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Structure of *N*²-*p*-Bromophenyl-*N*¹-methyl-*N*¹-(*p*-tolyl)acetamidine

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Abstract. C₁₆H₁₇BrN₂, *M_r* = 317.2, monoclinic, *C*2/*c*, *a* = 30.665 (9), *b* = 6.100 (2), *c* = 23.199 (5) Å, β = 135.50 (2)°, *V* = 3041 (2) Å³, *Z* = 8, *D_m* = 1.39, *D_x* = 1.39 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 2.615 mm⁻¹, *F*(000) = 1296, room temperature, *R* = 0.054 for 1144 observed reflexions. The N¹–C and C–N² bonds are different [1.366 (8) and 1.273 (8) Å, respectively]. The *p*-bromophenyl and *p*-tolyl rings are twisted relative to the central acetamidine plane by 90.1 (2) and 67.0 (2)°, respectively. The N¹ and *p*-bromophenyl substituents at the C=N² double bond are in *trans* configuration.

Introduction. This work is part of a series of structural studies on amidine systems carried out in our laboratory.† We are looking for the changes induced in the geometry of the amidine group by different substituents and the factors determining *cis*–*trans* (the C=N² bond) and *syn*–*anti* (the C–N¹ bond) isomerism of amidine systems.

Experimental. The title compound was synthesized and characterized by Raczynska, Oszczapowicz & Walczak (1985). Needle-shaped crystals obtained from absolute ethanol, *D_m* by flotation, space group from Weissenberg photographs, crystal 0.2 × 0.6 × 0.6 mm, Syntex P2₁ diffractometer, cell parameters from least-squares treatment of setting angles of 15 reflexions with

13 ≤ 2θ ≤ 20°. No absorption correction. 1922 reflexions measured in range *h*: 0→32, *k*: 0→6, *l*: –23→16. No significant intensity variation for two standard reflexions recorded every 1.5 h. Maximum value of sinθ = 0.538. Peak profile analysis according to Lehmann & Larsen (1974), 1145 observed reflexions with *I* ≥ 2σ(*I*). Structure solved by heavy-atom and Fourier techniques using *SHELX76* (Sheldrick, 1976) program. Full-matrix least-squares refinement on *F_c*, H atoms from molecular geometry included as fixed isotropic contribution to *F_c*, the methyl groups refined as rigid groups, anisotropic thermal parameters for non-H atoms, empirical isotropic extinction *x* refined to 1.0 (7) × 10⁻⁷ and *F_c* multiplied by (1 – *xF_c*²)/sin²θ. Reflexion 11,1,6 with large Δ*F*/σ excluded from final refinement cycle. *R* = 0.054, *wR* = 0.048, *S* = 5.63, *w* = 2.67/σ²(*F*), (Δ/σ)_{max} = 0.2, (Δρ)_{max} = 0.74, (Δρ)_{min} = –0.69 e Å⁻³ (around Br). Computer programs: *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 are given in Table 1, bond lengths and angles in Table 2.‡

‡ 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 43820 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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† Previous paper: Oszczapowicz, Tykarska, Jaskólski & Kosturkiewicz (1986).

An ORTEP stereodrawing showing the atom labelling system is presented in Fig. 1. The N(1)–C(1) and C(1)–N(2) bonds are significantly different: 1.366 (8) and 1.273 (8) Å, respectively. From the semiempirical correlation functions, ($r = r_0 - 0.18p$) between π -bond orders (p) and bond distances (r), where r_0 is a standard single-bond distance (1.458 Å for C–N bonds) (Norrestam, Mertz & Crossland, 1983), the following π -bond orders are obtained in the present structure: 0.5 for the C(1)–N(1) and 1.0 for the C(1)–N(2). The former is, therefore, intermediate between a single and a double bond, while the latter is a typical double bond.

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

$$U_{eq} = \frac{1}{3} \sum_i \sum_k U_{ik} a_i^* a_k^* (\mathbf{a}_i, \mathbf{a}_k).$$

	x	y	z	U_{eq}
Br(1)	−0.02525 (5)	0.1320 (2)	0.05056 (6)	0.209
C(1)	0.1496 (4)	0.554 (1)	0.4364 (4)	0.088
C(2)	0.1175 (3)	0.380 (1)	0.3220 (4)	0.094
C(3)	0.1042 (4)	0.508 (1)	0.2607 (5)	0.119
C(4)	0.0617 (4)	0.433 (2)	0.1795 (5)	0.127
C(5)	0.0330 (4)	0.236 (2)	0.1601 (5)	0.122
C(6)	0.0459 (4)	0.107 (1)	0.2193 (5)	0.143
C(7)	0.0878 (4)	0.181 (2)	0.2998 (5)	0.139
C(8)	0.2598 (3)	0.527 (1)	0.5671 (4)	0.105
C(9)	0.1869 (4)	0.732 (1)	0.5617 (4)	0.096
C(10)	0.2149 (4)	0.933 (1)	0.5925 (4)	0.108
C(11)	0.2089 (4)	1.055 (1)	0.6373 (5)	0.186
C(12)	0.1748 (4)	0.978 (2)	0.6511 (4)	0.106
C(13)	0.1474 (4)	0.774 (2)	0.6203 (5)	0.118
C(14)	0.1536 (3)	0.651 (1)	0.5764 (4)	0.110
C(15)	0.1676 (4)	1.110 (2)	0.6983 (5)	0.147
C(16)	0.0846 (3)	0.636 (1)	0.3898 (4)	0.120
N(1)	0.1959 (3)	0.602 (1)	0.5184 (3)	0.095
N(2)	0.1639 (3)	0.447 (1)	0.4049 (3)	0.105

