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Structure of N^1,N^2-Di(*p*-tolyl)acetamidine

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Abstract. $C_{16}H_{18}N_2$, $M_r = 238{\cdot}3$, orthorhombic, *Pbca*, $a = 24{\cdot}558$ (4), $b = 12{\cdot}534$ (3), $c = 9{\cdot}211$ (1) Å, $V = 2835{\cdot}2$ (9) Å^3, $Z = 8$, $D_m = 1{\cdot}10$, $D_x = 1{\cdot}12$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0{\cdot}440$ mm^{-1}, $F(000) = 1024$, room temperature, $R = 0{\cdot}056$ for 1364 observed reflexions. The N^1—C and C—N^2 bonds are different [1·368 (4) and 1·283 (4) Å, respectively]. The N^1 atom and the *p*-tolyl substituent at the C=N^2 double bond are in a *trans* (*E*) configuration. The phenyl rings at N^1 and N^2 are twisted relative to the central amidine plane by 39·4 (4) and 88·1 (4)°, respectively. An intermolecular N^1—H···N^2 hydrogen bond joins the molecules into chains parallel to **c**.

Introduction. This work is part of a series of investigations carried out in this laboratory† to determine the changes induced in the geometry of the amidine core by its intra- and intermolecular environment. As the molecule belongs to the group of symmetrically substituted amidines with secondary amine nitrogen, which have two identical tautomeric forms, we expected the C—N bonds to be of equal length due to tautomerism and/or H-bond formation.

Experimental. The title compound was synthesized by Oszczapowicz, Orliński & Hejchman (1979). Plate-shaped crystals obtained from absolute ethanol; D_m by flotation; space group from Weissenberg photographs; crystal 0·15 × 0·20 × 0·45 mm; Syntex $P2_1$ diffractometer; cell parameters from least-squares treatment of setting angles of 15 reflexions with $16 \le 2\theta \le 22°$. No absorption correction. 1881 reflexions with $2\theta \le 115°$ measured in the range h: 0→+26, k: 0→+12, l: 0→+10; no significant intensity variation (±3·4%) for two standard reflexions (112, 4$\bar{1}$0) recorded every hour. Peak-profile analysis according to Lehmann & Larsen (1974); 1364 observed reflexions with $I \ge 2\sigma(I)$. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Phenyl H atoms and amine H atom from $\Delta\rho$ map, remaining H atoms calculated from methyl-group geometry and optimized with fixed U_{iso} (0·08 Å^2). Full-matrix least-squares refinement [function minimized: $\sum w(F_o - F_c)^2$] of anisotropic non-H atoms and isotropic H atoms found in $\Delta\rho$ map. F_c values multiplied by $(1 - xF_c^2/\sin 2\theta)$ where x is the empirical isotropic extinction parameter refined to 29 (9) × 10^{-7}. $R = 0{\cdot}056$, $wR = 0{\cdot}079$, $S = 3{\cdot}14$, $w = 1/[\sigma^2(F_o) + 0{\cdot}0003F_o^2]$, $(\Delta/\sigma)_{max} = 0{\cdot}1$, $(\Delta\rho)_{max} = 0{\cdot}19$, $(\Delta\rho)_{min} = -0{\cdot}28$ e Å^{-3}. Computer programs: *MULTAN*80 (Main *et al.*, 1980), *SHELX*76 (Sheldrick, 1976) and local programs (Jaskólski, 1982*a*). 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 parameters are given in Table 1, bond lengths and angles in Table 2.†

An *ORTEP* stereodrawing showing the atom labelling system is presented in Fig. 1. The N(1)—C(1) and C(1)—N(2) bond lengths are significantly different. From a semiempirical correlation ($r = r_0 - 0{\cdot}18p$) between π-bond orders (p) and bond distances (r) where r_0 is a standard single-bond distance (1·458 Å for C—N

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† Previous paper: Ciszak, Gdaniec, Jaskólski, Kosturkiewicz, Owsiański & Tykarska (1989).

