significance level. Hence the hypothesis that the structure is described by the alternative enantiomorph was rejected at the 0·005 significance level. The main result of the present study is that the conformation of the alcohol is unambiguously determined to be that of (IV), as indicated in Fig. 1. Such information is an invaluable help in understanding the reaction mechanism involving this substance.

O(1) of one molecule is hydrogen bonded to O(1) of the other independent one, which in turn is hydrogen bonded to the O(1) related to the first one by the twofold screw axis, giving rise to an infinite helical arrangement of hydrogen bonds around the symmetry axis $|O(1)\cdots O(1') = 2\cdot79$ (2), $2\cdot80$ (2) Å; $O(1)-H(O1) = 0\cdot97$ (2), $0\cdot95$ (2) Å; $H(O1)\cdots O(1') = 1\cdot94$ (2), $1\cdot89$ (2) Å; $O(1)-H(O1)\cdots O(1') = 146$ (1), 159 (1)° |.

References

BROCKSOM, T. J., CANEVAROLO, E. T. & LOPES, F. T. (1985). To be published.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KABSCH, W. (1976). *Acta Cryst.* **A32**, 922–923.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SYDNES, L. & SKATTEBØL, L. (1975). *Tetrahedron Lett.* pp. 4603–4606.

ZUKERMAN-SCHPECTOR, J., CASTELLANO, E. E., OLIVA, G., BROCKSOM, T. J. & CANEVAROLO, E. T. (1984). *Can. J. Chem.* **62**, 570–573.

Structure of N^2-(m-Chlorophenyl)-N^1,N^1-pentamethylenebenzamidine

BY E. TYKARSKA, M. JASKÓLSKI AND Z. KOSTURKIEWICZ*

Department of Crystallography, Faculty of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland

Abstract. 3-Chloro-N-(α-piperidinobenzylidene)aniline, $C_{18}H_{19}ClN_2$, $M_r = 298\cdot82$, orthorhombic, $P2_12_12_1$, $a = 10\cdot096$ (1), $b = 17\cdot128$ (2), $c = 9\cdot220$ (1) Å, $V = 1594\cdot4$ (3) Å^3, $Z = 4$, $D_m = 1\cdot25$, $D_x = 1\cdot24$ Mg m^{-3}, $\lambda(Cu\,K\alpha) = 1\cdot57178$ Å, $\mu = 2\cdot06$ mm^{-1}, $F(000) = 632$, room temperature, $R = 0\cdot044$ for 1090 observed reflexions. The N=C(—C)—N amidine group is planar ($\chi^2 = 5\cdot02$). The C—N_{imine} and C—N_{amine} bond lengths are different, 1·290 (6) and 1·365 (6) Å, respectively. The phenyl ring is twisted by 60·2° and the m-chlorophenyl ring by 59·7° relative to the amidine plane, indicating there is no conjugation between the amidine and aromatic fragments.

Introduction. Compounds based on the amidine skeleton possess anaesthetic properties and are used in medicine for blocking nervous conduction. The title compound was synthetized and characterized by spectroscopic methods by Oszczapowicz, Raczyńska & Pawlik (1984). The present X-ray crystal structure analysis has been undertaken in order to reveal the details of the geometry of the benzamidine molecule. Our aim is to compare how the disposition of the side fragments relative to the central amidine group depends on the character and dimensions of those fragments. So far, no structural data have been reported for benzamidine derivatives. Benzamidines are based on a formamidine skeleton, $-N_I=C_F N_A<$, with the H atom substituted by a phenyl group. N_{imine} and N_{amine} are formally different. Nevertheless, X-ray and IR spectroscopic investigations of formamidines (Krajewski *et al.*, 1981) and acetamidines (Norrestam, Mertz & Crossland, 1983; Norrestam, 1984) show that the amidine group is planar with both nitrogen atoms having sp^2 hybridization. It is of interest to investigate the changes

---

* To whom correspondence should be addressed.

brought about when the hydrogen is substituted by a phenyl ring. In particular, we would like to answer the questions about the amount of equalization of the N—C bonds, the degree of conjugation between the amidine and phenyl groups, and the overall conformation of the benzamidine molecule.

