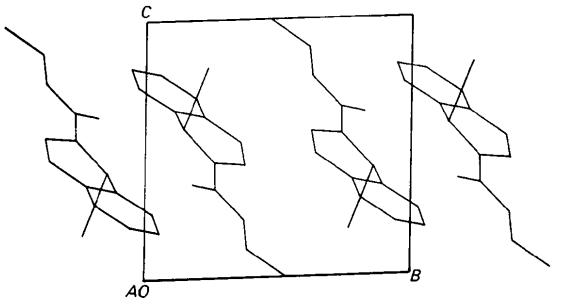

Fig. 2. Projection of the structure down **a**.

a consequence of steric hindrance between O(14) and H(C3) in the other possible rotational isomer. In a molecule with a bulky dimethoxybenzoyl substitutent at C(1) (Pavkovic, Glowinski, Feng & Brown, 1981) the carbonyl group is oriented *syn* relative to the N(2)–C(3) bond, indicating that the disposition of the C(3)–O(14) bond is a compromise between steric interactions with the neighboring substituents at C(1) and C(3).

The heterocyclic ring has a sofa conformation in (I), a 1,3-diplanar form in (II) and a half-chair form in (III). In the present compound (IV) it is intermediate between 1,3-diplanar and sofa conformations. Asymmetry parameters (Duax & Norton, 1975) $\Delta C_2^{1,2} = 7{\cdot}99$ and $\Delta C_s^1 = 7{\cdot}02$ indicate better consistency with the sofa conformation.

Fig. 2 presents the molecular packing of (IV) in the unit cell. In the racemic structure two chiral molecules [asymmetric C(1)] across the inversion center $(00\frac{1}{2})$ are joined by a weak C(1)–H(11)···O(14) hydrogen bond. The H(11)···O(14) distance equals 2·33 (2) Å and according to Taylor & Kennard (1982) can be considered as a hydrogen bond. All other contacts are in the ranges of the van der Waals distances.

The authors are indebted to Doc. Dr M. Rozwadowska and Dr D. Brózda for providing a sample of the compound.

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Structure of N^2-(*p*-Methoxyphenyl)-N^1,N^1-pentamethylenebenzamidine

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(*Received* 30 *September* 1985; *accepted* 2 *January* 1986)

Abstract. 4-Methoxy-*N*-(α-piperidinobenzylidene)-aniline, $C_{19}H_{22}N_2O$, $M_r = 294{\cdot}40$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}525$ (1), $b = 19{\cdot}680$ (2), $c = 8{\cdot}757$ (1) Å, $V = 1641{\cdot}4$ (3) Å^3, $Z = 4$, $D_m = 1{\cdot}18$, $D_x = 1{\cdot}19$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 5{\cdot}05$ cm^{-1}, $F(000) = 632$, room temperature, $R = 0{\cdot}047$ for 1189 observed reflexions. The benzamidine phenyl ring and the methoxyphenyl fragment (both approximately planar) are twisted with respect to the central amidine plane by 61·6 (4) and 54·6 (3)°, respectively. The piperidine ring is in a chair conformation. The C–N^1 and C–N^2 bonds are different [1·283 (5) and 1·372 (5) Å, respectively].

