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Structure of N^2-*p*-Nitrophenylbenzamidine

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Abstract. $C_{13}H_{11}N_3O_2$, $M_r = 241\cdot3$, monoclinic, $C2/c$, $a = 20\cdot885\,(3)$, $b = 5\cdot7616\,(6)$, $c = 19\cdot603\,(2)$ Å, $\beta = 94\cdot791\,(8)°$, $V = 2350\cdot7\,(5)$ Å^3, $Z = 8$, $D_m = 1\cdot35$, $D_x = 1\cdot362$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot54178$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 0\cdot694$ mm^{-1}, $F(000) = 1008$, room temperature, $R = 0\cdot046$ for 1016 observed reflexions. The N^1—C and N^2=C bonds are different [1·355 (5) and 1·280 (5) Å respectively]. The N^1 and *p*-nitrophenyl substituents at the C=N^2 double bond are in *cis* configuration. The N^1—C—N^2 angle [125·9 (3)°] is different from that found in *trans* benzamidine derivatives (about 118°). The *p*-nitrophenyl and phenyl rings are twisted by 78·9 (4) and 21·2 (4)° relative to the amidine fragment.

Introduction. This work is part of a series of structural studies on the amidine system carried out in this laboratory.† We are looking for the changes induced in the geometry of the amidine group by different substituents and for factors controlling the *cis–trans* isomerism around the C=N^2 bond. Also, we would like to find out how the disposition of the side groups relative to the central amidine groups depends on the character and dimensions of those groups.

Experimental. The title compound was synthetized by one of us (JO). Prismatic yellow crystals obtained from absolute ethanol, D_m by flotation, space group from Weissenberg photographs, crystal 0·1 × 0·1 × 0·25 mm, Syntex $P2_1$ diffractometer, cell parameters from least-squares treatment of setting angles of 15 reflexions with $14 \le 2\theta \le 20°$. 1513 reflexions measured in the range: h: 0→22, k: 0→6, l: −21→+21. No significant intensity variation for two standard reflexions recorded every 1·5 h. Maximum value of $2\theta = 115°$. Peak profile analysis according to Lehmann & Larsen (1974), 1017 observed reflexions with $I \ge 2\sigma(I)$. Structure solved by direct methods using *SHELX*76 (Sheldrick, 1976) program. Full-matrix least-squares refinement on F, H atoms from $\Delta\rho$ map, anisotropic thermal parameters for non-H atoms,

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† Previous paper: Ciszak, Gdaniec & Kosturkiewicz (1987).

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isotropic for H atoms, empirical isotropic extinction parameter x refined to $7{\cdot}5\,(6) \times 10^{-7}$ and F_c multiplied by $(1 - xF_c^2)/\sin\theta$. Reflexion $40\bar{4}$ with large $\Delta F/\sigma$ excluded from final refinement. $R = 0{\cdot}046$, $wR = 0{\cdot}052$, $S = 2{\cdot}826$, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{\max} = 0{\cdot}28$, $(\Delta\rho)_{\max} = 0{\cdot}17$, $(\Delta\rho)_{\min} = -0{\cdot}19$ e Å^{-3}. Computer programs: *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).

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* An *ORTEP* drawing showing the atom-labelling system is presented in Fig. 1. The N(1)—C(1) and C(1)—N(2) bonds are significantly different: 1·355 (5) and 1·280 (5) Å, respectively. From a semi-empirical correlation $r = r_0 - 0{\cdot}18p$ (Norrestam, Mertz & Crossland, 1983) where r_0 is a standard single-bond distance (1·458 Å for C—N) the following π-bond orders are calculated for the present molecule: 0·57 for C(1)—N(1) and 0·99 for C(1)—N(2). The former is, therefore, intermediate between a single and double bond, while the latter is a typical double bond. Two isomeric forms are thus possible depending on the disposition of the substituents at the amidine $C{=}N^2$ double bond. The substituent at N^2 can be positioned *trans* or *cis* to the N^1 amine atom. In contrast to the *trans* benzamidines investigated so far (Oszczapowicz, Tykarska, Jaskólski & Kosturkiewicz, 1986), the present structure has the *p*-nitrophenyl group in *cis* position, the N(1)—C(1)—N(2)—C(2) torsion angle being −3·1 (4)°. The *cis* configuration was also found in unsubstituted acetamidine (Norrestam, Mertz & Crossland, 1983) and in 2,6-*cis*-dimethylpiperidyl-*N*-phenyl-2,2-dimethylpropionamidine (Gilli & Bertolasi, 1979).

