

(B. A. Frenz & Associates, Inc., 1983). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters of non-H atoms are in Table 1.* Bond distances and angles and macrocyclic torsion angles are given in Table 2, whereas some important non-bonded distances and hydrogen bonds in the crystal structure of the complex are given in Table 3. Atom numbering in the macrocycle is shown in Fig. 1.

Related literature. Crystal structures of the uncomplexed 4-pyridohemispherand (Dijkstra, den Hertog, van Eerden, Harkema & Reinhoudt, 1988), the Na.picrate complex (Dijkstra, den Hertog, van Steen, Zijlstra, Skowronska-Ptasinska, Reinhoudt, van Eerden & Harkema, 1987) and the complex with malononitrile (van Eerden, Grootenhuis, Dijkstra van Staveren, Harkema & Reinhoudt, 1986) have been reported.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete lists of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53289 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Upon complexation of water but also with Na⁺ and malononitrile a rather strong reorganization takes place: in the crystal structure of the uncomplexed ligand the two methoxy groups are on either side of the mean macrocyclic plane, whereby one of the methoxy groups partly converges into the cavity which is partly filled by the methyl groups.

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Structure of 1-(3-Methylphenyl)-4-(2- β -quinolylethyl)piperazine: Centhaquin

BY ALAIN CARPY

URA 605 CNRS, Faculté de Pharmacie, Université de Bordeaux II, 3 Place de la Victoire,
33076 Bordeaux CEDEX, France

AND ANIL K. SAXENA

Central Drug Research Institute, Chattar Manzil, P. B. n^o 173, Lucknow-226001, India

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Abstract. C₂₂H₂₅N₃, centrally active hypotensive agent, antihypertensive, $M_r = 331.46$, monoclinic, $P2_1/c$, $a = 9.122$ (2), $b = 22.108$ (3), $c = 9.165$ (2) Å, $\beta = 102.20$ (1)°, $V = 1806.6$ Å³, $Z = 4$, $D_x = 1.22$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 5.67$ cm⁻¹, $F(000) = 712$, room temperature, $R = 0.043$ for 1360 observed reflections. The methylphenyl substituted nitrogen exhibits sp^2 character. The resonance of its axial lone pair with the phenyl ring is evidenced by the shortening of the bridge bond and by the almost parallel position of the phenyl ring and of the mean plane of the piperazine ring.

Experimental. White prisms, dimensions 0.20 × 0.15 × 0.08 mm. Density not measured. Unit-cell parameters and intensity data obtained on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation in ω/θ scan mode ($0 < \theta < 65^\circ$). Cell dimensions refined by least-squares fitting of θ values of 25 reflections. No appreciable drop in intensity of two standard reflections ($\bar{2}10, 040$) checked every 5400 s. 3081 independent reflections collected in $h, k, \pm l$, range 0, 0, $\bar{1}0$ to 10, 26, 10; 1360 unique reflections with $I \geq 3\sigma(I)$ used in subsequent calculations. Intensities corrected

for Lorentz and polarization effects but not for absorption. Scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 201–209) and for H from Stewart, Davidson & Simpson (1965). The Wilson statistical test showed a centrosymmetric intensity distribution. Structure solved with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and standard Fourier techniques. H atoms located by ΔF synthesis. Block-diagonal-matrix least-squares refinement on F of observed reflections, $w = 1$ if $|F_o| < P$, $P = [F_o^2(\max)/10]^{1/2}$, $w = (P/F_o)^2$ if $|F_o| > P$; anisotropic thermal parameters for C and N atoms and isotropic ones for H atoms. Final $R = 0.043$, $wR = 0.053$, $S = 0.718$ (1360 reflections, 326 parameters). In final cycle, mean and max. Δ/σ 0.1 and 0.3. Residual electron density within $\pm 0.3 \text{ e } \text{\AA}^{-3}$. Calculations carried out on a Mini 6–92 CII Honeywell Bull computer (unpublished programs from Laboratoire de Cristallographie, Université de Bordeaux I, F-33400 Talence).*

A projection of the molecule is given in Fig. 1. Coordinates for non-H atoms are presented in Table 1. Bond lengths and angles are summarized in Table 2. The piperazine ring is in the expected chair conformation. N(13) is sp^3 hybridized (average valence angles 109.6°). Due to the 3-methylphenyl substituent the hybridization state of N(16) exhibits sp^2 character (average valence angles 115.6°), the axial lone pair being able to participate in resonance with the phenyl ring [$\text{N}(16)\text{—C}(19) = 1.403(4) \text{ \AA}$].

Evidence of resonance is also provided by the position of the phenyl ring vs. the mean plane of the piperazine chair. The angle between the two planes being $13(1)^\circ$, they are almost parallel.

* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53316 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

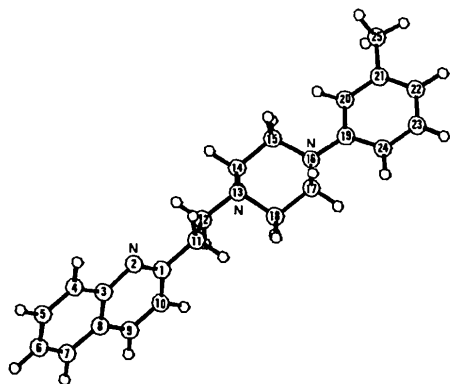


Fig. 1. Projection of the molecule showing the numbering of atoms.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
C(1)	-4944 (4)	-914 (2)	3081 (4)	3.9 (1)
N(2)	-5992 (3)	-832 (1)	3850 (3)	4.0 (1)
C(3)	-7126 (4)	-1249 (1)	3691 (4)	3.9 (1)
C(4)	-8214 (4)	-1175 (2)	4575 (4)	4.6 (2)
C(5)	-9374 (4)	-1582 (2)	4455 (5)	5.4 (2)
C(6)	-9497 (4)	-2070 (2)	3458 (5)	5.8 (2)
C(7)	-8451 (5)	-2158 (2)	2603 (5)	5.7 (2)
C(8)	-7228 (4)	-1745 (2)	2714 (4)	4.3 (1)
C(9)	-6109 (5)	-1807 (2)	1875 (4)	5.2 (2)
C(10)	-4967 (4)	-1400 (2)	2064 (4)	4.8 (2)
C(11)	-3660 (4)	-473 (2)	3324 (4)	4.7 (2)
C(12)	-3449 (4)	-177 (2)	1863 (4)	4.4 (2)
N(13)	-2143 (3)	221 (1)	2113 (3)	3.9 (1)
C(14)	-2183 (4)	597 (2)	800 (4)	5.1 (2)
C(15)	-875 (4)	1046 (2)	1081 (5)	5.3 (2)
N(16)	564 (3)	739 (1)	1509 (3)	4.0 (1)
C(17)	596 (4)	300 (2)	2692 (4)	4.6 (2)
C(18)	-739 (4)	-119 (2)	2362 (4)	4.9 (2)
C(19)	1851 (4)	1094 (2)	1568 (4)	3.8 (1)
C(20)	1810 (4)	1621 (2)	711 (4)	4.2 (1)
C(21)	3085 (4)	1968 (2)	723 (4)	4.5 (2)
C(22)	4454 (4)	1788 (2)	1594 (4)	4.7 (2)
C(23)	4514 (4)	1262 (2)	2431 (4)	5.1 (2)
C(24)	3237 (4)	917 (2)	2444 (4)	4.8 (2)
C(25)	2963 (5)	2545 (2)	-187 (5)	5.8 (2)

Table 2. Bond distances (\AA) and angles ($^\circ$)

C(1)—N(2)	1.315 (4)	C(12)—N(13)	1.460 (4)
C(1)—C(10)	1.421 (5)	N(13)—C(14)	1.455 (4)
C(1)—C(11)	1.503 (5)	N(13)—C(18)	1.461 (4)
N(2)—C(3)	1.370 (4)	C(14)—C(15)	1.531 (5)
C(3)—C(4)	1.417 (4)	C(15)—N(16)	1.457 (4)
C(3)—C(8)	1.407 (4)	N(16)—C(17)	1.451 (4)
C(4)—C(5)	1.375 (5)	N(16)—C(19)	1.403 (4)
C(5)—C(6)	1.403 (5)	C(17)—C(18)	1.509 (5)
C(6)—C(7)	1.371 (5)	C(19)—C(20)	1.402 (4)
C(7)—C(8)	1.429 (5)	C(19)—C(24)	1.403 (5)
C(8)—C(9)	1.408 (5)	C(20)—C(21)	1.391 (5)
C(9)—C(10)	1.359 (5)	C(21)—C(22)	1.391 (5)
C(11)—C(12)	1.538 (5)	C(21)—C(25)	1.515 (5)
N(2)—C(1)—C(10)	122.9 (3)	C(12)—N(13)—C(18)	111.9 (2)
N(2)—C(1)—C(11)	117.6 (3)	C(14)—N(13)—C(18)	106.9 (2)
C(10)—C(1)—C(11)	119.4 (3)	N(13)—C(14)—C(15)	110.4 (3)
C(1)—N(2)—C(3)	118.0 (2)	C(14)—C(15)—N(16)	111.7 (3)
N(2)—C(3)—C(4)	117.8 (3)	C(15)—N(16)—C(17)	112.8 (2)
N(2)—C(3)—C(8)	122.6 (3)	C(15)—N(16)—C(19)	116.7 (2)
C(4)—C(3)—C(8)	119.5 (3)	C(17)—N(16)—C(19)	117.4 (2)
C(3)—C(4)—C(5)	120.0 (3)	N(16)—C(17)—C(18)	111.9 (3)
C(4)—C(5)—C(6)	120.6 (3)	N(13)—C(18)—C(17)	111.0 (3)
C(5)—C(6)—C(7)	120.8 (3)	N(16)—C(19)—C(20)	121.3 (3)
C(6)—C(7)—C(8)	119.6 (3)	N(16)—C(19)—C(24)	120.8 (3)
C(3)—C(8)—C(7)	119.3 (3)	C(20)—C(19)—C(24)	117.8 (3)
C(3)—C(8)—C(9)	117.7 (3)	C(19)—C(20)—C(21)	122.0 (3)
C(7)—C(8)—C(9)	122.9 (3)	C(20)—C(21)—C(22)	119.7 (3)
C(8)—C(9)—C(10)	119.4 (3)	C(20)—C(21)—C(25)	119.7 (3)
C(1)—C(10)—C(9)	119.2 (3)	C(22)—C(21)—C(25)	120.6 (3)
C(1)—C(11)—C(12)	112.5 (3)	C(21)—C(22)—C(23)	118.8 (3)
C(11)—C(12)—N(13)	111.6 (3)	C(22)—C(23)—C(24)	121.9 (3)
C(12)—N(13)—C(14)	109.7 (2)	C(19)—C(24)—C(23)	119.7 (3)