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Introduction. The present structural study is the second of a series of investigations on amidines carried out in this laboratory. The title compound was synthetized and characterized by Oszczapowicz, Raczyńska & Pawlik (1984). This structure investigation has been undertaken to determine the effect of the substituents on the amidine group. Our aim was also to compare the dispositions of the side fragments relative to the central amidine group and their dependence on the character and dimensions of those fragments.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
N(1)	0·3130 (3)	0·2534 (1)	0·6949 (4)	0·048 (1)
C(2)	0·1990 (4)	0·2196 (2)	0·7125 (5)	0·045 (1)
N(3)	0·1967 (3)	0·1517 (1)	0·6765 (4)	0·047 (1)
C(4)	0·1046 (4)	0·1032 (2)	0·7552 (5)	0·053 (1)
C(5)	0·0599 (5)	0·0480 (2)	0·6440 (6)	0·062 (2)
C(6)	0·1836 (5)	0·0137 (2)	0·5713 (6)	0·068 (2)
C(7)	0·2820 (5)	0·0658 (2)	0·4998 (6)	0·065 (2)
C(8)	0·3234 (5)	0·1202 (2)	0·6126 (5)	0·056 (2)
C(9)	0·0627 (4)	0·2497 (2)	0·7660 (5)	0·043 (1)
C(10)	0·0566 (4)	0·2858 (2)	0·9004 (5)	0·048 (1)
C(11)	−0·0674 (5)	0·3148 (2)	0·9485 (5)	0·060 (2)
C(12)	−0·1867 (5)	0·3091 (2)	0·8601 (6)	0·062 (2)
C(13)	−0·1830 (5)	0·2733 (2)	0·7238 (6)	0·062 (2)
C(14)	−0·0578 (5)	0·2436 (2)	0·6773 (5)	0·053 (2)
C(15)	0·3172 (4)	0·3251 (2)	0·7085 (5)	0·048 (1)
C(16)	0·2382 (4)	0·3692 (2)	0·6196 (5)	0·052 (1)
C(17)	0·2553 (5)	0·4391 (2)	0·6309 (5)	0·053 (2)
C(18)	0·3531 (4)	0·4654 (2)	0·7297 (6)	0·055 (2)
C(19)	0·4328 (5)	0·4220 (2)	0·8206 (6)	0·062 (2)
C(20)	0·4157 (4)	0·3531 (2)	0·8075 (5)	0·058 (2)
O(21)	0·3807 (3)	0·5340 (1)	0·7514 (5)	0·070 (1)
C(22)	0·3042 (6)	0·5806 (2)	0·6610 (8)	0·079 (2)

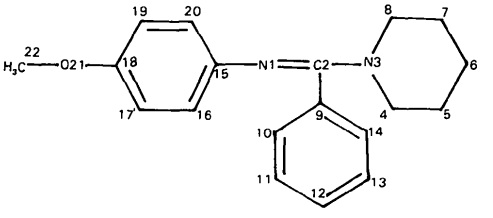
Table 2. *Bond lengths* (Å) *and angles* (°)

N(1)–C(2)	1·283 (5)	C(12)–C(13)	1·387 (7)
C(2)–N(3)	1·372 (5)	C(13)–C(14)	1·389 (6)
N(3)–C(4)	1·468 (5)	C(14)–C(9)	1·391 (6)
C(4)–C(5)	1·520 (6)	N(1)–C(15)	1·416 (5)
C(5)–C(6)	1·500 (7)	C(15)–C(16)	1·388 (6)
C(6)–C(7)	1·523 (7)	C(16)–C(17)	1·390 (6)
C(7)–C(8)	1·509 (6)	C(17)–C(18)	1·372 (6)
C(8)–N(3)	1·467 (5)	C(18)–C(19)	1·393 (6)
C(2)–C(9)	1·502 (6)	C(19)–C(20)	1·369 (6)
C(9)–C(10)	1·376 (6)	C(20)–C(15)	1·391 (6)
C(10)–C(11)	1·377 (6)	C(18)–O(21)	1·388 (5)
C(11)–C(12)	1·379 (7)	O(21)–C(22)	1·415 (7)
N(1)–C(2)–N(3)	119·4 (3)	C(13)–C(14)–C(9)	120·4 (4)
C(2)–N(3)–C(4)	122·3 (3)	C(14)–C(9)–C(10)	119·2 (3)
N(3)–C(4)–C(5)	109·3 (3)	N(1)–C(2)–C(9)	124·4 (3)
C(4)–C(5)–C(6)	112·0 (3)	C(2)–N(1)–C(15)	122·0 (3)
C(5)–C(6)–C(7)	110·8 (4)	N(1)–C(15)–C(16)	124·1 (3)
C(6)–C(7)–C(8)	111·7 (4)	C(15)–C(16)–C(17)	121·1 (3)
C(7)–C(8)–N(3)	109·6 (3)	C(16)–C(17)–C(18)	119·9 (4)
C(8)–N(3)–C(4)	113·3 (3)	C(17)–C(18)–C(19)	119·9 (4)
C(8)–N(3)–C(2)	119·1 (3)	C(18)–C(19)–C(20)	119·6 (4)
N(3)–C(2)–C(9)	116·2 (3)	C(19)–C(20)–C(15)	121·7 (4)
C(2)–C(9)–C(10)	120·4 (3)	C(20)–C(15)–N(1)	117·9 (3)
C(9)–C(10)–C(11)	120·7 (4)	C(17)–C(18)–O(21)	125·6 (3)
C(10)–C(11)–C(12)	120·1 (4)	C(19)–C(18)–O(21)	114·5 (3)
C(11)–C(12)–C(13)	120·2 (4)	C(18)–O(21)–C(22)	117·2 (3)
C(12)–C(13)–C(14)	119·2 (4)		

