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2,4,6,8,10,12-Hexabenzyl-5-(nitromethylene)-2,4,6,8,10,12-hexaazatricyclo[7.3.0.0^{3,7}]dodecane

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Key indicators

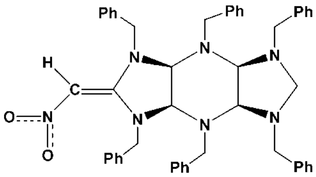
Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.003 Å
R factor = 0.059
wR factor = 0.116
Data-to-parameter ratio = 15.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

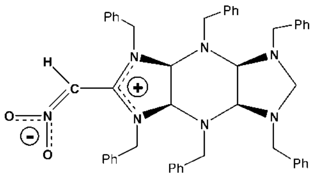
The title compound, $C_{49}H_{49}N_7O_2$, is a crowded tricyclic heterocycle substituted with six benzyl groups. It is related to the hexaazaisowurtzitane family of high-density, high-energy polycyclic cage compounds. The central six-membered ring adopts a boat conformation which minimizes the steric repulsion of the six benzyl substituents. The nitromethylene substituent on the methylene C atom of one of the five-membered rings has a considerable influence on the metric parameters of that ring. From the bond distances in the nitro group and the five-membered ring it appears that the molecule is zwitterionic, rather than neutral, in the vicinity of the nitro group.

Comment

The title compound, (I), is a benzyl substituted 'open' tricyclic hexaazadodecane. By open, it is meant that the fused ring system can be drawn as a flat system, as opposed to a 'caged' ring system, such as an adamantane or cubane. It is related to the hexaazaisowurtzitane family of high-density high-energy compounds (Batsanov *et al.*, 1994; Crampton *et al.*, 1993; Nielsen *et al.*, 1990, 1998; Qiu *et al.*, 1998), which are caged tetracyclohexaazadodecane compounds. The present compound lacks one C—C bond that closes the cage and thus is open. Despite this significant difference, there are similarities; the central six-membered rings of the title molecule and of the hexaazaisowurtzitanes all adopt a boat conformation. As a result, both types of molecule have a cup-like cavity, and both 'open' and 'caged' systems are far from flat.



(I)



(II)

The nitromethylene substituent on the methylene C atom of one of the five-membered rings has a considerable influence on the metric parameters in its vicinity. From the metric parameters of the nitro group and the five-membered ring, it appears that zwitterionic form (II) may contribute as much as, or more then, neutral form (I) to a description of the electronic ground state of the molecule. This can be seen from a comparison of the metric parameters and conformations of the two five-membered rings. From an examination of the local geometry, it appears as though some electronic charge may be

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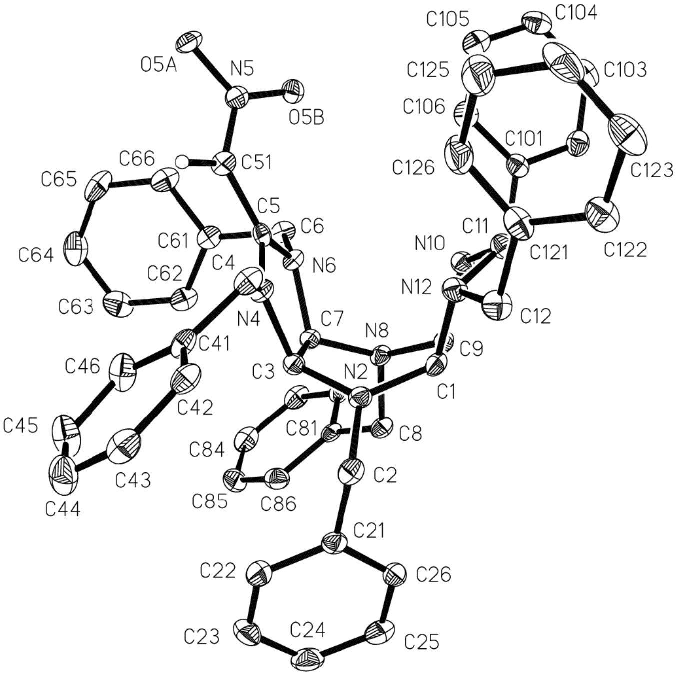

Figure 1
View of the title compound. Displacement ellipsoids are drawn at the 50% probability level; all H atoms except that of the nitromethylene group have been omitted for clarity.

