Cl9—P6—N5	107.9 (3)	C14—C11—C12	107.3 (8)
Cl9—P6—N6	108.8 (2)	C14—C11—C13	109.0 (8)
Cl8—P6—N5	109.7 (3)		
C2—C1—C6—C7	154.9 (7)	O1—P1—P4—N6	66.5 (6)
C6—C1—C2—C11	−156.6 (7)	O1—P1—P4—Cl5	−179.4 (4)
C2—C1—O1—P1	90.9 (6)	O1—P1—P4—N4	−66.0 (6)
C1—O1—P1—P4	−179.1 (4)	N2—P1—O1—C1	−66.2 (7)
N1—P1—O1—C1	67.9 (6)	N2—P1—P4—N4	177.7 (6)

The H atoms were geometrically positioned 1.0 Å from their corresponding atoms and a riding model was used in the refinement process. Initially, a unit-weighting scheme was used, but in the final stages of the refinement the weights were assigned using the method described by Carruthers & Watkin (1979), as incorporated in the CRYSTALS package (Watkin, Carruthers & Betteridge, 1985). Other programs used were SHELXS86 (Sheldrick, 1990) and SNOOPI (Davies, 1983).

References

Allcock, H. R. (1972). Chem. Rev. 72, 315–356.
Allcock, H. R., Connolly, M. S. & Harris, P. J. (1982). J. Am. Chem. Soc. 104, 2482–2490.
Allcock, H. R., Karen, D. L., Riding, G. H., Suszko, P. R. & Whittle, R. R. (1984). J. Am. Chem. Soc. 106, 2337–2347.
Allcock, H. R., Mang, M. N., McDonnel, G. S. & Parvez, M. (1987). Macromolecules, 20, 2060–2067.
Allcock, H. R., Manners, I., Mang, M. N. & Parvez, M. (1990). Inorg. Chem. 29, 522–529.
Allcock, H. R., Riding, G. H. & Whittle, R. R. (1984). J. Am. Chem. Soc. 106, 5561–5567.
Bandoli, G., Casellato, U., Gleria, M., Grassi, A., Montoneri, E. & Pappalardo, G. C. (1989). J. Chem. Soc. Dalton Trans. pp. 757–760.
Carruthers, J. R. & Watkin, D. J. (1979). Acta Cryst. A35, 698–699.
Çetinkaya, B., Gümrükçü, I. & Lappert, M. F. (1980). J. Am. Chem. Soc. 102, 2086–2087.
Contractor, S. R., Hursthouse, M. B., Shaw, L. S., Shaw, R. A. & Yılmaz, H. (1985). Acta Cryst. B41, 122–131.
Davies, K. (1983). SNOOPI. Program for Drawing Crystal and Molecular Diagrams. Univ. of Oxford, England.
Fincham, J. K., Hursthouse, M. B., Parkes, H. G., Shaw, L. S. & Shaw, R. A. (1986). Acta Cryst. B42, 462–472.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). Acta Cryst. A24, 351–359.
Sheldrick, G. M. (1990). Acta Cryst. A46, 467–473.
Watkin, D. J., Carruthers, J. R. & Betteridge, D. W. (1985). CRYSTALS User Guide. Chemical Crystallography Laboratory, Univ. of Oxford, England.

N^1,N^2-Di(p-tolyl)benzamidine, $C_{21}H_{20}N_2$

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J. Barker

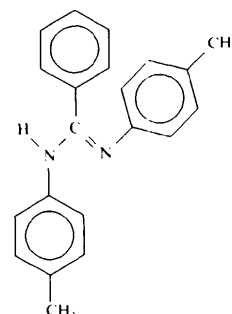The Associated Octel Co. Ltd, Ellesmere Port, South Wirral L65 4HF, England

Abstract

The C—N bonds in the amidine skeleton show distinct amine and imine characteristics; the N—C—N bond angle is 120.8 (7)°. An E,Z configuration is observed and the solid is held together in infinite chains containing N—H···N hydrogen bonding.

Comment

The structures of amidines continue to attract attention (Alcock, Barker & Kilner, 1988; Kosturkiewicz, Ciszak & Tykarska, 1992) because of their biological and ligating properties. The asymmetric unit in N^1,N^2-di(p-tolyl)benzamidine(1) contains two molecules, one of which is shown in Fig. 1.

(1)

The geometry of the amidine N—C—N skeleton is of interest since this is the portion which is particularly prone to structural changes upon coordination to a metal. The C—N bond lengths alternate as expected, with a mean C—N distance of 1.368 (10) Å and a mean C=N distance of 1.281 (11) Å; these values are not significantly different from those reported (Alcock, Barker & Kilner, 1988) for N^1,N^2-diphenylbenzamidine. The mean N—C—N bond angle of 120.8 (7)° is very close to the ideal value for

sp^2 hybridization; in general this angle is dependent upon the conformation of the molecule and the size of the substituents.

