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(2*RS*,5*RS*,8*RS*,11*RS*)-1,4,7,10-Tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane

By Tosio Sakurai, Kimiko Kobayashi, Kaoru Tsuboyama
and Sei Tsuboyama

The Institute of Physical and Chemical Research (Rikagaku Kenkyusho), Wako-shi, Saitama 351, *Japan*

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Abstract. $C_{44}H_{60}N_4$, monoclinic, $P2_1/a$, $a = 22{\cdot}710\,(2)$, $b = 14{\cdot}639\,(1)$, $c = 11{\cdot}831\,(1)$ Å, $\beta = 90{\cdot}5\,(2)^\circ$, $U = 3933{\cdot}1\,(3)$ Å^3, $D_m = 1{\cdot}08$, $D_c = 1{\cdot}09$ g cm^{-3}, $Z = 4$. The skeleton of the molecule consists of the typical 12-membered square conformation. Compared with other related structures and the conformational-energy calculation, the molecular shape is found to be flexible, in both the N atom positions and the benzyl conformations.

Introduction. This paper is a part of a series of investigations on the cyclic tetramers of chiral aziridines. The synthesis and the identification of the title compound (Fig. 1) were described in previous papers (Tsuboyama, Tsuboyama, Uzawa & Higashi, 1974; Tsuboyama, Tsuboyama, Higashi & Yanagita, 1970). Single crystals were obtained by recrystallization from benzene solution. A clear, colorless plate crystal, 0·4 × 0·3 × 0·1 mm, was used for the study. X-ray diffraction data were measured on a Rigaku

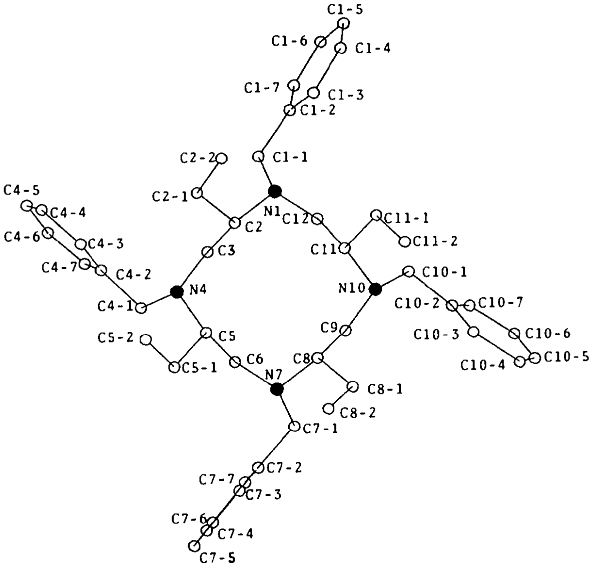


Fig. 1. The numbering of atoms in the molecule.

Table 1. *Atomic parameters*

Positional parameters are multiplied by 10^4 for C, N atoms, and 10^3 for H atoms. The equivalent temperature factors (Å^2) are given in the last column.

