from 1·504 (3) to 1·519 (4) Å while the two methano bonds at the spiro fusion center are 1·543 (3) and 1·531 (2) Å. Because of fusion the six ethano bonds are also connecting bonds (between ethano and methano bridges) and range from 1·553 (3) to 1·578 (4) Å. The three pure connecting bonds range from 1·521 (3) to 1·523 (3) Å. In general, this pattern is repeated in the other cage; however, the bicyclo[2.2.2]octanone moiety introduces additional variations. The carbonyl C atom is slightly pyramidalized with C(22) lying 0·021 (3) Å out of the plane of the three connecting atoms. The shortest significant contact between the two cages is 2·12 (4) Å between H(10) and H(12).

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Stereochemistry of Rings. XVII.* Norbornane Derivatives. 1. 2-(*p*-Methoxyphenyl)-3-phenylbicyclo[2.2.1]heptane (I) and 2-(*p*-Nitrophenyl)-3-phenylbicyclo[2.2.1]heptane (II)

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Abstract. (I): $C_{20}H_{22}O$, monoclinic, $P2_1/a$, $M_r = 278·4$, $a = 22·039$ (2), $b = 5·910$ (2), $c = 11·722$ (2) Å, $\beta = 92·75$ (3)°, $V = 1525·0$ (6) Å^3, $Z = 4$, $D_x = 1·21$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5·22$ cm^{-1}, $F(000) = 600$, room temperature. (II): $C_{19}H_{19}NO_2$, monoclinic, $P2_1/n$, $a = 9·141$ (2), $b = 13·048$ (2), $c = 13·091$ (3) Å, $\beta = 92·47$ (3)°, $V = 1559·9$ (6) Å^3, $Z = 4$, $D_x = 1·25$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 6·06$ cm^{-1}, $F(000) = 624$, room temperature. $R = 0·049$ for 1953 reflections above $2\sigma(I)$ for compound (I) and $R = 0·060$ and $wR = 0·068$ for 2169 reflections above $2\sigma(I)$ for compound (II). Only small conformational differences, due to the differently substituted benzene groups and the methylene bridge, are remarkable in the two six-membered rings of the norbornane skeletons which show boat conformations. The planar phenyl rings are all in equatorial positions and form dihedral angles of 43·4 (1) and 51·8 (1)° to each other in (I) and (II) respectively.

Introduction. Extensive structural analysis on norbornane derivatives has been carried out in recent years in view of their increasing importance in organic synthesis. In particular, in the course of studies aimed at the synthesis of rigid systems containing adjacent aromatic nuclei, two derivatives of bicyclo[2.2.1]heptane with two different aryl groups in 2,3 positions were prepared starting from bicycloheptane, aryl bromides and sodium tetraphenylborate under the catalytic action of a Pd complex (Catellani, Chiusoli, Fornasari & Concari, 1989). In view of the spectroscopic properties and reactivity of these compounds and as part of our program of investigations on ring deformations induced by substituents it has been deemed useful to determine the conformation of the two molecules by X-ray methods.

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* Part XVI: Bocelli & Rizzoli (1989).

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Experimental. Siemens AED single-crystal diffractometer equipped with an IBM PS2/30 personal computer, prismatic crystals of about 0·3 × 0·3 × 0·6 and 0·4 × 0·5 × 0·8 mm for compounds (I) and (II) respectively, unit-cell parameters resulted from a least-squares fit to 19 reflections ($21 \geq \theta \geq 30°$) for compound (I) and to 29 reflections ($14 \geq \theta \geq 39°$) for compound (II), reflections measured using a modified version (Belletti, Cantoni & Pasquinelli, 1988) of the Lehmann & Larsen (1974) method, nickel-filtered Cu $K\alpha$ radiation, θ range 3–70°, one check reflection monitored every 50 measurements without significant variations, intensities corrected for Lorentz and polarization effects but not for absorption. Compound (I): 3027 reflections collected (index range: h −26/26, k 0/7, l 0/12), 2891 independent (R_{int} = 0·033) and 1958 with $I \geq 2\sigma(I)$ observed. Compound (II): 3091 reflections collected (index range: h −11/10, k 0/15, l 0/15), 2964 independent (R_{int} = 0·015), 2176 with $I \geq 2\sigma(I)$ observed. Direct methods with *SHELX76* (Sheldrick, 1976), block-matrix anisotropic least squares, H atoms found in difference Fourier maps and refined isotropically, $\sum w\Delta F^2$ minimized, unit weights for compound (I), weighting scheme $w = 1/(\sigma^2 F + 0{\cdot}01548F^2)$ for compound (II), five reflections for compound (I) and seven for compound (II) omitted because probably affected by extinction, $\Delta\rho_{\text{max}}$ 0·21 and 0·18 e Å^{-3} for (I) and (II) respectively, final refinements converged to R = 0·049 and S = 0·78 for compound (I) and to R = 0·060, wR = 0·068 and S = 0·66 for (II), maximum shifts/e.s.d. 0·55 and 0·86. Atomic scattering factors of *SHELX76*.*

