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Crystal and Molecular Structure of *trans*-2,5-Dimethylpiperazine

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Synopsis. The crystal structure of *trans*-2,5-dimethylpiperazine has been determined by means of the X-ray method. The molecule is centrosymmetric, the piperazine ring having a *chair* form. The methyl groups are in the equatorial position. The molecules are linked together by N–H···N hydrogen bonds (N···N=3.305(3) Å) to form infinite ribbons along [011].

As a part of conformation studies of piperazine derivatives, we wish hence to report our structure analysis of *trans*-2,5-dimethylpiperazine(mp 119 °C). The structure thus far determined by means of the X-ray method are *cis*- and *trans*-1,4-dibenzoyl-2,5-dimethylpiperazine(DDP).[1,2)]

Experimental and Structure Determination

Colorless prisms elongated along the b axis were obtained by the slow evaporation of a petroleum-benzene solution of the title compound. A prismatic crystal was ground to a cylinder 0.3 mm in diameter and 0.5 mm in length. As the substance was hygroscopic, the sample was sealed in a glass capillary tube 0.3 mm in diameter. The crystal data are as follows: $C_6H_{14}N_2$, F.W.=114.0, space group $P2_1/c$, $a=8.582(2)$, $b=5.231(1)$, $c=8.953(2)$ Å, $\beta=118.09$ (2)°, $V=354.7(3)$ Å^3, $Z=2$, $D_m=1.06$ g cm^{-3} (flotation method), $D_c=1.067$ g cm^{-3}, $\mu=0.711$ cm^{-1} for Mo $K\alpha$ radiation. The intensity data were obtained for 1097 independent reflections with $|F_o|\geqq 3\sigma(F_o)$ by measuring all the reflections within $2\theta\leqq 60.0°$. Correction for Lorentz-polarization factor was made as usual.

The structure was solved by an interpretation of the three-dimensional Patterson map. Refinement was made with a block-diagonal least-squares program, HBLS V[3)]. The calculations were carried out on two computers, the CDC-6600 in the Century Research Center Co., Ltd., and the NEAC-2200/575 in the National Defense Academy. The final R value was 0.059. The atomic parameters are given in Table 1.***

Discussion

The numbering scheme and the thermal ellipsoids are illustrated in Fig. 1, while the bond distances and angles are given in Table 2. The molecule is centrosymmetric, showing that the piperazine ring has

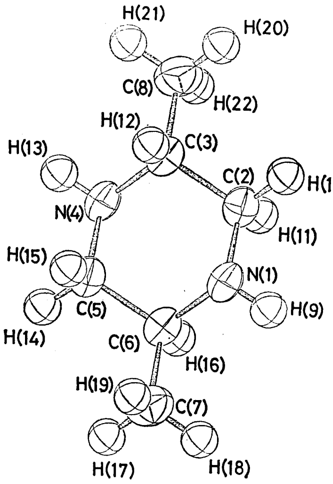

Fig. 1. Thermal vibration ellipsoids[10)] for non-hydrogen atoms are drawn at the 50% probability level, viewed along the normal to the C(2), C(3), C(5), C(6) plane. H atoms are shown as spheres with radii of 0.2 Å.

Table 1. Fractional atomic coordinates (×10^4, for H atoms ×10^3) and equivalent or isotropic thermal parameters

The estimated standard deviations given in parentheses refer to the last decimal position.

Atom	x	y	z	$B_{\mathrm{eq}}^{\mathrm{a)}}$ or B_{iso}/Å^2	Bonding atom
N(1)	71(2)	1315(1)	1405(1)	5.6	
C(2)	−1558(2)	1222(2)	−204(2)	5.6	
C(3)	−1623(2)	−1249(2)	−1129(2)	5.5	
C(7)	3299(3)	1420(2)	2812(2)	6.9	
H(9)	10(2)	272(2)	193(2)	6.4(14)	N(1)
H(10)	−263(2)	127(2)	4(2)	3.4(8)	C(2)
H(11)	−167(2)	274(2)	−96(2)	2.9(7)	C(2)
H(12)	−162(2)	−268(2)	−42(2)	3.5(8)	C(3)
H(17)	437(2)	137(2)	265(2)	4.9(10)	C(7)
H(18)	335(2)	312(2)	339(2)	6.7(12)	C(7)
H(19)	337(2)	−3(2)	352(2)	6.0(12)	C(7)

a) Calculated from the refined anisotropic thermal parameters (deposited) by the method of Willis and Pryor.[11)]

***The complete F_o-F_c data are deposited as Document No. 8209 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

Table 2. Bond distances(l/Å) and bond angles(θ/°)

The estimated standard deviations given in parentheses refer to the least significant figure.

