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Cyclodecyl 4-nitrophenylacetate

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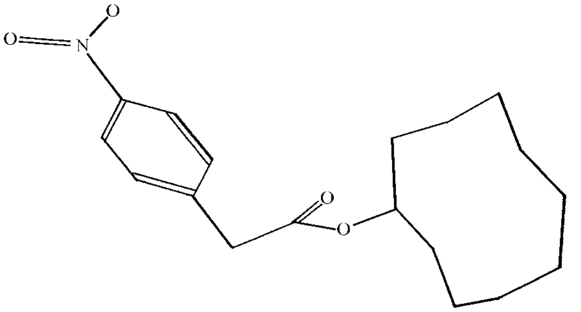
Cyclodecyl 4-nitrophenylacetate, $C_{18}H_{25}NO_4$, has its ten-membered ring in the expected diamond-lattice boat–chair–boat [2323] conformation, with the substituent 4-nitrophenylacetoxy group in the BCB III*e* position. The ester unit has the expected *Z* conformation, with an O=C—O—C torsion angle of −0.3 (3)°, and the connection to the benzene ring is nearly perpendicular to the ester, with an O=C—C—C torsion angle of 85.5 (2)°. An intermolecular contact exists between the ester C atom and a nitro O atom, having a C···O distance of 2.909 (2) Å.

Comment

The conformations of cyclodecane, (2), and its derivatives have been of interest for a long time. The boat–chair–boat conformation (BCB), (2*a*), was found for the solid state by X-ray diffraction near 173 K (Shenhav & Schaeffer, 1981) and by ^{13}C NMR at 145 K (Drotloff, 1987). This conformation has C_{2h} symmetry as in Fig. 1, with the three types of C atoms labeled I, II and III. The mirror plane bisects the type I C atoms, and the axis bisects the bonds connecting the type III C atoms. The axial H atoms on the six C atoms of type I or type III form two planes, above and below the ring, with substantial non-bonded interactions. These intraannular positions are drawn as closed circles, and the open circles represent extra-annular positions, which are relatively strain free and will be occupied by groups larger than hydrogen.

A dynamic NMR study of (2) (Pawar *et al.*, 1998) found the expected three ^{13}C peaks for (2*a*) in solution by 102 K. Additional absorption for the twist-boat–chair–chair conformation (TBCC), (2*b*), about 0.7 kcal mol^{-1} higher in free energy than (2*a*), was also found at higher temperatures by these authors. The possible presence of a small amount of the twist-boat–chair conformation (TBC), (2*c*), could not be verified or disproved by the low-temperature NMR spectra.

Calculations confirm a low energy for BCB and provide estimates of relative energies for other conformations (Hendrickson, 1967; Saunders, 1991; Kolossvary & Guida, 1993; Pawar *et al.*, 1998). *Ab initio* calculations at the MP2/6–311+G* level (Wiberg, 2003) predict that six conformations of (2) will have populations of 10% or greater at 298 K, with TBCC most populated (23%), followed by BCB (21%).



(1)

Interconversion of carbon sites in the BCB conformation is expected to occur by way of TBC. Cheng (1973) has described the itinerary for this process, which equilibrates C atoms 1 and 4, *etc.*, of (2*a*). Kolossvary & Guida (1993) carried out a comprehensive study of conformational equilibration for (2) with Allinger's *MM2* program and concluded that (2*a*) equilibrates only with (2*c*) within a 12 kcal mol^{-1} window. Wiberg (2003) calculated a free-energy barrier of 5.4 kcal mol^{-1} for the BCB to TBC conversion at room temperature, in good agreement with a later experimental determination of this barrier (5.54 kcal mol^{-1} at 136 K; Pawar *et al.*, 2006).

1,1-Difluorocyclodecane was found by ^{19}F NMR to have the F atoms at the II*e* and II*a* positions (Noe & Roberts, 1972). *trans*-1,6-Disubstituted cyclodecanes have four possible BCB conformations that avoid intraannular positions, and examples of three of them have been found by X-ray diffraction, *viz.* a monoclinic modification of *trans*-1,6-diaminocyclodecane dihydrochloride (II*a*, II*a*; Huber-Buser & Dunitz, 1966), *trans*-1,6-cyclodecanediol (II*a*, II*a*; Ermer *et al.*, 1973), a triclinic modification of *trans*-1,6-diaminocyclodecane dihydrochloride (II*e*, II*e*; Huber-Buser & Dunitz, 1960, 1961) and *trans*-1,6-dibromocyclodecane (III*e*, III*e*; Dunitz & Weber, 1964). Disubstitution at the type I*e* positions would also avoid the intraannular positions but has not been observed. This conformation lacks the *R*ln2 contribution to entropy that would favor the enantiomeric pairs of the observed conformations. Similarly, substitution at the I*e* position has not been

