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Structure of N^1-Methyl-N^1-phenyl-N^2-(p-tolyl)benzamidine

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Abstract. $C_{21}H_{20}N_2$, $M_r = 300.4$, orthorhombic, $P2_12_12_1$, $a = 12.232$ (2), $b = 15.543$ (1), $c = 9.165$ (1) Å, $V = 1742.6$ (3) Å³, $Z = 4$, $D_m = 1.14$, $D_x = 1.145$ Mg m⁻³, $\lambda(Cu\,K\alpha) = 1.54178$ Å, $\mu(Cu\,K\alpha) = 0.447$ mm⁻¹, $F(000) = 640$, room temperature, $R = 0.048$ for 1174 observed reflexions. The C–N¹ and C–N² bonds are different [1.365 (5) and 1.286 (6) Å, respectively]. The angles which the amidine group makes with the phenyl rings attached to N¹, $C_{amidine}$ and N² [63.1 (1), 60.0 (2) and 70.2 (1)°] attest to a lack of conjugation between the amidine group and the aromatic fragments. The molecule is highly overcrowded.

Introduction. The present study is the third part of a series of structural investigations on benzamidines carried out in this laboratory. The title compound was synthetized and characterized by Oszczapowicz, Raczyńska & Orliński (1981). The structure investigation has been undertaken to determine the effect of substituents on the amidine group. Our aim was also to see how the disposition of the side substituents, relative to the central amidine group, depends on the character and dimensions of those fragments.

Experimental. Suitable crystals obtained from ethanol. D_m by flotation. Space group from Weissenberg photographs. Crystal 0·28 × 0·32 × 0·39 mm. Syntex $P2_1$ diffractometer. Cell parameters from least-squares treatment of setting angles of 15 reflexions with $2\theta = 2\theta \leq 30°$. No absorption or extinction correction. Profile analysis according to Lehmann & Larsen (1974). Max. sin $\theta/\lambda = 0.547$ Å⁻¹, 1337 reflexions measured in range $h\,0–13$, $k\,0–16$, $l\,0–10$. No significant intensity variation for two standard reflexions recorded every 1·5 h. 1174 observed reflexions with $I \geq 2\sigma(I)$. Structure solved by direct methods using MULTAN80 (Main et al., 1980). Full-matrix least-squares refinement on F, $w^{-1} = \sigma^2(F)$, H atoms from molecular geometry and included as fixed isotropic

contribution to F_c, seven extinction-affected reflexions (200, 112, 011, 211, 021, 041, 012) excluded from final refinement, anisotropic thermal parameters for non-H atoms. $R = 0.048$, $wR = 0.054$, $S = 4.83$, $(\Delta/\sigma)_{max} = 0.2$, $(\Delta\rho)_{max} = 0.36$, $(\Delta\rho)_{min} = -0.20$ e Å⁻³. Computer programs: MULTAN80 (Main et al., 1980), SHELX76 (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).

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
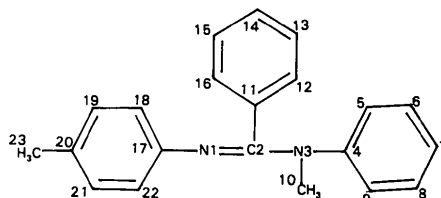
and a stereoscopic view of the molecule is presented in Fig. 1. The N(1)C(2)N(3)C(11) group is planar ($\chi^2 = 7.81$) with C(4) and C(17) −0·347 (4) and 0·195 (5) Å out of plane. The sum of the valency angles around N(3) equals 359·4 (4)°, showing nonsignificant pyramidization of that atom. The N(1)–C(2) and C(2)–N(3) bonds are different [1·286 (6) and 1·365 (5) Å, respectively]. The C(2)–N(3) bond is intermediate between a single and double bond, while N(1)–C(2) has a predominant double-bond character. Nevertheless, the C(17)–N(1)–C(2)–N(3)

