Crystal and Molecular Structure of *trans*-1,4-Dibenzoyl-2,5-dimethylpiperazine†

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The crystal structure of *trans*-1,4-dibenzoyl-2,5-dimethyl-piperazine has been determined by the X-ray method. The space group is $P2_1/c$, with $a=7.483$, $b=6.577$, $c=19.939$ Å, $\beta=116.71°$ and $Z=2$. The structure was solved by the direct method and refined by the least-squares method to the final R factor of 0.094 for 2559 independent reflections. A nitrogen atom and three carbon atoms bonded to the nitrogen atom are approximately in a plane. The molecule is centrosymmetric, the piperazine ring having a *chair*-form. The methyl groups are in the axial position. The oxygen atom is approximately in a plane formed by N, C(carbonyl), and C(benzene). The dihedral angle between this plane and the benzene ring is approximetely 70°.

1,4-Dibenzoyl-2,5-dimethylpiperazine (DDP) has two isomers, the *trans*-form (mp 225 °C) and the *cis*-form (mp 146 °C). The crystal structure of the *cis*-form was reported by Sakurai *et al.*[1] We have studied the *trans*-form in order to discuss the molecular geometry in both forms. The results are given below.

Experimental

Colorless prisms elongated along the b axis were obtained by slow evaporation from an ethanol solution of *trans*-DDP. The crystal is built upon a monoclinic unit cell.

Crystal Data. Oscillation and Weissenberg photographs were taken with Cu $K\alpha$ radiation. The systematically absent reflections indicated that the space group is $P2_1/c$. The cell dimensions were refined by least-squares calculations on the basis of higher-order reflections measured on a diffractometer. The density of the crystal was measured by the flotation method. Since there are two formula units per cell, the molecule has a center of symmetry. The crystal data are summarized in Table 1.

Intensity Data. A prismatic crystal was ground to a cylinder 0.4 mm in diameter and 0.4 mm in length. This was mounted on a four-circle diffractometer (Rigaku AFC-III) with Nb-filtered Mo $K\alpha$ radiation from a graphite monochromator, and the intensity data were collected for 2559 independent reflections with $|F_o| \geqq 3\sigma(F_o)$ with $2\theta \leqq 60.0°$, using the ω-2θ scan technique with a scanning speed of 4° min^{-1} in 2θ. No corrections were made for absorption or extinction.

Table 1. Crystal data

Experimental error given in parentheses refers to the last figure.

Molecular formula	$C_{20}H_{22}N_2O_2$
Formula weight	322.4
Mp	225 °C
Crystal system	Monoclinic
a	7.483 (1) Å
b	6.577 (1)
c	19.939 (4)
β	116.71 (2)°
Space group	$P2_1/c$
V	876.5 (7) Å^3
Z	2
D_m	1.229 g cm^{-1}
D_x	1.221
μ(Mo $K\alpha$)	0.856 cm^{-1}

Structure Determination

The structure was analyzed by the direct method using MULTAN.[2] Phases were determined for the 346 reflections with $|E|>1.50$, eight E maps being calculated. The phases set with the lowest residual (33.1) and the highest figure of merit (1.10) produced a significant E map, which revealed the positions of all the non-hydrogen atoms. The atomic coordinates and temperature factors were refined by the block-diagonal matrix least-squares method until R was reduced to 0.190. Locations of the hydrogen atoms were obtained by assuming a tetrahedral angle for each carbon atom and a bond length of 1.09 Å for each C–H bond. Further refinements were made on a CDC-6600 computer at Century Research Center Co., Tokyo, using anisotropic thermal parameters for the non-hydrogen atoms and isotropic B for the hydrogen atoms. Convergence was attained with $R=0.094$ after six cycles of the procedure. The atomic scattering factors were taken from International Tables for X-Ray Crystallography[3]. The final parameters with their standard deviations are given in Tables 2 and 3***.

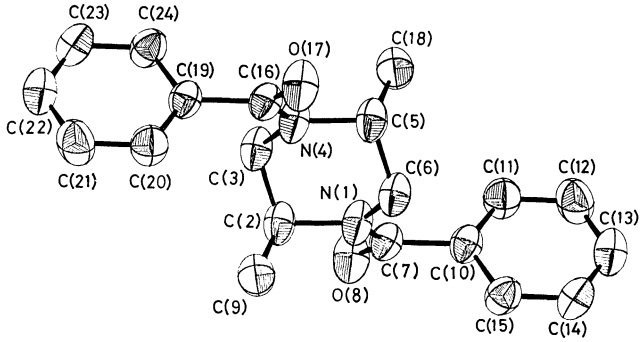

Fig. 1. The thermal vibration ellipsoids of non-hydrogen atoms drawn by ORTEP.[7]

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*** The complete F_o-F_c data are deposited as Document No. 7921 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

Table 2. Atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$) of the non-hydrogen atoms