	x	y	z	B_{eq}
N(1)	349 (1)	2781 (2)	4369 (3)	2·6
N(4)	1211 (2)	3467 (3)	7020 (3)	2·8
N(7)	2477 (2)	4279 (3)	5201 (3)	3·0
N(10)	1644 (2)	3518 (3)	2543 (3)	3·2
C(2)	503 (2)	3321 (3)	5380 (4)	2·5
C(3)	944 (2)	2843 (3)	6178 (4)	2·8
C(5)	1616 (2)	4150 (3)	6516 (4)	2·8
C(6)	2182 (2)	3713 (3)	6054 (4)	3·1
C(8)	2148 (2)	4384 (3)	4123 (4)	3·1
C(9)	2107 (2)	3498 (3)	3423 (4)	3·2
C(11)	1026 (2)	3579 (3)	3019 (4)	3·1
C(12)	832 (2)	2675 (3)	3558 (4)	2·9
C(2)1	−50 (2)	3614 (4)	6050 (4)	3·5
C(2)2	−542 (2)	4004 (4)	5295 (5)	4·6
C(5)1	1768 (2)	4924 (4)	7344 (5)	4·2
C(5)2	1215 (3)	5405 (4)	7804 (6)	6·4
C(8)1	2377 (2)	5180 (4)	3411 (5)	4·6
C(8)2	2350 (3)	6091 (4)	3992 (6)	7·1
C(11)1	586 (2)	3906 (4)	2114 (4)	4·6
C(11)2	750 (3)	4794 (5)	1543 (5)	6·2
C(1)1	106 (2)	1873 (3)	4631 (4)	3·2
C(1)2	−308 (2)	1515 (3)	3715 (4)	3·1
C(1)3	−639 (2)	2093 (4)	3049 (5)	4·5
C(1)4	−1041 (2)	1729 (5)	2246 (5)	5·3
C(1)5	−1093 (2)	798 (5)	2134 (5)	5·2
C(1)6	−758 (3)	221 (4)	2795 (5)	5·5
C(1)7	−365 (2)	590 (4)	3573 (5)	4·4
C(4)1	1476 (2)	2946 (4)	7951 (4)	3·8
C(4)2	1023 (2)	2482 (4)	8692 (4)	4·2
C(4)3	510 (3)	2941 (5)	8983 (4)	5·5
C(4)4	111 (3)	2460 (6)	9721 (5)	7·5
C(4)5	258 (4)	1590 (5)	10111 (5)	8·1
C(4)6	774 (4)	1159 (5)	9806 (6)	8·0
C(4)7	1138 (3)	1613 (4)	9105 (5)	5·5
C(7)1	3091 (2)	3918 (4)	5024 (4)	3·9
C(7)2	3481 (2)	4109 (4)	6038 (4)	3·5
C(7)3	3505 (2)	4969 (4)	6516 (5)	5·1
C(7)4	3888 (3)	5144 (4)	7432 (6)	6·2
C(7)5	4247 (2)	4450 (4)	7842 (5)	5·0
C(7)6	4221 (2)	3604 (4)	7380 (5)	4·9
C(7)7	3836 (2)	3422 (4)	6470 (4)	4·2
C(10)1	1706 (2)	2740 (4)	1779 (4)	4·4
C(10)2	2221 (2)	2843 (5)	972 (4)	5·6
C(10)3	2367 (3)	3716 (6)	557 (5)	7·9
C(10)4	2856 (3)	3737 (8)	−321 (6)	11·1
C(10)5	3084 (4)	2870 (9)	−609 (7)	12·2
C(10)6	2957 (4)	2014 (9)	−203 (8)	12·9
C(10)7	2492 (3)	2010 (7)	647 (6)	8·9
H(1)1	−11 (2)	189 (3)	543 (4)	5·0 (1·2)
H(1)2	46 (2)	138 (3)	476 (4)	4·8 (1·2)
H(1)3	−58 (2)	283 (3)	311 (4)	5·4 (1·3)
H(1)4	−127 (3)	227 (4)	157 (5)	9·8 (1·9)
H(1)5	−136 (3)	48 (4)	139 (5)	9·2 (1·7)
H(1)6	−73 (3)	−54 (4)	265 (5)	8·5 (1·7)
H(1)7	−20 (2)	18 (4)	409 (5)	7·5 (1·6)
H(2)1	68 (2)	396 (3)	504 (3)	2·7 (0·9)
H(2)2	5 (2)	411 (3)	675 (4)	4·3 (1·1)
H(2)3	−19 (2)	306 (3)	662 (4)	3·9 (1·1)
H(2)4	−75 (2)	350 (4)	478 (4)	6·1 (1·3)
H(2)5	−45 (2)	452 (4)	477 (4)	5·7 (1·3)
H(2)6	−79 (2)	433 (4)	582 (4)	6·7 (1·4)
H(3)1	125 (2)	246 (3)	568 (3)	2·7 (0·9)
H(3)2	71 (2)	232 (3)	664 (4)	3·7 (1·0)
H(4)1	169 (2)	345 (4)	856 (4)	6·0 (1·3)
H(4)2	178 (2)	239 (4)	764 (4)	5·8 (1·3)
H(4)3	40 (2)	360 (4)	862 (4)	5·5 (1·3)
H(4)4	−22 (2)	294 (4)	976 (5)	7·1 (1·6)
H(4)6	95 (3)	35 (5)	1023 (5)	10·0 (1·9)
H(4)7	157 (3)	122 (5)	886 (5)	10·5 (1·9)
H(5)1	139 (2)	448 (3)	581 (3)	2·3 (0·9)
H(5)2	201 (2)	551 (4)	686 (4)	5·8 (1·3)
H(5)3	200 (2)	471 (3)	801 (4)	5·1 (1·2)
H(5)4	111 (3)	502 (5)	868 (6)	13·7 (2·3)
H(5)6	139 (3)	594 (4)	830 (5)	8·1 (1·6)
H(6)1	208 (2)	305 (3)	575 (3)	2·6 (0·9)
H(6)2	245 (2)	359 (3)	684 (3)	3·2 (1·0)
H(7)1	329 (2)	433 (4)	431 (4)	5·7 (1·3)
H(7)2	316 (2)	316 (4)	481 (4)	6·7 (1·4)
H(7)3	324 (3)	560 (4)	614 (5)	8·5 (1·7)
H(7)4	395 (3)	581 (4)	796 (5)	9·4 (1·8)
H(7)5	451 (2)	462 (3)	851 (4)	5·5 (1·3)
H(7)6	451 (2)	305 (4)	769 (5)	7·2 (1·5)
H(7)7	383 (2)	276 (4)	603 (4)	5·7 (1·3)
H(8)1	171 (2)	460 (3)	443 (4)	4·5 (1·2)
H(8)2	217 (2)	527 (3)	262 (4)	5·5 (1·3)
H(8)3	274 (2)	506 (4)	306 (5)	7·1 (1·5)
H(8)4	261 (2)	610 (4)	452 (5)	7·7 (1·5)
H(8)5	213 (3)	616 (4)	472 (5)	9·9 (1·8)
H(8)6	243 (2)	659 (4)	326 (5)	7·1 (1·5)
H(9)1	206 (2)	291 (3)	396 (3)	3·1 (1·0)
H(9)2	249 (2)	340 (3)	291 (4)	4·5 (1·1)
H(10)1	132 (2)	267 (4)	111 (4)	6·6 (1·4)
H(10)2	184 (2)	210 (4)	222 (4)	6·6 (1·4)
H(11)1	101 (2)	409 (3)	372 (3)	3·2 (1·0)
H(11)2	21 (2)	401 (4)	256 (4)	6·2 (1·4)
H(11)3	55 (2)	338 (3)	145 (4)	4·1 (1·1)
H(11)4	108 (3)	471 (4)	92 (5)	9·1 (1·7)
H(11)5	80 (2)	527 (4)	213 (4)	6·4 (1·4)
H(11)6	51 (3)	502 (4)	105 (5)	8·6 (1·7)
H(12)1	121 (2)	228 (4)	406 (4)	6·0 (1·3)
H(12)2	63 (2)	227 (3)	285 (3)	3·5 (1·0)

