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α,β-Bis(*N*-methylanilino)stilbene

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Abstract. $C_{28}H_{26}N_2$, monoclinic, $P2_1$, $a = 9{\cdot}94\ (2)$, $b = 14{\cdot}58\ (3)$, $c = 7{\cdot}91\ (2)$ Å, $\beta = 106{\cdot}5\ (2)°$, $V = 1099{\cdot}86$ Å^3, $Z = 2$; $D_m = 1{\cdot}177$, $D_x = 1{\cdot}179$ g cm^{-3}; $F(000) = 416$. Full-matrix least-squares refinement gave $R = 0{\cdot}084$ and $R_w = 0{\cdot}072$ for 375 parameters and 1928 significant reflexions. The molecule exhibits a *cis* configuration and the phenyl groups are twisted out of the plane of the ethylene group to avoid steric hindrance. The N atoms have a planar configuration.

Introduction. An unsolved configuration led us to investigate the structure of $C_{28}H_{26}N_2$. Yellow-orange crystals, recrystallized from benzene at room temperature, were provided by Henning Lund.

A crystal 0·78 × 0·40 × 0·25 mm was mounted along *a*. Weissenberg photographs showed systematic absences of reflexions 0*k*0 for *k* odd. Intensities were collected with a linear diffractometer (Arndt & Phillips, 1961), using monochromated Mo *K*α radiation up to $\sin\theta_{\max} = 0{\cdot}5$. The background-peak-background method was employed. Intensities were corrected for Lorentz and polarization effects but no absorption correction was made ($\mu = 0{\cdot}75$ cm^{-1}).

Direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) were applied. Normalized structure factors were obtained (*SYMBAD*, Danielsen, 1969) from 2662 observed reflexions of which 393 with $E \geq 1{\cdot}4$ were used. The calculations indicated the absence of a centre of symmetry hence the space group $P2_1$.

Positions of all 30 non-hydrogen atoms were found from the *E* map corresponding to the second lowest value of 'RESID' and the fourth highest 'ABSFOM' as given by *MULTAN*.

A structure factor calculation at this point gave $R = 0{\cdot}65$, indicating that the positions for the atoms were only approximate, which made it best to start refinement by using constraints (Pawley, 1971). Starting with the innermost 73 reflexions and four fragments of seven atoms each, and allowing only the scale factor, Euler angles and centres of gravity to move, the *R* value fell to 0·24. In spite of the initial *R* being so high the trial structure was confirmed and the shifts were small and unsystematic. After a gradual increase in the number of reflexions and inclusion of atoms, the *R* value was 0·131 for 1654 reflexions and 98 parameters. Further refinement was continued using full-matrix least squares (*LINUS*, Coppens & Hamilton, 1970) minimizing the quantity $r = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$ where $w = \{[\sigma(F_o^2) + 1{\cdot}02F_o^2]^{1/2} - |F_o|\}^{-2}$.

The scattering factors used for C and N were those of Cromer & Mann (1968) and of Stewart, Davidson & Simpson (1965) for H. Final refinement of the coordinates, overall scale factor, thermal parameters (anisotropic for C and N, isotropic for H) gave an *R* value of 0·084 ($wR = 0{\cdot}070$) for 56 atoms, 1928 reflexions $[>2\sigma(I)]$ and 375 parameters refined in batches of 210.[*] Illustrations were drawn by *ORTEP* (Johnson, 1965) while interatomic distances, angles, least-squares planes and dihedral angles were calculated with *ORFFE* (Busing, Martin & Levy, 1964).

Discussion. The molecule with the numbering of atoms is shown in Fig. 1. The configuration around the double bond is *cis* and a pseudo twofold axis is present.

The final coordinates, interatomic distances and bond angles are listed in Tables 1, 2, and 3, respectively. The ethylenic bond, C(1)–C(2) (1·356 Å), agrees well with the corresponding bond, α–β (1·35 Å),

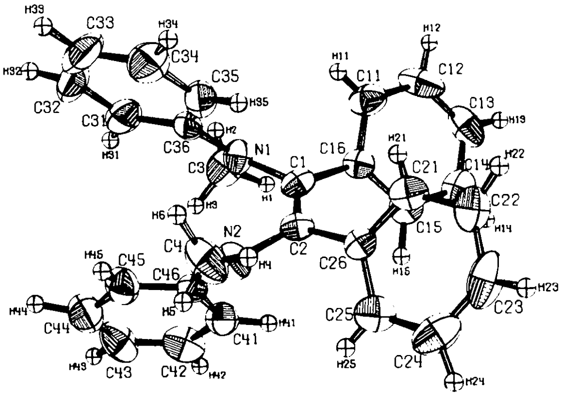

Fig. 1. View of the molecule illustrating thermal ellipsoids (50% probability) and atom numbering.

