ionic radii of Hg and S atoms, 2·95 Å (Pauling, 1960). The bond length 2·749 Å is intermediate between the tetrahedral covalent and ionic distances.

The S—Hg—S bond angles of the distorted tetrahedral configuration range from 81·8 to 148·8°; the widest takes the value intermediate between those of tetrahedral and linear bicovalent arrangements. It occurs between the two shortest bonds. The observed distortion of the metal—sulphur tetrahedral arrangement increases in the order: $Zn(SSCOC_2H_5)_2$, $Cd(SSCOC_2H_5)_2$ and $Hg(SSCOC_2H_5)_2$.

Calculations were carried out on a FACOM 230-75 computer with the program system UNICS2 (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). Fig. 1 was drawn with ORTEP (Johnson, 1965). The author wishes to thank Professor H. Hagihara for his valuable advice.

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(RS)-1,4-Dibenzoyl-cis-2,5-dimethylpiperazine

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Abstract. $C_{20}H_{22}N_2O_2$, monoclinic, $P2_1/a$, $Z = 4$, $a = 11\cdot220$ (6), $b = 14\cdot571$ (6), $c = 10\cdot688$ (7) Å, $\beta = 99\cdot38$ (8)°, $U = 1724$ (2) Å^3, $d_m = 1\cdot22$, $d_c = 1\cdot24$ g cm^{-3}. The six-membered piperazine ring forms a twist-boat conformation.

Introduction. Ordinary N-containing six-membered rings have been known to form the chair conformation (Kellie & Riddell, 1974). During the NMR study of chiral piperazines, a twist-boat conformation of the piperazine ring was proposed for the title compound (Tsuboyama et al., 1977). To verify this result an X-ray diffraction study was performed

Single crystals were grown by the slow evaporation of an ethyl acetate solution. Two different crystal forms were obtained from the same batch: one is prismatic, and the other is thick tabular. A careful examination of Weissenberg photographs revealed that these two forms have an identical unit cell. The prismatic form is elongated in the a direction, and the tabular face is {001}. The tabular crystals were used for further X-ray investigations. Diffraction intensities were collected on a Rigaku automated four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation and $2\theta \leq$ 140°. The size of the crystal used was $0\cdot3 \times 0\cdot4 \times 0\cdot5$ mm. The usual Lorentz and polarization corrections were applied. The number of observed reflections was 2190.

The structure was solved by a direct phasing method, and all H atoms were deduced from successive difference Fourier syntheses. The structure was refined by the block-diagonal least-squares method. Unit weight was given to all reflections, and anisotropic temperature factors were used for all non-hydrogen atoms. The final R index was 5·6%. Atomic parameters are given in Table 1.†

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Table 1. *Atomic parameters* ($\times 10^4$, *for* H $\times 10^3$)

The atom-numbering scheme is shown in Fig. 2. The H atoms are numbered according to the atoms to which they are attached.