Table 2. *Torsion angles for the benzyl groups* (°)

Bond	$n = 1$	4	7	10	Mean
C(n − 2)–C(n − 1)–N(n)–C(n)1	166·9	162·6	165·8	168·9	166
C(n + 2)–C(n + 1)–N(n)–C(n)1	56·8	58·4	56·2	52·7	56
C(n − 1)–N(n)–C(n)1–C(n)2	−78·8	−69·7	−70·7	−74·0	−73
C(n + 1)–N(n)–C(n)1–C(n)2	152·3	161·6	160·9	158·9	158
N(n)–C(n)1–C(n)2–C(n)3	−29·7	−41·0	−48·5	−34·7	−38
N(n)–C(n)1–C(n)2–C(n)7	152·0	141·2	133·8	148·9	144

automated four-circle diffractometer, AFC, with graphite-monochromatized Cu $K\alpha$ radiation. Within the range of $2\theta \leq 140°$, 4459 independent reflections were observed. In the previous study on (2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane (TETA) (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978), the square conformation of the 12-membered ring was established. Based on this ring conformation, a molecular model for the title compound with C_4 symmetry was calculated (Tsuboyama, Tsuboyama, Uzawa, Kobayashi & Sakurai, 1977). The intensity distribution within reciprocal space shows a pseudo tetragonal pattern, with the *b* axis as the symmetry axis. Therefore, the structure analysis was first attempted by a trial and error method using the calculated model. However, no satisfactory result was obtained. Then the direct phasing method was applied. 40 atoms were obtained in the first *E* map. The whole structure was deduced from the successive Fourier syntheses, and refined by the block-diagonal least-squares method. Of the 60 H atoms, 53 could be located. One of the phenyl groups is subjected to a large thermal vibration, and its H atoms were not located. The final *R* index is 7·9%, with anisotropic temperature factors for all the nonhydrogen atoms.* The atomic parameters are given in Table 1. Fig. 1 gives the numbering scheme and a stereodrawing is shown in Fig. 2.