Experimental. Crystals obtained from ethanol, prisms. Crystal 0·30 × 0·30 × 0·35 mm. D_m by flotation. Syntex $P2_1$ diffractometer, θ–2θ scan. Cell parameters from least-squares treatment of setting angles of 15 reflexions with $20 < 2\theta < 30°$. No absorption or extinction correction. Profile analysis according to Lehmann & Larsen (1974). Max. $\sin\theta/\lambda = 0{\cdot}547$ Å^{-1}, 1302 reflexions measured in range h: 0–10, k: 0–21, l: 0–9. No significant intensity variation for two standard reflexions recorded every 1·5 h. 1195 observed reflexions with $I \geq 2\sigma(I)$. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement on F, $w^{-1} = \sigma^2(F)$, 10 H atoms located in $\Delta\rho$ map, remaining determined geometrically. H atoms included with fixed isotropic thermal parameters in F_c, 6 extinction-affected reflexions excluded from final refinement; anisotropic thermal parameters for non-H atoms. $R = 0{\cdot}047$, $wR = 0{\cdot}054$, $S = 7{\cdot}7$; $(\Delta/\sigma)_{max} = 0{\cdot}13$; $(\Delta\rho)_{max} = 0{\cdot}14$, $(\Delta\rho)_{min} = -0{\cdot}19$ e Å^{-3}. Computer programs: *MULTAN*80 (Main *et al.*, 1980), *SHELX*76 (Sheldrick, 1976) and local programs (Jaskólski, 1982). Molecular illustrations drawn using *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1976). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed on an R-32 computer.

Discussion. Atomic coordinates and bond lengths and angles are given in Tables 1 and 2, respectively.*

The labelling sequence is shown in the formula below, and the stereoscopic view of the molecule is presented in Fig. 1. The values of bond lengths and angles as well as the endocyclic torsion angles in the piperidine ring are comparable with the values found in N^2-(*m*-chlorophenyl)-N^1,N^1-pentamethylenebenzamidine (Tykarska, Jaskólski & Kosturkiewicz, 1986) and are typical of a chair conformation. The mean of the endocyclic torsion angles of the piperidine ring is 56 (1)°. The C(9)–C(14) and C(15)–C(20) phenyl rings are planar, $\chi^2 = 5{\cdot}45$ and 8·00, respectively. The



* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42749 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

methoxy group is in the plane of the phenyl ring, the displacements of O(21) and C(22) are not significant. The C(17)–C(18)–O(21)–C(22) torsion angle is −1·8 (5)°. The C(18)–O(21) bond [1·388 (5) Å] is slightly longer than that [1·372 (3) Å] found by Cameron, Freer & Gilmore (1981) or those (1·362–1·376 Å) found by Pavkovic, Glowinski & Feng (1981) in other methoxyphenyl groups. The amidine group is planar, $\chi^2 = 9{\cdot}90$. The sum of the valence angles around N(3) is 354·7 (5)° which indicates a pronounced pyramidalization of this atom and a significant deviation from the sp^2 state. The N(1)–C(2) and C(2)–N(3) bonds differ more than in N^2-(*m*-chlorophenyl)-N^1,N^1-pentamethylenebenzamidine [1·209 (6) and 1·365 (6) Å] (Tykarska *et al.*, 1986) and in acetamidine [1·298 (1) and 1·334 (1) Å] (Norrestam, Mertz & Crossland, 1983). The C(2)–N(3) bond in the present structure [1·372 (5) Å] is intermediate between a single and double bond, while N(1)–C(2) [1·283 (5) Å] has a predominant double-bond character. The C(15)–N(1)–C(2)–N(3) torsion angle [170·6 (4)°] confirms that N(1)–C(2) is not a pure double bond. The N(1)–C(2)–N(3) angle [119·4 (3)°] is similar to that found in the above-cited chlorobenzamidine derivative, but it deviates considerably from the values reported for acetamidine [125·5 (1)°] by Norrestam, Mertz & Crossland (1983), for acetamidine complexes [121·9 (2)°] (Norrestam, 1985) and for N^1-hexylene-N^2-(*p*-nitrophenyl)-formamidine [122·1 (4)°] (Krajewski *et al.*, 1981). The torsion angle N(1)–C(2)–N(3)–C(4) is 149·9 (4)°. The mean plane through the piperidine ring is twisted by 22 (1)° with respect to the amidine group. The situation is different from that in N^1,N^1-(1,5-dimethylpentamethylene)-N^2-phenylacetamidine (Gilli & Bertolasi, 1979) where the amidine group and the mean plane through the piperidine ring are coplanar. Owing to the partial double-bond character of the C(2)–N(3) bond the C(4) and C(8) atoms tend to lie in the amidine plane but overcrowding in the present molecule makes it impossible. This is justified by the non-bonded contacts the piperidine moiety makes with the other parts of the molecule, *e.g.* C(2)···H(41) = 2·66 (4), C(2)···H(81) = 2·57 (4), C(9)···H(41) = 2·47 (4) and C(14)···H(41) = 2·54 (4) Å.

The angles the amidine group makes with the planes of the phenyl ring [61·6 (4)°] and the methoxyphenyl ring [54·6 (3)°] reveal the lack of conjugation between the amidine and aromatic fragments. The non-bonded intramolecular contacts N(1)···H(161) = 2·63 (4), C(2)···H(141) = 2·71 (5), N(3)···H(141) = 2·86 (4) and C(9)···H(161) = 2·84 (4) Å indicate the steric hindrance between the phenyl rings and the amidine group. The molecular packing is shown in Fig. 2. No intermolecular contacts significantly shorter than the sum of the van der Waals radii are observed.

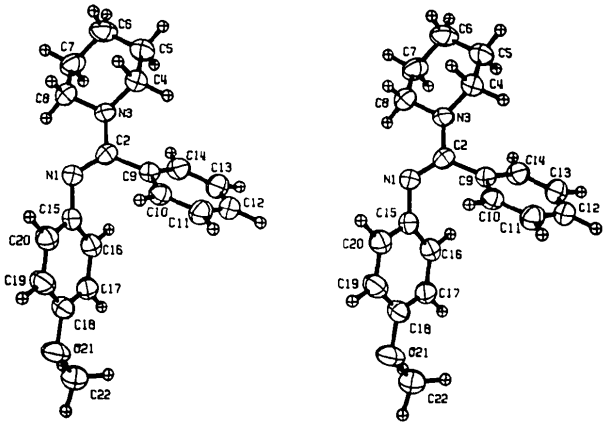


Fig. 1. Stereodrawing of the molecule (*ORTEP*; Johnson, 1976).