In all these structures the N^1—C—N^2 angle is larger than 120°, while in *trans*-amidine derivatives it is less than this value (about 118°). In the present structure it equals 125·9 (3)°. The widening of the N^1—C—N^2 angle seems to be a rule in *cis*-amidine systems.

The N(1)H(14)H(15)C(1) group in the present structure is planar within experimental error ($\chi^2 = 2{\cdot}21$). The sum of valence angles around N(1) is 360·0 (5)° and indicates that the hybridization of N(1) is close to sp^2.

The Winkler & Dunitz (1971) parameters determining deviations from planarity of amidine bonds are: $\chi_C = 0{\cdot}2\,(6)$, $\chi_N = 8{\cdot}3\,(4)$ and $\tau = 3{\cdot}7\,(5)$°. χ_C is small,

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

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	0·2315 (1)	0·0906 (6)	0·1243 (2)	0·045 (1)
C(2)	0·1699 (1)	−0·0476 (6)	0·0283 (2)	0·049 (1)
C(3)	0·1297 (2)	−0·2392 (7)	0·0335 (2)	0·060 (2)
C(4)	0·0741 (2)	−0·2620 (7)	−0·0089 (2)	0·059 (1)
C(5)	0·0584 (1)	−0·0918 (6)	−0·0559 (2)	0·050 (1)
C(6)	0·0975 (2)	0·0994 (7)	−0·0635 (2)	0·056 (1)
C(7)	0·1533 (2)	0·1196 (7)	−0·0204 (2)	0·055 (1)
C(8)	0·2930 (1)	0·0858 (6)	0·1691 (2)	0·044 (1)
C(9)	0·3339 (2)	−0·1027 (7)	0·1650 (2)	0·052 (1)
C(10)	0·3908 (2)	−0·1140 (8)	0·2070 (2)	0·058 (2)
C(11)	0·4076 (2)	0·0616 (8)	0·2519 (2)	0·063 (1)
C(12)	0·3675 (2)	0·2500 (8)	0·2562 (2)	0·066 (2)
C(13)	0·3105 (2)	0·2609 (7)	0·2147 (2)	0·057 (2)
N(1)	0·1846 (2)	0·2303 (7)	0·1449 (2)	0·062 (1)
N(2)	0·2276 (1)	−0·0361 (6)	0·0705 (1)	0·055 (1)
N(3)	−0·0009 (1)	−0·1152 (7)	−0·1007 (2)	0·064 (1)
O(1)	−0·0125 (1)	0·0268 (7)	−0·1459 (2)	0·102 (1)
O(2)	−0·0370 (1)	−0·2772 (6)	−0·0911 (1)	0·081 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—N(1)	1·355 (5)	N(1)—C(1)—N(2)	125·9 (3)
C(1)—N(2)	1·280 (5)	N(1)—C(1)—C(8)	116·3 (3)
C(1)—C(8)	1·495 (4)	N(2)—C(1)—C(8)	117·8 (3)
C(2)—N(2)	1·404 (4)	C(1)—N(2)—C(2)	120·4 (3)
C(2)—C(3)	1·396 (5)	N(2)—C(2)—C(3)	119·0 (3)
C(3)—C(4)	1·377 (5)	C(2)—C(3)—C(4)	120·8 (3)
C(4)—C(5)	1·367 (5)	C(3)—C(4)—C(5)	118·9 (3)
C(5)—C(6)	1·387 (5)	C(4)—C(5)—C(6)	122·0 (3)
C(6)—C(7)	1·385 (5)	C(5)—C(6)—C(7)	118·4 (3)
C(7)—C(2)	1·381 (5)	C(6)—C(7)—C(2)	120·9 (3)
C(5)—N(3)	1·463 (4)	C(7)—C(2)—C(3)	119·0 (3)
N(3)—O(1)	1·216 (5)	C(4)—C(5)—N(3)	118·9 (3)
N(3)—O(2)	1·223 (5)	C(6)—C(5)—N(3)	119·1 (3)
C(8)—C(9)	1·388 (5)	C(5)—N(3)—O(1)	118·8 (3)
C(9)—C(10)	1·390 (5)	C(5)—N(3)—O(2)	118·6 (3)
C(10)—C(11)	1·368 (6)	O(1)—N(3)—O(2)	122·6 (3)
C(11)—C(12)	1·378 (6)	N(2)—C(2)—C(7)	121·9 (3)
C(12)—C(13)	1·387 (5)	C(1)—C(8)—C(9)	118·9 (3)
C(13)—C(8)	1·377 (5)	C(1)—C(8)—C(13)	122·4 (3)
		C(8)—C(9)—C(10)	120·1 (3)
		C(9)—C(10)—C(11)	120·5 (3)
		C(10)—C(11)—C(12)	119·9 (3)
		C(11)—C(12)—C(13)	119·8 (3)
		C(12)—C(13)—C(8)	121·1 (3)
		C(13)—C(8)—C(9)	118·7 (3)

