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A Naphthalene-Fused Tricyclic Orthoamide

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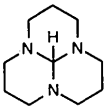
Abstract

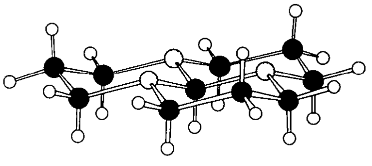
The crystal structure of 3a,6a,12b-triaza-1,2,3,3a,4,5,6,-6a,12b,12c-decahydroperylene, $C_{17}H_{19}N_3$, (6), shows that the naphthalene unit adopts an orientation orthogonal to the average plane of the triaza-*trans*-decalin moiety. This forces two aromatic N-atom lone pairs to orient equatorially and thus allows only partial overlap with the naphthalene π system.

Comment

We have been examining the effect of fusing aromatic rings onto hexahydro-3a,6a,9a-triazaphenalene, (1). The tricycle (1) displays the remarkable ability of extruding the central H atom as a hydride which then reacts with a proton to produce hydrogen gas at only 423 K (Erhardt & Wuest, 1980). This is attributed to its three-dimensional structure, (2) (Beddoes, Edwards, Joule, Mills & Street, 1987), which enables three N-atom lone pairs to assist the process by overlapping with the σ_{CH^*} orbital. [For the crystal structure of an analogue of (1) carrying a central methyl group instead of an H atom, see Seiler, Weisman, Glendening, Weinhold, Johnson & Dunitz (1987).]

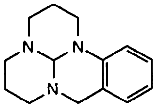


(1)

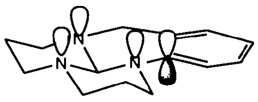


(2)

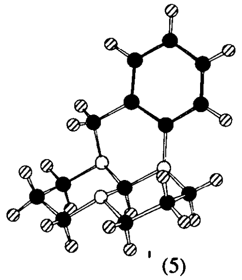
It was our aim to synthesize analogues of (1) and to test whether the energy necessary to drive hydride expulsion, and thus, hydrogen production could be made available by photochemical excitation. To this end we synthesized (3), incorporating a UV chromophore, in which we hoped that the π system of the aromatic ring would lie in the plane of the saturated part, in a conformation idealized as (4), thus allowing for electronic interactions between the π system and the N-atom lone pairs of the desired type. However, a crystal structure determination showed that in (3) the benzene ring actually adopts an orientation, shown in (5), orthogonal to the triaza-*trans*-decalin, which is inappropriate for our aims (Beddoes, Edwards, Joule, Mills & Street, 1987).



(3)

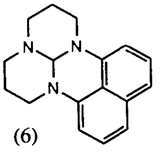


(4)

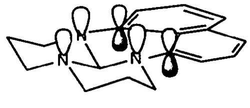


(5)

In order to increase, as we thought, the chances of achieving the desired orientation between the N atoms and the aromatic system, we synthesized the title compound 3a,6a,12b-triaza-1,2,3,3a,4,5,6,6a,12b,12c-decahydroperylene, (6), in which two of the N atoms are directly bonded to an aromatic system and so the additional overlap stabilization from the interaction of two N-atom lone pairs with two benzene rings would favour the desired conformation, idealized as (7).



(6)



(7)

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The crystal structure and the conformation discussed here show that the energy associated with normal resonance interaction between aniline lone pairs and associated benzene rings, is, in this molecule, more than offset by other factors. Chief among these may be the close approach which would have to occur between the aromatic protons *ortho* to the N atoms and the equatorial protons on the C atoms adjacent to the N atoms. Modelling indicates that this distance would be between 1.7 and 2.0 Å.

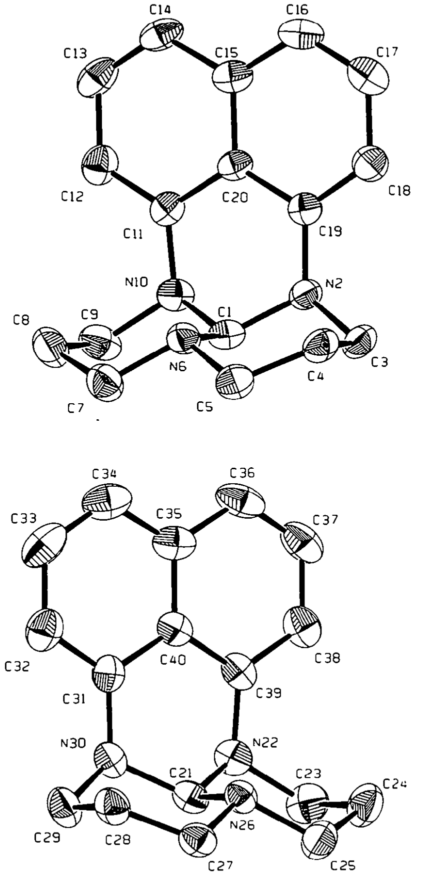
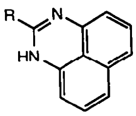