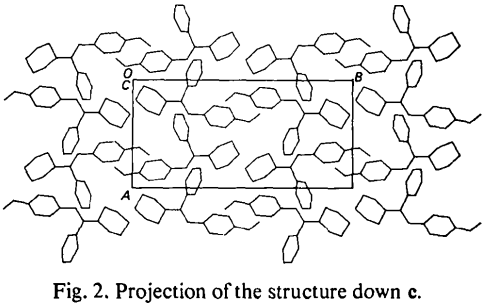


Fig. 2. Projection of the structure down c.

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Structure of (4*R**,4a*S**,8a*R**)-8a-Hydroxy-4-methylperhydrochroman-7-one, a Relay Material for Stereospecific Synthesis of β-Turmerone

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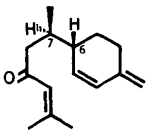
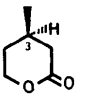
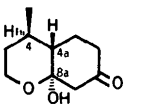
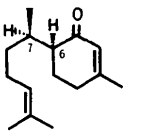
Abstract. $C_{10}H_{16}O_3$, $M_r = 184{\cdot}24$, monoclinic, $P2_1/c$, $a = 9{\cdot}778$ (6), $b = 8{\cdot}809$ (6), $c = 12{\cdot}189$ (6) Å, $\beta = 112{\cdot}10$ (5)°, $V = 973$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}258$ Mg m^{-3}, λ(Ag $K\alpha$) = 0·56083 Å, $\mu = 0{\cdot}06$ mm^{-1}, $F(000) = 400$, $T = 291$ (1) K. Final $R = 0{\cdot}056$ for 1436 unique observed reflexions. In the crystal two molecules are linked by two symmetrically equivalent hydrogen bonds [O···O 2·800 (2) Å, H···O 1·85 Å, ∠C–O–H 104°]. The two six-membered rings are both in similar chair conformations with corresponding parts of the two chairs coplanar. The 6*S*,7*R* configuration is unambiguously determined for (–)-β-turmerone.

Introduction. In 1982 B. T. Golding published some of his results regarding the constituents of turmeric, from the rhizomes of *Curcuma longa* (Golding, Pombo & Samuel, 1982). This material serves as part of the colour and odour component of various curry powders. That investigation *inter alia* led to the isolation and constitutional determination of β-turmerone (1) by careful and reliable assignment of the ^{1}H NMR spectrum. On the other hand, Golding's publication does not disclose anything about the relative and absolute configuration at the two adjacent chiral centres emerging from the structure of (1). Even its optical rotation is lacking, since the natural material was difficult to separate. When we decided to solve the question of stereochemistry in (1), a rule was originally applied, which we had found to work perfectly well with the 1-bisabolone class [*i.e.* (4); Bohlmann, Zdero & Schöneweiss, 1976], to establish the relative configuration by NMR; however, this method failed on turmerone (Preut, Kreiser, Müller & Jones, 1985). Apparently this failure was due to the fact that the ring keto group – with its dominant influence on the chemical shift of the secondary methyl signal – was lacking in (1). The corresponding shift value of (1) did not fit in either diastereomeric series. We therefore decided to prove the relative and absolute configuration of (1) by total synthesis.


(–)-(1)


(+)-(2)


rac-(3)


(+)-(4) (synthetic enantiomer)

Starting with optically active (+)-3-methyl-δ-valerolactone (2) of known absolute configuration (Jones, 1984), we passed two crystalline intermediates during this first preparation of (1). One of them proved unsuitable for X-ray examination. The second substance (3) displayed three asymmetric centres, of which the acetal chirality at C(8a) was destroyed later on during the course of the highly stereospecific synthesis. This material showed a melting point of 399 K. (For practical purposes the racemate was preferred for measurement.) In formula (3) the relative stereochemistry is already properly assigned according to the result of the X-ray determination. Since the centres C(4 and 4a) remain untouched until the final stage, they represent the conclusive arrangement of C(6 and 7) in (–)-β-turmerone (1). [The final product of a reaction sequence, which includes (3) as an intermediate, was shown to be identical to β-turmerone by ^{1}H

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