All calculations performed on an IBM PS2/80 personal computer with the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1987).

Table 1. *Atomic fractional coordinates* (× 10^4) *and* U_{eq} *values* (× 10^4 Å^2) (*Hamilton*, 1959) *for compound* (I)

	x	y	z	U_{eq}
O1	1825 (1)	−80 (4)	3606 (2)	573 (7)
C1	4363 (1)	−413 (5)	2877 (2)	424 (9)
C2	4573 (1)	−530 (5)	1585 (2)	433 (8)
C3	5072 (1)	−2332 (6)	1678 (3)	523 (11)
C4	5610 (2)	−1431 (8)	2438 (4)	632 (14)
C5	5385 (2)	−1620 (8)	3670 (3)	632 (14)
C6	4719 (1)	−2403 (6)	3449 (3)	505 (10)
C7	4797 (2)	−4096 (6)	2471 (3)	547 (11)
C8	3688 (1)	−367 (5)	3065 (2)	392 (8)
C9	3286 (1)	−2124 (5)	2757 (2)	452 (10)
C10	2673 (1)	−1984 (5)	2952 (2)	466 (9)
C11	2441 (1)	−67 (5)	3469 (2)	428 (9)
C12	2829 (1)	1670 (5)	3795 (2)	468 (10)
C13	3443 (1)	1502 (5)	3594 (2)	439 (9)
C14	1561 (2)	1928 (8)	4036 (3)	646 (14)
C15	4067 (1)	−916 (5)	679 (2)	434 (8)
C16	4006 (1)	−2906 (5)	55 (2)	544 (11)
C17	3525 (2)	−3195 (6)	−743 (3)	626 (12)
C18	3096 (2)	−1536 (6)	−933 (3)	635 (11)
C19	3156 (1)	481 (6)	−332 (3)	591 (11)
C20	3638 (1)	765 (5)	463 (2)	509 (10)

Table 2. *Atomic fractional coordinates* (× 10^4) *and* U_{eq} *values* (× 10^4 Å^2) (*Hamilton*, 1959) *for compound* (II)

	x	y	z	U_{eq}
O1	3195 (3)	4821 (1)	8384 (1)	901 (7)
O2	4432 (2)	5671 (1)	7297 (2)	925 (8)
N1	3750 (2)	4902 (1)	7553 (2)	650 (6)
C1	3210 (2)	1497 (2)	4769 (2)	534 (6)
C2	1712 (2)	1441 (2)	4098 (2)	554 (6)
C3	2263 (2)	1422 (2)	2991 (2)	643 (8)
C4	2859 (3)	343 (3)	2784 (3)	826 (10)
C5	4260 (3)	296 (2)	3502 (2)	834 (10)
C6	4359 (2)	1396 (2)	3946 (2)	641 (7)
C7	3691 (2)	2044 (2)	3072 (2)	667 (8)
C8	3376 (2)	2414 (1)	5473 (1)	494 (5)
C9	2643 (2)	2405 (2)	6388 (2)	591 (6)
C10	2756 (2)	3210 (2)	7077 (2)	613 (7)
C11	3608 (2)	4042 (2)	6837 (1)	524 (6)
C12	4363 (2)	4074 (2)	5951 (2)	589 (7)
C13	4246 (2)	3263 (2)	5274 (2)	582 (6)
C15	567 (2)	2238 (1)	4322 (1)	552 (5)
C16	541 (2)	3206 (2)	3887 (2)	723 (7)
C17	−535 (3)	3917 (2)	4115 (2)	870 (9)
C18	−1628 (3)	3653 (2)	4762 (2)	871 (9)
C19	−1629 (2)	2693 (2)	5188 (2)	798 (8)
C20	−544 (2)	1990 (2)	4974 (2)	665 (7)

Discussion. Final atomic fractional coordinates are listed in Tables 1 and 2 for compounds (I) and (II) respectively. Bond distances and bond angles are in Table 3. Projections of the molecules with arbitrary numbering schemes are in Figs. 1 and 2.

