

Fig. 3. Bond angles ($^{\circ}$). Numbers in parentheses are the estimated standard deviations in the last digits shown. For clarity, the H atoms attached to C atoms are omitted, except for H(7) on C(7), the mandelate chiral center.

$N-H(N1) \cdots O(2) = 150(3)^{\circ}$; those for $N-H(N2) \cdots O(3)$ are $2.75(1)$, $0.92(10)$, $1.87(10)$ Å, and $163(3)^{\circ}$, correspondingly. Since both observed $N \cdots O$ distances are smaller than the sum of the van der Waals radii (Bondi, 1964), and since both observed $N-H \cdots O$ angles are very favorable, the $N-H \cdots O$ interactions are strong. A third possible hydrogen bond is in the $O(1)-H(O) \cdots O(3)$ system, whose geometrical descriptions are $O(1) \cdots O(3) = 2.60(1)$, $O(1)-H(O) = 0.90(9)$, $H(O) \cdots O(3) = 1.91(10)$ Å, and the angle $O(1)-H(O) \cdots O(3) = 123(3)^{\circ}$. Atom O(3) is therefore involved in two hydrogen bonds, an interionic one to $N-H(2)$ as part of the infinite hydrogen-bonding chain, and an intraionic one to $O(1)-H(O)$, thereby forming the five membered ring $\overline{C(7)-O(1)-H(O) \cdots O(3)-C(8)}$.

Acta Cryst. (1980). B36, 173–176

trans-(2R,5R)-1-(p-Bromophenylsulfonyl)-2,5-dimethylpyrrolidine at 238 K

BY LING-KANG LIU AND RAYMOND E. DAVIS*

Department of Chemistry, University of Texas, Austin, Texas 78712, USA

(Received 29 May 1979; accepted 6 September 1979)

Abstract. $C_{12}H_{16}BrNO_2S$, $M_r = 318.24$, orthorhombic, $P2_12_12_1$, $Z = 4$, $F(000) = 648$, at 238 K, $a = 11.558(4)$, $b = 15.390(3)$, $c = 7.634(3)$ Å, $D_x = 1.56$, $D_m = 1.53$ Mg m $^{-3}$ (296 K, measured by flotation in an aqueous $AgNO_3$ solution). Full-matrix least-squares refinement of 1270 reflections resulted in a final R value of 0.029. Utilization of the anomalous-

This ring formation may be regarded as a weak interaction which restricts the hydroxyl H position in the crystalline state.

This work was supported by the Robert A. Welch Foundation (Grant No. F-233). We are also indebted to the National Science Foundation for the purchase of the Syntex $P2_1$ diffractometer (Grant No. GP-37028), and to Professor James K. Whitesell and Steve W. Felman for supplying the sample used in this work.

References

- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 DERVAN, P. B. & UYEHARA, J. (1976). *J. Am. Chem. Soc.* **98**, 2003–2005.
 HENSLEE, W. & DAVIS, R. E. (1975). *Acta Cryst.* **B31**, 1511–1519.
International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2A. Birmingham: Kynoch Press.
 KLYNE, W. & BUCKINGHAM, J. (1974). *Atlas of Stereochemistry*, p. viii. Oxford Univ. Press.
 MAIN, P., WOLFSON, M. M., DECLERCQ, J. P. & GERMAIN, G. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 OVERBERGER, C. G., PALMER, L. C., MARKS, B. S. & BYRD, N. R. (1955). *J. Am. Chem. Soc.* **77**, 4100–4104.
 RILEY, P. E. & DAVIS, R. E. (1975). *Inorg. Chem.* **14**, 2507–2513.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 WEI, K.-T. & WARD, D. L. (1977). *Acta Cryst.* **B33**, 797–800.
 WHITESSELL, J. K. & FELMAN, S. W. (1977). *J. Org. Chem.* **42**, 1663–1664.

dispersion effects of Br and S has allowed the direct determination of the absolute configuration of (–)-trans-2,5-dimethylpyrrolidine as 2R,5R.