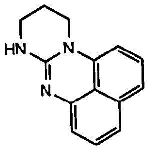
Fig. 1. *ORTEPII* (Johnson, 1976) views of the two molecules in the assymetric unit, with ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

Experimental

2-Chloroperimidine, (8*a*) (Gleiter & Uschmann, 1986), was reacted with 3-hydroxypropanamine at reflux in thf to produce the guanidine (8*b*), which was cyclized to (9) using methanesulfonyl chloride in pyridine. The final ring was added to (9) by reaction with 1,3-dibromopropane in the presence of sodium hydride, followed by reduction with sodium borohydride, giving (6). Crystals were obtained by recrystallization from methanol.



(8*a*) $R = Cl$
(8*b*) $R = NH(CH_2)_3OH$



(9)

Crystal data

$C_{17}H_{19}N_3$
$M_r = 265.34$
Monoclinic
$C2$
$a = 25.166$ (1) Å
$b = 8.588$ (1) Å
$c = 18.382$ (1) Å
$\beta = 136.53$ (4)°
$V = 2733.2$ Å^3
$Z = 8$
$D_x = 1.29$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 100 reflections
$\theta = 7.6$–12.8°
$\mu = 0.13$ mm^{-1}
$T = 296$ (1) K
Prismatic
0.36 × 0.26 × 0.16 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2664 measured reflections
2205 independent reflections
1901 observed reflections [$F > 3\sigma(F)$]
$R_{\rm int} = 0.04$

$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 28$
$k = 0 \rightarrow 10$
$l = -20 \rightarrow 14$
1 standard reflection monitored every 150 reflections intensity decay: insignificant

Refinement

Refinement on F
$R = 0.032$
$wR = 0.041$
$S = 1.12$
1901 reflections
361 parameters
H-atom parameters not refined

$w = 1/(0.62 - 0.024F + 0.008F^2)^{1/2}$
$(\Delta/\sigma)_{\rm max} = 0.09$
$\Delta\rho_{\rm max} = 0.5$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.5$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
C1	0.3084 (2)	0.4150	−0.0395 (2)	3.9 (3)
N2	0.2987 (1)	0.5527 (4)	−0.0044 (2)	3.9 (3)
C3	0.2686 (2)	0.6816 (5)	−0.0789 (3)	4.7 (4)
C4	0.3260 (2)	0.7194 (5)	−0.0821 (3)	4.6 (3)
C5	0.3412 (2)	0.5736 (5)	−0.1115 (3)	4.6 (4)
N6	0.3652 (2)	0.4419 (4)	−0.0414 (2)	3.9 (3)
C7	0.3705 (2)	0.3030 (5)	−0.0827 (3)	5.3 (4)
C8	0.3872 (3)	0.1563 (5)	−0.0222 (3)	6.1 (5)
C9	0.3286 (3)	0.1420 (5)	−0.0203 (3)	5.6 (5)
N10	0.3294 (2)	0.2830 (4)	0.0249 (2)	4.2 (3)
C11	0.3917 (2)	0.3046 (5)	0.1349 (3)	3.8 (3)
C12	0.4379 (2)	0.1848 (5)	0.2040 (3)	5.0 (4)
C13	0.4968 (2)	0.2129 (6)	0.3143 (3)	5.3 (4)
C14	0.5085 (2)	0.3560 (6)	0.3535 (3)	5.0 (4)
C15	0.4614 (2)	0.4825 (5)	0.2848 (3)	4.2 (3)