With respect to the N—C—N skeleton, the tolyl substituent at the imine N atom is in a *trans* (*E*) orientation while the tolyl substituent at the amine N atom is *cis* (*Z*). The overall conformation is thus described as *E,Z* (as for N^1,N^2-diphenylbenzamidine) and this implies that the imine lone pair and the N—H proton are on opposite sides of the molecule. This orientation results in the formation of infinite hydrogen-bonded chains along *b* in the solid state (Fig. 2). The hydrogen-bonded N⋯N distances are 3.16 Å between molecules in the asymmetric unit and 3.05 Å between other molecules.
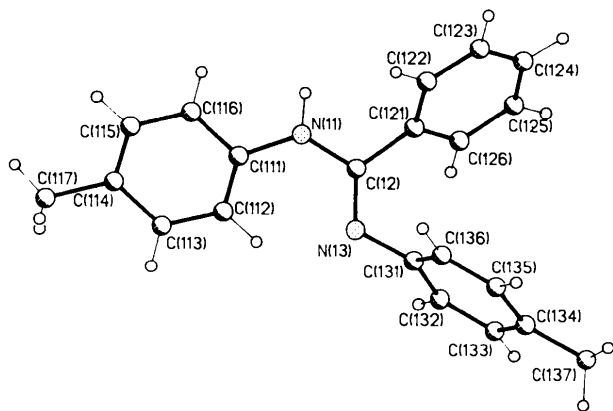

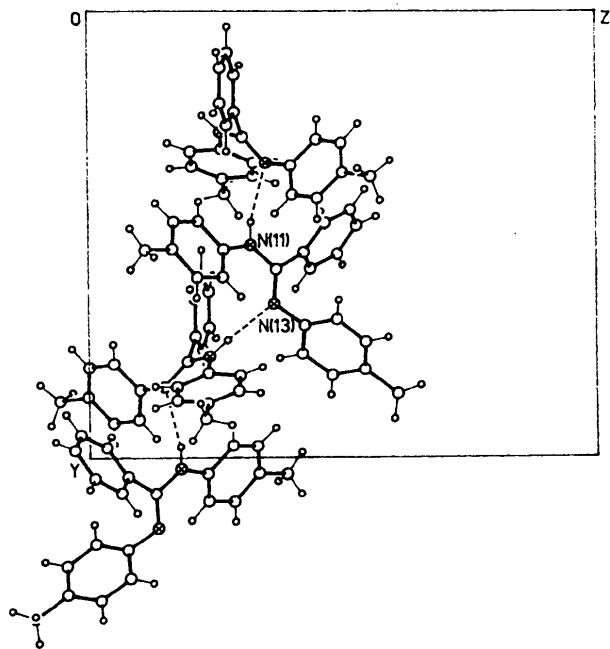Fig. 1. Molecular structure of N^1,N^2-di(*p*-tolyl)benzamidine.

Fig. 2. Partial packing diagram showing one of the hydrogen-bonded chains.

Experimental

The compound was supplied by the Associated Octel Co. Ltd and recrystallized from *n*-hexane.

Crystal data

$C_{21}H_{20}N_2$	Mo $K\alpha$ radiation
$M_r = 300.4$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 15
$P2_12_12_1$	reflections
$a = 11.364$ (2) Å	$\theta = 8\text{-}12°$
$b = 16.452$ (3) Å	$\mu = 0.07$ mm^{-1}
$c = 18.609$ (4) Å	$T = 290$ K
$V = 3479$ (4) Å^3	Irregular block
$Z = 8$	$0.51 \times 0.47 \times 0.28$ mm
$D_x = 1.15$ Mg m^{-3}	Colourless

Data collection

Siemens $P3R3$ diffractometer	$\theta_{max} = 21°$
ω-2θ scans	$h = 0 \rightarrow 11$
Absorption correction:	$k = 0 \rightarrow 16$
none	$l = 0 \rightarrow 18$
2146 measured reflections	3 standard reflections
2146 independent reflections	monitored every 200
1388 observed reflections	reflections
$[I \geq 2.0\sigma(I)]$	intensity variation: none

