

system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974) for the crystallography, *LSAM* (Main, Woolfson & Germain, 1972) for the direct phasing, and *MMB* (Sakurai & Kobayashi, 1972) for the conformational-energy calculation.

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## (S)-1,4-Dibenzoyl-cis-2,5-dimethylpiperazine

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**Abstract.** C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>, monoclinic, *P*2<sub>1</sub>, *Z* = 2, *a* = 10.789 (7), *b* = 14.251 (12), *c* = 5.889 (5) Å, β = 102.59 (6)°, *U* = 884 (1) Å<sup>3</sup>. *D<sub>m</sub>* = 1.21, *D<sub>c</sub>* = 1.21 g cm<sup>-3</sup>. The six-membered piperazine ring forms a twist-boat conformation. The molecule has limited flexibility for phenyl-group rotation.

**Introduction.** Recently, we found by NMR and X-ray diffraction that the N-containing six-membered ring of the racemic form of 1,4-dibenzoyl-*cis*-2,5-dimethylpiperazine formed a twist-boat conformation (Tsuboyama *et al.*, 1977; Sakurai, Nakamaru, Tsuboyama & Tsuboyama, 1977), and the carbonyl group was located by the side of the methyl group at the bow of the piperazine. In order to see the variation of the molecular conformation in a different environment, we have studied the title compound by X-ray diffraction.

The compound was derived from (*S*)-alanine (Tsuboyama, Tsuboyama, Tanji & Yanagita, 1976), and single crystals were grown by the slow evaporation of an ethyl alcohol solution. The size of the crystal used was 0.5 × 0.5 × 0.5 mm. Diffraction data were collected on a Rigaku automated four-circle diffractometer with graphite-monochromatized Mo *K*α radiation

in the range 2 < 2θ < 50°. The intensities were corrected for the Lorentz and polarization factors but no absorption correction was applied. 1166 independent reflections were observed.

The coordinates of all the non-hydrogen atoms were obtained with *MULTAN* (Main, Woolfson & Germain,

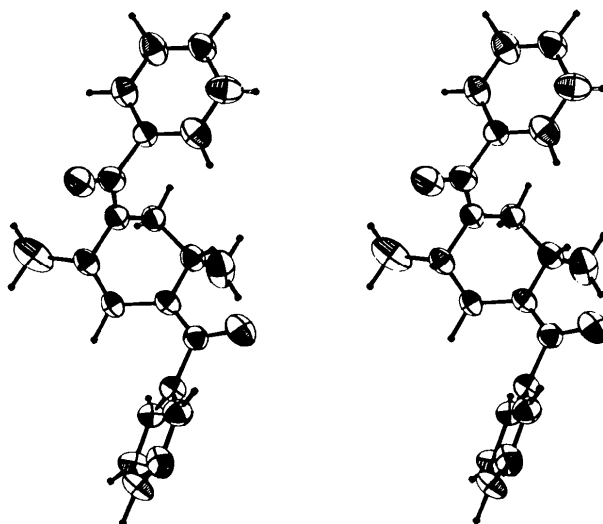


Fig. 1. A stereodrawing of the (*S*) molecule.

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1971). The reflections with non-zero  $k$  values were included in the starting set because no suitable  $h0l$  values were available. The structure was refined by the block-diagonal least-squares method to  $R = 0.097$ . Successive difference Fourier syntheses showed the positions of all the H atoms, which reduced  $R$  to 0.045. Unit weight was given to all reflections, and anisotropic temperature factors were used for all the non-

hydrogen atoms. Atomic parameters are given in Table 1.\*

**Discussion.** A stereodrawing of the molecules is shown in Fig. 1. Averaged values of the bond lengths and bond angles of the chemically equivalent bonds are shown in Fig. 2. The torsion angles are shown in

Table 1. Atomic parameters

Positional parameters are multiplied by  $10^4$  for C, N, O atoms, and  $10^3$  for H atoms. The equivalent temperature factors ( $\text{\AA}^2$ ) are given in the last column. The atom-numbering scheme is shown in Fig. 2, and the H atoms are represented by the numbering of the attached C atoms.