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43203 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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torsion angle [−170·4 (5)°] indicates that N(1)—C(2) is not a pure double bond. [The corresponding torsion angle around the C(2)—N(3) bond, C(4)—N(3)—C(2)—N(1), is −163·5 (5)°.] The N(1)—C(2)—N(3) angle [119·0 (3)°] is similar to that found in N^2-(p-methoxyphenyl-N^1,N^1-pentamethylenebenzamidine (Tykarska, Jaskólski & Kosturkiewicz, 1986) but it deviates considerably from the value reported for

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å²)

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

	x	y	z	U_{eq}
N(1)	0·1634 (3)	0·0370 (2)	0·6004 (4)	0·060 (1)
C(2)	0·1606 (3)	0·0927 (3)	0·4967 (5)	0·050 (1)
N(3)	0·2440 (3)	0·1507 (2)	0·4845 (4)	0·056 (1)
C(4)	0·2370 (3)	0·2273 (3)	0·4001 (5)	0·051 (2)
C(5)	0·1507 (4)	0·2851 (3)	0·4186 (5)	0·063 (2)
C(6)	0·1476 (4)	0·3599 (3)	0·3357 (7)	0·077 (2)
C(7)	0·2285 (4)	0·3786 (3)	0·2369 (6)	0·079 (2)
C(8)	0·3132 (4)	0·3212 (3)	0·2199 (5)	0·074 (2)
C(9)	0·3178 (3)	0·2461 (3)	0·3002 (5)	0·061 (2)
C(10)	0·3412 (4)	0·1413 (3)	0·5787 (6)	0·075 (2)
C(11)	0·0730 (3)	0·0969 (3)	0·3840 (4)	0·048 (1)
C(12)	0·0975 (4)	0·0842 (3)	0·2372 (5)	0·061 (2)
C(13)	0·0118 (5)	0·0845 (3)	0·1354 (5)	0·075 (2)
C(14)	−0·0940 (5)	0·0960 (4)	0·1813 (8)	0·087 (2)
C(15)	−0·1174 (4)	0·1098 (4)	0·3254 (7)	0·079 (2)
C(16)	−0·0348 (4)	0·1091 (3)	0·4259 (5)	0·062 (2)
C(17)	0·0867 (3)	−0·0316 (3)	0·6016 (5)	0·056 (2)
C(18)	0·0889 (4)	−0·0965 (3)	0·4985 (5)	0·063 (2)
C(19)	0·0143 (4)	−0·1643 (3)	0·5062 (5)	0·068 (2)
C(20)	−0·0625 (4)	−0·1694 (3)	0·6173 (6)	0·065 (2)
C(21)	−0·0622 (4)	−0·1050 (3)	0·7205 (6)	0·067 (2)
C(22)	0·0113 (4)	−0·0373 (3)	0·7149 (5)	0·063 (2)
C(23)	−0·1406 (4)	−0·2449 (4)	0·6250 (7)	0·091 (2)