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.04$
$R = 0.051$	$\Delta\rho_{max} = 0.14$ e Å^{-3}
$wR = 0.070$	$\Delta\rho_{min} = -0.15$ e Å^{-3}
$S = 1.16$	Extinction correction: none
1388 reflections	Atomic scattering factors
427 parameters	from *SHELXTL-Plus*
$w = 1/[\sigma^2(F) + 0.0012F^2]$	(Sheldrick, 1986)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N(11)	0.0101 (7)	0.5243 (4)	0.3203 (4)	0.072 (2)
N(13)	−0.0008 (6)	0.6551 (4)	0.3652 (3)	0.064 (2)
N(21)	−0.0162 (5)	0.2725 (4)	0.2613 (3)	0.053 (2)
N(23)	0.0807 (5)	0.3414 (4)	0.3506 (3)	0.056 (2)
C(12)	−0.0284 (7)	0.5787 (6)	0.3699 (4)	0.065 (3)
C(22)	0.0796 (7)	0.2842 (5)	0.3053 (4)	0.051 (2)
C(111)	0.0987 (7)	0.5348 (5)	0.2670 (4)	0.054 (2)
C(112)	0.1771 (8)	0.5956 (5)	0.2654 (5)	0.064 (2)
C(113)	0.2649 (8)	0.5956 (6)	0.2151 (5)	0.079 (3)
C(114)	0.2752 (9)	0.5340 (7)	0.1661 (5)	0.084 (3)
C(115)	0.1954 (9)	0.4742 (6)	0.1689 (5)	0.083 (3)
C(116)	0.1063 (9)	0.4728 (5)	0.2173 (4)	0.076 (3)
C(117)	0.3767 (9)	0.5357 (7)	0.1117 (5)	0.126 (3)
C(121)	−0.1091 (7)	0.5412 (5)	0.4246 (4)	0.054 (2)
C(122)	−0.0756 (8)	0.4768	0.4661 (4)	0.068 (3)
C(123)	−0.1443 (9)	0.4478 (6)	0.5169 (5)	0.090 (3)
C(124)	−0.2504 (11)	0.4825 (8)	0.5287 (5)	0.107 (3)
C(125)	−0.2878 (9)	0.5449 (7)	0.4903 (6)	0.104 (3)
C(126)	−0.2178 (8)	0.5771 (6)	0.4373 (5)	0.080 (3)
C(131)	−0.0250 (8)	0.7036 (5)	0.4258 (5)	0.059 (2)
C(132)	−0.0986 (9)	0.7669 (5)	0.4212 (5)	0.079 (3)
C(133)	−0.1176 (9)	0.8153 (5)	0.4792 (5)	0.087 (3)

$C_{21}H_{20}N_2$

C(134)	−0.0634 (9)	0.8022 (5)	0.5439 (5)	0.074 (3)
C(135)	0.0145 (8)	0.7398 (6)	0.5456 (5)	0.074 (3)
C(136)	0.0349 (7)	0.6901 (5)	0.4891 (4)	0.063 (2)
C(137)	−0.0838 (10)	0.8562 (6)	0.6083 (5)	0.113 (3)
C(211)	−0.1263 (7)	0.3104 (4)	0.2639 (5)	0.056 (2)
C(212)	−0.1896 (8)	0.3160 (5)	0.2023 (5)	0.070 (3)
C(213)	−0.3025 (9)	0.3500 (5)	0.2049 (6)	0.089 (3)
C(214)	−0.3506 (8)	0.3775 (6)	0.2655 (8)	0.102 (3)
C(215)	−0.2858 (8)	0.3711 (6)	0.3259 (6)	0.085 (3)
C(216)	−0.1740 (8)	0.3412 (5)	0.3265 (5)	0.077 (3)
C(217)	−0.4745 (8)	0.4119 (6)	0.2696 (7)	0.134 (3)
C(221)	0.1780 (7)	0.2280 (5)	0.2894 (4)	0.050 (2)
C(222)	0.2835 (8)	0.2577 (5)	0.2748 (5)	0.078 (3)
C(223)	0.3786 (9)	0.2084 (7)	0.2617 (6)	0.104 (3)
C(224)	0.3634 (10)	0.1275 (6)	0.2625 (5)	0.098 (3)
C(225)	0.2557 (10)	0.0938 (6)	0.2767 (5)	0.085 (3)
C(226)	0.1612 (8)	0.1446 (5)	0.2899 (4)	0.064 (3)
C(231)	0.1728 (7)	0.3477 (5)	0.3996 (4)	0.054 (2)
C(232)	0.2435 (7)	0.4135 (5)	0.4022 (5)	0.066 (2)
C(233)	0.3323 (7)	0.4210 (5)	0.4517 (5)	0.071 (3)
C(234)	0.3532 (8)	0.3632 (6)	0.5016 (5)	0.077 (3)
C(235)	0.2814 (10)	0.2976 (6)	0.4994 (5)	0.103 (3)
C(236)	0.1934 (9)	0.2896 (5)	0.4504 (5)	0.093 (3)
C(237)	0.4487 (8)	0.3721 (6)	0.5569 (5)	0.105 (3)