Discussion. The skeleton of the molecule consists of a square 12-membered ring, similar to TETA. However, in contrast to the methylene corner structure in TETA, the N atoms are situated at the corners, as in azacyclododecane (Dunitz & Weber, 1964). The torsion angles for the four benzyl groups are slightly different from each other (Table 2). The TETA part has an approximate C_4 symmetry. Therefore, only the geometry of the average structure with C_4 symmetry is given in Fig. 3. Because of the differences in the N-atom positions, the *S* molecule of the present structure can be compared with the *R* molecule of TETA [*cf.* Fig. 5 in the previous paper (Sakurai *et al.*, 1978)]. Though the torsion angles for the ethyl groups are considerably different from each other, the ring conformation is almost the same in both compounds.

The benzyl groups are extended away from the ring, making an open conformation. On the other hand, in the predicted model, besides the difference in the N atom positions, the phenyl groups came close to each other to make a closed conformation. In order to compare these conformations, the conformational energy was calculated with respect to the rotation about two single bonds in the benzyl group. In this calculation the TETA part was fixed, and the molecule was assumed to

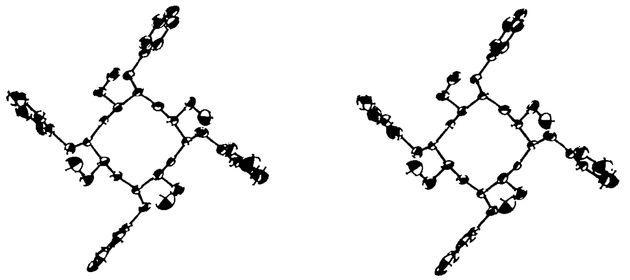
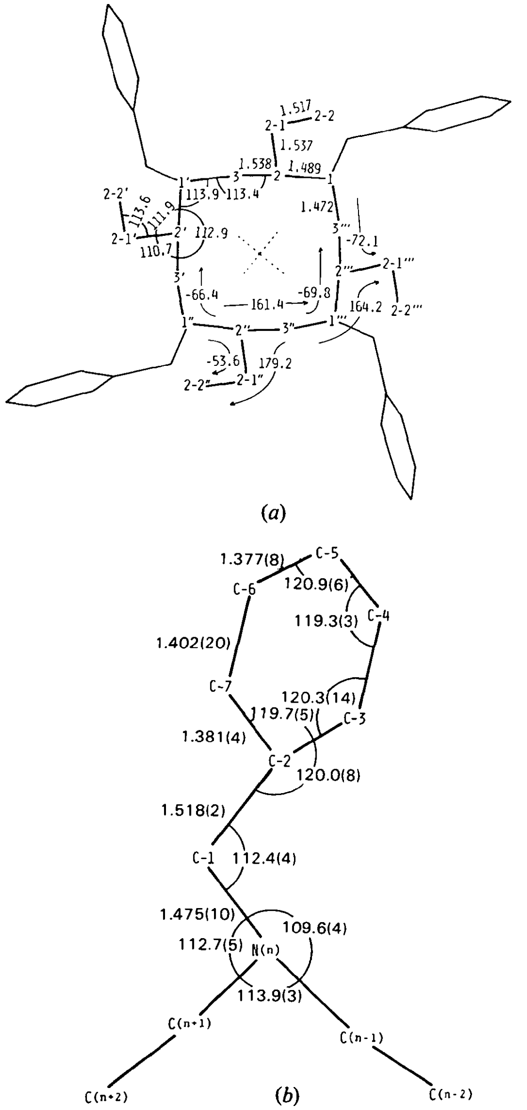


Fig. 2. A stereodrawing of the molecule.