The estimated standard deviations given in parentheses, refer to the last decimal position. The anisotropic temperature factors is of the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N (1)	908 (4)	1223 (4)	643 (2)	162 (2)	204 (7)	40 (1)	8 (5)	12 (2)	−19 (2)
C (2)	−1312 (5)	986 (6)	271 (2)	166 (7)	218 (8)	39 (1)	31 (6)	22 (2)	−7 (3)
C (3)	−1972 (5)	534 (5)	−553 (2)	172 (7)	204 (8)	38 (1)	15 (6)	17 (2)	−10 (3)
C (7)	1719 (5)	3030 (5)	960 (2)	190 (7)	202 (8)	28 (1)	−3 (6)	21 (2)	−7 (2)
O (8)	732 (4)	4524 (4)	946 (2)	217 (6)	213 (6)	55 (1)	11 (5)	27 (2)	−27 (2)
C (9)	−1963 (6)	−625 (7)	656 (2)	227 (9)	351 (13)	41 (1)	8 (9)	42 (3)	10 (4)
C (10)	3985 (5)	3128 (5)	1365 (2)	185 (7)	190 (7)	29 (1)	−1 (6)	21 (2)	−8 (2)
C (11)	5004 (6)	4358 (6)	1100 (2)	239 (9)	264 (10)	38 (1)	−1 (8)	37 (3)	19 (3)
C (12)	7082 (6)	4489 (7)	1479 (3)	246 (10)	325 (12)	52 (2)	−43 (9)	56 (4)	15 (4)
C (13)	8098 (5)	3427 (7)	2137 (2)	193 (8)	306 (12)	45 (2)	−17 (8)	24 (3)	−9 (4)
C (14)	7114 (6)	2239 (7)	2415 (2)	232 (9)	307 (11)	31 (1)	5 (8)	12 (3)	5 (3)
C (15)	5039 (5)	2068 (6)	2035 (2)	233 (8)	248 (9)	31 (1)	−27 (7)	26 (3)	11 (3)

Table 3. Atomic coordinates($\times 10^3$) of the hydrogen atoms

The estimated standard deviations are in parentheses.

Atom	x	y	z	B	Bonding atom
H (25)	−190 (5)	233 (6)	31 (2)	4.7 (0.8)	C (2)
H (26)	−156 (5)	177 (5)	−80 (2)	3.7 (0.7)	C (3)
H (27)	−339 (6)	21 (7)	−72 (2)	6.2 (1.0)	C (3)
H (31)	−175 (6)	−22 (7)	113 (2)	6.5 (1.0)	C (9)
H (32)	−135 (6)	−194 (7)	61 (2)	7.7 (1.2)	C (9)
H (33)	−331 (7)	−68 (8)	51 (3)	8.3 (1.3)	C (9)
H (34)	440 (6)	499 (7)	66 (2)	6.5 (1.0)	C (11)
H (35)	781 (6)	505 (7)	122 (2)	6.1 (1.0)	C (12)
H (36)	964 (7)	336 (7)	230 (2)	7.8 (1.2)	C (13)
H (37)	776 (6)	151 (7)	285 (2)	6.8 (1.1)	C (14)
H (38)	431 (5)	131 (6)	228 (2)	4.6 (0.8)	C (15)

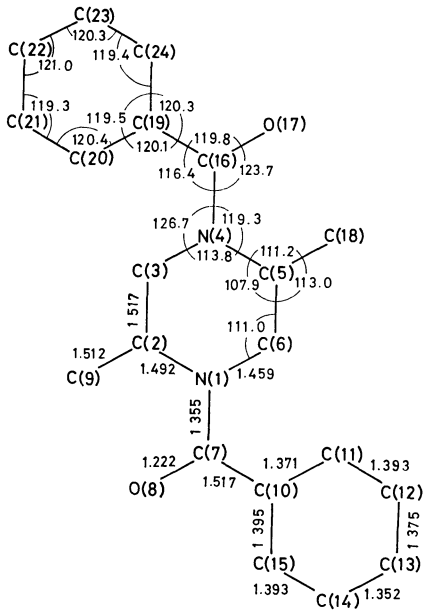

Fig. 2. Intramolecular interatomic distances and angles.

Discussion

Molecular Geometry and Conformation. Numbering scheme and the thermal ellipsoids of the non-hydrogen atoms are illustrated in Fig. 1, where thermal vibration ellipsoids are set to 50% probability. Bond distances and angles involving the non-hydrogen atoms are shown in Fig. 2. The standard deviations of these measurements are 0.004—0.008 Å for distances, and 0.1—0.4° for angles. Since the molecule is centrosymmetric, the piperazine ring has a *chair*-form.[4] The mean N–C bond length in the piperazine ring, 1.476 Å, is comparable to that of *cis*-1,4-dibenzoyl-2,5-dimethylpiperazine (*cis*-DDP).[1] The bond distances, 1.517 Å for C–C in the piperazine ring and 1.512 Å for C (piperazine)–C(methyl), are shorter than the C–C covalent bond length. The bond angles of carbon atoms in the piperazine ring are approximately tetrahedral. The value for C(5)–N(4)–C(3) is comparable to 115.7° of *cis*-DDP, or 112.6° of piperidine.[4,5]

The least-squares planes are given in Table 4 and the torsion angles in the molecule in Table 5. Exocyclic torsion angles for C(9)–C(2)–C(3)–N(4) and C(9)–C(2)–N(1)–C(6) show that C(9) is in the axial position. The shift of N(1) from the plane(1), containing C(2), C(3), C(5), and C(6), is 0.639 Å, and that of C(9) from the plane(1) is 1.383 Å.