	$x$	$y$	$z$	$B_{eq}$
O(1)	5650 (4)	2933 (3)	8854 (7)	5.0
O(2)	1073 (4)	1089 (3)	3553 (9)	6.4
N(1)	4906 (4)	2483 (3)	5153 (8)	3.6
N(4)	2499 (4)	2143 (3)	2877 (8)	3.7
C(2)	4042 (5)	3290 (4)	4756 (10)	4.2
C(3)	2959 (5)	3095 (4)	2671 (10)	4.1
C(5)	3406 (5)	1389 (4)	2764 (10)	4.1
C(6)	4749 (5)	1792 (4)	3264 (9)	3.7
C(21)	4772 (6)	4161 (5)	4263 (14)	7.1
C(51)	3122 (6)	909 (6)	377 (13)	6.8
C(11)	5720 (5)	2410 (4)	7209 (9)	3.7
C(12)	6759 (4)	1686 (4)	7525 (8)	3.3
C(13)	7586 (5)	1650 (4)	6005 (9)	3.9
C(14)	8601 (5)	1034 (5)	6423 (10)	4.5
C(15)	8778 (5)	451 (5)	8348 (11)	4.8
C(16)	7981 (6)	492 (5)	9850 (11)	5.0
C(17)	6975 (5)	1108 (5)	9451 (10)	4.4
C(41)	1366 (5)	1906 (4)	3362 (9)	4.1
C(42)	470 (5)	2681 (4)	3586 (9)	3.6
C(43)	580 (5)	3197 (5)	5610 (11)	5.0
C(44)	-310 (6)	3865 (5)	5802 (11)	5.5
C(45)	-1320 (5)	4027 (4)	3962 (11)	4.7
C(46)	-1432 (5)	3540 (5)	1965 (11)	5.2
C(47)	-548 (5)	2858 (4)	1766 (10)	4.4
H(2)	372 (4)	326 (3)	624 (8)	4.0 (1.2)
H(3)1	227 (4)	348 (3)	282 (7)	3.0 (1.0)
H(3)2	328 (5)	322 (4)	108 (10)	6.8 (1.6)
H(5)	326 (4)	88 (4)	392 (9)	4.7 (1.3)
H(6)1	541 (4)	117 (4)	360 (8)	4.2 (1.1)
H(6)2	489 (6)	223 (5)	160 (10)	7.7 (1.7)
H(21)1	416 (6)	475 (6)	407 (12)	10.7 (2.2)
H(21)2	476 (6)	431 (5)	278 (11)	9.0 (1.9)
H(21)3	555 (5)	422 (4)	524 (10)	6.2 (1.5)
H(51)1	377 (7)	37 (5)	29 (12)	9.7 (2.1)
H(51)2	223 (6)	67 (5)	-17 (12)	8.6 (1.9)
H(51)3	337 (7)	135 (5)	-116 (12)	10.9 (2.2)
H(13)	633 (5)	115 (4)	1056 (10)	6.4 (1.5)
H(14)	797 (5)	2 (5)	1112 (10)	7.2 (1.7)
H(15)	954 (4)	1 (3)	844 (8)	3.8 (1.1)
H(16)	912 (5)	87 (5)	516 (10)	7.3 (1.7)
H(17)	744 (4)	208 (4)	461 (8)	3.9 (1.1)
H(43)	127 (4)	297 (3)	710 (8)	4.2 (1.1)
H(44)	-20 (6)	412 (4)	721 (10)	6.9 (1.7)
H(45)	-196 (5)	456 (4)	423 (10)	6.6 (1.5)
H(46)	-226 (7)	361 (6)	36 (12)	11.3 (2.3)
H(47)	-59 (5)	260 (5)	3 (10)	7.6 (1.7)

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33772 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

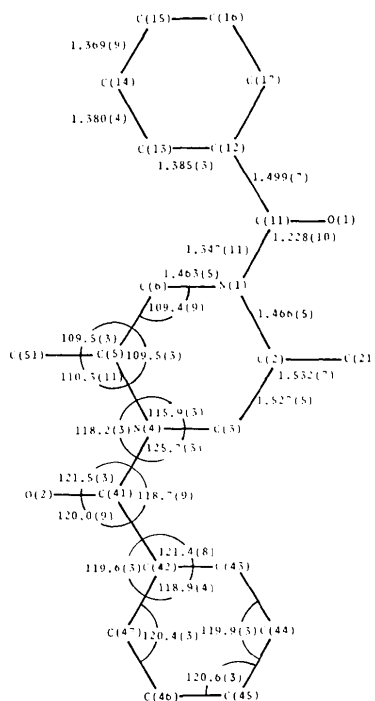


Fig. 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ). The mean values of the chemically equivalent bonds are shown.