N(1)-C(2)	1.463(3)	C(2)-H(10)	1.04(2)
N(1)-C(6)	1.465(3)	C(2)-H(11)	1.02(2)
C(2)-C(3)	1.521(3)	C(3)-H(12)	0.98(2)
C(6)-C(7)	1.521(3)	C(7)-H(17)	1.00(2)
		C(7)-H(18)	1.02(2)
N(1)-H(9)	0.87(2)	C(7)-H(19)	0.97(2)
N(1)-C(2)-C(3)	109.8(2)	C(3)-C(2)-H(11)	109(1)
C(2)-C(3)-N(4)	107.9(2)	H(10)-C(2)-H(11)	108(2)
C(2)-N(1)-C(6)	110.9(2)	N(4)-C(3)-H(12)	111(1)
C(5)-C(6)-C(7)	111.4(2)	C(2)-C(3)-H(12)	108(1)
N(1)-C(6)-C(7)	110.1(2)	C(8)-C(3)-H(12)	108(1)
		C(6)-C(7)-H(17)	111(1)
C(2)-N(1)-H(9)	110(1)	C(6)-C(7)-H(18)	111(1)
C(6)-N(1)-H(9)	108(1)	C(6)-C(7)-H(19)	110(1)
N(1)-C(2)-H(10)	109(1)	H(17)-C(7)-H(18)	106(2)
C(3)-C(2)-H(10)	109(1)	H(17)-C(7)-H(19)	107(2)
N(1)-C(2)-H(11)	112(1)	H(18)-C(7)-H(19)	112(2)

Table 3. Torsion angles (ϕ/°)

The torsion angle $A(i)$-$A(j)$-$A(k)$-$A(l)$ is viewed down $A(j)$-$A(k)$, with the clockwise rotation of $A(i)$ to $A(l)$ taken to be positive. The e.s.d.'s are 0.5—0.9°.

C(3)-C(2)-N(1)-C(6)	60.8	C(2)-N(1)-C(6)-C(7)	178.5
C(2)-N(1)-C(6)-C(5)	−59.7	C(7)-C(6)-C(5)-N(4)	180.0
N(1)-C(6)-C(5)-N(4)	59.0	C(3)-C(2)-N(1)-H(9)	−179.6
		C(5)-C(6)-N(1)-H(9)	−179.9
		C(7)-C(6)-N(1)-H(9)	−58.8

a *chair* form. The mean N–C bond length, 1.464 Å, is in good agreement with that of *trans*-DDP(1.476 Å),²⁾ that of *cis*-DDP(1.472 Å),¹⁾ and that of piperazine (1.467 Å).⁴⁾ The C–C bond distance is comparable to those found in *N*,*N*′-dimethylpiperazine(1.521 Å),⁵⁾ cyclohexane(1.536 Å),⁶⁾ *cis*-DDP(1.535 Å), and *trans*-DDP(1.517 Å). The C(2)–N(1)–C(6) bond angle is comparable to the 109.0° of piperazine or the 112.6° of piperidine.⁷⁾ The C(2)–N(1)–H(9) and C(6)–N(1)–H(9) bond angles agree with that of 109° for C–N–H in dimethylamine.⁸⁾

The torsion angles are given in Table 3. The values of the ring torsion angles correspond to the typical chair form. The exocyclic torsion angles show that C(7) is in the equatorial position. This result supports Sudmeier's suggestion.⁹⁾ The H(9) atom is in the equatorial position.

The molecular packing with intermolecular distances less than 4.000 Å is shown in Fig. 2. The shortest contact of 3.305 Å is seen between N(1) and the equivalent atom related by a two-fold screw axis. The value of the N-H···N′ angle (168°) suggests the presence of a weak hydrogen bond. These hydrogen bonds form infinite ribbons of molecules along the [011] direction. The ribbons of molecules are held together by the van der Waals interactions.

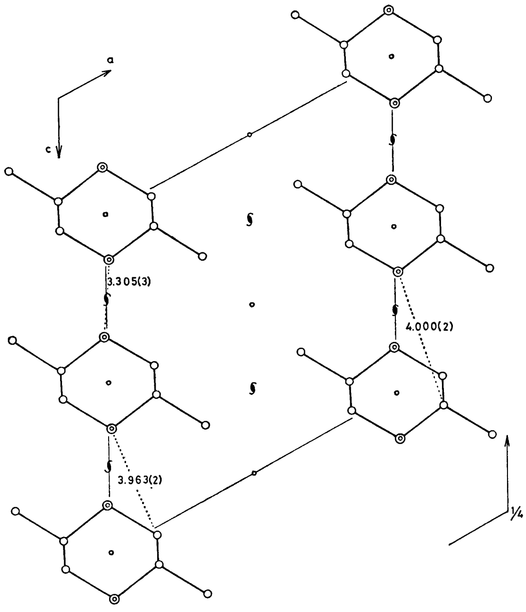

Fig. 2. The molecular packing viewed down the b axis, showing all intermolecular distances less than 4.000 Å.

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