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Structure of 2,4-Bis(4-methoxyphenyl)-3-nitroso-3-azabicyclo[3.3.1]nonan-9-one

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Abstract

The bicyclic rings adopt a twin-chair conformation with the phenyl rings in equatorial positions. The N atom at N(3) is sp^2 hybridized and the nitroso group makes an angle of approximately 35° with the C(2)—N(3)—C(4) atom plane of the piperidine ring. The crystal structure is stabilized by van der Waals interactions.

Comment

The crystal-structure analysis of the title compound (II) forms part of our work on the synthesis (Ravindran & Jeyaraman, 1991) and investigation of the conformational flexibility of the bicyclo[3.3.1]nonane ring in a series of cyclic nitrosamines (Priya, Shamala, Viswamitra, Senthil Kumar & Jeyaraman, 1992). The X-ray results are compared with those of 2,4-bis(*p*-methoxyphenyl)-3-azabicyclo[3.3.1]nonan-9-one, henceforth abbreviated as ABNOM (Cox, McCabe, Milne & Sim, 1985).

The bicyclo[3.3.1]nonane ring systems offer wide conformational flexibility owing to their existence as twin-chair (Brown, Eglinton, Martin, Parker & Sim, 1964; Dobler & Dunitz, 1964; Brown, Martin & Sim, 1965; Sim, 1979; Kimura, Kato, Okabayashi & Yasuoka, 1983), chair–boat (Tamura & Sim, 1968; Quast, Muller, Peters, Peters & Schnering, 1982; Levina, Potekhin, Rau, Struchkov, Palyulin & Zefirov, 1982; Smith-Verdier, Florencio & Garcia-Blanco, 1983), and twin-boat conformations (Kimoto, Imagawa & Kawanisi, 1972; Padegimas & Kovacic, 1972; Peters, Remijnse, van der Wiele & van Bekkum, 1971). However, the twin-chair conformer with various degrees of distortion of the cyclohexane ring has been found to be most favoured (Brown, Martin & Sim, 1965; Zefirov, 1975; Takeuchi, Scheiber & Takada, 1980).

In *N,N'*-dialkyl derivatives of 3,7-diazabicyclo[3.3.1]nonane, when the N atoms at the 3 and 7 positions are sp^3 hybridized, the boat–chair conformation is preferred to twin-chair, minimizing the lone-pair electron repulsion (McCabe, Milne & Sim, 1985). When one of the N atoms is replaced by an alkyl group, the system adopts a twin-chair conformation in order to reduce the repulsion between *endo* H atoms and lone-pair electrons (McCabe, Milne & Sim, 1985). Cox, McCabe, Milne & Sim (1985) emphasized that in the twin-chair conformation with an sp^3 -hybridized N atom at the 3 position and C(7)—H at the 7 position, the cyclohexane ring is distorted, which is attributed to the repulsion between the N-atom lone pair and the *endo* H atom of the C(7)—H group. They further argue that a bulky substituent in place of the alkyl H atom at the 7 position enforces the boat–chair conformation in order to minimize the steric hindrance between the substituent and the lone pair of electrons at the 3 position (Cox, McCabe, Milne & Sim, 1985). Our studies on the title compound show that even with sp^2 hybridization of the N atom at the 3 position, the bicyclic system adopts the twin-chair conformation as in ABNOM. However, there are differences in detail.

The bond lengths and bond angles of the bicyclic ring agree with those observed in ABNOM. The cyclohexane ring shows deviations from an ideal chair conformation. This is evident from the displacement of atoms C(7) and C(9) from the C(1)—C(5)—C(6)—C(8) plane by -0.612 (5) and 0.721 (6) Å respectively. Furthermore, the endocyclic angles at C(6) and C(8) are 112.5 (4) and 112.7 (4) $^\circ$ respectively, showing deviation from the tetrahedral value owing to flattening of the ring (Brown, Martin & Sim, 1965; Tamura & Sim, 1968). The torsion angles C(5)—C(6)—C(7)—C(8), C(6)—C(7)—C(8)—C(1) and C(7)—C(8)—C(1)—C(9) are 50.0 (5), -50.9 (5) and 56.6 (5) $^\circ$ in comparison with 46.0 , -45.5 and 52.7 $^\circ$ in ABNOM, respectively. The asymmetry parameter (Duax & Norton, 1975) of the cyclohexane ring for the best mirror passing through atoms C(7) and C(9) is $\Delta C_s = 1.76$ $^\circ$.