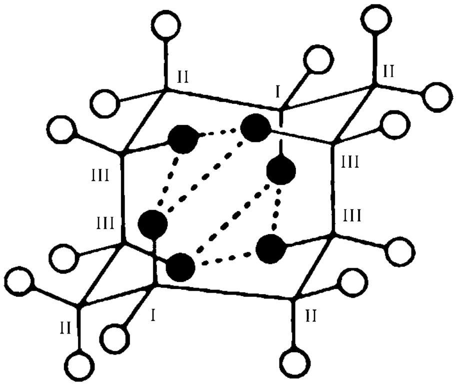


Figure 1
The boat–chair–boat conformation of cyclodecane.

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found for monosubstituted cyclodecanes. X-ray studies of cyclodecanol (Valente *et al.*, 1998) and cyclodecylamine hydrochloride sesquihydrate (Nowacki & Mladeck, 1961; Mladeck & Nowacki, 1964) found the substituents at the II*e* and III*e* positions of the BCB conformation, respectively.

The low-temperature ^{13}C spectrum of the substituted ring carbon of chlorocyclodecane, (3), in solution showed three peaks at δ 67.67, 66.14 and 61.63 [(3*a*), (3*b*) and (3*c*), respectively], with populations of 31.2, 14.9 and 53.9% (Pawar *et al.*, 1998). These peaks were assigned to II*e* BCB, II*a* BCB and a TBCC conformation, respectively, but the assignment for the major conformation, (3*c*), was later changed to III*e* BCB (Pawar *et al.*, 2006). The low-temperature ^{13}C spectra for cyclodecyl acetate, (4), in solution show three peaks for the substituted ring C atoms, with relative positions and intensities similar to those of (3), which suggested that the populated ring conformations are the same for (3) and (4) (Pawar *et al.*, 1998). In the present work, an X-ray diffraction study of cyclodecyl 4-nitrophenylacetate, (1) (Fig. 2), in which a 4-nitrophenyl group replaces a methyl H atom of (4), showed that the conformation in the solid state is III*e* BCB. This result suggests that III*e* BCB is the major conformation for (1) in solution, and by extension also for (3) and (4).

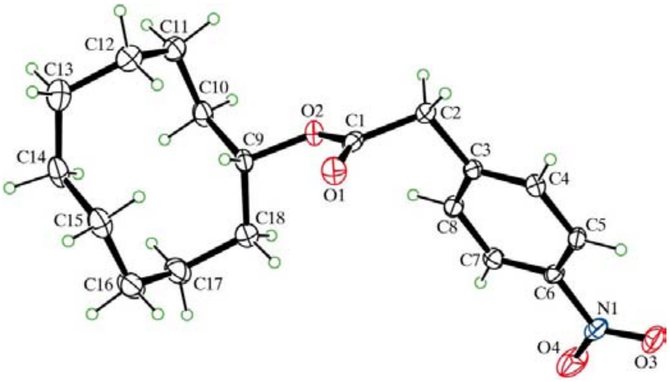

Figure 2
A displacement ellipsoid plot of (1) at the 50% probability level.

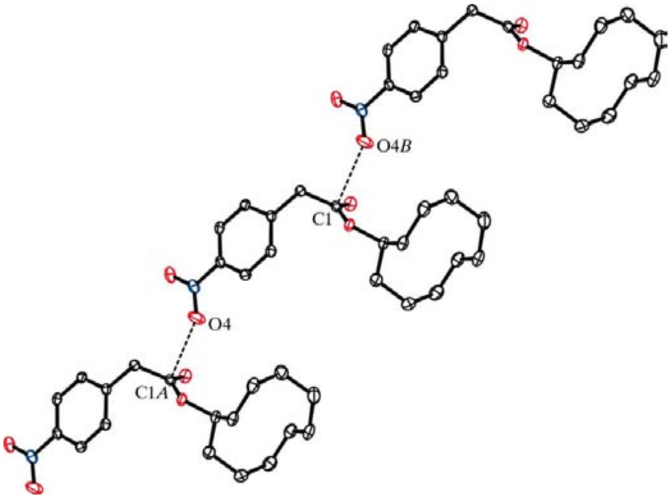

Figure 3
The intermolecular C$\cdots$O contacts in (1). [Symmetry codes: (*A*) $x + 1$, $y + 1$, z; (*B*) $x - 1$, $y - 1$, z.]