	x	y	z	B_{eq} (Å²)		x	y	z	B (Å²)
O(1)	1613 (3)	528 (2)	5932 (3)	4·3	H(2)	214 (3)	24 (3)	826 (4)	4·0 (1·0)
O(4)	4699 (2)	2087 (2)	10486 (3)	3·8	H(3)1	91 (4)	150 (3)	1008 (4)	5·3 (1·1)
N(1)	1549 (3)	1535 (2)	7508 (3)	2·6	H(3)2	188 (3)	62 (2)	1034 (3)	2·5 (0·8)
N(4)	2731 (3)	1768 (2)	9894 (3)	2·5	H(5)	346 (3)	264 (3)	860 (4)	3·3 (0·9)
C(2)	1410 (3)	777 (3)	8390 (4)	2·7	H(6)1	61 (3)	256 (3)	837 (4)	3·7 (0·9)
C(3)	1689 (3)	1150 (3)	9750 (4)	2·6	H(6)2	146 (3)	293 (2)	734 (3)	2·5 (0·8)
C(5)	2611 (3)	2593 (3)	9076 (4)	2·6	H(21)1	1 (5)	−13 (4)	875 (5)	6·8 (1·3)
C(6)	1516 (3)	2456 (2)	8038 (4)	2·5	H(21)2	−60 (4)	90 (3)	835 (5)	7·1 (1·3)
C(21)	131 (4)	372 (3)	8128 (5)	4·1	H(21)3	−10 (4)	14 (4)	718 (5)	6·7 (1·3)
C(51)	2479 (4)	3457 (3)	9840 (5)	3·8	H(51)1	243 (4)	399 (3)	932 (4)	5·7 (1·2)
C(11)	1690 (4)	1320 (3)	6312 (4)	3·0	H(51)2	320 (4)	359 (3)	1035 (5)	5·4 (1·2)
C(12)	1949 (4)	2083 (3)	5450 (4)	2·8	H(51)3	173 (5)	348 (4)	1037 (5)	7·4 (1·5)
C(13)	2947 (4)	2673 (3)	5766 (4)	3·5	H(13)	366 (5)	261 (4)	678 (5)	7·9 (1·5)
C(14)	3163 (4)	3352 (3)	4916 (5)	4·2	H(14)	409 (5)	381 (4)	524 (5)	8·7 (1·6)
C(15)	2406 (5)	3434 (3)	3763 (5)	4·6	H(15)	248 (5)	396 (4)	302 (5)	8·5 (1·6)
C(16)	1443 (5)	2839 (3)	3432 (4)	4·5	H(16)	86 (4)	283 (4)	256 (5)	6·9 (1·4)
C(17)	1215 (4)	2161 (3)	4280 (4)	3·7	H(17)	48 (3)	173 (3)	406 (4)	3·8 (1·0)
C(41)	3826 (3)	1610 (3)	10600 (4)	2·8	H(43)	233 (4)	124 (3)	1235 (4)	6·0 (1·2)
C(42)	3945 (3)	867 (3)	11583 (4)	2·7	H(44)	290 (4)	16 (3)	1410 (4)	5·8 (1·2)
C(43)	3192 (4)	825 (3)	12485 (4)	3·7	H(45)	461 (4)	−86 (3)	1428 (4)	5·3 (1·1)
C(44)	3403 (5)	188 (3)	13462 (4)	4·7	H(46)	589 (4)	−87 (3)	1265 (5)	6·8 (1·4)
C(45)	4367 (5)	−407 (3)	13536 (4)	4·7	H(47)	552 (4)	32 (3)	1099 (4)	4·5 (1·0)
C(46)	5120 (4)	−369 (3)	12653 (5)	4·6					
C(47)	4929 (4)	273 (3)	11673 (4)	3·5					

Discussion. A stereodrawing of the molecule is shown in Fig. 1. The molecule has a pair of chemically equivalent bonds: the bond lengths and bond angles in the pair are equal within experimental error. The values in each pair were therefore averaged and are shown in Fig. 2. However, because of the rotation about the single bonds, the steric structure lacks twofold symmetry. A most remarkable difference is the orientation of the phenyl group with respect to the amide plane: the dihedral angle between these two planes is about 55°.

However, the direction of the rotation is opposite for the N(1) and N(4) sides. Newman projections about the C(11)–C(12) and C(41)–C(42) bonds are shown in Fig. 3. N(1)–C(11) is 1·353 Å; this suggests that the ring N conjugates strongly with the carbonyl group. Therefore, the amide group is almost planar, as shown in Fig. 4.

In agreement with the NMR study, the piperazine ring takes a twist-boat form with C(3) and C(6) at the bows. Torsion angles are shown in Fig. 5 and Table 2.
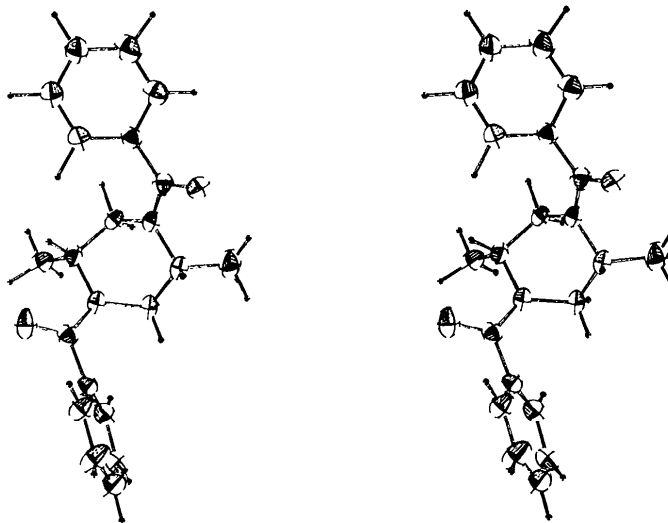