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

N(1)—C(2)	1·286 (6)	C(13)—C(14)	1·372 (9)
C(2)—N(3)	1·365 (5)	C(14)—C(15)	1·368 (9)
N(3)—C(4)	1·424 (6)	C(15)—C(16)	1·367 (7)
C(4)—C(5)	1·396 (6)	C(16)—C(11)	1·387 (6)
C(5)—C(6)	1·390 (7)	N(1)—C(17)	1·421 (6)
C(6)—C(7)	1·373 (8)	C(17)—C(18)	1·383 (7)
C(7)—C(8)	1·376 (7)	C(18)—C(19)	1·395 (7)
C(8)—C(9)	1·382 (7)	C(19)—C(20)	1·387 (7)
C(9)—C(4)	1·378 (6)	C(20)—C(21)	1·376 (7)
N(3)—C(10)	1·477 (6)	C(21)—C(22)	1·386 (7)
C(2)—C(11)	1·490 (6)	C(22)—C(17)	1·391 (6)
C(11)—C(12)	1·392 (6)	C(20)—C(23)	1·515 (7)
C(12)—C(13)	1·404 (8)		
N(1)—C(2)—N(3)	119·0 (3)	C(14)—C(15)—C(16)	119·6 (5)
C(2)—N(3)—C(4)	123·5 (3)	C(15)—C(16)—C(11)	121·2 (4)
N(3)—C(4)—C(5)	121·1 (3)	C(16)—C(11)—C(12)	119·4 (4)
C(4)—C(5)—C(6)	119·5 (4)	C(2)—N(1)—C(17)	119·5 (3)
C(5)—C(6)—C(7)	121·2 (4)	N(1)—C(17)—C(18)	122·0 (4)
C(6)—C(7)—C(8)	118·8 (4)	C(17)—C(18)—C(19)	120·2 (4)
C(7)—C(8)—C(9)	121·2 (4)	C(18)—C(19)—C(20)	121·6 (4)
C(8)—C(9)—C(4)	120·2 (4)	C(19)—C(20)—C(21)	117·4 (4)
C(9)—C(4)—C(5)	119·2 (4)	C(20)—C(21)—C(22)	121·9 (4)
N(3)—C(2)—C(11)	116·8 (3)	C(21)—C(22)—C(17)	120·4 (4)
C(2)—C(11)—C(12)	120·6 (3)	C(22)—C(17)—C(18)	118·5 (4)
C(11)—C(12)—C(13)	118·8 (4)	C(19)—C(20)—C(23)	120·4 (4)
C(12)—C(13)—C(14)	120·0 (5)	C(21)—C(20)—C(23)	122·2 (4)
C(13)—C(14)—C(15)	121·0 (5)		

acetamidine [125·5 (1)°] (Norrestam, Mertz & Crossland, 1983). The angles the amidine group makes with the C(4)—C(9), C(11)—C(16) and C(17)—C(22) phenyl rings are 63·1 (1), 60·0 (2) and 70·2 (1)°, and attest to a lack of conjugation between the amidine and aromatic fragments. Several intramolecular contacts shorter than the sum of the van der Waals radii are detected, the shortest ones being N(1)···C(10) = 2·720 (6) and C(11)···C(17) = 2·827 (6) Å. They can be considered as evidence of steric hindrance involving the amidine group and the substituents. Owing to the partial double-bond character of the C(2)—N(3) bond, the C(11)—C(16) and C(17)—C(22) rings tend to be coplanar with the amidine moiety but overcrowding renders this impossible.

The tolyl group is *trans* to the N_{amine} atom. The phenyl rings are situated on one side of the amidine moiety while the other side is occupied by the C(10) methyl group alone. Even though the two N—C bonds
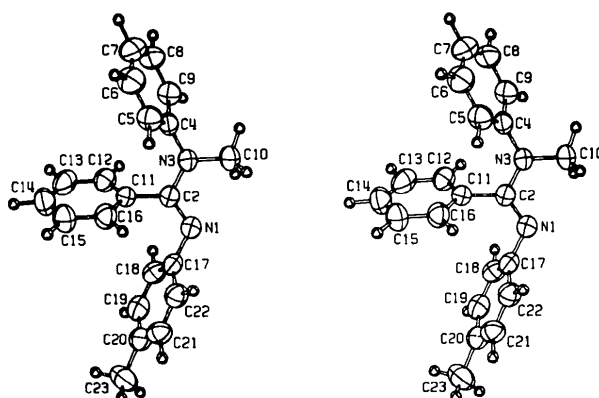

