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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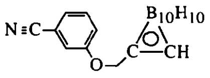
Abstract

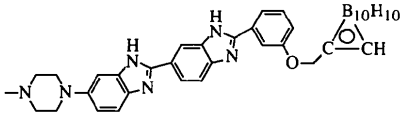
The title compound, $C_{10}H_{17}B_{10}NO$, contains a *closo* carbonane cage linked *via* a methyleneoxy tether to a substituted benzene ring. The carborane cage is essentially a regular dodecahedron with slight distortions owing to the presence of C—C and C—B bonds. The mean B—B bond distance is 1.77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

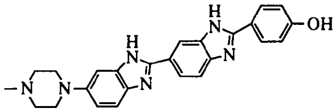
The title compound, (1), is a synthetic precursor to the *o*-(1,2-dicarba-*closo*-dodecacarboran-1-yl) substituted bibenzimidazole, (2). Compound (2) is related to the DNA minor-groove binding agent Hoechst 33258, (3) (Loewe & Urbanietz, 1974; Pjura, Grzeskowiak & Dickerson, 1987; Teng, Usman, Frederick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



(1)

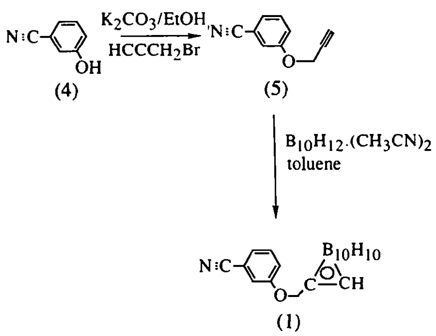


(2)



(3)

The carborane (1) was prepared in two steps from 3-cyanophenol (4) according to the reaction scheme below; treatment of the alkyne (5) with decaborane acetonitrile complex in refluxing toluene by an established procedure (Heying *et al.*, 1963) gave the carboranyl-substituted nitrile (1) in 52% yield.



The structure of the carborane cage is best described as a slightly distorted dodecahedron, the distortions being the result of the presence of the two C atoms in the cage. The mean B—B bond distance is 1.77 (1) Å, the mean C—B distance is 1.71 (1) Å and the cage C—C bond distance is 1.648 (2) Å; these values compare with other similar 1,2-carboranes (Shaw & Welch, 1992; Subrtova, Petricek & Maly, 1991; Scobie, Mahon & Threadgill, 1994). Surprisingly, atom C10 of the carborane cage showed no evidence for disorder with the B4, B3, B2 and B1 boron sites of the carborane cage (by rotation about the C8—C9 bond), attempts to refine the structure with C10 at either of these sites resulted in significantly higher *R* factors (0.5%). Furthermore, distribution of C10 over all five sites with an occupancy of 0.2 and the B atoms with occupancy of 0.8 also gave a significantly higher *R* factor.

The geometry of the linkage of the cage to the methyleneoxy tether is described by the selected torsion angles listed in Table 2. The C8—O1 bond bisects the carboranyl C10—B1 bond and the geometry about the C8—O1 bond is *trans*. The C8—O1 bond is close to coplanar with the substituted benzene ring; this geometry allows delocalization of the O-atom lone pair into the electron-deficient aromatic ring.

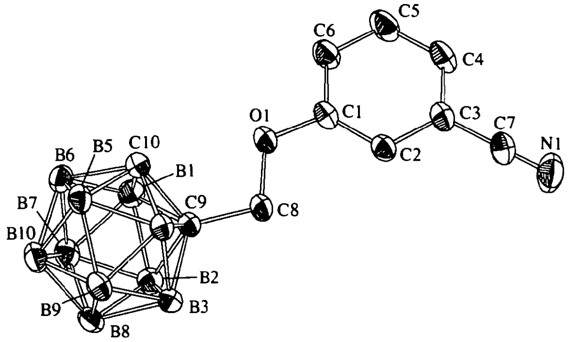


Fig. 1. *ZORTEP* (Zsolnai, 1994) diagram of (1). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Crystals of (1) were grown from dichloromethane/hexane.

Crystal data

$C_{10}H_{17}B_{10}NO$
$M_r = 275.35$
Triclinic
$P\bar{1}$
$a = 6.8995\,(4)$ Å
$b = 11.3444\,(6)$ Å
$c = 11.5370\,(10)$ Å
$\alpha = 114.436\,(7)°$
$\beta = 92.049\,(6)°$
$\gamma = 104.428\,(5)°$
$V = 786.26\,(9)$ Å^3
$Z = 2$
$D_x = 1.163$ Mg m^{-3}
D_m not measured

Cu *Kα* (Ni-filtered) radiation
$\lambda = 1.54180$ Å
Cell parameters from 25 reflections
$\theta = 25$–$30°$
$\mu = 0.458$ mm^{-1}
$T = 571\,(2)$ K
Block
0.4 × 0.35 × 0.3 mm
Colourless

Data collection

Enraf–Nonius CAD-4-MachS diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3389 measured reflections
3113 independent reflections
2790 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0102$
$\theta_{\rm max} = 74.84°$
$h = 0 \rightarrow 8$
$k = -14 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 9600s min
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0446$
$wR(F^2) = 0.1650$
$S = 0.809$
3112 reflections
268 parameters
H atoms refined isotropically without constraint
$w = 1/[\sigma^2(F_o^2) + (0.1265P)^2 + 0.1725P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.082$