Fig. 1. A stereodrawing for the (R) molecule.
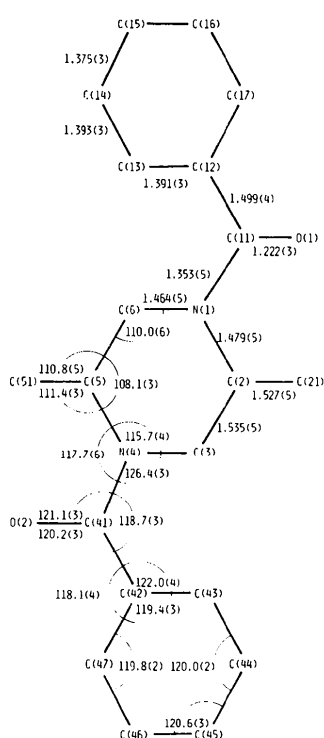
Fig. 2. Bond lengths (Å) and angles (°). These are the mean values of chemically equivalent bonds, and lengths and angles are shown in the upper and lower halves of the figure respectively.
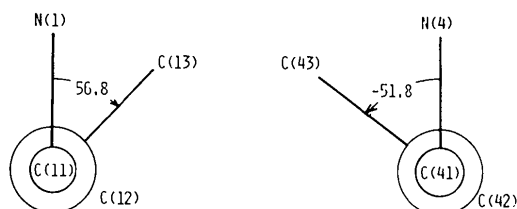

Fig. 5. Torsion angles (°) around the piperazine ring.

Table 2. *Important torsion angles* (°)

N(1)–C(2)–C(3)–N(4)	−41·2 (4)
C(2)–C(3)–N(4)–C(5)	60·6 (4)
C(3)–N(4)–C(5)–C(6)	−14·2 (4)
N(4)–C(5)–C(6)–N(1)	−45·7 (3)
C(5)–C(6)–N(1)–C(2)	65·8 (4)
C(6)–N(1)–C(2)–C(3)	−18·9 (3)
C(3)–N(4)–C(5)–C(51)	108·1 (3)
C(6)–N(1)–C(2)–C(21)	102·7 (3)
N(1)–C(6)–C(5)–C(51)	−168·0 (3)
N(4)–C(3)–C(2)–C(21)	−163·7 (3)
C(2)–N(1)–C(11)–O(1)	5·5 (5)
C(2)–N(1)–C(11)–C(12)	−174·3 (3)
N(1)–C(11)–C(12)–C(13)	56·8 (5)
C(5)–N(4)–C(41)–O(2)	−6·0 (5)
C(5)–N(4)–C(41)–C(42)	171·0 (3)
N(4)–C(41)–C(42)–C(43)	−51·8 (5)

Fig. 3. Newman projections about the C(11)–C(12) and C(41)–C(42) bonds.

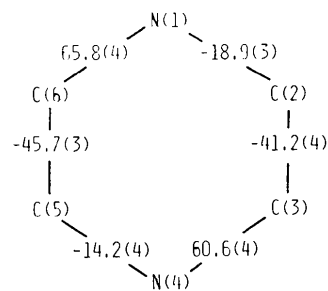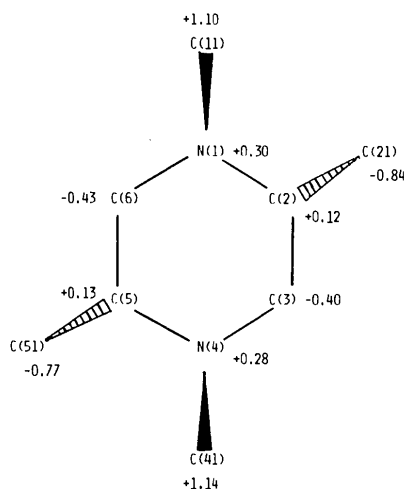Fig. 6. Deviations (Å) of atoms from the mean plane of the piperazine ring. The plane is calculated for N(1), C(2), C(3), N(4), C(5) and C(6).