Fig. 1. Stereodrawing of the molecule (*ORTEP*; Johnson, 1976).
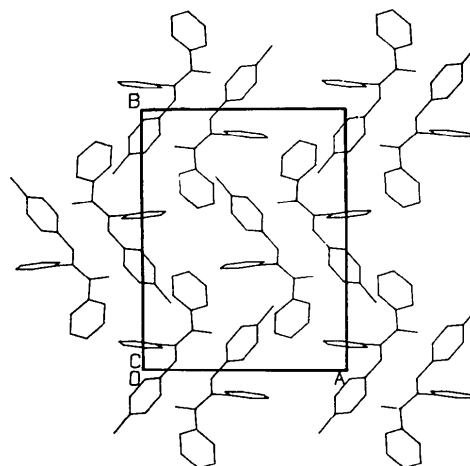

Fig. 2. Projection of the structure down c.

are different, an appreciable conjugation within the N^1—C=N^2 system can be expected. Therefore the rotation around the N^1—C bond is hindered and, in the case of unsymmetrically substituted N^1, two isomeric forms are possible. One can therefore conclude that the bulky methyl group can cause greater steric hindrance in a crystal structure than a flat phenyl ring.

Molecular packing is shown in Fig. 2. No intermolecular contacts significantly shorter than the sum of the van der Waals radii are observed.

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Structure of 1-{[(4-Carbamoylpyridinio)methoxy]methyl}-2-[(hydroxyimino)methyl]pyridinium Dichloride (A) and Diiodide (B) Monohydrates

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Abstract. (A): $C_{14}H_{16}N_4O_3^{2+}$.2Cl$^-$.H$_2$O, $M_r = 377.23$, monoclinic, $P2_1/n$, $a = 13.348$ (9), $b = 8.982$ (6), $c = 15.214$ (9) Å, $\beta = 106.09$ (5)°, $V = 1752.6$ (2) Å^3, $Z = 4$, $D_x = 1.430$ Mg m^{-3}, λ(Cu Kα) = 1.5418 Å, μ(Cu Kα) = 3.583 mm^{-1}, $F(000) = 784$, $T = 298$ K, final $R = 0.054$ for 1846 observed reflections. (B): $C_{14}H_{16}N_4O_3^{2+}$.2I$^-$.H$_2$O, $M_r = 560.13$, triclinic, $P\bar{1}$, $a = 18.448$ (7), $b = 7.964$ (4), $c = 8.032$ (4) Å, $\alpha = 119.85$ (4), $\beta = 95.46$ (3), $\gamma = 93.48$ (3)°, $V = 1010.9$ (9) Å^3, $Z = 2$, $D_x = 1.840$ Mg m^{-3}, λ(Mo Kα) = 0.7107 Å, μ(Mo Kα) = 3.174 mm^{-1}, $F(000) = 536$, $T = 298$ K, final $R = 0.075$ for 4368 observed reflections. The molecules of both compounds have similar but not identical shapes: the angle between the best planes through the two pyridinium rings amounts to 20.2 (1)° in (A) and 45.2 (4)° in (B). The interatomic distances between N from pyridine ring (i) and its oxime O and between N from pyridine ring (ii) and its carbonyl O are 4.638 (5) and 4.910 (6) Å in (A), and 4.605 (15) and 4.947 (14) Å in (B), respectively, and are very similar to such distances in nicotine and in the
nicotinic conformation of acetylcholine. This could be the reason for their antisoman activity.

Introduction. In recent years considerable attention has been given to the study of a bispyridinium oxime known under the code name HI-6 as a very efficient antidote against soman poisoning (Bošković, 1981). In order to contribute to the elucidation of the structure–activity relationship as well as to the explanation of the possible mechanism of the antidotal activity of this class of compounds we have undertaken the X-ray structure analysis of compound HI-6 in the form of its chloride and iodide (Kamenar & Vicković, 1984; Binenfeld, Deljac, Kamenar & Vicković, 1984).
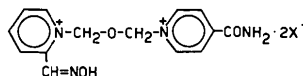
Experimental. (A) Prism-shaped specimen 0.15 × 0.04 × 0.44 mm. Unit cell from 18 reflections (12 ≤