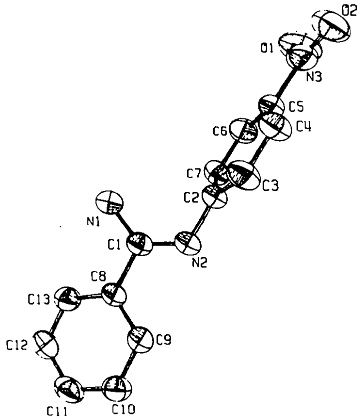

Fig. 1. An *ORTEP* plot showing the thermal ellipsoids (50% probability level) and the atom labelling.

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* 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 44761 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

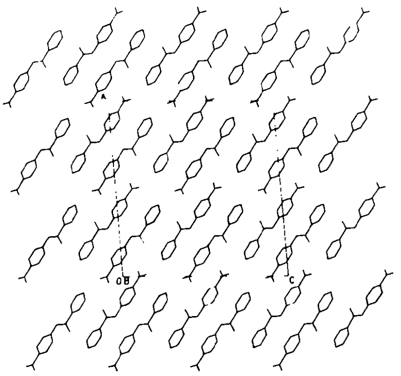

Fig. 2. Projection of the structure down **b**.

indicating that C(sp^2) has a stronger resistance against out-of-plane bending than the N^1 atom. The value of τ shows that the twist around C(1)—N(1) is minimal. As a result of molecular overcrowding, the *p*-nitrophenyl and phenyl rings are twisted from the amidine plane by 78·9 (4) and 21·2 (4)°, respectively, showing lack of conjugation. The nitro group is twisted by 4·8 (4)° relative to the C(2)—C(7) ring.

Molecular packing is shown in Fig. 2. The shortest intermolecular contact is O(2)···H(15)($-x$, $-y$, $-z$) 2·43 (4) Å. Molecules linked by these contacts are situated around a symmetry centre forming 'dimers', but the O···H distance is rather long for a hydrogen bond.

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Conformational Study of Optically Active Oxaziridines. Structures of (I) *N*-Isopropyl-, (II) *N*-*tert*-Butyl- and (III) *N*-Methylsulfonyldiphenyloxaziridine

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Abstract. (I) $C_{16}H_{17}NO$, $M_r = 239·3$, orthorhombic, $P2_12_12_1$, $a = 14·330$ (4), $b = 10·502$ (3), $c = 9·251$ (2) Å, $V = 1392·2$ (6) Å^3, $Z = 4$, $D_x = 1·14$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5·2$ cm^{-1}, $F(000) = 512$, $T = 293$ K, final conventional R 0·041 for 1259 symmetry-independent observed reflections. (II) $C_{17}H_{19}NO$, $M_r = 253·3$, orthorhombic, $P2_12_12_1$, $a = 14·110$ (4), $b = 10·805$ (3), $c = 9·498$ (2) Å, $V = 1448·1$ (7) Å^3, $Z = 4$, $D_x = 1·16$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418, $\mu = 5·3$ cm^{-1}, $F(000) = 544$, $T = 293$ K, final conventional R 0·035 for 1492 symmetry-independent observed reflections. (III) $C_{14}H_{13}NO_3S$, $M_r = 275·3$, monoclinic, $P2_1/c$, $a = 5·591$ (2), $b = 18·704$ (6), $c = 12·585$ (4) Å, $\beta = 100·2$ (1)°, $V = 1295·3$ (9) Å^3, $Z = 4$, $D_x = 1·41$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 22·1$ cm^{-1}, $F(000) = 576$, $T = 293$ K, final conventional R 0·046 for 1326 symmetry-independent observed reflections. The conformational geometry of the diphenyloxaziridine moiety is similar for the three compounds and seems not to be influenced by substituents at N. A small but significant shortening of the N—O distance in the oxaziridine ring is observed

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