C212	0.4484 (2)	0.6389 (3)	0.1065 (2)	0.0397 (9)
C213	0.4009 (2)	0.6662 (3)	0.0248 (2)	0.0430 (9)
C214	0.3615 (3)	0.7631 (3)	0.0093 (2)	0.0462 (10)
C215	0.3678 (2)	0.8305 (3)	0.0740 (2)	0.0427 (9)
C216	0.3935 (3)	0.5948 (4)	−0.0466 (3)	0.0681 (14)

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

S101—O102	1.443 (3)	S201—O202	1.445 (2)
S101—N1	1.560 (3)	S201—N2	1.559 (3)
S101—C101	1.783 (3)	S201—C201	1.781 (3)
S102—O104	1.432 (3)	S202—O204	1.434 (3)
S102—O103	1.436 (3)	S202—O203	1.438 (3)
S102—N1	1.630 (3)	S202—N2	1.632 (3)
O101—C101	1.383 (4)	O201—C201	1.418 (4)
O101—C102	1.466 (5)	O201—C202	1.461 (4)
C101—C102	1.455 (5)	C201—C202	1.469 (4)
C102—C103	1.485 (5)	C202—C203	1.488 (5)
S101—N1—S102	118.8 (2)	S201—N2—S202	118.5 (2)
C101—O101—C102	61.3 (2)	C201—O201—C202	61.4 (2)
O101—C101—C102	62.1 (2)	O201—C201—C202	60.7 (2)
C101—C102—O101	56.5 (2)	O201—C202—C201	57.9 (2)

C101—S101—N1—S102	177.2 (2)
C110—S102—N1—S101	−99.2 (2)
O102—S101—C101—C102	−11.7 (3)
S101—C101—C102—C103	−155.9 (3)
C101—S101—C104—C105	−109.5 (3)
C201—S201—N2—S202	171.5 (2)
C210—S202—N2—S201	−89.6 (2)
O202—S201—C201—C202	−8.7 (3)
S201—C201—C202—C203	−157.0 (3)
C201—S201—C204—C205	−114.1 (3)

The measured data consisted of a complete unique set together with a partial set of Friedel opposites. In view of the marked decline in intensity at higher Bragg angles (mean $I/\sigma < 0.6$ at $\theta = 22°$) and the significant decay in standard reflections, data collection was restricted to $\theta_{\max} = 24°$.

H atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom.

Checks on cell symmetry show that the two independent molecules are related by an approximate non-crystallographic inversion centre.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1221). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-4-*tert*-Butylcyclohexyl 2,4-Dinitrobenzenesulfenate

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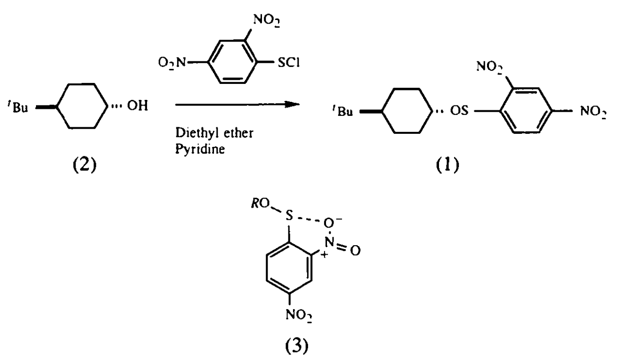
Abstract

The low-temperature structure of *trans*-4-*tert*-butylcyclohexyl 2,4-dinitrobenzenesulfenate, $C_{16}H_{22}N_2O_5S$, is reported. The C—O bond distance is 1.473 (2) Å. A close contact exists between a 2-nitro O atom and the sulfenate S atom which is evidence for a significant interaction between these two; the pattern of bond distances in the aromatic ring and the nitro groups is consistent with this.

Comment

As part of our structural studies on the factors influencing C—O bond distances (White, 1995; White & Robertson, 1992), we required accurate C—O bond distances for an equatorial cyclohexyl 2,4-dinitrobenzenesulfenate ester for comparison purposes. The C—O bond distance is a useful probe for detecting the presence of electronic interactions in organic compounds (Amos, Handy, Jones & Kirby, 1992; White, 1995; White & Robertson, 1992). We chose *trans*-4-*tert*-butylcyclohexyl 2,4-dinitrobenzenesulfenate, (1), for this study.

Compound (1) was prepared by esterification of *trans*-4-*tert*-butylcyclohexanol, (2), with 2,4-nitrobenzenesulfenyl chloride in diethyl ether in the presence of one equivalent of pyridine.