The piperidine ring is considerably deformed from the ideal chair form. The torsion angles involving N(3) deviate significantly from 60° . The ring is flattened at N(3) and the mean value of the ring torsion angle is 45.9 $^\circ$, in comparison with 59° in ABNOM. There is a marginal increase in the N(3)⋯C(7) distance from 2.93 Å in ABNOM to 3.150 (6) Å in (II), owing to flattening at the N end of the molecule. The C—N—C angle is enlarged to 125.2 (4) $^\circ$ in (II) from 113.1 $^\circ$ in ABNOM. The asymmetry parameter ΔC_s (Duax & Norton, 1975) is equal to 1.11 $^\circ$ for the piperidine ring and corresponds to the mirror passing through the N3 and C9 atoms. The endocyclic N

atom exhibits slight pyramidal character. In (II), the sum of the three bond angles at the N atom is 350° and the displacement of N(3) from the C(2)–C(4)–N(27) plane is $0.256(4) \text{ \AA}$.

The phenyl rings are in equatorial positions in ABNOM whereas they are in quasi-equatorial positions in (II) owing to flattening at the N end as is evident from the torsion angles C(9)–C(1)–C(2)–C(11) of $-169.9(4)$ and C(9)–C(5)–C(4)–C(19) of $171.0(4)^\circ$ in (II), as compared to 178.2 and -177.9° in ABNOM, respectively. The crystal structure is stabilized by van der Waals interactions.

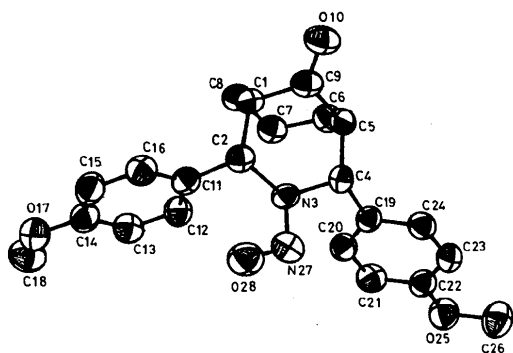


Fig. 1. ORTEP (Johnson, 1976) plot showing the atomic numbering scheme.

Experimental

Crystal data

$C_{22}H_{24}N_2O_4$

$M_r = 380.41$

Orthorhombic

$P2_12_12_1$

$a = 7.521(1) \text{ \AA}$

$b = 10.872(2) \text{ \AA}$

$c = 22.901(3) \text{ \AA}$

$V = 1872.6 \text{ \AA}^3$

$Z = 4$

$D_x = 1.35 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 24 reflections

$\theta = 8-55^\circ$

$\mu = 0.67 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Parallelepiped

$0.3 \times 0.2 \times 0.1 \text{ mm}$

Yellow

Crystal source: crystallization from ethanol solution

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

2499 measured reflections

1968 independent reflections

1537 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 65^\circ$

$h = 0 \rightarrow 9$

$k = 0 \rightarrow 13$

$l = 0 \rightarrow 22$

2 standard reflections

frequency: 60 min

intensity variation: $< 3\%$

Refinement

Refinement on F

Final $R = 0.059$

$wR = 0.050$

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.31 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

$S = 1.87$

1537 reflections

279 parameters

Only H-atom U 's refined

$w = 2.1461/[\sigma^2(|F|)$

$+ 0.000178|F_o|^2]$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Data collection: *SDP* (Enraf-Nonius, 1985). Program(s) used to solve structure: *MULTAN87* (Debaeremaeker, Germain, Main, Tate & Woolfson, 1987). Program(s) used to refine structure: *SHELX400* [enhanced version of *SHELX76* (Sheldrick, 1976)].

