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Cyclopentadecanone

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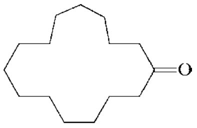
In the crystal structure, the title compound (exaltone), $C_{15}H_{28}O$, exhibits no disorder, and the 15-membered ring exists in the quinquangular [13353] C_1 symmetry conformation. The crystal exhibits nonmerohedral twinning by twofold rotation about [100], but adjustment of the temperature to 90 K causes the [101] distance to equal the c axial length, allowing the twinning to be treated as pseudo-merohedral. The literature description of the structure as disordered orthorhombic with halved a-axis length is corrected.

Comment

The conformations of cyclic ketones have been studied in solution by dynamic NMR spectroscopy (*e.g.* Anet *et al.*, 1973, 1974) and in the solid state by X-ray crystallography (*e.g.* Groth, 1974, 1975, 1976, 1979). Completely ordered crystals were found for cyclodecanone at 113 K (Groth, 1976) and cycloundecanone at 108 K (Groth, 1974); the conformation in each case was based on a stable conformation of the parent hydrocarbon {[2323] (Pawar *et al.*, 1998) or [335] (Pawar *et al.*, 2006)}.



(I)

The ring skeletons for cyclododecanone (Groth, 1979) and cyclotetradecanone (Groth, 1975) matched those of cyclododecane ([3333]; Dunitz & Shearer, 1960) and cyclotetradecane ([3434]; Anet *et al.*, 1972), but the crystals were disordered with respect to placement of the carbonyl groups. Groth (1979) concluded from preliminary studies of cyclotridecanone and cycloheptadecanone that the crystals were disordered, and the structures were not determined. Crystals of cyclopentadecanone [the title compound, (I)] and cyclohexadecanone were reported to be orthorhombic, and cell dimensions were given [incorrectly for compound (I); see below] by Groth (1976). The author concluded that the crystals were disordered, and attempts to solve both structures were unsuccessful.

Attempts to study the conformations of (I) in solution by low-temperature ^{1}H and ^{13}C NMR spectroscopy were inconclusive, and conformational assignments were not made (Cheng, 1973). Cyclopentadecanone phenylsemicarbazone has been reported to have a [3435] conformation in the solid state by X-ray diffraction (van den Hoek *et al.*, 1979), and a [12345] conformation was found for the 2,4-dintrophenylhydrazone of (I) by the same method (Noe *et al.*, 2008). Strain energies have been calculated using *MOLBUILD* (Boyd *et al.*, 1973) for several conformations of cyclopentadecane, and the [33333] conformation was predicted to be the most stable of those considered (Anet & Rawdah, 1978).

The molecular structure of (I) is shown in Fig. 1. The cyclopentadecane ring exists in the quinquangular [13353] conformation with corner positions at C atoms 3, 4, 7, 10 and 15, as described by the torsion angles in Table 1. The atoms of the C_{15} ring are coplanar, with a mean deviation of 0.382 Å and a maximum deviation of 0.603 (2) Å for atom C8. The O atom lies 1.646 (2) Å out of this plane, and the ketone plane (O1/C1/C2/C15) forms a dihedral angle of 66.12 (2)° with it.

While the unit cell has monoclinic symmetry, the lattice has a nearly *C*-centered orthorhombic metric, with the transformation $(\bar{1}00, 102, 010)$ yielding a cell with dimensions a = 15.663 Å, b = 31.719 Å and c = 5.553 Å, and $\alpha = \beta = 90°$ and

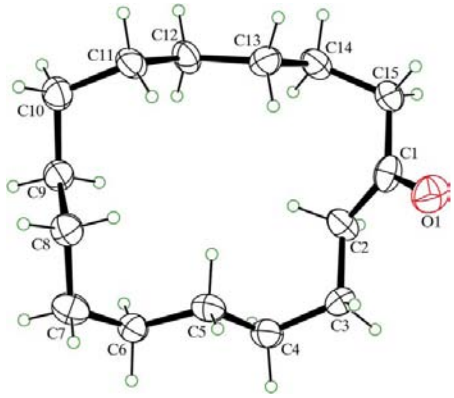


Figure 1
The molecule of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

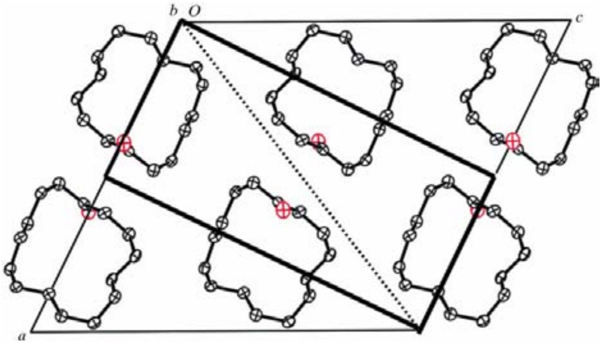


Figure 2
A unit-cell diagram for (I), viewed down the symmetry direction. The bold lines correspond to the cell reported by Groth (1976), and the dotted line, [101], has a length equal to that of the c axis in this twinned structure.