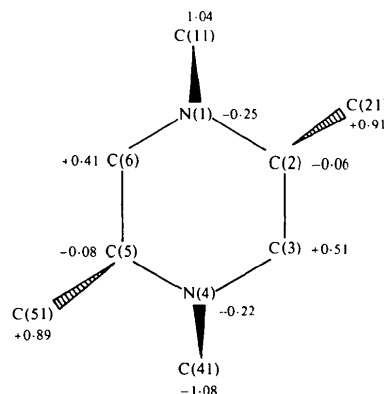


Fig. 3. Deviations ( $\text{\AA}$ ) of atoms from the mean plane of the piperazine ring. The plane is calculated for N(1), C(2), C(3), N(4), C(5) and C(6).

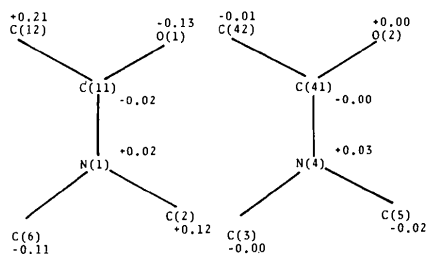


Fig. 4. Deviations (Å) of atoms from the mean amide plane.

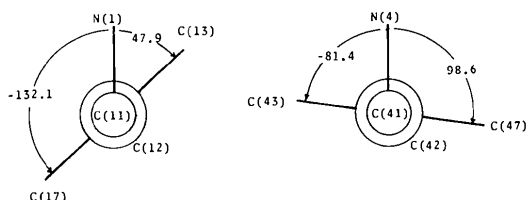


Fig. 5. Newman projections about the C(11)-C(12) and C(41)-C(42) bonds.

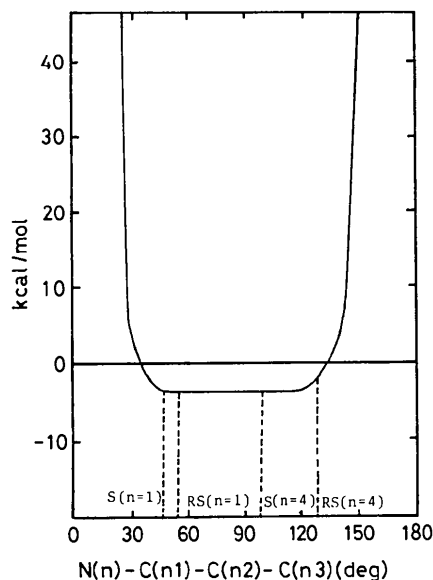


Fig. 6. The van der Waals energy (kcal mol<sup>-1</sup>) with respect to the rotation of the phenyl group ( $n = 1$  or  $4$ ). RS: the racemic form. S: the left-handed form.

Table 2, and the deviations of atoms from the mean plane of the piperazine ring are shown in Fig. 3. These results show that this molecule takes the twist-boat form, similar to the racemic one. In this compound, however, there is *ca* 50° difference in the two dihedral angles between the amide (Fig. 4) and the phenyl planes as shown in the Newman projection (Fig. 5). To

Table 2. Important torsion angles (°)

N(1)-C(2)-C(3)-N(4)	45.0 (6)
C(2)-C(3)-N(4)-C(5)	-64.2 (6)
C(3)-N(4)-C(5)-C(6)	18.8 (6)
N(4)-C(5)-C(6)-N(1)	40.5 (6)
C(5)-C(6)-N(1)-C(2)	-59.1 (6)
C(6)-N(1)-C(2)-C(3)	13.7 (6)
C(3)-N(4)-C(5)-C(51)	-102.6 (6)
C(6)-N(1)-C(2)-C(21)	-106.0 (5)
N(1)-C(6)-C(5)-C(51)	163.0 (5)
N(4)-C(3)-C(2)-C(21)	164.6 (5)
C(2)-N(1)-C(11)-O(1)	9.2 (8)
C(2)-N(1)-C(11)-C(12)	-169.8 (5)
N(1)-C(11)-C(12)-C(13)	-132.1 (6)
C(5)-N(4)-C(41)-O(2)	-4.6 (8)
C(5)-N(4)-C(41)-C(42)	177.2 (5)
N(4)-C(41)-C(42)-C(43)	-81.4 (7)

estimate the allowed range of this dihedral angle, the van der Waals energy between the phenyl and the other groups was calculated as a function of the rotation angle N( $n$ )-C( $n1$ )-C( $n2$ )-C( $n3$ ) ( $n = 1$  or  $4$ ). A broad low-energy range appears between 40–130° as shown in Fig. 6. The structures of both the present and the racemic compounds are contained in this range. Therefore, the conformation of the molecule in solution will have flexibility within this range.

The calculations were performed on the FACOM 230-75 computer of this Institute, using the UNICS II program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). The research was supported, in part, by a Scientific Grant (134041) from the Ministry of Education.

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