The conformation of the cyclohexane ring is a chair with the sulfenate ester occupying an equatorial position. The geometry about the S—O1 bond as represented by the C1—O1—S—C11 torsion angle is −91.97°. This conformation minimizes lone-pair repulsion between the *p*-type lone pairs on the S and O atoms of the sulfenate group (Wolfe, 1972). The S—O bond is essentially coplanar with the aromatic ring, allowing for maximum delocalization of the S-atom lone pair into the electron-deficient aromatic ring. Both the 2- and 4-nitro groups are coplanar with the aromatic ring; interestingly, this results in one of the 2-nitro O atoms, O2, coming into very close contact with the S atom. The non-bonded distance O2···S is 2.519 (2) Å, which is well inside the sum of the van der Waals radii of S and O (1.52 for O plus 1.8 Å for S; Bondi 1964), suggesting a significant interaction between the nitro O atom and the S atom, as represented by (3) in the scheme above. Consistent with this is the observation that the N1—O2 bond distance is significantly longer than the N1—O3 bond distance. Furthermore, the C12—N1 distance is significantly shorter than the C14—N2 distance implying a greater degree of delocalization of the S-atom lone pair onto the 2-nitro O atoms than the 4-nitro O atoms. The variation in the C—C bond lengths of the aromatic ring is consistent with significant delocalization of S-atom lone pair into the aromatic ring. The O2···S—O1 angle is close to 180°; this favourable for interaction between the 2-nitro O-atom and the S-atom *d* and *p* orbitals or, alternatively, interaction with the low-lying σ^* (S—O) orbital (Kucsman, Kapovits, Parkanyi, Argay & Kálmán, 1984).

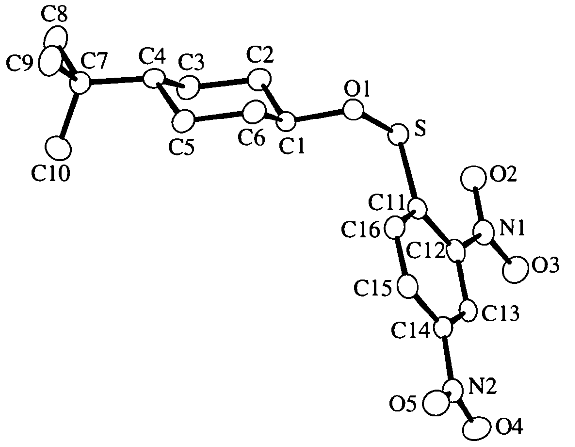


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of (1). Displacement ellipsoids are shown in projection at the 50% probability level. H atoms are omitted for clarity.

Experimental

(1) was prepared by esterification of commercially available *trans*-4-*tert*-butylcyclohexanol, (2), with 2,4-nitrobenzenesulfenyl chloride in diethyl ether in the presence of one equivalent of pyridine. Yellow needles of (1) (m.p. 420 K) were grown from methanol.

Crystal data

$C_{16}H_{22}N_2O_5S$
$M_r = 354.43$
Orthorhombic
Pbca
$a = 13.841$ (2) Å
$b = 9.308$ (3) Å
$c = 26.308$ (6) Å
$V = 3389.3$ (14) Å^3
$Z = 8$
$D_x = 1.389$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ (Ni-filtered) radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 20$–30°
$\mu = 1.956$ mm^{-1}
$T = 200.0$ (1) K
Needle
0.38 × 0.10 × 0.07 mm
Yellow

Data collection

Enraf–Nonius CAD-4*S* diffractometer
ω–2θ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
$T_{\min} = 0.68$, $T_{\max} = 0.90$
3480 measured reflections
3480 independent reflections

2738 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max} = 74.86°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 11$
$l = -32 \rightarrow 0$
3 standard reflections
frequency: 160 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0384$
$wR(F^2) = 0.1001$
$S = 1.028$
3480 reflections
306 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 1.3682P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.334$ e Å^{-3}
$\Delta\rho_{\min} = -0.269$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00081 (9)
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*	$U_{\rm eq}$
S	0.67112 (3)	0.22421 (5)	0.46062 (2)	0.02286 (13)
C1	0.78243 (13)	0.2040 (2)	0.38024 (7)	0.0203 (4)
C2	0.70351 (14)	0.1938 (2)	0.34053 (7)	0.0238 (4)

C3	0.73782 (14)	0.2546 (2)	0.28956 (7)	0.0238 (4)
C4	0.83045 (13)	0.1817 (2)	0.27071 (7)	0.0200 (4)
C5	0.90765 (14)	0.1930 (2)	0.31245 (7)	0.0244 (4)
C6	0.87353 (14)	0.1292 (2)	0.36293 (7)	0.0245 (4)
C7	0.86496 (14)	0.2350 (2)	0.21762 (7)	0.0234 (4)
C8	0.7824 (2)	0.2277 (3)	0.17926 (8)	0.0340 (5)
C9	0.9457 (2)	0.1367 (3)	0.19795 (9)	0.0348 (5)
C10	0.9039 (2)	0.3884 (3)	0.21931 (9)	0.0395 (6)
C11	0.74761 (14)	0.3220 (2)	0.50090 (7)	0.0202 (4)
C12	0.71377 (12)	0.4206 (2)	0.53706 (7)	0.0202 (4)
C13	0.77436 (13)	0.5026 (2)	0.56700 (7)	0.0210 (4)
C14	0.87233 (13)	0.4826 (2)	0.56178 (7)	0.0208 (4)
C15	0.90991 (13)	0.3807 (2)	0.52855 (7)	0.0218 (4)
C16	0.84851 (13)	0.3024 (2)	0.49838 (7)	0.0218 (4)
O1	0.75136 (10)	0.13367 (14)	0.42765 (5)	0.0236 (3)
O2	0.55753 (10)	0.3613 (2)	0.51759 (5)	0.0302 (3)
O3	0.58036 (10)	0.5268 (2)	0.57456 (6)	0.0326 (4)
O4	0.90401 (11)	0.6749 (2)	0.61467 (6)	0.0337 (4)
O5	1.02474 (10)	0.5430 (2)	0.59027 (5)	0.0314 (3)
N1	0.61039 (11)	0.4390 (2)	0.54384 (6)	0.0239 (3)
N2	0.93842 (11)	0.5732 (2)	0.59103 (6)	0.0244 (3)