Experimental. Suitable crystals obtained from ethanol; D_m by flotation; approximate unit-cell dimensions and space group from oscillation and Weissenberg photographs; crystal $0.33 \times 0.33 \times 0.22$ mm, Syntex $P2_1$ diffractometer, Cu $K\alpha$ radiation, graphite monochromator; precise cell parameters from least-squares treatment of setting angles of 15 reflexions; max. $\sin\theta/\lambda = 0.547$ Å^{-1}; profiles measured for 1250 independent reflexions with $2\theta \leq 115°$, h:0–11, k:0–18, l: 0–10; profile analysis according to Lehmann & Larsen (1974); no significant intensity variation for two standard reflexions monitored every 1·5 h; no absorption correction; 1094 observed reflexions with $I \geq 1.96\sigma(I)$; structure solved by direct methods using *MULTAN*80; full-matrix least-squares refinement on F, $w^{-1} = \sigma^2(F)$; H atoms (from molecular geometry) included as fixed isotropic contribution to F_c; positional and anisotropic thermal parameters for non-H atoms refined in final cycles; 4 extinction-affected reflexions excluded from final refinement; $R = 0.044$, $wR = 0.048$, $S = 5.3$, $(\Delta/\sigma)_{max} = 0.005$, max. and min. $\Delta\rho$ in final difference Fourier map $+0.13$ and -0.18 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 a stereoscopic view of the molecule is presented in Fig. 1.
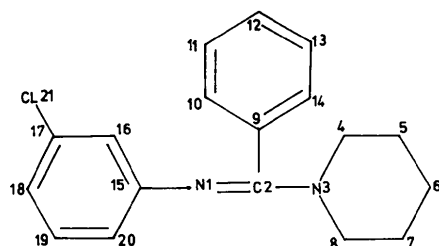
* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42548 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

$$U_{eq} = \Sigma_i \Sigma_k U_{ik} a_i^* a_k^* (\mathbf{a}_i . \mathbf{a}_k).$$

	x	y	z	U_{eq}
N(1)	0·4445 (4)	0·1271 (2)	0·3824 (4)	0·058
C(2)	0·5596 (5)	0·1374 (2)	0·4399 (5)	0·047
N(3)	0·5680 (4)	0·1796 (2)	0·5652 (4)	0·059
C(4)	0·6903 (5)	0·2120 (3)	0·6268 (6)	0·056
C(5)	0·6989 (5)	0·1911 (3)	0·7860 (7)	0·073
C(6)	0·5740 (7)	0·2188 (4)	0·8668 (6)	0·094
C(7)	0·4498 (6)	0·1880 (3)	0·7963 (6)	0·075
C(8)	0·4476 (6)	0·2086 (3)	0·6365 (6)	0·066
C(9)	0·6861 (4)	0·1075 (2)	0·3760 (6)	0·047
C(10)	0·7216 (5)	0·1312 (3)	0·2365 (5)	0·057
C(11)	0·8380 (6)	0·1033 (3)	0·1752 (6)	0·072
C(12)	0·9162 (5)	0·0521 (3)	0·2501 (8)	0·080
C(13)	0·8815 (5)	0·0278 (3)	0·3873 (8)	0·072
C(14)	0·7670 (5)	0·0558 (3)	0·4510 (6)	0·057
C(15)	0·4185 (4)	0·0709 (3)	0·2755 (5)	0·053
C(16)	0·4527 (4)	−0·0067 (3)	0·2896 (5)	0·052
C(17)	0·4044 (5)	−0·0602 (3)	0·1895 (6)	0·059
C(18)	0·3246 (5)	−0·0391 (4)	0·0745 (6)	0·072
C(19)	0·2936 (5)	0·0392 (4)	0·0615 (6)	0·072
C(20)	0·3385 (5)	0·0931 (3)	0·1584 (6)	0·068
Cl(21)	0·4460 (2)	−0·15871 (8)	0·2112 (2)	0·096

Table 2. *Bond lengths* (Å) *and angles* (°) *and torsion angles* (°) *determining molecular conformation*