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	-0.0781 (6)	-0.0538 (4)	0.5013 (2)	0.044 (2)
C(2)	0.0189 (6)	0.0662 (4)	0.5198 (2)	0.044 (3)
N(3)	0.0937 (5)	0.1315 (3)	0.4681 (2)	0.039 (2)
C(4)	0.0193 (7)	0.1269 (4)	0.4083 (2)	0.038 (2)
C(5)	-0.0742 (7)	0.0023 (4)	0.3961 (2)	0.046 (3)
C(6)	0.0479 (7)	-0.1073 (5)	0.3823 (2)	0.057 (3)
C(7)	0.1576 (7)	-0.1475 (4)	0.4349 (2)	0.049 (3)
C(8)	0.0418 (7)	-0.1653 (4)	0.4890 (2)	0.049 (3)
C(9)	-0.1860 (8)	-0.0338 (4)	0.4474 (2)	0.045 (3)
O(10)	-0.3436 (5)	-0.0567 (3)	0.4436 (2)	0.045 (3)
C(11)	0.1535 (7)	0.0431 (4)	0.5675 (2)	0.059 (2)
C(12)	0.0989 (7)	0.0522 (5)	0.6242 (2)	0.048 (3)
C(13)	0.2101 (8)	0.0316 (5)	0.6704 (2)	0.061 (4)
C(14)	0.3854 (8)	0.0009 (5)	0.6599 (2)	0.048 (3)
C(15)	0.4454 (8)	-0.0064 (5)	0.6038 (3)	0.052 (3)
C(16)	0.3302 (8)	0.0165 (5)	0.5570 (2)	0.054 (3)
O(17)	0.4896 (5)	-0.0152 (4)	0.7084 (2)	0.067 (3)
C(18)	0.6627 (10)	-0.0619 (6)	0.7013 (3)	0.080 (4)
C(19)	0.1566 (7)	0.1592 (4)	0.3624 (2)	0.042 (2)
C(20)	0.3352 (7)	0.1304 (5)	0.3674 (2)	0.050 (3)
C(21)	0.4488 (7)	0.1607 (5)	0.3223 (2)	0.051 (3)
C(22)	0.3888 (7)	0.2178 (5)	0.2724 (2)	0.049 (3)
C(23)	0.2136 (7)	0.2472 (5)	0.2677 (2)	0.049 (3)
C(24)	0.1003 (7)	0.2187 (5)	0.3132 (2)	0.045 (3)
O(25)	0.5148 (5)	0.2422 (4)	0.2310 (1)	0.065 (2)
C(26)	0.4571 (9)	0.2994 (6)	0.1777 (3)	0.077 (4)
N(27)	0.1620 (6)	0.2466 (4)	0.4758 (2)	0.058 (3)
O(28)	0.1708 (5)	0.2761 (4)	0.5279 (2)	0.063 (2)

Table 2. Geometric parameters (\AA , $^\circ$)

C(1)–C(2)	1.548 (6)	C(1)–C(8)	1.532 (6)
C(1)–C(9)	1.493 (7)	C(2)–N(3)	1.489 (6)
C(2)–C(11)	1.510 (7)	N(3)–C(4)	1.480 (7)
N(3)–N(27)	1.359 (6)	C(4)–C(5)	1.546 (6)
C(4)–C(19)	1.514 (7)	C(5)–C(6)	1.533 (7)
C(5)–C(9)	1.497 (7)	C(6)–C(7)	1.524 (7)
C(7)–C(8)	1.527 (7)	C(9)–O(10)	1.214 (7)
C(11)–C(16)	1.381 (8)	C(11)–C(12)	1.365 (7)
C(16)–C(15)	1.400 (8)	C(15)–C(14)	1.364 (8)
C(14)–C(13)	1.381 (8)	C(14)–O(17)	1.371 (7)
C(13)–C(12)	1.367 (7)	O(17)–C(18)	1.406 (8)
C(19)–C(24)	1.365 (7)	C(19)–C(20)	1.384 (7)
C(24)–C(23)	1.380 (6)	C(23)–C(22)	1.360 (8)
C(22)–O(25)	1.366 (6)	C(22)–C(21)	1.375 (7)
C(21)–C(20)	1.380 (7)	O(25)–C(26)	1.436 (7)
N(27)–O(28)	1.237 (7)		
C(2)–C(1)–C(8)	115.7 (4)	C(4)–C(19)–C(24)	118.1 (4)
C(8)–C(1)–C(9)	106.4 (4)	C(2)–C(1)–C(9)	111.1 (4)
C(1)–C(2)–C(11)	112.0 (4)	C(1)–C(2)–N(3)	111.0 (4)
C(2)–N(3)–C(4)	125.2 (4)	N(3)–C(2)–C(11)	113.6 (4)
C(4)–N(3)–N(27)	107.1 (4)	C(2)–N(3)–N(27)	118.3 (4)
N(3)–C(4)–C(19)	112.1 (4)	N(3)–C(4)–C(5)	111.6 (4)
C(4)–C(5)–C(6)	116.1 (4)	C(5)–C(4)–C(19)	112.7 (4)
C(6)–C(5)–C(9)	107.3 (4)	C(4)–C(5)–C(9)	110.0 (4)
C(6)–C(7)–C(8)	111.6 (4)	C(5)–C(6)–C(7)	112.5 (4)
C(1)–C(9)–C(5)	112.4 (4)	C(1)–C(8)–C(7)	112.7 (4)