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

C(1)–N(1)	1.366 (8)	C(6)–C(7)	1.386 (10)
C(1)–N(2)	1.273 (8)	C(8)–N(1)	1.474 (8)
C(1)–C(16)	1.522 (10)	C(9)–N(1)	1.448 (9)
C(2)–C(3)	1.401 (10)	C(9)–C(10)	1.373 (10)
C(2)–C(7)	1.378 (10)	C(9)–C(14)	1.379 (10)
C(2)–N(2)	1.408 (8)	C(10)–C(11)	1.392 (10)
C(3)–C(4)	1.398 (9)	C(11)–C(12)	1.379 (10)
C(4)–C(5)	1.364 (11)	C(12)–C(13)	1.381 (11)
C(5)–C(6)	1.373 (10)	C(12)–C(15)	1.497 (10)
C(5)–Br(1)	1.891 (8)	C(13)–C(14)	1.386 (10)
N(1)–C(1)–N(2)	118.0 (7)	C(10)–C(9)–N(1)	119.5 (9)
N(1)–C(1)–C(16)	116.9 (7)	N(1)–C(9)–C(14)	121.1 (8)
N(2)–C(1)–C(16)	125.1 (7)	C(9)–C(10)–C(11)	120.1 (8)
N(2)–C(2)–C(3)	120.3 (8)	C(10)–C(11)–C(12)	121.3 (8)
N(2)–C(2)–C(7)	121.1 (8)	C(11)–C(12)–C(13)	117.9 (8)
C(3)–C(2)–C(7)	118.3 (7)	C(11)–C(12)–C(15)	121.4 (9)
C(2)–C(3)–C(4)	120.2 (8)	C(13)–C(12)–C(15)	120.7 (11)
C(3)–C(4)–C(5)	119.6 (8)	C(12)–C(13)–C(14)	121.3 (8)
C(4)–C(5)–C(6)	121.2 (8)	C(13)–C(14)–C(9)	120.1 (8)
C(4)–C(5)–Br(1)	120.5 (7)	C(1)–N(1)–C(9)	124.0 (7)
C(6)–C(5)–Br(1)	118.3 (7)	C(1)–N(1)–C(8)	119.5 (6)
C(5)–C(6)–C(7)	119.3 (9)	C(8)–N(1)–C(9)	116.4 (6)
C(2)–C(7)–C(6)	121.4 (8)	C(1)–N(2)–C(2)	120.5 (7)
C(10)–C(9)–C(14)	119.3 (8)		

The N(1)C(1)N(2)C(16) group is planar ($\chi^2 = 0.03$) and C(2), C(8), C(9) deviate by -0.09 (1), -0.01 (1), 0.06 (1) Å, respectively, from the best plane through this group. The bond-order scheme is in agreement with the planar arrangement about C(1) and N(1) and with the tendency pointed out by Bellucci, Bertolasi, Ferretti & Gilli (1985).

Two isomeric forms are possible, depending on the disposition of the substituents at the amidine C=N² double bond. The substituent at N² can be positioned *trans* or *cis* to the N¹_{amine} atom. In the present structure the *p*-bromophenyl group is in *trans* configuration. Owing to the partial double-bond character of the N¹–C_{amidine} bond, rotation about this bond is hindered and for unsymmetrically substituted N¹ two isomeric forms can exist. As in N¹-methyl-N¹-phenyl-N²-(*p*-tolyl)-benzamidinium (Oszczapowicz, Tykarska, Jaskólski & Kosturkiewicz, 1986), the methyl group seems to cause greater steric hindrance than a flat, twisted phenyl ring and therefore in the present structure two methyl groups are in *anti* disposition. The Winkler & Dunitz (1971) parameters have the following values for the present structure: $\tau_1 = 178.4$ (9), $\tau_2 = 179.6$ (10), $\chi_C = -0.2$ (10), $\chi_N = 2.2$ (9). Small values of the χ_C and χ_N parameters characterizing the out-of-plane bending at C(1) and N(1) indicate a planar arrangement of bonds around these atoms. The values of τ show that the twist about the C(1)–N(1) bond is minimal. The value of N(1)–C(1)–N(2) [118.0 (7)°] is similar to the values found in the majority of the *trans* amidine derivatives substituted at the C_{amidine} atom investigated so far. For the *cis* amidine system this angle is larger than 120° and in *cis*-acetamidinium it equals 125.5 (1)° (Norrestam, Mertz & Crossland, 1983). As a result of