† 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 51248 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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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}
C(1)	0·4013 (1)	0·1782 (3)	0·0682 (3)	0·053 (1)
C(2)	0·4104 (2)	0·0389 (3)	0·2349 (3)	0·054 (1)
C(3)	0·4597 (2)	0·0118 (3)	0·2965 (4)	0·065 (1)
C(4)	0·4689 (2)	−0·0924 (3)	0·3459 (4)	0·069 (2)
C(5)	0·4296 (2)	−0·1696 (3)	0·3370 (4)	0·064 (1)
C(6)	0·3806 (2)	−0·1419 (3)	0·2737 (5)	0·072 (2)
C(7)	0·3709 (2)	−0·0398 (3)	0·2233 (4)	0·066 (1)
C(8)	0·3541 (1)	0·3513 (2)	0·1151 (3)	0·051 (1)
C(9)	0·3630 (2)	0·4594 (3)	0·0969 (4)	0·057 (1)
C(10)	0·3339 (2)	0·5334 (3)	0·1783 (4)	0·061 (1)
C(11)	0·2962 (1)	0·5022 (3)	0·2826 (4)	0·063 (1)
C(12)	0·2872 (2)	0·3938 (3)	0·2958 (5)	0·072 (2)
C(13)	0·3150 (2)	0·3186 (3)	0·2143 (4)	0·066 (1)
C(14)	0·4391 (2)	−0·2804 (3)	0·3962 (6)	0·098 (2)
C(15)	0·2671 (2)	0·5829 (3)	0·3755 (5)	0·085 (2)
C(16)	0·4258 (1)	0·1142 (3)	−0·0522 (3)	0·060 (1)
N(1)	0·3837 (1)	0·2778 (2)	0·0293 (3)	0·058 (1)
N(2)	0·3973 (1)	0·1461 (2)	0·2001 (3)	0·060 (1)

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

C(1)–N(1)	1·368 (4)	C(8)–C(9)	1·382 (5)
C(1)–N(2)	1·283 (4)	C(9)–C(10)	1·391 (5)
N(2)–C(2)	1·419 (4)	C(10)–C(11)	1·390 (5)
C(2)–C(3)	1·380 (6)	C(11)–C(12)	1·382 (6)
C(3)–C(4)	1·401 (6)	C(12)–C(13)	1·385 (6)
C(4)–C(5)	1·370 (6)	C(13)–C(8)	1·387 (5)
C(5)–C(6)	1·381 (6)	C(5)–C(14)	1·510 (6)
C(6)–C(7)	1·382 (5)	C(11)–C(15)	1·506 (6)
C(7)–C(2)	1·387 (6)	C(1)–C(16)	1·496 (5)
N(1)–C(8)	1·416 (4)	N(1)–H(1)	0·82 (4)

N(1)–C(1)–N(2)	120·7 (3)	C(10)–C(11)–C(12)	116·4 (3)
N(1)–C(1)–C(16)	114·9 (3)	C(11)–C(12)–C(13)	122·8 (3)
N(2)–C(1)–C(16)	124·4 (3)	C(12)–C(13)–C(8)	119·9 (3)
C(1)–N(2)–C(2)	119·6 (3)	C(13)–C(8)–C(9)	118·6 (3)
N(2)–C(2)–C(3)	121·7 (3)	C(13)–C(8)–N(1)	122·1 (3)
C(2)–C(3)–C(4)	120·3 (3)	C(7)–C(2)–N(2)	119·9 (3)
C(3)–C(4)–C(5)	121·7 (3)	C(3)–C(2)–C(7)	118·0 (3)
C(4)–C(5)–C(6)	117·5 (3)	C(4)–C(5)–C(14)	121·3 (3)
C(5)–C(6)–C(7)	121·7 (3)	C(6)–C(5)–C(14)	121·2 (3)
C(6)–C(7)–C(2)	120·8 (3)	C(10)–C(11)–C(15)	121·3 (3)
C(1)–N(1)–C(8)	127·6 (3)	C(12)–C(11)–C(15)	122·3 (3)
N(1)–C(8)–C(9)	119·3 (3)	C(1)–N(1)–H(1)	114 (2)
C(8)–C(9)–C(10)	120·5 (3)	C(8)–N(1)–H(1)	118 (3)
C(9)–C(10)–C(11)	121·8 (3)		

bonds) (Norrestam, Mertz & Crossland, 1983), the following π-bond orders are obtained in the present structure: 0·5 for C(1)–N(1) and 1·0 for C(1)–N(2). The former bond is, therefore, intermediate between a single and a double bond, while the latter is a typical double bond. In a similar compound, N^1,N^2-diphenylformamidine (Anulewicz, Krygowski & Pniewska, 1987), the difference between C–N¹ and C–N² (Δ) is very small [$\Delta = 0{\cdot}009$ (4) Å for molecule A and 0·012 (4) Å for molecule B]. In another formamidine with different substituents at N^1 and N^2 [N^1,N^1-hexamethylene-N^2-p-nitrophenylformamidine (Krajewski *et al.*, 1981)], this difference is 0·032 (9) Å, and in N^1,N^1-dimethyl-N^2-p-nitrophenylformamidine (Ciszak *et al.*, 1989), $\Delta = 0{\cdot}043$ (6) and 0·042 (6) Å for the two independent molecules. In acet-, benz- and pival-amidines investigated in this laboratory (Surma, Jaskólski, Kosturkiewicz & Oszczapowicz, 1988; Ciszak *et al.*, 1989), Δ varies from 0·052 (8) Å in N^1,N^1-dimethyl-N^2-p-nitrophenylacetamidine to 0·087 (4) Å in N^1,N^1-dimethyl-N^2-p-nitrophenyl-2,2-dimethylpropionamidine. In the present structure Δ is 0·085 (6) Å although N¹ and N² have identical substituents. In conclusion we can say that it is the presence of an H atom at C(1) that permits an equalization of N¹–C and C–N² while symmetrical substitution at N¹ and N² and the presence of an H atom at N¹ seem to play a minor role.