(*a*)

(*b*)

Fig. 3. The averaged bond lengths (Å), angles (°) and torsion angles (°) of the chemically equivalent bonds in the (*S*) molecule. (*a*) TETA part. (*b*) Benzyl group.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33771 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

keep C_4 symmetry. The calculation shows a broad low-energy region with three minima *A*, *B* and *C* (Fig. 4). The regions *A* and *B* correspond to the open form, and the present structure is situated within the lowest energy region *A*. The third minimum *C* is the closed conformation as shown in the stereodrawing in Fig. 5. The *A* and *B* minima are connected by a broad low-energy region. This fact, together with the difference in the N atom positions due to the different substituent, suggests that the molecular shape may have considerable flexibility in solution. However, the open conformation is more preferable than the closed one.

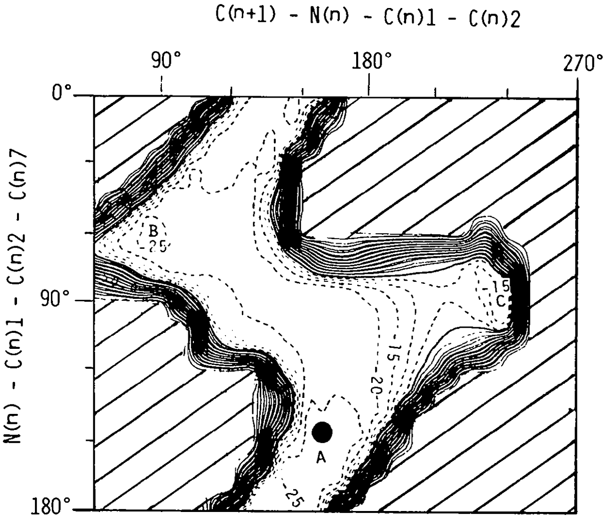

Fig. 4. Conformational-energy map. The molecule was assumed to keep C_4 symmetry. The contour lines are drawn at every 5 kcal mol^{-1}. The three energy minima are indicated by *A*, *B* and *C*, and the present structure is marked by a black circle.

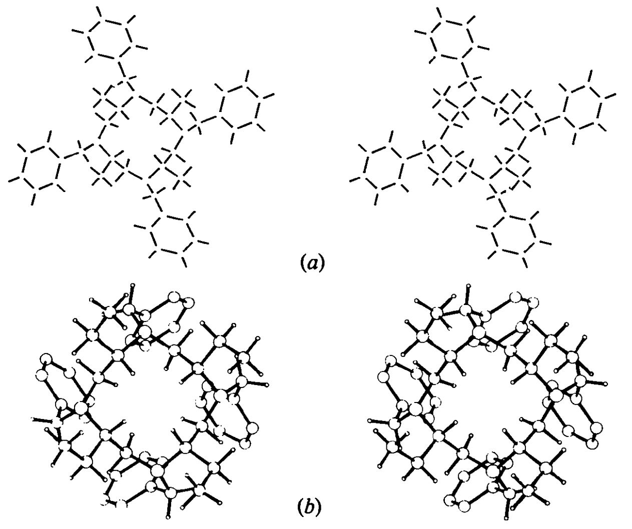

Fig. 5. Stereodrawings of the molecular models at subsidiary minima. (*a*) Open conformation at the region *B*. C(*n* + 1)—N(*n*)—C(*n*)1—C(*n*)2 = 90°, N(*n*)—C(*n*)1—C(*n*)2—C(*n*)7 = 60°. (*b*) Closed conformation at the region *C*. C(*n* + 1)—N(*n*)—C(*n*)1—C(*n*)2 = 240°, N(*n*)—C(*n*)1—C(*n*)2—C(*n*)7 = 80°.

The intermolecular C—C distances in the crystal, shorter than 3·7 Å, are shown in Fig. 6. These are mainly between the phenyl groups. The phenyl group attached to the N atom N(10) has less interaction than the other group, and large temperature factors are observed for this group.

Calculations were performed on the FACOM 230-75 computer of this Institute using the *UNICS* II program

