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cis- and *trans*-2-(4-*tert*-Butylcyclohexyloxy)-1,3,5-trinitrobenzene

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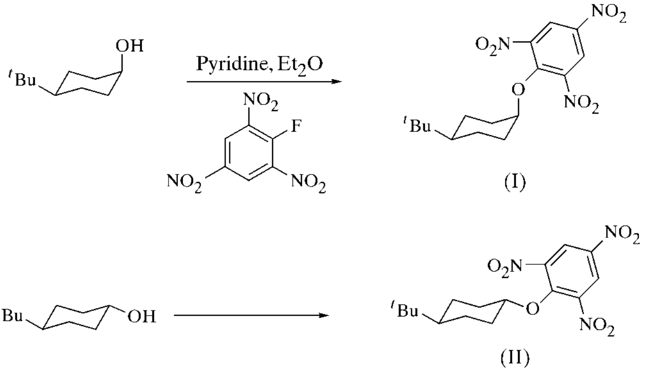
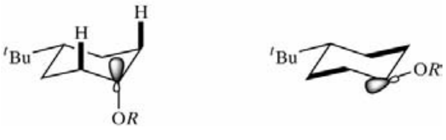
The structures of *cis*- and *trans*-2-(4-*tert*-butylcyclohexyloxy)-1,3,5-trinitrobenzene, $C_{16}H_{21}N_3O_7$, (I) and (II), respectively, were determined at low temperature in order to obtain accurate structural parameters for comparison purposes. The $C_{alkyl}-O_{ether}$ bond distances are 1.497 (2) and 1.491 (2) Å for (I) and (II), respectively.

Comment

This report forms part of our structural studies on cyclohexanes substituted with ester and ether derivatives of varying electron demand (White & Robertson, 1992; White *et al.*, 1996, 2000). Previous work reported by Kirby and co-workers (Kirby & Allen, 1984; Briggs *et al.*, 1984) has shown that Csp^3-O bond distances are sensitive both to the donor ability of bonds which are antiperiplanar to the oxygen substituent, and also to the electron demand of the oxygen substituent itself. The Csp^3-O bond distance was found to be linearly related to the electron demand of the oxygen substituent, and the slope of the plot was sensitive to the donor ability of bonds which were antiperiplanar to the C—O bond and therefore able to donate electron density into the C—O antibonding orbital. This structural method for detecting electronic interactions in the ground state was referred to as the 'variable oxygen probe' (Kirby *et al.*, 1992).



The present low-temperature structural study is part of our efforts to apply the variable oxygen probe to the important question, 'which is the better donor, a C—H or a C—C bond?'. Thus, we have embarked on a series of structural studies on ester and ether derivatives of cyclohexane in which the oxygen substituent is constrained to occupy both axial and equatorial positions. An axial oxygen substituent has two antiperiplanar C—H bonds which can donate electron density into the C—O antibonding orbital (see *Scheme* below), whereas an equatorial oxygen substituent has two ring C—C bonds which can donate electron density into the C—O antibonding orbital. It is hoped that a comparison of the plots obtained for a range of oxygen substituents of varying electron demand will allow the distinction of the donor abilities of C—H and C—C bonds.



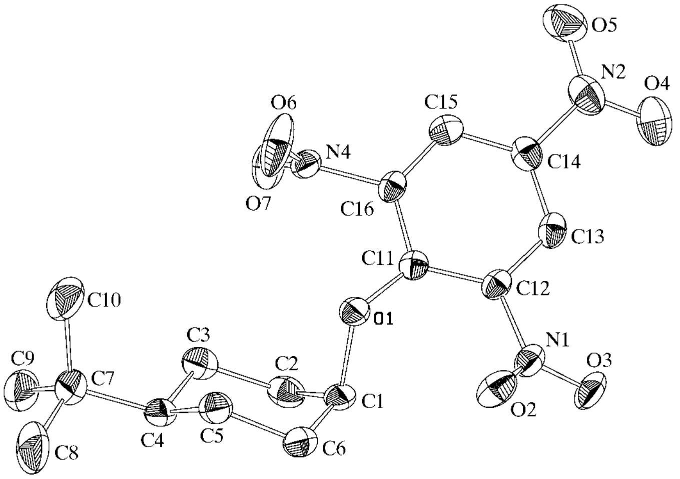


Figure 1
A view of the molecule of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

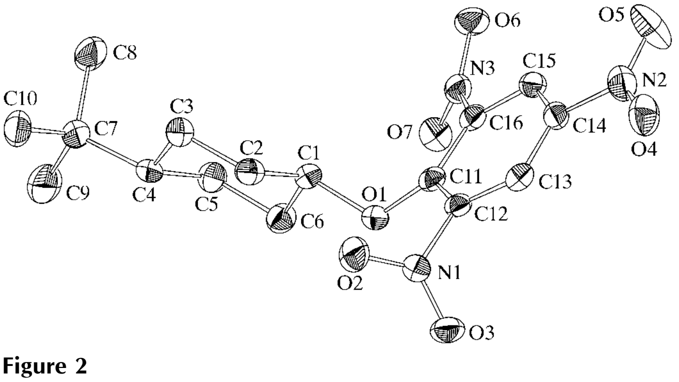


Figure 2
A view of the molecule of (II). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

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The results for the title compounds, (I) and (II), are presented here.