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[*] Lists of structure factors, thermal parameters, hydrogen atom coordinates and C–H distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33721 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* (×10⁴)

	x	*y*	*z*
C(11)	1617 (6)	5552 (4)	2981 (7)
C(12)	2500 (7)	5801 (5)	1992 (8)
C(13)	3304 (6)	5166 (5)	1467 (8)
C(14)	3230 (6)	4266 (5)	1932 (7)
C(15)	2354 (5)	4007 (3)	2926 (6)
C(16)	1537 (5)	4640 (4)	3484 (6)
C(21)	3478 (5)	4224 (4)	7265 (6)
C(22)	4850 (5)	4015 (5)	8166 (7)
C(23)	5180 (6)	3131 (6)	8666 (7)
C(24)	4179 (7)	2453 (5)	8270 (9)
C(25)	2822 (6)	2680 (4)	7377 (8)
C(26)	2430 (5)	3570 (4)	6848 (6)
C(1)	582 (5)	4383 (3)	4531 (6)
C(2)	949 (5)	3787 (3)	5900 (6)
C(31)	2853 (6)	350 (4)	5290 (8)
C(32)	3443 (7)	811 (5)	4153 (10)
C(33)	2628 (8)	1132 (5)	2570 (11)
C(34)	1201 (7)	973 (5)	2089 (9)
C(35)	599 (6)	517 (4)	3233 (8)
C(36)	1397 (5)	196 (3)	4843 (7)
C(41)	8824 (5)	2503 (4)	3903 (7)
C(42)	7645 (6)	2103 (4)	2763 (8)
C(43)	6384 (6)	2163 (5)	3105 (9)
C(44)	6235 (6)	2627 (5)	4531 (9)
C(45)	7404 (6)	3038 (4)	5669 (8)
C(46)	8707 (4)	2980 (3)	5363 (6)
N(1)	788 (4)	−235 (3)	6032 (5)
N(2)	9924 (4)	3361 (3)	6558 (5)
C(3)	8381 (6)	4633 (5)	2158 (7)
C(4)	8 (6)	3412 (5)	8436 (7)

Table 2. *Interatomic distances* (Å)

C(11)–C(12)	1·383 (7)	C(41)–C(42)	1·385 (7)
C(12)–C(13)	1·364 (9)	C(42)–C(43)	1·359 (8)
C(13)–C(14)	1·371 (9)	C(43)–C(44)	1·361 (9)
C(14)–C(15)	1·384 (7)	C(44)–C(45)	1·385 (8)
C(15)–C(16)	1·383 (7)	C(45)–C(46)	1·386 (6)
C(16)–C(11)	1·398 (7)	C(46)–C(41)	1·383 (7)
C(21)–C(22)	1·378 (7)	C(1)–C(2)	1·356 (6)
C(22)–C(23)	1·361 (9)	C(1)–C(16)	1·477 (6)
C(23)–C(24)	1·374 (9)	C(2)–C(26)	1·481 (6)
C(24)–C(25)	1·371 (8)	C(1)–N(1)	1·420 (6)
C(25)–C(26)	1·386 (7)	C(2)–N(2)	1·414 (6)
C(26)–C(21)	1·381 (7)		
C(31)–C(32)	1·384 (8)	N(1)–C(36)	1·406 (6)
C(32)–C(33)	1·364 (9)	N(2)–C(46)	1·417 (6)
C(33)–C(34)	1·379 (8)	N(1)–C(3)	1·447 (6)
C(34)–C(35)	1·390 (7)	N(2)–C(4)	1·467 (6)
C(35)–C(36)	1·375 (7)		
C(36)–C(31)	1·405 (6)		

Table 3. *Bond angles* (°)

(*a*) Angles inside the benzene rings

C(11)	120·7 (5)	C(31)	120·8 (6)
C(12)	121·1 (5)	C(32)	120·9 (6)
C(13)	119·1 (5)	C(33)	119·2 (6)
C(14)	120·4 (5)	C(34)	120·1 (6)
C(15)	121·5 (5)	C(35)	121·7 (5)
C(16)	117·3 (4)	C(36)	117·2 (5)
C(21)	122·4 (5)	C(41)	119·8 (5)
C(22)	118·6 (5)	C(42)	119·9 (5)
C(23)	121·3 (5)	C(43)	121·6 (5)
C(24)	118·8 (6)	C(44)	118·8 (5)
C(25)	122·1 (5)	C(45)	120·9 (5)
C(26)	116·6 (4)	C(46)	118·9 (5)

(*b*) Angles around the ethylene carbon and the nitrogen atoms

N(1)–C(1)–C(16)	116·0 (4)	N(2)–C(2)–C(26)	115·8 (4)
C(16)–C(1)–C(2)	122·9(4)	C(26)–C(2)–C(1)	122·8 (4)
C(2)–C(1)–N(1)	121·0 (4)	C(1)–C(2)–N(2)	121·4 (4)
C(1)–N(1)–C(3)	118·7 (4)	C(2)–N(2)–C(4)	121·0 (4)
C(3)–N(1)–C(36)	119·4 (4)	C(4)–N(2)–C(46)	119·0 (4)
C(36)–N(1)–C(1)	121·6 (4)	C(46)–N(2)–C(2)	119·5 (4)