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γ = 90.04°. Groth (1976) reported an orthorhombic cell at 113 K having dimensions 7.814 (4), 15.990 (8) and 5.589 (3) Å, noting that its cell volume (half ours) would yield Z = 2 and require disorder of the molecule. We note that the Groth cell has two of its dimensions near half those of the *C*-centered cell from our data. Examination of the packing in Fig. 2 suggests how the incorrect description of the unit-cell dimensions came about for this soft weakly scattering compound. The centroid of the 15-membered ring is very near $(\frac{3}{4}, \frac{1}{2}, \frac{1}{2})$, and thus its equivalent by inversion through the center of the cell is related to it by an approximate translation of $a/2$, corresponding to the 7.81 Å cell dimension of the Groth cell. The vector from the origin to $(\frac{1}{2}, 0, \frac{1}{2})$ is nearly orthogonal to our a axis, and corresponds to Groth's 15.99 Å cell dimension, half the 31.7 Å axis of the *C*-centered metric. The molecules related by the $a/2$ approximate translation would not overlap exactly, so would necessarily be disordered in the smaller cell, as pointed out by Groth (1976).

We noted splitting of spots in the diffraction pattern at nearer ambient temperatures, hinting that crystals of (I) are twinned. The twinning is a twofold rotation about [100], bringing the [101] and [00$\bar{1}$] vectors into near coincidence. At T = 150 K, these two distances differ by 0.6%, but we found that lowering the temperature to 90 K caused anisotropic shrinkage of the cell, making the [101] distance equal to the c axis and causing the split spots to coalesce (Fronczek & Fox, 2007). Thus, we measured diffraction data at 90 K, and were able to treat the twin as essentially perfectly pseudo-merohedral. Introducing one TWIN and one BASF command into the refinement in *SHELXL97* (Sheldrick, 1997) lowered the R value from 0.296 to 0.059.

Experimental

A commercial sample (Aldrich Chemical Company) of cyclopentadecanone was recrystallized from ethanol [m.p. 336.5 K; literature m.p. 338.5 K (Giral, 1935)]. Purity was determined by a room-temperature ^{13}C NMR spectrum.

Crystal data

$C_{15}H_{28}O$
M_r = 224.37
Monoclinic, $P2_1/c$
a = 15.6634 (16) Å
b = 5.5531 (5) Å
c = 17.6928 (18) Å
β = 116.315 (8)°
V = 1379.4 (3) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.48 mm^{-1}
T = 90 K
0.34 × 0.12 × 0.07 mm

Data collection

Bruker Kappa-APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.853, T_{max} = 0.967
5210 measured reflections
2359 independent reflections
2007 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.164
S = 1.08
2359 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected torsion angles (°).

C15—C1—C2—C3	−177.3 (3)	C8—C9—C10—C11	70.2 (3)
C1—C2—C3—C4	144.6 (3)	C9—C10—C11—C12	70.3 (3)
C2—C3—C4—C5	−72.9 (3)	C10—C11—C12—C13	−154.0 (3)
C3—C4—C5—C6	168.1 (2)	C11—C12—C13—C14	174.2 (3)
C4—C5—C6—C7	172.8 (3)	C12—C13—C14—C15	−157.6 (3)
C5—C6—C7—C8	52.9 (4)	C2—C1—C15—C14	47.6 (4)
C6—C7—C8—C9	59.9 (4)	C13—C14—C15—C1	58.6 (3)
C7—C8—C9—C10	−178.9 (2)		

H atoms were placed in calculated positions, guided by difference maps, with C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and thereafter treated as riding. The structure was refined as a pseudo-merohedral twin with twin law (100, 0$\bar{1}$0, $\bar{1}$0$\bar{1}$). The twinning was perfect, with the BASF parameter refining to 0.500 (2).

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *XSHELL* (Bruker, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3125). Services for accessing these data are described at the back of the journal.

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