The structures of (I) and (II) were determined at 130 K to minimize the unwanted effects of thermal motion. Selected structural parameters for (I) and (II) are summarized in Tables 1 and 2, respectively.

The picrate moiety (1,3,5-trinitrobenzene) in both structures adopts the same conformation with respect to both the nitro substituents and the O-alkyl substituent. In both structures, the *para*-nitro substituent is essentially coplanar with the aromatic ring, and one of the *ortho*-nitro substituents is twisted slightly from the plane of the aromatic ring (*ca* 30°), while the second *ortho*-nitro substituent is close to orthogonal. The conformation of the *ortho*-nitro substituents presumably represents a compromise between the electron preference of the nitro group to be coplanar with the aromatic ring and the need to minimize steric interactions with the neighbouring oxygen substituent.

The conformation of the O-alkyl substituent, as defined by the dihedral angles C1—O1—C11—C12 and C1—O1—C11—C16, is essentially identical in each structure. While this conformation does not allow effective delocalization of an oxygen lone pair into the electron-deficient aromatic ring, a coplanar conformation would suffer from severe steric interaction between atom C1 and one of the *ortho*-nitro substituents.

An examination of bond angles O1—C1—C2 and O1—C1—C6 suggests that there is no significant strain associated with the axial substituent. This is consistent with the findings of Steiner (Steiner & Saenger, 1998), who examined a number of oxo-substituted cyclohexanes.

The C1—O1 distances in (I) and (II) are 1.497 (2) and 1.491 (2) Å, respectively. Although the axial picrate moiety appears to have a slightly longer C—O bond than the corresponding equatorial picrate, this is barely significant. The C—C bond distances within the cyclohexane rings of both structures follow similar patterns, with the C1—C2 and C1—C6 bonds being shorter than both the C2—C3 and C5—C6 bonds, and the C3—C4 and C4—C5 bonds, reflecting the expected effects of the strongly electron-withdrawing picryl substituent.

There are no significant differences in the C2—C3 and C5—C6 bond distances between the two structures. Thus, there are no observable structural effects of hyperconjugation of the antiperiplanar C—C bonds with the C1—O1 antibonding orbital in (II).

Experimental

Compounds (I) and (II) were prepared by reaction of *cis*- and *trans*-cyclohexanol with 2,4,6-trinitrofluorobenzene in diethyl ether in the presence of one equivalent of pyridine. *cis*-4-*tert*-Butylcyclohexanol in pyridine–diethyl ether was treated with picryl fluoride to afford (I). Brown needles (m.p. 382–385 K) were grown from methanol. *trans*-4-*tert*-Butylcyclohexanol was treated in the same manner to prepare (II); recrystallization from pentane gave dark-brown slabs (m.p. 381–383 K).

Compound (I)

Crystal data

$C_{16}H_{21}N_3O_7$
$M_r = 367.36$
Monoclinic, $P2_1/c$
$a = 15.257$ (3) Å
$b = 8.954$ (2) Å
$c = 13.623$ (2) Å
$\beta = 102.71$ (2)°
$V = 1815.5$ (6) Å^3
$Z = 4$
$D_x = 1.344$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.11$ mm^{-1}
$T = 130.0$ (2) K
Needle, brown
0.6 × 0.1 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
3341 measured reflections
3191 independent reflections
2589 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.071$
$\theta_{\rm max} = 25°$
$h = -18 \rightarrow 17$
$k = -10 \rightarrow 0$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 160 min
intensity decay: 2%