C(5)—C(9)—O(10)	123.1 (5)	C(1)—C(9)—O(10)	124.1 (5)
C(2)—C(11)—C(12)	118.3 (4)	C(2)—C(11)—C(16)	123.6 (4)
C(13)—C(14)—O(17)	115.8 (4)	C(15)—C(14)—O(17)	124.5 (5)
N(3)—N(27)—O(28)	112.5 (4)	C(22)—O(25)—C(26)	117.6 (4)
C(4)—C(19)—C(20)	123.5 (4)	C(14)—O(17)—C(18)	118.8 (5)

Table 3. Torsion angles ($^{\circ}$) for the title compound and ABNOM

	(II)	ABNOM
Cyclohexane ring		
C(8)—C(1)—C(9)—C(5)	-64.8 (5)	-63.1
C(1)—C(9)—C(5)—C(6)	64.5 (5)	63.5
C(9)—C(5)—C(6)—C(7)	-55.1 (5)	-54.0
C(5)—C(6)—C(7)—C(8)	50.0 (5)	46.0
C(6)—C(7)—C(8)—C(1)	-50.9 (5)	-45.5
C(7)—C(8)—C(1)—C(9)	56.6 (5)	52.7
Piperidine ring		
C(1)—C(2)—N(3)—C(4)	29.1 (6)	58.0
C(2)—N(3)—C(4)—C(5)	-30.5 (6)	-57.5
N(3)—C(4)—C(5)—C(9)	43.8 (5)	57.3
C(4)—C(5)—C(9)—C(1)	-62.6 (5)	-61.8
C(5)—C(9)—C(1)—C(2)	61.9 (5)	61.8
C(9)—C(1)—N(2)—N(3)	-41.7 (5)	-57.7
Torsion angles about the phenyl rings		
C(5)—C(4)—C(19)—C(24)	85.7 (5)	92.2
C(5)—C(4)—C(19)—C(20)	-93.5 (6)	-85.7
N(3)—C(4)—C(19)—C(20)	33.5 (6)	38.1
N(3)—C(4)—C(19)—C(24)	-147.3 (4)	-143.8
C(1)—C(2)—C(11)—C(16)	91.7 (6)	101.6
C(1)—C(2)—C(11)—C(12)	-90.1 (5)	-79.6
N(3)—C(2)—C(11)—C(16)	-35.0 (6)	-22.2
N(3)—C(2)—C(11)—C(12)	43.2 (4)	156.9

H atoms were located by difference Fourier synthesis and allowed to ride on their corresponding non-H atoms (C—H = 1.08 Å). For the methoxy groups, one H atom of each (namely HA18 and HA26) was located from difference maps while the others were fixed geometrically.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55784 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1028]

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Structures of Muscarine Picrate and Muscarine Tetraphenylborate

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Abstract

The tetrahydrofuran ring of the muscarine ion [(±)-(2*S*,4*R*,5*S*)-tetrahydro-4-hydroxy-*N,N,N*,5-tetramethyl-2-furanaminium] of muscarine picrate, as well as that of muscarine tetraphenylborate, is observed in a distorted twist conformation, 4T_3 . This is different from the conformation observed in the crystal structure of muscarine chloride, but nearly the same as the conformation known from the crystal structure of muscarine iodide. The ring conformations are, however, not exactly identical as can be seen from the different pucker amplitudes. The crystal packing of muscarine tetraphenylborate shows disorder, which is especially dominant for the muscarine ion. The conformation of the tetrahydrofuran ring is undoubtedly an average of different conformations, and therefore the