N(1)–C(2)	1·290 (6)	C(12)–C(13)	1·377 (10)
C(2)–N(3)	1·365 (6)	C(13)–C(14)	1·383 (8)
N(3)–C(4)	1·468 (7)	C(14)–C(9)	1·389 (7)
C(4)–C(5)	1·514 (8)	N(1)–C(15)	1·402 (6)
C(5)–C(6)	1·539 (9)	C(15)–C(16)	1·380 (7)
C(6)–C(7)	1·508 (9)	C(16)–C(17)	1·389 (7)
C(7)–C(8)	1·515 (8)	C(17)–C(18)	1·380 (8)
C(8)–N(3)	1·468 (7)	C(18)–C(19)	1·382 (9)
C(2)–C(9)	1·497 (7)	C(19)–C(20)	1·363 (8)
C(9)–C(10)	1·395 (7)	C(20)–C(15)	1·401 (7)
C(10)–C(11)	1·389 (8)	Cl(21)–C(17)	1·751 (5)
C(11)–C(12)	1·367 (8)		

N(1)–C(2)–N(3)	118·4 (4)	C(12)–C(13)–C(14)	119·9 (5)
C(2)–N(3)–C(4)	125·4 (4)	C(13)–C(14)–C(9)	120·1 (4)
N(3)–C(4)–C(5)	109·5 (4)	C(2)–C(9)–C(14)	121·6 (4)
C(4)–C(5)–C(6)	110·4 (4)	C(2)–N(1)–C(15)	123·5 (3)
C(5)–C(6)–C(7)	111·4 (5)	N(1)–C(15)–C(16)	123·3 (4)
C(6)–C(7)–C(8)	110·5 (4)	C(15)–C(16)–C(17)	119·0 (4)
C(7)–C(8)–N(3)	110·2 (4)	C(16)–C(17)–C(18)	122·9 (4)
N(3)–C(2)–C(9)	117·5 (4)	C(17)–C(18)–C(19)	116·9 (5)
C(2)–C(9)–C(10)	118·8 (4)	C(18)–C(19)–C(20)	121·7 (5)
C(9)–C(10)–C(11)	119·4 (4)	C(19)–C(20)–C(15)	120·9 (4)
C(10)–C(11)–C(12)	120·3 (5)	C(16)–C(17)–Cl(21)	118·4 (3)
C(11)–C(12)–C(13)	120·7 (5)	C(18)–C(17)–Cl(21)	118·7 (4)

C(15)–N(1)–C(2)–N(3)	−164·5 (5)
C(15)–N(1)–C(2)–C(9)	17·0 (5)
C(16)–C(15)–N(1)–C(2)	51·3 (5)
C(2)–N(1)–C(15)–C(20)	−137·4 (5)
N(1)–C(2)–N(3)–C(4)	−165·2 (5)
N(1)–C(2)–N(3)–C(8)	3·5 (5)
N(1)–C(2)–C(9)–C(10)	58·6 (6)
N(1)–C(2)–C(9)–C(14)	−120·1 (5)
C(2)–N(3)–C(4)–C(5)	−131·1 (5)
C(2)–N(3)–C(8)–C(7)	130·5 (5)
N(3)–C(4)–C(5)–C(6)	−55·4 (6)
C(4)–C(5)–C(6)–C(7)	54·2 (6)
C(5)–C(6)–C(7)–C(8)	−53·8 (6)
C(6)–C(7)–C(8)–N(3)	55·4 (6)
C(4)–N(3)–C(8)–C(7)	−59·5 (5)
C(5)–C(4)–N(3)–C(8)	59·5 (5)

The bond lengths and angles in the piperidine ring are comparable with previously reported values (Jaskólski, Gdaniec & Kosturkiewicz, 1977; Jaskólski, 1978). Torsion angles around the piperidine ring indicate that it has the chair conformation. The mean absolute value of the endocyclic torsion angles is 56·3 (6)°. Both phenyl rings are planar $[\chi^2 = 3·24$ for the C(9)–C(14) ring and 6·32 for the C(15)–C(20) ring]. The N(3) and C(15) atoms are *trans* relative to the N(1)–C(2) bond. Atoms N(1)C(2)N(3)C(9) form a plane $(\chi^2 = 5·02)$ with atoms C(4), C(8) and C(15) deviating from it by 0·298 (6), −0·053 (5) and −0·318 (5) Å, respectively. The atoms around N(3) form a very flat pyramid [sum of bond angles 359·2 (6)°], the distance of N(3) from the C(2)C(4)C(8) plane being 0·076 (4) Å. The torsion angles N(1)–C(2)–N(3)–C(8) [3·5 (5)°] and N(1)–C(2)–N(3)–C(4) [−165·2 (5)°] attest to the distortion of the *sp²* character of the amine N(3) atom. The N(1)–C(2) and C(2)–N(3) bonds show much more pronounced differentiation [1·290 (6) and 1·365 (6) Å, respectively] than in the substituted formamidine molecule [1·302 (6) and 1·334 (5) Å, respectively]