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

S—O1	1.6419 (14)	C11—C12	1.402 (3)
S—C11	1.753 (2)	C11—C16	1.410 (3)
C1—O1	1.473 (2)	C12—C13	1.381 (3)
C1—C6	1.511 (3)	C12—N1	1.452 (2)
C1—C2	1.514 (3)	C13—C14	1.376 (3)
C2—C3	1.531 (3)	C14—C15	1.390 (3)
C3—C4	1.533 (3)	C14—N2	1.463 (2)
C4—C5	1.536 (3)	C15—C16	1.373 (3)
C4—C7	1.557 (3)	O2—N1	1.239 (2)
C5—C6	1.529 (3)	O3—N1	1.222 (2)
C7—C8	1.526 (3)	O4—N2	1.229 (2)
C7—C10	1.527 (3)	O5—N2	1.228 (2)
C7—C9	1.534 (3)	O2· · ·S	2.519 (2)
O1—S—C11	100.22 (8)	C12—C11—S	123.25 (15)
O1—C1—C6	107.11 (15)	C16—C11—S	120.16 (15)
O1—C1—C2	110.22 (15)	C13—C12—C11	123.1 (2)
C6—C1—C2	111.4 (2)	C13—C12—N1	117.6 (2)
C1—C2—C3	110.9 (2)	C11—C12—N1	119.3 (2)
C2—C3—C4	112.3 (2)	C14—C13—C12	117.8 (2)
C3—C4—C5	108.7 (2)	C13—C14—C15	121.6 (2)
C3—C4—C7	113.9 (2)	C13—C14—N2	119.1 (2)
C5—C4—C7	114.0 (2)	C15—C14—N2	119.3 (2)
C6—C5—C4	112.3 (2)	C16—C15—C14	119.6 (2)
C1—C6—C5	109.9 (2)	C15—C16—C11	121.1 (2)
C8—C7—C10	109.0 (2)	C1—O1—S	114.63 (12)
C8—C7—C9	107.2 (2)	O3—N1—O2	123.9 (2)
C10—C7—C9	108.1 (2)	O3—N1—C12	119.7 (2)
C8—C7—C4	110.4 (2)	O2—N1—C12	116.4 (2)
C10—C7—C4	112.3 (2)	O5—N2—O4	124.2 (2)
C9—C7—C4	109.6 (2)	O5—N2—C14	117.9 (2)
C12—C11—C16	116.6 (2)	O4—N2—C14	117.9 (2)
O1—C1—C2—C3	−175.0 (2)	C16—C11—C12—C13	4.0 (3)
O1—C1—C6—C5	177.65 (15)	C6—C1—O1—S	164.64 (12)
O1—S—C11—C12	178.90 (15)	C2—C1—O1—S	−74.0 (2)
O1—S—C11—C16	−1.9 (2)	C11—S—O1—C1	−91.97 (13)

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). Refinement was performed with *SHELXL*93 (Sheldrick, 1993) using anisotropic displacement parameters for all non-H atoms and isotropic for the H atoms. Molecular graphics were prepared using *ORTEP*II (Johnson, 1976) and the material for publication using *SHELXL*93. All calculations were carried out on a VAXStation 4000VLC computer system.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-[1,2-Dicarba-*closo*-dodecacarboranyl-(methyleneoxy)]benzonitrile

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Abstract

The title compound, $C_{10}H_{17}B_{10}NO$, contains a *closo* carbonane cage linked *via* a methyleneoxy tether to a substituted benzene ring. The carborane cage is essentially a regular dodecahedron with slight distortions owing to the presence of C—C and C—B bonds. The mean B—B bond distance is 1.77 (1) Å, the mean C—B bond distance is 1.71 (1) Å and the cage C—C distance is 1.648 (2) Å.

Comment

The title compound, (1), is a synthetic precursor to the *o*-(1,2-dicarba-*closo*-dodecacarboran-1-yl) substituted bibenzimidazole, (2). Compound (2) is related to the DNA minor-groove binding agent Hoechst 33258, (3) (Loewe & Urbanietz, 1974; Pjura, Grzeskowiak & Dickerson, 1987; Teng, Usman, Frederick & Wang, 1988) and was seen to be a potentially useful drug for use in boron neutron-capture therapy (Kelly *et al.*, 1994; Hawthorne 1993).