donated by atoms N4 and N6 to increase the bond order of the C—N bonds N4—C5 [1.353 (2) Å] and C5—N6 [1.344 (2) Å], which are shorter than typically found for a C—N single bond [1.469 (10) Å; Allen *et al.*, 1991]. As shown in form (II), the exocyclic bond, C5—C51, which is an olefin bond in form (I), is lengthened [to a distance of 1.420 (3) Å] by withdrawal of charge by the strongly electron-withdrawing nitro group. Also, the C—NO_2 bond length is 1.359 (2) Å, which is shorter than typically found; *e.g.* a search of the Cambridge Structural Database (Allen *et al.*, 1991) gave 2106 observations of nitro groups on benzene rings with no *ortho* substituents and with $R < 0.05$, and the mean C—NO_2 bond length was 1.467 (2) Å. The N5—O5*A* and N5—O5*B* distances are longer than typically found, at 1.274 (2) and 1.258 (2) Å, while the O5A—N5—O5*B* bond angle is 120.18 (15)°, which is much smaller than typically found [compare with values of 1.219 (1) Å and 123.8 (1)° from the aforementioned database search]. The five-membered ring, comprised of atoms C3, N4, C5, N6, and C7, is planar (mean deviation from a least-squares plane is 0.02 Å), while the other five-membered ring is non-planar, as is expected for a fully saturated five-membered ring. These changes are all consistent with the bonding seen in the charged form, (II).

Experimental

Crystals of the title compound were supplied by Dr Michael Chaykovsky, Naval Surface Warfare Center – White Oak, Silver Spring, MD. Crystal and reflection data were obtained using standard procedures (Butcher *et al.*, 1995).

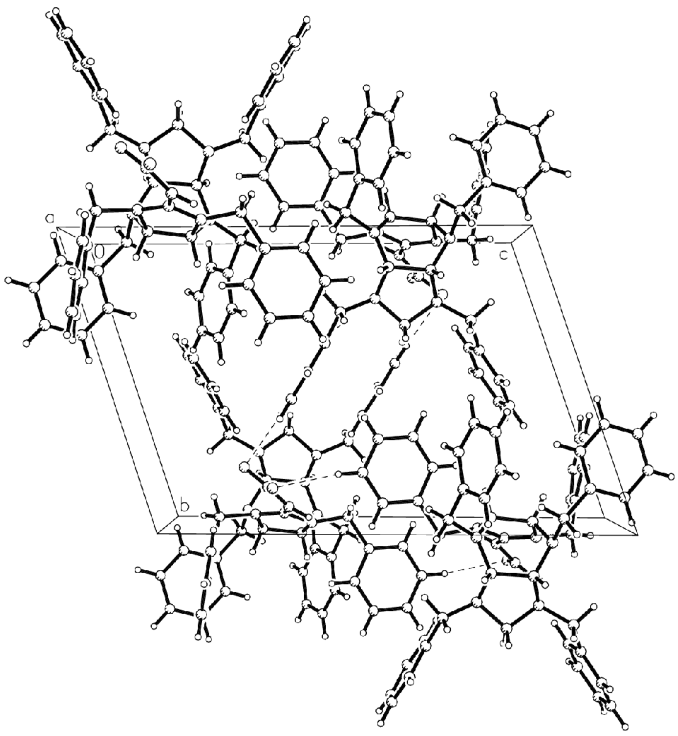

Figure 2
Packing diagram of the title compound. Dashed lines mark weak (2.44 < CH···O < 2.56 Å) hydrogen bonds to nitro-O atoms.

Crystal data

$C_{49}H_{49}N_7O_2$
$M_r = 767.95$
Triclinic, $P\bar{1}$
$a = 10.4199$ (15) Å
$b = 11.7594$ (17) Å
$c = 17.288$ (3) Å
$\alpha = 71.449$ (2)°
$\beta = 86.811$ (3)°
$\gamma = 86.953$ (3)°
$V = 2003.7$ (5) Å^3
$Z = 2$
$D_x = 1.273$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7939 reflections
$\theta = 2.3$–28.3°
$\mu = 0.08$ mm^{-1}
$T = 93$ (2) K
Slab, colorless
0.52 × 0.26 × 0.10 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: by integration (Wuensch & Prewitt, 1965)
$T_{\min} = 0.976$, $T_{\max} = 0.992$
13583 measured reflections
8141 independent reflections
5974 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 26.4$°
$h = -13 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.116$
$S = 1.06$
8141 reflections
524 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.7713P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0031 (7)

Table 1
Selected geometric parameters (Å, °).

N4—C5	1.353 (2)	C51—N5	1.359 (2)
C5—N6	1.344 (2)	N5—O5*B*	1.258 (2)
C5—C51	1.420 (3)	N5—O5*A*	1.2738 (19)
O5*B*—N5—O5*A*	120.18 (15)		

H atoms were found in difference maps; all H atoms were constrained in the refinement to ideal positions, with phenyl C—H distances of 0.95 Å and angles as close to 120° as possible, and with sp^3 C—H distances of 0.99 or 1.00 Å, and angles as close to 109.5° as possible. Each was assigned a $U_{\rm iso}$ equal to $1.2U_{\rm eq}$ of the neighboring C atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS* (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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