The geometry of the norbornane moieties is consistent with that reported in other norbornanes. In particular, as observed in other norbornane derivatives [95·55 (30)°: Albinati, Zocchi, Germain & Declercq, 1973; 94·3 (4) and 94·5 (5)°: Moews, Knox & Vaughan, 1978; 94·11 (42)°: Baker & Wood, 1978; 94·4 (4) and 96·6 (4)°: Bocelli, 1984; 96·2 (3), 96·6 (2) and 96·7 (2)°: Gallucci, Kravetz, Green & Paquette, 1985], the values of the C3—C7—C6 angles [94·1 (3) and 94·0 (2)°] are markedly different from the tetrahedral value. The norbornane skeleton is composed of two fused five-membered rings in envelope conformations or of a six-membered ring held in a boat conformation by a bridging methylene group. Following the Cremer & Pople (1975) notation the spherical polar set values for the six-membered rings are Q = 0·970 (4) Å, φ = −54·4 (2)°, θ = 88·9 (2)° for compound (I) and Q = 0·978 (3) Å, φ =

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* Lists of structure-factor amplitudes, hydrogen coordinates with isotropic thermal parameters, anisotropic thermal parameters of heavy atoms, bond distances and angles involving H atoms and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52255 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and angles* (°) *for compounds* (I) *and* (II)

	(I)	(II)		(I)	(II)
O1—C11	1·375 (3)		C6—C7	1·538 (5)	1·529 (4)
O1—C14	1·424 (5)		C8—C9	1·401 (4)	1·398 (3)
O1—N1		1·225 (3)	C8—C13	1·389 (4)	1·395 (4)
O2—N1		1·235 (2)	C9—C10	1·383 (3)	1·385 (4)
N1—C11		1·464 (3)	C10—C11	1·394 (4)	1·380 (3)
C1—C2	1·606 (3)	1·596 (3)	C11—C12	1·378 (4)	1·376 (3)
C1—C6	1·549 (4)	1·542 (3)	C12—C13	1·388 (3)	1·382 (4)
C1—C8	1·515 (3)	1·514 (3)	C15—C16	1·388 (4)	1·385 (3)
C2—C3	1·531 (4)	1·555 (4)	C15—C20	1·386 (4)	1·393 (3)
C2—C15	1·520 (3)	1·513 (3)	C16—C17	1·390 (5)	1·394 (4)
C3—C4	1·543 (5)	1·538 (5)	C17—C18	1·373 (6)	1·381 (4)
C3—C7	1·540 (5)	1·537 (3)	C18—C19	1·388 (5)	1·371 (4)
C4—C5	1·553 (6)	1·557 (4)	C19—C20	1·389 (4)	1·388 (3)
C5—C6	1·549 (5)	1·550 (4)			
C11—O1—C14	117·3 (3)		C1—C8—C13	119·0 (2)	123·8 (1)
O1—N1—O2		123·0 (2)	C1—C8—C9	124·2 (2)	118·4 (1)
O2—N1—C11		118·7 (1)	C9—C8—C13	116·7 (2)	117·7 (1)
O1—N1—C11		118·3 (1)	C8—C9—C10	121·6 (3)	121·8 (2)
C6—C1—C8	115·6 (2)	116·1 (1)	C9—C10—C11	120·1 (2)	118·4 (2)
C2—C1—C8	117·9 (2)	115·6 (1)	N1—C11—C10		119·5 (1)
C2—C1—C6	102·3 (2)	101·9 (1)	O1—C11—C10	115·6 (2)	
C1—C2—C15	115·5 (2)	116·5 (1)	C10—C11—C12	119·4 (2)	121·6 (2)
C1—C2—C3	101·6 (2)	102·1 (1)	N1—C11—C12		118·9 (2)
C3—C2—C15	116·5 (2)	116·5 (2)	O1—C11—C12	125·1 (2)	
C2—C3—C7	102·2 (2)	103·6 (2)	C11—C12—C13	119·8 (3)	119·3 (2)
C2—C3—C4	109·3 (3)	108·1 (2)	C8—C13—C12	122·4 (3)	121·2 (2)
C4—C3—C7	101·5 (2)	100·9 (1)	C2—C15—C20	119·4 (2)	119·2 (1)
C3—C4—C5	104·0 (3)	102·6 (2)	C2—C15—C16	123·0 (2)	123·1 (1)
C4—C5—C6	102·0 (3)	102·9 (2)	C16—C15—C20	117·6 (2)	117·6 (1)
C1—C6—C5	107·6 (3)	108·1 (1)	C15—C16—C17	120·7 (3)	121·2 (2)
C5—C6—C7	100·4 (3)	102·5 (2)	C16—C17—C18	121·2 (3)	120·1 (2)
C1—C6—C7	104·1 (3)	102·3 (1)	C17—C18—C19	118·9 (4)	119·4 (2)
C3—C7—C6	94·1 (3)	94·0 (1)	C18—C19—C20	119·7 (3)	120·6 (2)
			C15—C20—C19	121·9 (3)	121·1 (2)