Introduction. Single crystals of $C_{12}H_{16}BrNO_2S$ were grown by slow evaporation from a methanol solution. With an air tumbler, several large, clear prisms were ground to spheroids of diameter ca 0.4 mm. X-ray diffraction work was carried out with a Syntex $P2_1$

* To whom all correspondence should be addressed.

autodiffractometer using graphite-monochromatized Mo $K\alpha$ radiation and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system to cool the data crystal to 238 K. Intensity data were measured by the ω -scan technique such that each reflection was scanned symmetrically over 1.0° about the $K\alpha_{1,2}$ maximum with a variable scan rate from 1.5 to $5.0^\circ \text{ min}^{-1}$ according to the intensity of the reflection. Background counts were offset $\pm 1.0^\circ$ from the $K\alpha_{1,2}$ maximum. Four monitor reflections were remeasured after every 96 reflections. An analysis of the monitor reflections throughout the 33.5 h data-collection time indicated no crystal decomposition or misalignment (Henslee & Davis, 1975). The net intensities were corrected for spherical absorption ($\mu = 3.29 \text{ mm}^{-1}$) and for Lorentz and polarization effects; standard deviations based on counting statistics were assigned to the data, details of which have been described elsewhere (Riley & Davis, 1975). A p factor included in the weighting scheme was 0.05 (Corfield, Doedens & Ibers, 1967). The intensity data were then converted to the structure factor amplitudes, $|F_o|$. Of 1791 unique reflections measured in the range $4^\circ \leq 2\theta \leq 55^\circ$, only 1270 with $I_o \geq 3\sigma(I_o)$ were used in structure solution and refinement.

Solution of the Patterson map suggested the atomic fractional coordinates of Br. Three successive Fourier maps, phased initially with the Br atom, revealed the positions of all non-hydrogen atoms of the structure. Two enantiomers – one model related to the other by the transformation (x, y, z) to $(-x, -y, -z)$ – were refined in parallel to least-squares convergence with the inclusion of the real (f') and the imaginary (f'') corrections due to anomalous dispersion of Br and S (*International Tables for X-ray Crystallography*, 1974). Neutral-atom scattering factors for O, N, C (*International Tables for X-ray Crystallography*, 1974) and H (Stewart, Davidson & Simpson, 1965) were used. The function minimized in the refinement was $(\sum w||F_o| - |F_c||^2)$; the weight, w , was taken as the reciprocal square of the standard deviation of each observation, $|F_o|$.

Refinement of the first model bearing a *trans*-(2*R*,5*R*)-2,5-dimethylpyrrolidine moiety resulted in a final R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.029 and a final R_w [$= (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2}$] of 0.036, and the second, 2*S*,5*S*, resulted in $R = 0.050$ and $R_w = 0.061$. While a comparison of the R values suggested a preference for the 2*R*,5*R* configuration, a statistical judgment of the R ratio accepts the 2*R*,5*R* configuration to be correct over the 2*S*,5*S* at far above the 99.995% confidence level (Hamilton, 1965). In the final cycle of refinement of the 2*R*,5*R* configuration, all non-hydrogen atoms were refined anisotropically and all H atoms were included ideally. No parameters shifted more than 0.08σ in the final cycle; no residual peaks were greater than $0.36 \text{ e } \text{ \AA}^{-3}$. The final estimated standard deviation per unit weight reflection was 1.02.

Table 1. Final atomic fractional coordinates with *e.s.d.*'s

	<i>x</i>	<i>y</i>	<i>z</i>
Br	0.23068 (5)	0.40463 (3)	0.54671 (9)
S	0.27845 (9)	0.81963 (3)	0.55173 (14)
O(1)	0.1686 (3)	0.8507 (2)	0.4919 (4)
O(2)	0.3817 (2)	0.8415 (2)	0.4584 (4)
N	0.2965 (3)	0.8523 (2)	0.7502 (4)
C(1)	0.2450 (4)	0.5277 (3)	0.5505 (7)
C(2)	0.3525 (4)	0.5635 (3)	0.5241 (8)
C(3)	0.3640 (4)	0.6531 (3)	0.5258 (8)
C(4)	0.2664 (4)	0.7049 (2)	0.5521 (6)
C(5)	0.1586 (4)	0.6666 (3)	0.5775 (7)
C(6)	0.1487 (4)	0.5771 (3)	0.5764 (7)
C(7)	0.4129 (4)	0.8658 (3)	0.8297 (6)
C(8)	0.3772 (5)	0.9017 (4)	1.0098 (7)
C(9)	0.2684 (5)	0.8502 (3)	1.0554 (7)
C(10)	0.2014 (4)	0.8471 (3)	0.8812 (6)
C(11)	0.4839 (4)	0.7834 (4)	0.8457 (7)
C(12)	0.1156 (5)	0.9209 (4)	0.8646 (7)