The C–O distance of 1.222 Å is in agreement with 1.222 Å of *cis*-DDP, and 1.229 Å of *N,N'*-dibenzoyl-*p*-phenylenediamine(DPD).[6] The N–C(carbonyl) distance is 1.355 Å, corresponding to 1.357 Å in DPD, and 1.353 Å in *cis*-DDP. The C(carbonyl)–C(benzene) distance is 1.517 Å, being comparable to 1.499 Å of *cis*-DDP, and 1.502 Å of DPD.

The mean value of the C–C bond distance in the benzene ring is 1.380 Å, being shorter than 1.397 Å of benzene. The corresponding values for *cis*-DDP and DPD are both 1.386 Å.

The dihedral angle between the planes(2) and (3) is 70.5°. The angle in *cis*-DDP is about 55°. The dihedral angle between planes(1) and (2) is 56.0°, and that between planes(1) and (3) is 61.1°.

Table 4. Least-squares plane through various groups of atoms and the deviations(l/Å) of the atoms from the plane

The equation is of the form $AX+BY+CZ=D$, where X, Y, and Z are the coordinates in Å along the a, b, and c* axes, respectively. (Atoms marked by ** are not included in the least-squares calculation.)

Plane(1)			
$-0.4311X-0.8956Y+0.1096Z=0.0000$			
C (2)	0.000	C (3)	0.000
C (5)	0.000	C (6)	0.000
N (1)**	−0.639	C (7)**	−1.781
O (8)**	−2.351	C (9)**	1.383
C (10)**	−2.334		
Plane(2)			
$0.3979X+0.3280Y-0.8568Z=-0.6488$			
N (1)	−0.027	C (2)	−0.039
C (6)	0.080	C (7)	0.007
O (8)	0.063	C (10)	−0.061
Plane(3)			
$0.3591X-0.7755Y-0.5193Z=-2.2367$			
C (10)	0.010	C (11)	−0.013
C (12)	0.007	C (13)	0.001
C (14)	−0.004	C (15)	−0.001

Table 5. Torsion angles (ϕ)

Torsion angle $A(i)$-$A(j)$-$A(k)$-$A(l)$ is viewed down $A(j)$-$A(k)$ with a clockwise rotation of $A(i)$ to $A(l)$ taken to be positive.

Ring torsion angles	ϕ/°
N (1)--C (2)--C (3)--N (4)	54.7
C (2)--N (1)--C (6)--C (5)	58.1
C (3)--C (2)--N (1)--C (6)	−56.4
Exocyclic torsion angles	
C (7)--N (1)--C (6)--C (5)	−115.5
C (9)--C (2)--N (1)--C (6)	68.0
C (9)--C (2)--N (1)--C (7)	−117.8
C (3)--C (2)--N (1)--C (7)	117.8
C (9)--C (2)--C (3)--N (4)	−68.6
Bridge torsion angles	
C (6)--N (1)--C (7)--O (8)	171.5
C (2)--N (1)--C (7)--O (8)	−1.9
C (6)--N (1)--C (7)--C (10)	−9.9
C (2)--N (1)--C (7)--C (10)	176.7
N (1)--C (7)--C (10)-C (11)	114.8
N (1)--C (7)--C (10)-C (15)	−69.2
O (8)--C (7)--C (10)-C (11)	−66.6
O (8)--C (7)--C (10)-C (15)	109.4

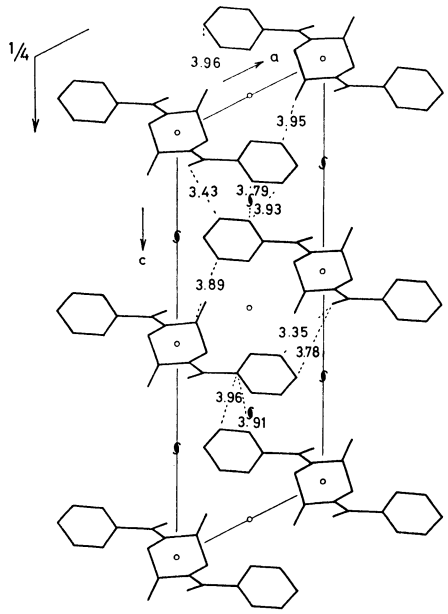

Fig. 3. The molecular packing viewed down the b axis, showing all intermolecular distances (the non-hydrogen atoms) of less than 4.00 Å.

Molecular Packing. The molecular packing in the unit cell with intermolecular distances less than 4.00 Å is shown in Fig. 3. The shortest contact of 3.35 Å is seen between C(12) and O(8) related by a translation along the a axis. The second shortest contact of 3.43 Å is seen between O(8) and C(14) related by a two-fold screw axis. No other significant contact can be seen in this structure. The molecules are held together in the crystal by the van der Waals forces.

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