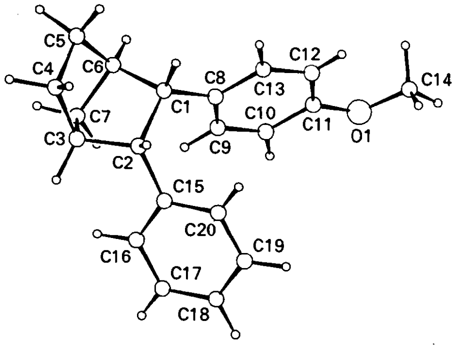

Fig. 1. Projection of compound (I).

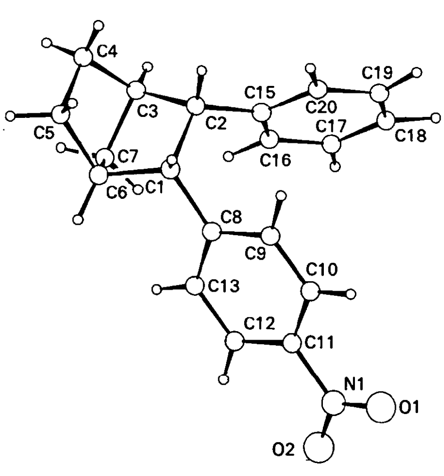

Fig. 2. Projection of compound (II).

115·0 (2)°, $\theta = 90{\cdot}0\,(2)°$ for (II). These values are very near to those corresponding to an ideal boat conformation ($\theta = 90°$, $\varphi = 120°$). The dihedral angles between the planar fragments C3,C2,C1,C6 (*A*), C3,C7,C6 (*B*) and C3,C4,C5,C6 (*C*) are 125·1 (3), 122·4 (3), 112·4 (2)° and 124·6 (2), 123·9 (2), 111·5 (1)° for *A–B*, *B–C* and *A–C* in compounds (I) and (II) respectively. These values are comparable with those [121·1 (5), 125·0 (5), 113·9 (6)°] determined by Kashyap, Watson, Wu & Bartlett (1984) for a similar derivative. The deformations in the six-membered rings induced by the different substituents and by the methylene bridge with respect to the ideal values reported for a boat conformation (Bucourt, 1974) show some differences in the two derivatives. These differences reverberate on the internal torsion angles which, in going from C1 to C6 in numerical sequence, are −7·4 (3), −65·9 (3), 75·9 (4), −5·1 (4), −68·5 (3) and 77·2 (3)° for compound (I) and −5·2 (2), 75·8 (3), −68·6 (3), −5·3 (3), 76·4 (3) and −68·1 (2)° for (II).

The benzene rings, which occupy equatorial positions in both compounds, are planar with only slight deviations from planarity and form dihedral angles of 43·4 (1) and 51·8 (1)° to each other in compounds (I) and (II) respectively. The methoxy and nitro groups are tilted by 5·5 (2) and 6·3 (2)° with respect to their aromatic rings.