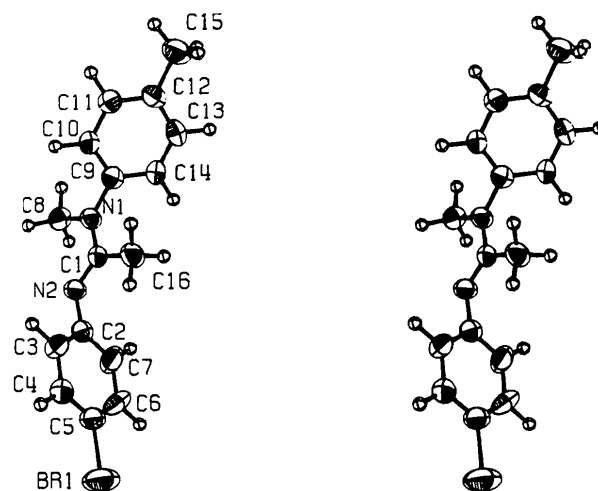


Fig. 1. Stereodrawing of the molecule (ORTEP; Johnson, 1976) showing the thermal ellipsoids (50% probability level) and the atom labelling.

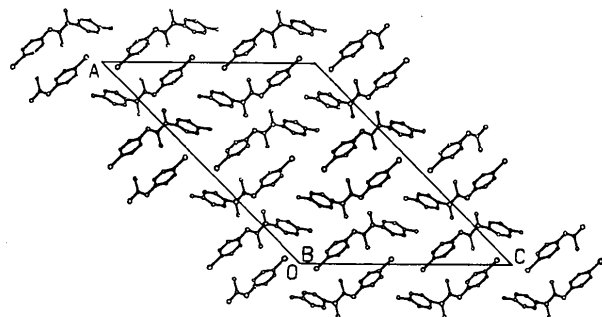


Fig. 2. Projection of the structure down *b*.

molecular overcrowding the phenyl rings are twisted relative to the plane of the amidine group by 90.1 (2) (*p*-bromophenyl) and 67.0 (2)° (*p*-tolyl), showing lack of conjugation between the amidine and the aromatic fragments.

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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Structures of Two Bicyclic Octanes

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Abstract. (3*S*,8*S*)-6-Benzyl-3-methoxy-6-aza-2-oxa-bicyclo[3.2.1]octane-8-carbonitrile (4), $C_{15}H_{18}N_2O_2$, $M_r = 258.31$, m.p. 370–372 K, $[\alpha]_D^{19} -15.9^\circ$ ($c = 3.5 \text{ g dm}^{-3}$ in chloroform), orthorhombic, $P2_12_12_1$, $a = 8.116$ (1), $b = 9.659$ (1), $c = 17.526$ (2) Å, $V = 1373.9 \text{ Å}^3$, $Z = 4$, $D_x = 1.25 \text{ g cm}^{-3}$, $\lambda(\text{Cu K}\alpha) = 1.5418 \text{ Å}$, $\mu(\text{Cu K}\alpha) = 5.93 \text{ cm}^{-1}$, $F(000) = 552$, $T = 295 \text{ K}$, final $R = 0.078$, $wR = 0.053$ for 1356 unique observed [$I > 2\sigma(I)$] reflections. (3*S*,8*S*)-6-Benzyl-8-chloro-3-methoxy-6-aza-2-oxabicyclo[3.2.1]octane (3), $C_{14}H_{18}ClNO_2$, $M_r = 267.75$, m.p. 360–361 K, orthorhombic, $P2_12_12_1$, $a = 8.056$ (4), $b = 9.622$ (2), $c = 17.512$ (3) Å, $V = 1357.4 \text{ Å}^3$, $Z = 4$, $D_x = 1.31 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ Å}$, $\mu(\text{Mo K}\alpha) = 2.31 \text{ cm}^{-1}$, $F(000) = 568$, $T = 295 \text{ K}$, final $R = 0.053$, $wR = 0.037$ for 1745 unique ($I > 0$) reflections. The conformations of the two bicyclic octanes are nearly identical and are determined by geometric restrictions

imposed by the two-atom bridge between C(1) and C(5). The pyranose rings adopt highly puckered distorted chair conformations, and the five-membered rings are halfway between envelope and twist forms with C(5) and C(8) out of the plane.

Introduction. In our program of heteroprostaglandin research, a route for the stereospecific synthesis of a chiral synthon (5) for 9-azaprostaglandins has been developed (Holzapfel, Koekemoer & Verdoorn, 1987). A crucial step in the synthesis involved the introduction of a nitrile group at C(8) of the bicyclic compound (1) as a one-carbon moiety required for completion of the prostaglandin ω side chain. Two compounds were isolated after substitution of the sulfonate group of (2) with cyanide. The major product was spectroscopically characterized as the nitrile (4) [stereochemistry at C(8) unknown], while the minor