Table 1 lists the final atomic fractional coordinates of the correct enantiomorph.*

Discussion. The present work has been carried out to directly determine the absolute configuration of (–)-*trans*-2,5-dimethylpyrrolidine,† which was assumed to be 2*R*,5*R* in an asymmetric induction study by Whitesell & Felman (1977). A *p*-bromobenzenesulfonamide derivative of (–)-*trans*-2,5-dimethylpyrrolidine was chosen for X-ray diffraction experiments because the incorporation of Br and S in an optically active crystal would show enhanced effects of anomalous dispersion due to Br and S, and would consequently permit a direct determination of the absolute stereochemistry (Bijvoet, Peerdeman & van Bommel, 1951).

One method of establishing the absolute configuration from the effects of anomalous dispersion is to calculate the structure factors for both possible enantiomers as described above. Another method is to measure the intensities of Bijvoet pairs of reflections and then to compare the intensity ratio with the computed ratio. The correct configuration is selected when agreement between the observed ratios and the calculated ratios is reached. Therefore, as a confirmation, the intensity ratios were calculated for Bijvoet pairs, assuming the 2*R*,5*R* configuration and including the effects of anomalous dispersion due to Br and S: for Bijvoet pairs

* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34748 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† A single-crystal X-ray diffraction study of (–)-*trans*-2,5-dimethylpyrrolidinium (+)-mandelate performed in this laboratory reveals a (2*R*,5*R* amine; *S* acid) structure (Liu & Davis, 1979).

Table 2. Calculated and observed ratios for several Bijvoet pairs with large intensity differences

<i>h k l</i>	<i>I</i> / <i>ī</i>	
	Calculated*	Observed†
4 4 2	1.397	1.426
4 1 4	1.394	1.404
4 4 3	1.342	1.360
4 8 3	1.327	1.345
3 6 2	1.323	1.303
2 3 2	0.824	0.826
4 10 3	0.823	0.824
5 5 2	0.819	0.817
4 5 2	0.794	0.771
2 6 2	0.779	0.751

* Calculated with coordinates for the 2*R*,5*R* configuration and with inclusion of *f''* and *f'''* with values of -0.374 and 2.456 for Br and 0.110 and 0.124 for S, respectively. The intensity ratios calculated for the 2*S*,5*S* configuration would be the reciprocals of those shown.

† Observed intensities of Bijvoet equivalent reflections were averaged for better statistics; *I* is an average intensity of *I*_o(*hkl*), *I*_o(*h* \bar{k} *l*), *I*_o(*hkl*), and *I*_o(*h* \bar{k} \bar{l}), while \bar{I} is an average of *I*_o(*h* \bar{k} *l*), *I*_o(*hkl*), *I*_o(*h* \bar{k} \bar{l}), and *I*_o(*hkl*). Based only on counting statistics, the estimated errors in the observed intensity ratios do not exceed 2%.

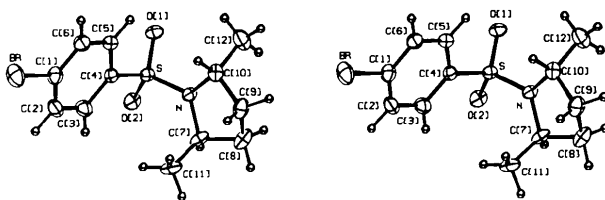


Fig. 1. A stereoview of *trans*-(2*R*,5*R*)-1-(*p*-bromophenylsulfonyl)-2,5-dimethylpyrrolidine, illustrating atomic-numbering scheme and molecular chirality. For non-hydrogen atoms, thermal ellipsoids of 40% probability are given; for hydrogen atoms, spheres are of radius 0.1 Å.

with calculated ratios quite different from 1.0 and with sufficient intensity to ensure small random counting errors, the intensity ratios were determined experimentally using the data crystal. The results of these measurements are shown in Table 2. The uniform agreement of the calculated and observed ratios further substantiates the correctness of the 2*R*,5*R* configuration for (-)-*trans*-2,5-dimethylpyrrolidine. Fig. 1 represents the determined stereochemistry and the atomic-numbering scheme. Selected bond distances and bond angles are given in Figs. 2 and 3, respectively.

trans-(2*R*,5*R*)-2,5-Dimethylpyrrolidine has *C*₂ symmetry. Although the *C*₂ symmetry does not exist in the sulfonamide derivative, the *trans*-(2*R*,5*R*)-2,5-dimethylpyrrolidine group has its originally chemically equivalent bonds equal in length within 0.001 Å and originally chemically equivalent bond angles differing by less than *ca* 2°; the C—C and C—N bond distances in the group are normal. The N atom displays trigonal geometry, as revealed by the bond angles.