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C11	1.3383 (19)	C2—C3	1.522 (2)
O1—C1	1.4964 (18)	C3—C4	1.532 (2)
O2—N1	1.2259 (18)	C4—C5	1.535 (3)
O3—N1	1.2281 (17)	C4—C7	1.553 (2)
O4—N2	1.217 (2)	C5—C6	1.529 (2)
O5—N2	1.228 (2)	C7—C8	1.526 (3)
O6—N3	1.2052 (19)	C7—C9	1.534 (3)
O7—N3	1.2103 (18)	C7—C10	1.541 (2)
N1—C12	1.467 (2)	C11—C12	1.403 (2)
N2—C14	1.471 (2)	C11—C16	1.404 (2)
N3—C16	1.471 (2)	C12—C13	1.384 (2)
C1—C6	1.507 (2)	C13—C14	1.378 (2)
C1—C2	1.508 (3)		
C11—O1—C1	120.13 (11)	C3—C4—C5	108.62 (14)
O1—C1—C6	105.18 (13)	C3—C4—C7	113.40 (15)
O1—C1—C2	108.65 (13)	C5—C4—C7	114.04 (14)
C1—C2—C3	113.94 (14)	C6—C5—C4	111.29 (14)
C2—C3—C4	112.56 (14)	C1—C6—C5	111.69 (14)
C11—O1—C1—C6	155.11 (14)	O3—N1—C12—C11	151.64 (14)
C11—O1—C1—C2	−83.98 (17)	O4—N2—C14—C13	12.2 (3)
O1—C1—C2—C3	−67.89 (17)	O5—N2—C14—C13	−167.98 (16)
O1—C1—C6—C5	66.86 (17)	O4—N2—C14—C15	−168.67 (17)
C1—O1—C11—C12	−56.7 (2)	O5—N2—C14—C15	11.2 (2)
C1—O1—C11—C16	126.24 (15)	O6—N3—C16—C15	−104.03 (19)
O2—N1—C12—C13	144.63 (15)	O7—N3—C16—C15	75.94 (18)
O3—N1—C12—C13	−32.9 (2)	O6—N3—C16—C11	76.4 (2)
O2—N1—C12—C11	−30.8 (2)	O7—N3—C16—C11	−103.64 (17)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.107$
$S = 1.01$
3191 reflections
232 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.7679P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

O1—C1	1.492 (3)	C3—C4	1.539 (4)
O2—N1	1.218 (3)	C4—C5	1.525 (4)
O3—N1	1.220 (2)	C4—C7	1.565 (3)
O4—N2	1.221 (3)	C5—C6	1.531 (3)
O5—N2	1.226 (3)	C7—C10	1.523 (4)
O6—N3	1.230 (2)	C7—C9	1.530 (4)
O7—N3	1.230 (3)	C7—C8	1.530 (3)
N1—C12	1.476 (3)	C11—C12	1.403 (3)
N2—C14	1.472 (3)	C11—C16	1.403 (3)
N3—C16	1.472 (3)	C12—C13	1.372 (3)
C1—C6	1.503 (3)	C13—C14	1.388 (3)
C1—C2	1.504 (3)	C14—C15	1.377 (3)
C2—C3	1.533 (3)	C15—C16	1.383 (3)
C11—O1—C1	120.24 (17)	C5—C4—C3	109.35 (19)
O1—C1—C6	107.60 (19)	C5—C4—C7	113.8 (2)
O1—C1—C2	109.37 (19)	C3—C4—C7	113.8 (2)
C1—C2—C3	109.4 (2)	C4—C5—C6	112.1 (2)
C2—C3—C4	112.4 (2)	C1—C6—C5	108.8 (2)
O1—C1—C2—C3	−177.80 (18)	O4—N2—C14—C15	−175.5 (2)
O1—C1—C6—C5	179.92 (19)	O5—N2—C14—C15	4.5 (3)
C1—O1—C11—C12	131.1 (2)	O4—N2—C14—C13	3.4 (3)
C1—O1—C11—C16	−53.0 (3)	O5—N2—C14—C13	−176.7 (2)
O2—N1—C12—C13	109.7 (2)	O7—N3—C16—C15	144.3 (2)
O3—N1—C12—C13	−69.2 (3)	O6—N3—C16—C15	−32.6 (3)
O2—N1—C12—C11	−70.7 (3)	O7—N3—C16—C11	−30.5 (3)
O3—N1—C12—C11	110.4 (2)	O6—N3—C16—C11	152.6 (2)

Compound (II)

Crystal data

$C_{16}H_{21}N_3O_7$
$M_r = 367.37$
Monoclinic, $P2_1/c$
$a = 14.950$ (3) Å
$b = 8.3490$ (10) Å
$c = 14.292$ (5) Å
$\beta = 94.22$ (3)°
$V = 1779.1$ (7) Å^3
$Z = 4$
$D_x = 1.375$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.11$ mm^{-1}
$T = 130$ K
Slab, dark brown
0.50 × 0.25 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
3248 measured reflections
3108 independent reflections
2092 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 25°$
$h = -17 \rightarrow 17$
$k = -9 \rightarrow 0$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 160 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.112$
$S = 1.04$
3104 reflections
256 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.7612P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

For both compounds, H atoms were placed in geometrical positions and treated as riding, with C—H = 0.95–1.00 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

For both compounds, data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: *PROCESS_DATA* (Gable *et al.*, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1354). Services for accessing these data are described at the back of the journal.

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