—C12*A*	1.52 (2)		
C6*A*—C1—C2	112 (2)	O2*B*—C9—C4	115 (2)
C2—C1—C6*B*	108 (1)	O1*B*—C9—C4	121 (2)
C3—C2—C7	122 (2)	C11*A*—C10*A*—C3	108 (2)
C3—C2—C1	121 (1)	C10*A*—C11*A*—C12*A*	107 (3)
C7—C2—C1	116 (2)	C17*A*—C12*A*—C13*A*	113 (4)
C2—C3—C4	122 (1)	C17*A*—C12*A*—C11*A*	121 (4)
C2—C3—C10*B*	119 (1)	C13*A*—C12*A*—C11*A*	126 (4)

C4—C3—C10*B*	117 (1)	C12*A*—C13*A*—C14*A*	122 (4)
C2—C3—C10*A*	123 (2)	C15*A*—C14*A*—C13*A*	121 (4)
C4—C3—C10*A*	113 (1)	C14*A*—C15*A*—C16*A*	114 (4)
C9—C4—C3	112 (1)	C17*A*—C16*A*—C15*A*	125 (4)
C8—C4—C3	113 (2)	C16*A*—C17*A*—C12*A*	123 (4)
C9—C4—C5	110 (1)	C5—C6*B*—C1	109 (2)
C8—C4—C5	106 (2)	C11*B*—C10*B*—C3	115 (1)
C3—C4—C5	114 (1)	C10*B*—C11*B*—C12*B*	111 (2)
C6*B*—C5—C4	114 (1)	C17*B*—C12*B*—C13*B*	113 (3)
C4—C5—C6*A*	112 (2)	C17*B*—C12*B*—C11*B*	120 (3)
C1—C6*A*—C5	109 (3)	C13*B*—C12*B*—C11*B*	123 (3)
O3*A*—C7—C2	110 (2)	C14*B*—C13*B*—C12*B*	126 (4)
O3*B*—C7—C2	128 (2)	C15*B*—C14*B*—C13*B*	113 (4)
O2*A*—C8—O1*A*	125 (3)	C14*B*—C15*B*—C16*B*	119 (4)
O2*A*—C8—C4	121 (3)	C17*B*—C16*B*—C15*B*	123 (4)
O1*A*—C8—C4	114 (3)	C12*B*—C17*B*—C16*B*	122 (4)
O2*B*—C9—O1*B*	122 (2)		

C1—C2—C3—C4	−3 (2)
C3—C4—C5—C6*A*	34 (3)
C4—C5—C6*A*—C1	−61 (3)
C5—C6*A*—C1—C2	55 (3)
C6*A*—C1—C2—C3	−24 (3)
C2—C3—C10*A*—C11*A*	−80 (3)
C3—C10*A*—C11*A*—C12*A*	179 (3)
C2—C3—C4—C5	−2 (2)
C3—C4—C5—C6*B*	−27 (2)
C4—C5—C6*B*—C1	58 (2)
C5—C6*B*—C1—C2	−60 (2)
C6*B*—C1—C2—C3	34 (2)
C2—C3—C10*B*—C11*B*	82 (2)
C4—C3—C10*B*—C11*B*	−112 (2)
C3—C10*B*—C11*B*—C12*B*	165 (2)

All calculations were performed using a VAX3400 computer at the Computer Center, Indian Association for the Cultivation of Science.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(1-Hydroxy-4,4-dimethyl-2-oxobutyl)-4-methoxy-1-naphtholactone

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Abstract

The crystal structure of the tricyclic keto lactone, $C_{18}H_{18}O_4$, has been determined by X-ray diffraction. The eight-membered heterocyclic ring in the molecule displays a distorted boat conformation in contrast to the boat–chair conformation more favoured in various oxygen-containing eight-membered ring systems.

Comment

Medium-sized-ring lactone compounds (having a ring containing 8–11 atoms), which are among the ever-growing number of natural products (Rousseau, 1995), are becoming increasingly important. Several eight-membered-ring lactones having marine-plant origin have been isolated recently and characterized (Proksa, Uhrin, Adamcova & Fuska, 1992; Fang *et al.*, 1993; Brown, 1994). A systematic knowledge of the crystal structures and the effect of substituents on the conformation of the lactone rings is seen to play a vital rôle in the development of efficient methods for the synthesis of compounds possessing this framework. A tricyclic enedione (2) was obtained as the major product (60% yield) during an acid-induced intramolecular cyclization of the diazomethyl ketone (1) leading to the stereocontrolled synthesis of the angularly ester-substituted *trans*-octahydrophenanthrene ring systems related to diterpenes