described by Krajewski *et al.* (1981). The present N(1)–C(2) bond has marked double-bond character. On the other hand, the torsion angle C(15)–N(1)–C(2)–N(3) [−164·5 (5)°] indicates that N(1)–C(2) is not a pure double bond. The N(1)–C(15) distance [1·402 (6) Å] is longer than the value of 1·387 (5) Å found in the above formamidine structure. The C(2)–C(9) distance [1·497 (7) Å] is in agreement with the value reported by Little & Morimoto (1981). The N(1)–C(2)–N(3) angle [118·4 (4)°] deviates considerably from the value reported in the above work [122·1 (4)°] and from the value found in acetamidine [125·5 (1)°] (Norrestam, Mertz & Crossland, 1983). The angles the amidine group makes with the phenyl ring (60·2°) and with the chlorophenyl ring (59·7°) reveal the lack of conjugation between the amidine and aromatic fragments. Steric hindrances seem to be responsible for these effects since several intramolecular contacts shorter than the sum of the van der Waals radii have been detected in the molecule. A molecular packing diagram is shown in Fig. 2. No unusually short intermolecular contacts are present in the crystal.
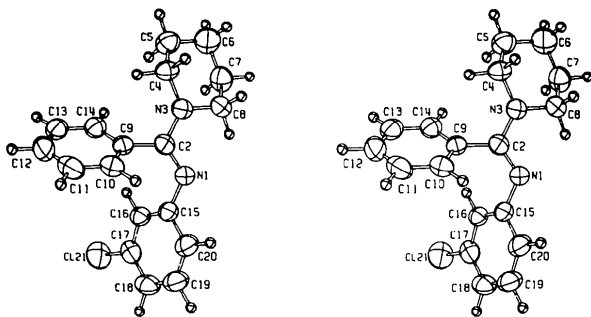
Fig. 1. Stereodrawing of the molecule (Johnson, 1976).
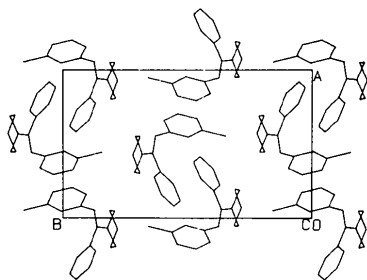

Fig. 2. Projection of the structure down **c**.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JASKÓLSKI, M. (1978). *Acta Cryst.* B34, 3429–3430.

JASKÓLSKI, M. (1982). *Fourth Symposium on Organic Crystal Chemistry*, Poznań, September 1982, edited by Z. KAŁUSKI, pp. 70–71. A. Mickiewicz Univ.

JASKÓLSKI, M., GDANIEC, M. & KOSTURKIEWICZ, Z. (1977). *Acta Cryst.* B33, 1627–1630.

JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KRAJEWSKI, J. W., URBAŃCZYK-LIPKOWSKA, Z., GLUZIŃSKI, P., BUŚKO-OSZCZAPOWICZ, J., OSZCZAPOWICZ, J., BLEIDELIS, J. & KEMME, A. (1981). *Pol. J. Chem.* 55, 1015–1024.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A30, 580–584.

LITTLE, R. G. & MORIMOTO, G. (1981). *Acta Cryst.* B37, 1637–1640.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NORRESTAM, R. (1984). *Acta Cryst.* C40, 955–957.

NORRESTAM, R., MERTZ, S. & CROSSLAND, I. (1983). *Acta Cryst.* C39, 1554–1556.

OSZCZAPOWICZ, J., RACZYŃSKA, E. & PAWLIK, T. (1984). *Pol. J. Chem.* 58, 117–124.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.