The conformation of the 2- β -quinolyethyl moiety is defined by the torsion angles $\text{N}(2)\text{—C}(1)\text{—C}(11)\text{—C}(12) = -125(1)$, $\text{C}(1)\text{—C}(11)\text{—C}(12)\text{—N}(13) = -177(1)$ and $\text{C}(11)\text{—C}(12)\text{—N}(13)\text{—C}(14) = -167(1)^\circ$.

Related literature. Several 1-aryl-4-(β -2-quinolyl/1-isoquinolyethyl)piperazines and related compounds have been synthesized and evaluated for their hypotensive activity (Murti, Bhandari, Ram, Prabhakar, Saxena, Jain, Gulati, Srimal, Dhawan, Nityanand & Anand, 1989). Most of the compounds exhibited prominent hypotensive activity and weak diuretic, antiinflammatory and CNS depressant activities. Among them, the centrally acting title compound, centhaquin, was found to possess the most suitable profile of hypotensive activity.

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(E)-1,2-Bis(2,3,5,6-tetrafluoro-4-pyridyl)diazene 1,2-Dioxide*

BY R. G. PRITCHARD, R. E. BANKS, A. E. TIPPING AND P. HAIDER

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester, M60 1QD, England

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Abstract. $C_{10}F_8N_4O_2$, $M_r = 360.12$, monoclinic, $P2_1/n$, $a = 6.012$ (2), $b = 5.653$ (2), $c = 18.174$ (3) Å, $\beta = 97.74$ (2)°, $V = 612.0$ Å³, $Z = 2.0$, $D_x = 1.95$ Mg m⁻³, $F(000) = 352.0$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.161$ mm⁻¹, $T = 293$ K, $R = 0.042$ for 776 unique reflexions [$F \geq 3\sigma(F)$]. The structure is composed of centrosymmetric *trans*-dimers of 2,3,5,6-tetrafluoro-4-nitrosopyridine [N—N 1.320 (4) Å]. This contrasts with the benzene analogue, where *cis*-dimer coexists with monomer [Prout, Coda, Forder & Kamenar (1974). *Cryst. Struct. Commun.* **3**, 39-40].

Experimental. Initial sample preparation employed the method of Banks, Du Boisson, Marraccini, Sekhri & Tipping (1987). However, purification of the green mixture thus produced relied on flash column chromatography (silica eluted with light petroleum). The first (blue-green) fraction was distilled to remove most of the eluent and the stillpot residue cooled to 195 K to afford white crystals suitable for X-ray investigation.

Crystal size 0.30 × 0.40 × 0.40 mm, Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, unit-cell dimensions from setting angles of 25 accurately centred reflexions ($7.6 \leq \theta \leq 8.7^\circ$), ω - 2θ scan mode, ω -scan width ($0.70 + 0.35 \tan \theta$)° and scan speed ranging from 1.4 to

5.0° min⁻¹ according to the intensity gathered in a pre-scan, $-7 \leq h \leq 7$, $0 \leq k \leq 6$, $0 \leq l \leq 21$, $0 \leq \theta \leq 25^\circ$, 1321 reflexions measured, 931 unique ($R_{\text{int}} = 0.010$), 776 observed ($F \geq 3\sigma(F)$), intensity standards ($\bar{1}16$; $\bar{1}15$; $2\bar{1}0$) measured every 2.5 h, 15% decay, Lp and decomposition corrections applied, absorption ignored. *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) used to solve the phase problem, all atoms found in Fourier map, full-matrix least squares based on F using *SHELX76* (Sheldrick, 1976), final $R = 0.042$, $wR = 0.045$, $w = 2.6449/[\sigma^2(F) + 0.0005F^2]$, anisotropic thermal parameters for all atoms. Maximum fluctuation in final ΔF map in range -0.2 to 0.2 e Å⁻³, maximum Δ/σ 0.004. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), computation carried out on the Amdahl 5890 system of the University of Manchester Computing Centre. Literature surveyed via the Cambridge Structural Database using the Crystal Structure Search and Retrieval interactive system (CSSR, 1984). Fractional atomic coordinates and vibrational parameters are presented in Table 1† and selected bond lengths and angles in Table 2. The molecule including atomic labelling is displayed in Fig. 1.

† 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 53272 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Alternative name: 2,2',3,3',5,5',6,6'-octafluoro-4,4'-azopyridine *N,N'*-dioxide.