The value of the N(1)–C(1)–N(2) angle, 120·7 (3)°, is larger than in many other *trans*-amidine derivatives substituted at the $C_{amidine}$ atom. Intermolecular forces seem to be the reason for this widening of angle.

As a result of molecular overcrowding, the N^1- and N^2-p-tolyl rings are twisted relative to the central amidine plane by 39·4 (4) and 88·1 (4)°, respectively.

N¹ and the p-tolyl group at N² are in a *trans* (E) configuration relative to the C(1)=N(2) double bond. Owing to the partial double-bond character of N(1)–C(1), rotation about this bond is hindered and two isomeric forms can exist. N² and the p-tolyl group at N(1) are in a *syn* (Z) configuration relative to the C(1)–N(1) bond. This configuration is different from

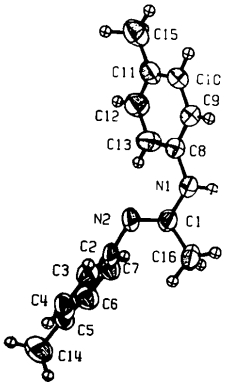

Fig. 1. View of the molecule with atom numbering.

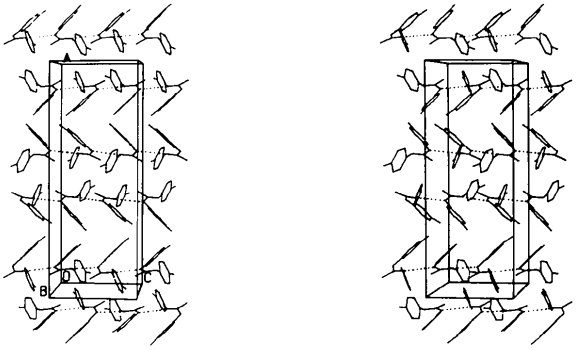

Fig. 2. A stereoview packing diagram.

that found in N^1,N^2-diphenylformamidine (Anulewicz *et al.*, 1987), where a different H-bond pattern was also found. The molecules of this formamidine form H-bonded dimers; such a dimerization is possible owing to the location of the lone pair at N^2 and the N^1—H donor on the same side of the molecule. In the present di(*p*-tolyl)acetamidine the lone pair at N^2 and the N^1—H are situated on opposite sides of the molecule, leading to a different pattern of H bonds in the crystal. The molecular packing is shown in Fig. 2. An intermolecular hydrogen bond between the molecules related by a glide plane [N(1)···N(2^i) 3·196 (4), H(1)···N(2^i) 2·38 (4) Å, N(1)—H(1)···N(2^i) 170 (2)°; (i) x, 0·5—y, —0·5+z] joins the molecules into infinite chains parallel to c. According to its ΔHA parameters (Jaskólski, 1982*b*), this hydrogen bond can be considered as medium weak ($\Delta HA = 12{\cdot}5$).

According to Sohàr (1967), solid *N,N'*-diphenylacetamidine shows an IR spectrum indicating the formation of a cyclic dimeric structure. The X-ray analysis of di-*p*-tolylacetamidine shows a different H-bond pattern and does not confirm the rule drawn from inspection of the IR spectrum.

As can be seen in Fig. 2, the *E,Z* configuration of the molecules makes possible the formation of infinite chains joined by hydrogen bonds.

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Structure of *rel*-(1*S*,2*S*,3*S*,6*S*,7*R*)-6-Acetoxy-5-bromo-1,2-dimethoxycarbonyl-3,7-dimethylcyclohept-4-ene

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Abstract. Dimethyl *rel*-(1*S*,2*S*,3*S*,6*S*,7*R*)-6-acetoxy-5-bromo-1,2-dimethoxycarbonyl-3,7-dimethylcyclohept-4-ene-1,2-dicarboxylate, $C_{15}H_{21}BrO_6$, $M_r = 377{\cdot}24$, monoclinic, $P2_1/n$, $a = 26{\cdot}004$ (2), $b = 7{\cdot}746$ (1), $c = 8{\cdot}540$ (3) Å, $\beta = 98{\cdot}90$ (1)°, $V = 1699{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}474$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) =

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