The O1=C1—O2—C9 torsion angle in (1) (Table 1) is experimentally indistinguishable from zero, showing that the ester has the expected *Z* conformation. The bond connecting the benzene ring to the CH$_2$ C atom is nearly perpendicular to the ester group [O1=C1—C2—C3 = 85.5 (2)°].

A notable intermolecular interaction exists (Fig. 3) involving the ester C atom and a nitrate O atom. It is quite similar to the perpendicular motif carbonyl–carbonyl interaction described by Allen *et al.* (1998). They found a median C$\cdots$O distance of 3.35 Å in a population from the Cambridge Structural Database (Allen, 2002) having C$\cdots$O < 3.6 Å. In (1), the C1$\cdots$O4($x - 1$, $y - 1$, z) distance is 2.909 (2) Å. For the perpendicular motif, Allen *et al.* (1998) find a mean C=O$\cdots$C angle of 159.7 (7)° and a mean O$\cdots$C=O angle of 97.2 (12)°. The analogous angles in (1) are 132.1 (2) and 97.2 (2)°, respectively. These interactions form chains in the [110] direction, as illustrated in Fig. 3.

Experimental

To a refluxing solution of 2.0 g of cyclodecanol and 1.64 g of dimethylaniline dissolved in 5 ml of ether was added 2.55 g of 4-nitrophenylacetyl chloride. After approximately two-thirds of the acid chloride had been added, dimethylaniline hydrochloride began to precipitate and the mixture refluxed vigorously. An ice bath was applied immediately, and after refluxed ceased, the remainder of the acid chloride was added. The mixture was heated for an hour on a water bath, cooled, and approximately 5 ml of water was added with stirring until all of the solid material dissolved. The ether layer was separated, extracted three times with 10 ml portions of 10% H$_2$SO$_4$, washed with saturated sodium bicarbonate, dried over Drierite, and the ether was evaporated to yield 2.48 g of cyclodecyl 4-nitrophenylacetate. The crude sample of (1) was recrystallized from hexane (m.p. 330 K) and the purity of the sample was established by ^{13}C NMR spectroscopy. Crystals suitable for X-ray analysis were obtained from ethyl acetate by slow evaporation.

Crystal data

$C_{18}H_{25}NO_4$
$M_r = 319.39$
Monoclinic, $P2_1$
$a = 7.5050$ (15) Å
$b = 5.8492$ (10) Å
$c = 19.381$ (4) Å
$\beta = 100.289$ (10)°
$V = 837.1$ (3) Å^3
$Z = 2$
$D_x = 1.267$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 115$ K
Plate, colorless
0.35 × 0.30 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
(with an Oxford Cryosystems Cryostream cooler)
ω scans with κ offsets
10156 measured reflections
2326 independent reflections
2008 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 29.9$°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.087$
$S = 1.04$
2326 reflections
209 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 0.2312P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.043 (5)

Acta Cryst. (2006). C**62**, o628–o630 Brown *et al.* • $C_{18}H_{25}NO_4$ **o629**

Table 1
Selected torsion angles (°).

C9—O2—C1—O1	−0.3 (3)	C12—C13—C14—C15	56.2 (3)
O1—C1—C2—C3	85.5 (2)	C13—C14—C15—C16	−150.6 (2)
C18—C9—C10—C11	155.83 (18)	C14—C15—C16—C17	56.1 (3)
C9—C10—C11—C12	−54.3 (2)	C15—C16—C17—C18	65.1 (3)
C10—C11—C12—C13	−66.1 (3)	C10—C9—C18—C17	−57.1 (3)
C11—C12—C13—C14	64.4 (3)	C16—C17—C18—C9	−65.0 (3)

H atoms were placed in calculated positions, guided by difference maps, with C—H bond distances of 0.95–1.00 Å and U_{iso}(H) values of $1.2U_{eq}$ of the attached C atom, and thereafter treated as riding. The absolute structure could not be established from the X-ray data, and the positive direction of the polar axis is an arbitrary choice. Friedel pairs were averaged.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3048). Services for accessing these data are described at the back of the journal.

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o630 Brown *et al.* • $C_{18}H_{25}NO_4$ *Acta Cryst.* (2006). C**62**, o628–o630