

Das Molekül hat die Punktsymmetrie 1 ( $C_1$ ). Im Kristall (Fig. 2) liegt nur eins der beiden bei Raumtemperatur nach rascher Isomerisierung in Lösung beobachteten Konfigurationsisomeren, die sich auf Grund des  $^{31}\text{P}\{^1\text{H}\}$ -NMR-Spektrums in der Stellung der *tert*-Butyl-Gruppe am Atom P5 unterscheiden, als Enantiomeren-Paar vor. Bemerkenswerte zwischenmolekulare Wechselwirkungen werden nicht beobachtet. Die Kontaktabstände zwischen Wasserstoffatomen beginnen bei 2,58 Å [H(6)···H(13)].

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## Structure of 2-Morpholino-4-phenylbicyclo[3.3.1]nonan-9-one\*

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**Abstract.**  $\text{C}_{19}\text{H}_{25}\text{NO}_2$ ,  $M_r = 299.4$ , orthorhombic, *Pcab*,  $a = 7.781$  (1),  $b = 9.959$  (1),  $c = 43.031$  (4) Å,  $V = 3334.5$  (6) Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.21$ ,  $D_x = 1.19$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 0.082$  mm<sup>-1</sup>,  $F(000) = 1296$ ,  $T = 293$  K,  $R = 0.057$  for 875 reflections. The bicyclo[3.3.1]nonane system adopts a boat–chair conformation. The ring with the morpholine and phenyl substituents is in a boat conformation while the other ring has a chair conformation. The morpholine ring adopts a chair conformation.

**Introduction.** Bicyclo[3.3.1]nonanes are useful synthetic intermediates and have been used in the synthesis of naturally occurring compounds (Evans, Hewson & Wadsworth, 1985). Some of the bicyclo[3.3.1]nonan-9-one derivatives have also been employed in perfume and flavour compositions (Kretschmor & Herbert, 1970). Considerable debate exists in the literature regarding the exact conformation of 2,4-disubstituted bicyclo[3.3.1]nonan-9-one systems. A simplified synthesis of 2-morpholino-4-phenylbicyclo[3.3.1]nonan-9-one was achieved in a one-pot reaction (Lakshmy, Geetha & Trivedi, 1985) of cyclohexanone, morpholine and cinnamaldehyde in tetrahydrofuran in the presence of anhydrous  $\text{CeCl}_3$ . The crude solid when recrystallized from hexane gave colourless single crystals of the

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title compound. In order to establish uniquely the conformation of this bicyclo[3.3.1]nonane system with substituents at C(2) and C(4), an X-ray crystal structure analysis was carried out.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters for non-H atoms with e.s.d.'s in parentheses

$B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$				
	x	y	z	$B_{eq}(\text{\AA}^2)$
N	1672 (12)	4420 (9)	702 (2)	7.39
O(1)	2678 (15)	5001 (12)	94 (2)	12.52
O(2)	-389 (9)	7600 (7)	1266 (2)	6.02
C(1)	-810 (14)	5540 (11)	998 (3)	6.42
C(2)	655 (15)	4428 (11)	993 (3)	6.19
C(3)	1808 (12)	4518 (10)	1270 (3)	5.18
C(4)	758 (13)	4455 (11)	1573 (3)	5.81
C(5)	-596 (14)	5634 (11)	1579 (3)	5.97
C(6)	-2420 (16)	5134 (15)	1622 (4)	9.53
C(7)	-2943 (17)	4311 (16)	1358 (5)	10.66
C(8)	-2667 (15)	4880 (16)	1031 (4)	10.43
C(9)	-543 (13)	6403 (10)	1277 (3)	4.91
C(10)	662 (12)	3958 (8)	439 (2)	10.17
C(11)	1851 (15)	3778 (10)	160 (2)	13.28
C(12)	3684 (12)	5454 (10)	351 (2)	11.06
C(13)	2574 (10)	5646 (7)	632 (1)	7.78
C(14)	1871 (7)	4459 (5)	1856 (1)	5.47
C(15)	1725 (15)	3406 (12)	2068 (3)	7.00
C(16)	2719 (18)	3360 (15)	2326 (3)	9.15
C(17)	3847 (18)	4373 (15)	2392 (3)	8.25
C(18)	4038 (17)	5423 (15)	2183 (3)	8.06
C(19)	3040 (14)	5471 (11)	1918 (2)	6.32

Table 2. Bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with e.s.d.'s in parentheses