Table 2. *Selected geometric parameters* (Å, °)

N(11)—C(12)	1.359 (11)	N(11)—C(111)	1.424 (11)
N(13)—C(12)	1.299 (12)	N(13)—C(131)	1.409 (11)
N(21)—C(22)	1.376 (10)	N(21)—C(211)	1.400 (10)
N(23)—C(22)	1.263 (10)	N(23)—C(231)	1.391 (10)
C(12)—C(121)	1.503 (12)	C(22)—C(221)	1.481 (11)
C(12)—N(11)—C(111)	128.4 (7)	C(12)—N(13)—C(131)	116.5 (7)
C(22)—N(21)—C(211)	128.6 (7)	C(22)—N(23)—C(231)	120.1 (7)
N(11)—C(12)—N(13)	120.9 (7)	N(11)—C(12)—C(121)	112.7 (8)
N(13)—C(12)—C(121)	126.2 (8)	N(21)—C(22)—N(23)	120.7 (7)
N(21)—C(22)—C(221)	113.0 (6)	N(23)—C(22)—C(221)	126.2 (7)
N(11)—C(111)—C(112)	125.2 (7)	N(11)—C(111)—C(116)	114.9 (7)

The crystal was mounted in a Lindemann tube. The scan speed was 5–29° min^{-1} in ω, depending upon the intensity of a 2 s prescan; backgrounds were measured at each end of the scan for $\frac{1}{4}$ of the scan time. Reflections were processed using profile analysis. The structure was solved by direct methods using *SHELXTL-Plus* (Sheldrick, 1986). Anisotropic temperature factors were used for all non-H atoms. H atoms were given fixed isotropic temperature factors, $U = 0.08$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; Me groups were treated as rigid CH$_3$ units. The absolute structure was not determined. Computation was performed with *SHELXTL-Plus* on a DEC MicroVAX II.

References

Alcock, N. W., Barker, J. & Kilner, M. (1988). *Acta Cryst.* **C44**, 712–715.
Kosturkiewicz, Z., Ciszak, E. & Tykarska, E. (1992). *Acta Cryst.* **B48**, 471–476.
Sheldrick, G. M. (1986). *SHELXTL-Plus User's Manual.* Nicolet Instrument Corporation, Madison, Wisconsin, USA.

2'-Bromo-4-[N-(2-cyanoethyl)-N-(2-phenyl-ethyl)]amino-4'-nitroazobenzene

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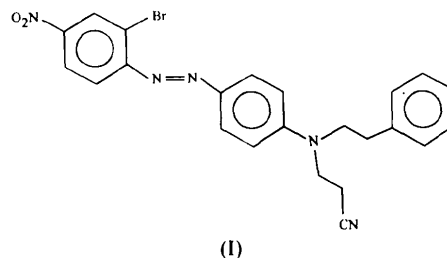*Institute of General and Ecological Chemistry, Technical University of Łódz, Żwirki 36, 90-924 Łódź, Poland*

Abstract

The structure of the title compound 3-{[4-(2-bromo-4-nitrophenylazo)phenyl](2-phenylethyl)amino}propanenitrile, $C_{23}H_{20}BrN_5O_2$, shows characteristic features of azobenzene derivatives. The rings in the azobenzene frame are twisted by 28.4 (4) and 9.9 (4)° in relation to the azo group plane. The larger twist is associated with the nitrobenzene ring and correlates with a longer N—C bond.

Comment

Crystals of the title compound (I) were obtained from a toluene solution of commercially available material (Samaronscharlach RGSL FH-Hoechst, C.I. Disperse Red 183) by evaporation of the solvent.

(I)

The most interesting feature of the structure is the significant twist of one of the phenyl rings within the azobenzene frame. Only nine azobenzene structures among 21 entries found in the Cambridge Structural Database (1992) show significant conjugation of the whole azobenzene system, as evidenced by planarity and shortening of the two N—C bonds. In these structures, the values of both C—C—N—N torsion angles are below 8° and the average N—C bond length is 1.405 (8) Å. In eight other structures, the C—C—N—N torsion angles are greater (usually over 40°) and the average C—N bond length is 1.445 (5) Å (Table 2). There are also azobenzene derivatives with only one benzene ring coplanar with the azo system, similar to the title compound. The nitro group is twisted by 3.7 (2)° in relation to the