Table 4. *Distances* (Å) *of atoms from least-squares planes through:* (*a*) *the ethylene group and the atoms bonded to it,* (*b*) N(1) *and its neighbours,* (*c*) N(2) *and its neighbours*

Plane (*a*)		Plane (*b*)		Plane (*c*)	
C(1)	0·0058	C(36)	0·0101	C(46)	−0·0160
C(2)	−0·0083	C(3)	−0·0215	C(4)	−0·0317
C(16)	−0·2160	N(1)	0·0256	N(2)	0·0378
C(26)	0·1972	C(1)	−0·0117	C(2)	−0·0138
N(1)	0·1726				
N(2)	−0·1655				

in 2,6-dibromo-α-cyanostilbene (d'Enghien & Van Meerssche, 1962), where the stilbene group is in a *cis* configuration, and with Pariser–Parr–Pople calculations. It is slightly longer than the corresponding bonds, 1·336, 1·305 Å in *trans*-stilbene (Hoekstra, Meertens & Vos, 1975; Bernstein, 1975*b*; Finder, Newton & Allinger, 1974), 1·343 Å in 4,4′-dimethoxystilbene (Ruban & Luger, 1975), 1·334 Å in α,β-bis(phenylazo)stilbene (Chesick, 1973), and 1·339 Å in a *cis*-stilbene derivative, 1,2-diphenylcyclopentene (Bernstein, 1975*a*). C(1)–C(16) (1·477 Å) and C(2)–C(26) (1·481 Å) are as expected for single bonds adjacent to a phenyl ring and a double bond. Similar bond lengths are found in the stilbenes mentioned above except in 2,6-dibromo-α-cyanostilbene (d'Enghien & Van Meerssche, 1962) where the corresponding bonds are shorter [1·42 and 1·36 (4) Å].

All other bond distances and angles are within the range of normal values. It is notable that in all four phenyl rings the bonds furthest away from the outer bond are shorter than the others, possibly due to the effects of thermal motion. Separate analyses of the thermal motion of the atoms (Schomaker & Trueblood, 1968) for the entire molecule as one rigid body, as well as for each phenyl ring together with the atom to which it is bonded), did not, however, give elucidative results.

The aromatic rings are planar. The N atoms have planar bonding configurations (see Table 4). The same was observed by Chiaroni (1971) for the amino nitrogen of 4-methyl-3-nitro-*N*-methylaniline and by Nielsen (1975) for cyanamide. The angles around the N atoms approximate to 120° in all three compounds. This indicates strongly that the bonding around N may be described as sp^2 hybridization. This can only be

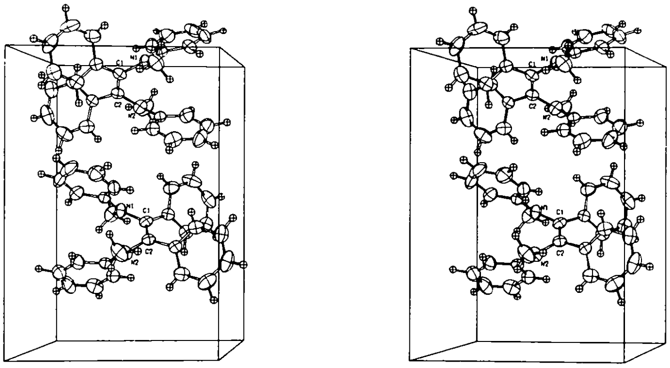

Fig. 2. Stereoscopic view of the unit cell showing the molecular packing.

energetically favourable, compared to the common pyramidal configuration (sp^3 hybridization), because of the interaction of the N lone pair with the π-electron system of the phenyl ring. Extensive discussions about the influence of the N lone pair on the geometry of N-containing molecules are given by Genson & Christoffersen (1972). The angle between the phenyl ring and the plane of coordination around N is 15 and 35°, whereas the torsion angles C(36)–N(1)–C(1)–C(2) and C(46)–N(2)–C(2)–C(1) are 52 and 46°, respectively, so that interaction between the lone pairs and the ethylenic bond is less likely.

The molecule is considerably twisted around both the double bond (17·5°) and the two C–C single bonds (44·3 and 41·7°) in order to avoid steric hindrance between the two phenyl groups in *cis* positions. Similar angles were found in the *cis*-stilbene derivative 1,2-diphenylcyclopentene (Bernstein, 1975*a*),

The packing of molecules in the unit cell is shown in Fig. 2. No intermolecular contacts shorter than normal van der Waals distances were found.

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