N—C(2)	1.480 (15)	C(5)—C(6)	1.516 (17)
N—C(10)	1.454 (12)	C(5)—C(9)	1.509 (17)
N—C(13)	1.441 (12)	C(6)—C(7)	1.458 (24)
O(1)—C(11)	1.407 (16)	C(7)—C(8)	1.530 (27)
O(1)—C(12)	1.428 (13)	C(10)—C(11)	1.527 (13)
O(2)—C(9)	1.199 (12)	C(12)—C(13)	1.498 (10)
C(1)—C(2)	1.590 (16)	C(14)—C(15)	1.394 (13)
C(1)—C(8)	1.594 (17)	C(14)—C(19)	1.384 (12)
C(1)—C(9)	1.489 (17)	C(15)—C(16)	1.356 (18)
C(2)—C(3)	1.492 (16)	C(16)—C(17)	1.367 (20)
C(3)—C(4)	1.542 (16)	C(17)—C(18)	1.388 (20)
C(4)—C(5)	1.578 (15)	C(18)—C(19)	1.379 (17)
C(4)—C(14)	1.494 (13)		
C(2)—N—C(10)	111.8 (8)	C(5)—C(6)—C(7)	110.6 (12)
C(2)—N—C(13)	115.7 (8)	C(6)—C(7)—C(8)	117.8 (14)
C(10)—N—C(13)	111.5 (7)	C(1)—C(8)—C(7)	111.3 (12)
C(11)—O(1)—C(12)	111.6 (9)	O(2)—C(9)—C(1)	123.8 (10)
C(2)—C(1)—C(8)	111.3 (10)	O(2)—C(9)—C(5)	122.7 (10)
C(2)—C(1)—C(9)	108.2 (9)	C(1)—C(9)—C(5)	113.4 (10)
C(8)—C(1)—C(9)	107.0 (10)	N—C(10)—C(11)	108.9 (7)
N—C(2)—C(1)	113.5 (9)	O(1)—C(11)—C(10)	109.5 (8)
N—C(2)—C(3)	110.7 (9)	O(1)—C(12)—C(13)	110.5 (8)
C(1)—C(2)—C(3)	112.2 (9)	N—C(13)—C(12)	110.0 (7)
C(2)—C(3)—C(4)	110.8 (9)	C(4)—C(14)—C(15)	119.0 (7)
C(3)—C(4)—C(5)	109.7 (9)	C(4)—C(14)—C(19)	122.8 (7)
C(3)—C(4)—C(14)	112.5 (8)	C(15)—C(14)—C(19)	118.3 (8)
C(5)—C(4)—C(14)	111.8 (8)	C(14)—C(15)—C(16)	121.1 (11)
C(4)—C(5)—C(6)	112.5 (10)	C(15)—C(16)—C(17)	120.7 (13)
C(4)—C(5)—C(9)	110.2 (9)	C(16)—C(17)—C(18)	119.4 (13)
C(6)—C(5)—C(9)	107.2 (10)	C(17)—C(18)—C(19)	120.1 (12)

**Experimental.** Crystal of approximate dimensions  $0.9 \times 0.5 \times 0.3$  mm; density by flotation in KI solution; lattice parameters from 20 reflections ( $10 \leq 2\theta \leq 21^\circ$ ); intensity data collected on an Enraf-Nonius CAD-4F-11M single-crystal X-ray diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\omega/2\theta$  scan mode, scan speed  $1^\circ \text{ min}^{-1}$ ,  $\theta < 23.5^\circ$  for 2457 reflections collected ( $h = 0-8$ ,  $k = 0-11$ ,  $l = 0-48$ ), 875 were judged significant ( $|F_o| \leq 3\sigma|F_o|$ ). Three standard reflections (2,2,16, 1,4,12 and 3,1,18) measured every 2000 s, 4% variation in intensity, intensities not corrected for absorption; structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) using a modified procedure (Tavale & Guru Row, 1986), full-matrix refinement of scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, geometrically fixed) converged to an  $R$  of 0.057 and  $wR = 0.055$ ,  $S = 2.98$ ;  $(|F_o| - |F_c|)^2$  minimized where  $w = [11.0 + 1.0|F_o| + 0.014|F_o|^2]$ ;  $(\Delta/\sigma)_{\text{max}} = 0.1$ , final  $\Delta\rho$  excursions  $\leq 10.3 \text{ e \AA}^{-3}$ , no correction for secondary extinction; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); *LALS* (Gantzel, Sparks & Trueblood, 1961) used for the refinement.