C16	0.4706 (2)	0.6325 (6)	0.3230 (3)	5.2 (3)
C17	0.4246 (2)	0.7511 (5)	0.2551 (3)	5.4 (5)
C18	0.3678 (2)	0.7284 (5)	0.1452 (3)	4.6 (3)
C19	0.3565 (2)	0.5841 (5)	0.1037 (2)	3.7 (3)
C20	0.4027 (2)	0.4565 (5)	0.1736 (2)	3.6 (3)
C21	0.1607 (2)	0.2598 (5)	0.3420 (3)	4.1 (2)
N22	0.2080 (2)	0.3913 (4)	0.3702 (2)	4.5 (2)
C23	0.1619 (3)	0.5328 (5)	0.3243 (4)	5.7 (5)
C24	0.0981 (3)	0.5191 (5)	0.2050 (4)	6.2 (5)
C25	0.0512 (2)	0.3746 (5)	0.1732 (3)	5.5 (4)
N26	0.0998 (2)	0.2346 (4)	0.2271 (2)	3.9 (2)
C27	0.0502 (2)	0.1036 (5)	0.1991 (3)	4.6 (3)
C28	0.0961 (2)	−0.0417 (5)	0.2602 (3)	4.7 (3)
C29	0.1583 (2)	−0.0050 (5)	0.3780 (3)	5.2 (4)
N30	0.2072 (2)	0.1226 (4)	0.3992 (2)	4.3 (3)
C31	0.2624 (2)	0.0902 (5)	0.4006 (2)	4.0 (2)
C32	0.2943 (2)	−0.0545 (5)	0.4226 (3)	5.4 (3)
C33	0.3512 (2)	−0.0775 (6)	0.4260 (3)	6.5 (5)
C34	0.3754 (2)	0.0373 (6)	0.4058 (3)	6.1 (5)
C35	0.3447 (2)	0.1887 (5)	0.3834 (3)	4.9 (3)
C36	0.3686 (2)	0.3145 (7)	0.3625 (3)	5.9 (4)
C37	0.3395 (2)	0.4580 (6)	0.3444 (3)	6.0 (5)
C38	0.2848 (2)	0.4879 (5)	0.3444 (3)	5.2 (4)
C39	0.2594 (2)	0.3680 (5)	0.3632 (2)	4.1 (2)
C40	0.2881 (2)	0.2165 (5)	0.3814 (2)	4.0 (2)

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

N2—C1	1.450 (5)	N22—C21	1.438 (4)
N2—C3	1.473 (6)	N22—C23	1.453 (5)
N2—C19	1.395 (4)	N22—C39	1.405 (4)
N6—C1	1.471 (4)	N26—C21	1.465 (4)
N6—C5	1.475 (6)	N26—C25	1.471 (4)
N6—C7	1.471 (4)	N26—C27	1.468 (6)
N10—C1	1.434 (4)	N30—C21	1.444 (4)
N10—C9	1.459 (5)	N30—C29	1.474 (4)
N10—C11	1.410 (4)	N30—C31	1.402 (4)
C1—N2—C3	109.9 (2)	C21—N22—C23	110.0 (3)
C1—N2—C19	116.9 (2)	C21—N22—C39	115.6 (3)
C3—N2—C19	119.0 (3)	C23—N22—C39	118.1 (3)
C1—N6—C5	110.4 (2)	C21—N26—C25	109.7 (3)
C1—N6—C7	110.1 (2)	C21—N26—C27	110.5 (2)
C5—N6—C7	107.9 (2)	C25—N26—C27	108.3 (2)
C1—N10—C9	110.3 (2)	C21—N30—C29	109.7 (2)
C1—N10—C11	115.9 (3)	C21—N30—C31	116.3 (3)
C9—N10—C11	117.9 (3)	C29—N30—C31	119.0 (3)

The structure was determined by direct methods using *MULTAN*80 (Main *et al.*, 1980) and contains two independent molecules. H atoms were found by difference Fourier then recalculated in steric positions. The H atoms were placed in calculated positions (C—H = 0.98 Å) at the beginning of each least-squares cycle, with a *B* value of 4.8 Å^2, and not refined. Dispersion corrections were taken from Cromer (1974).

Data collection: CAD-4 diffractometer software. Cell refinement: CAD-4 diffractometer software. Data reduction: local program. Structure solution: *MULTAN*80. Structure refinement: local program. Molecular graphics: *ORTEP*II (Johnson, 1976). Preparation of material for publication: local program.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6-(3,5-Di-*O*-acetyl-β-D-2-deoxyribofuranosyl)-3,4-dihydro-8*H*-pyrimido[4,5-*c*][1,2]oxazin-7(6*H*)-one

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Abstract

The title compound, $C_{15}H_{19}N_3O_7$ (P), crystallizes with two molecules in the asymmetric unit which differ in sugar and oxazino ring puckering; both occur as the imino tautomer and form P:P wobble base pairs.

Comment

The preferred *syn* conformation of the methoxyl group, with respect to N3, in the base analogue N^4-methoxycytosine M (Van Meervelt, 1991) destabilizes Watson–Crick M:A and M:G base pairs in oligonucleotide duplexes. In the left-handed double helical fragment d(CGCGMG)$_2$, wobble base pairing is found for the M:G base pairs with M in the imino form (Van

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