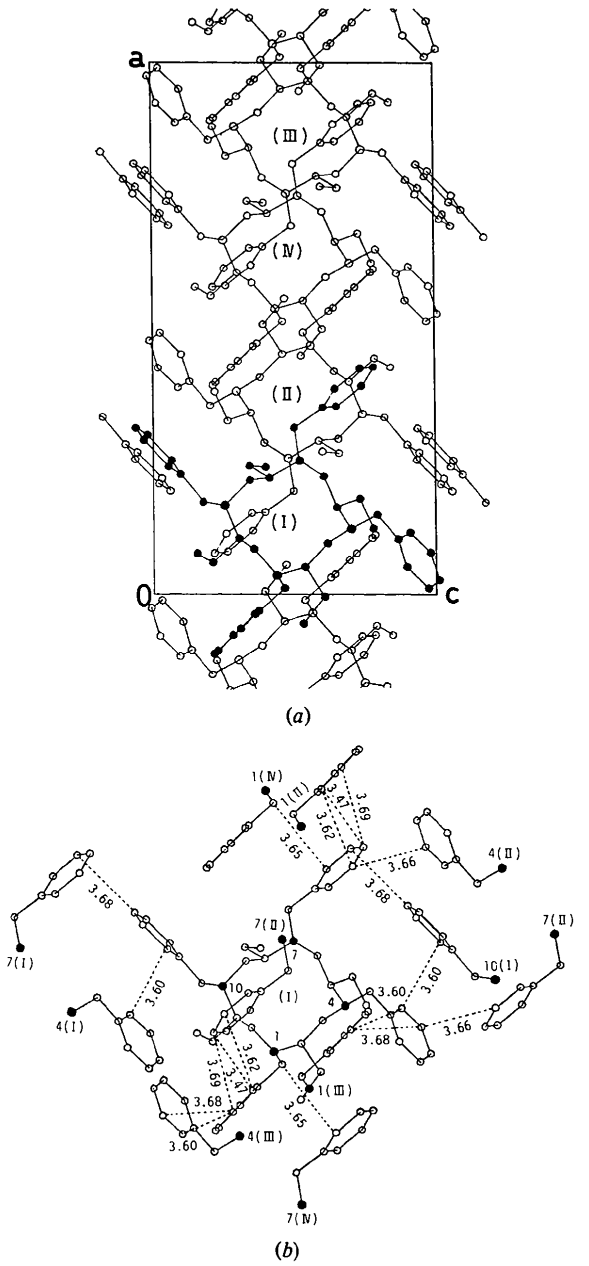

Fig. 6. (*a*) The crystal structure, projected along the *b* axis. (*b*) Intermolecular interactions. C—C distances shorter than 3·7 Å are indicated. The symmetry-related molecules are expressed as (I) *x*,*y*,*z*; (II) $-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z$; (III) $-x,-y,-z$; (IV) $x-\frac{1}{2}$, $-y-\frac{1}{2}$, z; or their unit-cell-translated equivalents.

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

By Hideo Hiramatsu, Tosio Sakurai,* Sei Tsuboyama
and Kaoru Tsuboyama

The Institute of Physical and Chemical Research (*Rikagaku Kenkyusho*), *Wako-shi, Saitama* 351, *Japan*

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Abstract. $C_{20}H_{22}N_2O_2$, monoclinic, $P2_1$, $Z = 2$, $a = 10{\cdot}789\,(7)$, $b = 14{\cdot}251\,(12)$, $c = 5{\cdot}889\,(5)$ Å, $\beta = 102{\cdot}59\,(6)^\circ$, $U = 884\,(1)$ Å^3, $D_m = 1{\cdot}21$, $D_c = 1{\cdot}21$ g cm^{-3}. 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 $K\alpha$ radiation in the range $2 < 2\theta < 50^\circ$. 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,

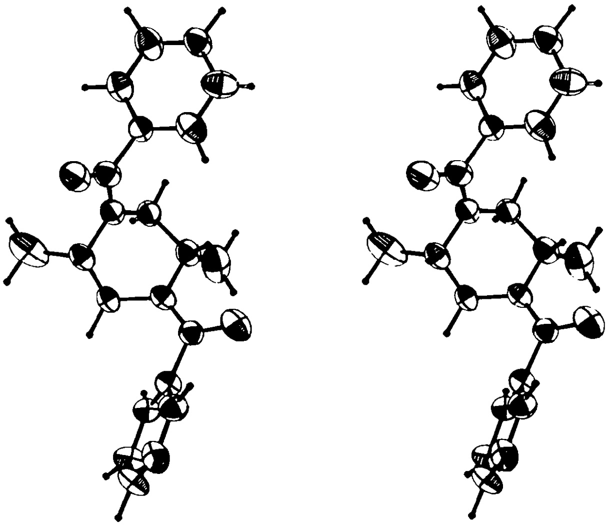

Fig. 1. A stereodrawing of the (*S*) molecule.

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* To whom correspondence should be addressed.