In the crystals the molecules of compound (I) are joined together by van der Waals forces only; short contacts of compound (II) are: $H9\cdots O1^{i} = 2{\cdot}53\,(3)$, $C9\cdots O1^{i} = 3{\cdot}473\,(3)$ Å, $C9—H9\cdots O1^{i} = 151\,(2)°$; $H9\cdots O2^{i} = 2{\cdot}51\,(3)$, $C9\cdots O2^{i} = 3{\cdot}459\,(3)$ Å, $C9—H9\cdots O2^{i} = 151\,(2)°$ [(i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$].

Thanks are due to Professor G. P. Chiusoli for supplying the crystals.

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Structure of a Pyridyl-Containing Macrobicyclic Molecule, Potential Transition-Metal Complexing Agent and NADH Model Precursor

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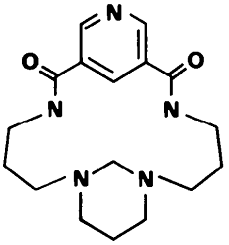
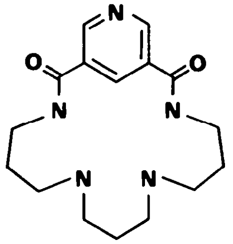
Abstract. $C_{17}H_{25}N_5O_2$, 1,5,9,13,17-pentaazatricyclo[15.3.1.$1^{7,11}$]docosa-7,9,11-triene-6,12-dione, M_r = 331·42, orthorhombic, $Pbn2_1$, a = 10·734 (9), b = 20·806 (10), c = 7·625 (6) Å, V = 1703 (4) Å^3, Z = 4, D_x = 1·293 Mg m^{-3}, Mo $K\bar{\alpha}$, λ = 0·7107 Å, μ = 0·095 mm^{-1}, $F(000)$ = 712, T = 294 K, final R = 0·055 for 2702 reflections. The molecule defines a macrocyclic cavity with convergent amine N-atom lone pairs and amide H atoms. The hexahydropyrimidine ring is in a chair conformation and is roughly perpendicular to the main plane defined by the tetraazamacrocycle. The pyridine ring makes an angle of 21·7° to the macrocyclic plane. The molecule provides a well organized cavity for potential metal-ion recognition.

Introduction. Within the past decade, the chemistry of macrocyclic ring systems has developed rapidly, particularly related to host–guest chemistry which mimics biological complexation (Melson, 1979; Lehn, 1988). As part of our efforts to design and synthesize NADH models, we have focused our work on pyridyl-containing polyazamacrocycles (Dutasta, Gellon, Leuchter & Pierre, 1988). Some have a polycyclic structure as depicted below. (1) is the prototype of a new series of polyazamacrocyclic structures for which the conformation and the molecular shape are of great interest; the macrocyclic cavity must be defined in order to estimate its complexing properties toward metal ions. In this paper we describe the X-ray crystal structure of the pyridyl-containing tetraazamacrobicyclic molecule (1). The hexahydropyrimidine ring introduces rigidity compared to the parent compound (2), and imposes a well defined conformation. In solution at room temperature, the ^{1}H and ^{13}C NMR spectra are in agreement with the existence of one preferred rigid conformer.



(1)



(2)

Experimental. The synthesis and the characterization of the macrocyclic molecule (1) is described elsewhere (Dutasta *et al.*, 1988). Crystal size: 0·25 × 0·32 × 0·20 mm. Density not measured. Nonius CAD-4 diffractometer, graphite monochromator. 25 reflections (10·0 < θ < 16·3°) for refining unit-cell dimensions. ω scan, scan width: 1·20°, scan speed variable between 0·02 and 0·04° s^{-1}, total background measuring time: between 28 and 57 s. 3390 reflections collected; 3 < θ < 30°; h, k, l; h max. = 17, k max. = 33, l max. = 12. Existence conditions: $h0l$ ($h + l = 2n$), $0kl$ ($k = 2n$). Two orientation ($\bar{2}$,16,0 and 2,16,0) and two intensity ($\bar{5}31$ and $\bar{2}$,$\overline{16}$,0) control reflections with no significant variation. Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN77*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977). H atoms located by difference-Fourier synthesis. Anisotropic full-matrix least-squares refinements (on F),

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