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

The difference between the chemically equivalent torsion angles is about 5°. This difference is attributed to the crystalline field, and will allow the same order of flexibility in solution. The deviations of atoms from the mean piperazine plane are shown in Fig. 6.

For the cyclohexane ring, the chair form is known to

have a lower energy than the twist-boat form (Hendrickson, 1961). A similar situation will occur for the piperazine ring. Therefore, all the reported piperazine structures have the chair form (Rérat, 1960; Koshino, Sasaki & Haisa, 1973; Mouillé, Cotrait, Hospital & Marsau, 1975; Okamoto, Sekido, Noguchi, Ono & Hirokawa, 1977). In the present compound, if the ring conformation takes a chair form, a large steric repulsion between the amide group and the vicinal equatorial methyl group is expected. This strain is relieved by the twist-boat conformation. Further details about the effects of other substituents will be discussed elsewhere (Tsuboyama et al., 1977).

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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cis-Dichloro(dimethyl sulphoxide)(2-picoline)platinum(II)

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Abstract. $PtCl_2C_8H_{13}NOS$, $M_r = 437.26$; monoclinic $P2_1/c$, $a = 8.004$ (7), $b = 17.508$ (8), $c = 9.176$ (5) Å, $\beta = 105.29$ (6)°, $Z = 4$, $V = 1240$ (1) Å^3, $D_x = 2.341$, $D_m = 2.33$ (1) g cm^{-3} (flotation); $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 124.6$ cm^{-1}, $t = 22°C$. Positional and anisotropic thermal parameters were refined by full-matrix least-squares calculations to $R = 0.049$ and $R_w = 0.036$. The coordination around Pt is planar. The cis Pt–Cl (relative to DMSO) bond length is 2.288 Å while trans Pt–Cl is 2.307 Å. The Pt–S distance is 2.200, and Pt–N 2.062 Å. The 2-picoline ring lies perpendicular to the coordination plane of the Pt atom (87.1°).

Introduction. Recently, we have studied by NMR the reactions of some dimethyl sulphoxide complexes of Pt with pyridine derivatives (py) and the isomerization of [Pt(DMSO)(py)Cl$_2$] (Kong, Iyamuremye & Rochon, 1976). In order to confirm the cis configurations assigned by NMR, we have studied by X-ray diffraction, the crystal structure of cis-[Pt(DMSO)(2-picoline)Cl$_2$].

The compound was synthesized from the isomerization of trans-[Pt(DMSO)(2-picoline)Cl$_2$] in DMSO solution by the method recently described (Kong et al., 1976). The crystals were recrystallized from acetone. A set of precession photographs showed that the $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ reflections are systematic absences indicating the $P2_1/c$ space group. The cell parameters were obtained by least-squares refinement from the setting angles of 15 automatically centred reflections on a Syntex P1̄ diffractometer with graphite-monochromatized Mo $K\alpha$ radiation.

The intensity data were collected from a crystal measuring $0.211 \times 0.135 \times 0.135$ mm elongated along a and bounded by the faces {100}, {1̄00}, {021}, {02̄1̄}, {021̄}, and {02̄1}. 3995 independent reflections were measured in the region of $2\theta < 60°$ by the $2\theta/\theta$ scan technique with Mo $K\alpha$ radiation. The data collection was done at a variable speed (24 to 1° min^{-1}). Most of the measurements were made at a speed of 1° min^{-1}. A 2θ scan range of $1.0°$ below $K\alpha_1$ and $1.0°$ above $K\alpha_2$ was selected. The background to scan time ratio was 0.40. During the data collection three standard reflections were measured after every 47 reflections. Their variations were less than 2% of their respective means. The reflections for which $I < 2.5\sigma(I)$ were