**Discussion.** The atomic parameters with their e.s.d.'s and equivalent isotropic thermal parameters are given in Table 1.\* Bond lengths and bond angles involving the non-H atoms are given in Table 2. Fig. 1 gives a perspective view of the molecule together with the crystallographic numbering of atoms.

The bicyclo[3.3.1]nonane system is of considerable stereochemical interest because it can be constructed by

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43747 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

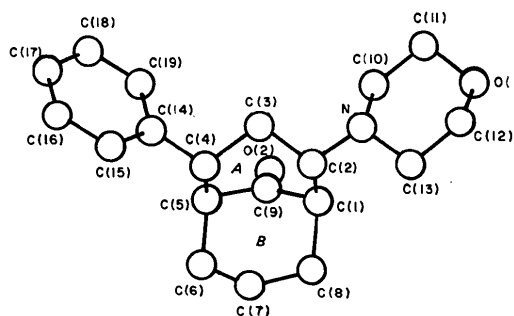


Fig. 1. Perspective view of the molecule with numbering scheme.

a fusion of two cyclohexane moieties. Obviously, the most 'strain-free' configuration of such a system would be chair-chair. However, this system is highly flexible under the influence of bulky substituents and can adopt either boat-chair or boat-boat conformations. However, energetically boat-boat is very unstable. In the present study this system has boat-chair conformation. Ring *A* (Fig. 1) is in a chair conformation. Ring *A* adopts a boat conformation rather than the preferred chair in order to avoid steric interaction between the external ring substituents at C(2) and C(4). An analysis of the conformation of the bicyclo[3.3.1]nonane system by Bhattacharjee & Chacko (1979) indicated that bulky substituents at C(3) and C(7) would result in a chair-boat configuration. In the present study, it is seen that even substitution on the same ring (ring *A*, Fig. 1) at C(2) and C(4) also results in a boat-chair conformation. This conformation purely occurs because of steric reasons and enables a less distorted configuration to be adopted.

The morpholine ring has a chair conformation. The phenyl ring at C(4) is at an angle of  $73.0(1)^\circ$  to the C(3), C(4), C(5) plane while the morpholine ring at C(2) [plane through C(10), N, C(13)] makes an angle of  $69.5(1)^\circ$  with the plane through C(1), C(2), C(3)

respectively. The molecules are held together by van der Waals interactions.

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### ***trans*-Isomeres des cyclischen Hydrazidophosphorsäurephenylester-Dimeren mit Twistkonformation**

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**Abstract.** *trans*-3,6-Dioxo-3,6-diphenoxy-1,2,4,5-tetraaza-3 $\lambda^5$ ,6 $\lambda^5$ -diphosphacyclohexane, C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>P<sub>2</sub>, *M*<sub>r</sub> = 340.216, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.318 (6), *b* = 5.854 (5), *c* = 29.261 (13) Å,  $\beta$  = 95.5 (4)°, *V* = 1589 (4) Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.423 g cm<sup>-3</sup>, *F*(000) = 704,  $\mu$  = 2.69 cm<sup>-1</sup>, *R* = 0.049 (*wR* = 0.053) for 2087 unique contributing reflections. Mo *K*α (monochromator),  $\lambda$  = 0.71069 Å, *T* = 293 K. The compound has been prepared in our laboratory for comparison with the corresponding 3,6-dithioxo compound. The molecule is the *trans* isomer. The six-membered saturated heterocycle adopts a twist conformation in the crystal in contrast to the *trans* isomer of the *N*-unsubstituted 3,6-dithioxo compound, which has a chair conformation. Strong hydrogen bridges

between hydrazine H's and terminal O's at P of adjacent molecules are apparently the reason for this ring distortion: interplanar (torsion) angles  $\pm 59.5(4)$  and  $\pm 63.5(4)^\circ$ , NNPN  $\pm 29.6(20)^\circ$  (mean). Mean bond distances N–N 1.419 (6), P–N 1.63 (1), P=O 1.476 (3), P–O 1.585 (6) and O–C 1.401 (8) Å.

**Einleitung.** *cis*- und *trans*-Isomere des Titel-Ringsystems (1) und (2) mit verschiedenen Substituenten an den Phosphor- bzw. Stickstoffatomen sind in unserer Arbeitsgruppe in größerer Zahl dargestellt worden. Die Thiophosphorsäure-Derivate (1a) bzw. (2a) lassen sich relative leicht kristallisieren und Strukturuntersuchungen an den Isomeren-Paaren haben interessante konformative Besonderheiten