$\Delta\rho_{\rm max} = 0.210$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.177$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0050 (27)
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)*

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

	x	y	z	U_{eq}
O1	0.14279 (15)	0.29429 (9)	0.05084 (9)	0.0573 (3)
N1	−0.5442 (3)	−0.2015 (2)	−0.1738 (2)	0.0944 (6)
C1	0.0587 (2)	0.16772 (12)	−0.04813 (12)	0.0469 (3)
C2	−0.1322 (2)	0.08593 (13)	−0.05789 (12)	0.0471 (3)
C3	−0.1982 (2)	−0.04148 (13)	−0.16375 (13)	0.0509 (3)
C4	−0.0785 (3)	−0.08442 (15)	−0.25690 (15)	0.0648 (4)
C5	0.1131 (3)	−0.0010 (2)	−0.2429 (2)	0.0730 (5)
C6	0.1821 (3)	0.12440 (15)	−0.13873 (15)	0.0614 (4)
C7	−0.3928 (3)	−0.1303 (2)	−0.17104 (15)	0.0642 (4)
C8	0.0133 (2)	0.35420 (13)	0.13228 (13)	0.0495 (3)
C9	0.1358 (2)	0.49633 (11)	0.22773 (11)	0.0400 (3)
C10	0.3776 (2)	0.52616 (13)	0.27737 (13)	0.0484 (3)
B1	0.3117 (2)	0.5938 (2)	0.17760 (15)	0.0501 (4)
B2	0.0886 (2)	0.63598 (15)	0.22530 (14)	0.0477 (3)
B3	0.0228 (2)	0.58566 (14)	0.34845 (13)	0.0449 (3)
B4	0.2085 (2)	0.51669 (14)	0.37983 (13)	0.0436 (3)
B5	0.4435 (2)	0.64000 (15)	0.4363 (2)	0.0507 (4)
B6	0.5086 (2)	0.6884 (2)	0.3119 (2)	0.0531 (4)
B7	0.3257 (3)	0.7622 (2)	0.2827 (2)	0.0532 (4)
B8	0.1452 (3)	0.75783 (15)	0.3885 (2)	0.0523 (4)
B9	0.2186 (3)	0.6816 (2)	0.48370 (14)	0.0510 (4)
B10	0.4055 (3)	0.79075 (15)	0.4431 (2)	0.0538 (4)

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

O1—C1	1.3723 (15)	B1—B6	1.774 (2)
O1—C8	1.406 (2)	B1—H1B	1.08 (2)
N1—C7	1.140 (2)	B2—B8	1.770 (2)
C1—C2	1.379 (2)	B2—B7	1.771 (2)
C1—C6	1.381 (2)	B2—B3	1.772 (2)
C2—C3	1.400 (2)	B2—H2B	1.06 (2)
C3—C4	1.380 (2)	B3—B4	1.756 (2)
C3—C7	1.440 (2)	B3—B8	1.773 (2)
C4—C5	1.380 (3)	B3—B9	1.776 (2)
C5—C6	1.379 (2)	B4—B9	1.736 (2)
C8—C9	1.521 (2)	B4—B5	1.747 (2)
C9—C10	1.648 (2)	B5—B10	1.765 (2)
C9—B3	1.697 (2)	B5—B6	1.771 (2)
C9—B2	1.706 (2)	B5—B9	1.772 (2)
C9—B4	1.711 (2)	B6—B7	1.771 (2)
C9—B1	1.714 (2)	B6—B10	1.783 (3)
C10—B6	1.703 (2)	B7—B8	1.781 (2)
C10—B4	1.707 (2)	B7—B10	1.781 (2)
C10—B5	1.711 (2)	B8—B10	1.775 (2)
C10—B1	1.728 (2)	B8—B9	1.782 (2)
B1—B2	1.763 (2)	B9—B10	1.773 (2)
B1—B7	1.764 (2)		
C8—C9—C10	119.29 (10)	C8—C9—B4	115.74 (10)
C8—C9—B3	117.88 (10)	C8—C9—B1	119.98 (10)
C8—C9—B2	121.52 (10)		
C8—O1—C1—C2	−13.1 (2)	O1—C8—C9—C10	−33.1 (2)
C8—O1—C1—C6	168.38 (13)	O1—C8—C9—B1	39.4 (2)
C1—O1—C8—C9	−176.12 (11)		

All calcutions were carried out on a VAXstation 4000VLC computer system.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). 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: KH1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Studies on Condensed Heterocyclic Compounds.† XIII. 6-(4-Methylphenyl)-3-(1-naphthylmethylene)-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole

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Abstract

6-(4-Methylphenyl)-3-(1-naphthylmethylene)-*s*-triazolo[3,4-*b*][1,3,4]thiadiazole, $C_{21}H_{16}N_4S$, was prepared by cyclization of 3-(1-naphthylmethylene)-4-amino-5-mercapto-1,2,4-triazole with *p*-methyl benzoic acid in the presence of phosphorus oxychloride. The structure of the compound was determined by elemental analysis, IR and ^{1}H NMR spectroscopy,and X-ray diffraction. The phenyl group and the heteronucleus are almost coplanar. The dihedral angle between the naphthyl group and the heteronucleus is 83.54 (6)°.

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