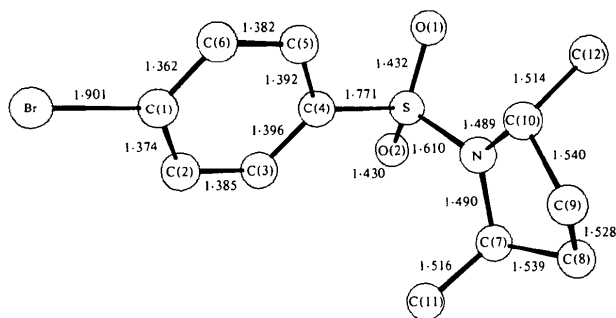


Fig. 2. Bond distances (Å). The estimated standard deviations are 0.003–0.004 Å for bonds associated with Br or S, and 0.006–0.007 Å for other non-hydrogen bonds.

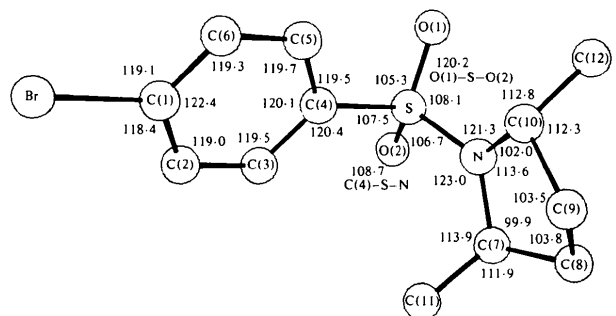


Fig. 3. Bond angles (°). The estimated standard deviations are 0.3–0.4°.

The C—C bond distances in the benzene rings are affected by the substituents. The C—C bonds neighboring the SO₂ group are longer by *ca* 0.02 Å than those neighboring Br. The difference in bond distances of the benzene ring could be appreciable for other similar structures. The S atom has a tetrahedral configuration as confirmed by the angles around S. The SO₂ plane makes angles with S—N and S—C(4) of 53 and 56° respectively, *i.e.* the SO₂ plane bisects N—S—C(4). A plane made up with the N atom and its three neighboring atoms makes a dihedral angle of 105° with a second plane involving the Br, S, and the six benzene C atoms. Furthermore, these two planes make dihedral angles of 49 and 56°, respectively, with the SO₂ plane, *i.e.* the SO₂ plane also approximately bisects two further planes.

This work was supported by the Robert A. Welch Foundation (Grant No. F-233). We are also indebted to the National Science Foundation for the purchase of the Syntex *P*₂ diffractometer (Grant No. GP-37028) and to Professor James K. Whitesell and Steve W. Felman for kindly supplying the sample used in this work.

References

- BLIVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature (London)*, **168**, 271–272.
- CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- HENSLEE, W. & DAVIS, R. E. (1975). *Acta Cryst.* **B31**, 1511–1519.

- International Tables for X-ray Crystallography* (1974). Vol. IV, Table 2.2A. Birmingham: Kynoch Press.
- LIU, L.-K. & DAVIS, R. E. (1980). *Acta Cryst.* **B36**, 171–173.
- RILEY, P. E. & DAVIS, R. E. (1975). *Inorg. Chem.* **14**, 2507–2513.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WHITESSELL, J. K. & FELMAN, S. W. (1977). *J. Org. Chem.* **42**, 1663–1664.

Acta Cryst. (1980). **B36**, 176–178

The Structure of 5,6-Cyclopentenopyrido[3,2- α]carbazole, Lys-P-1, a Potent Mutagenic Product from the Dry Distillation of L-Lysine

BY KENTARO YAMAGUCHI, YOICHI IITAKA, KOICHI SHUDO AND TOSHIHIKO OKAMOTO

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

(Received 19 July 1979; accepted 7 September 1979)

Abstract. C₁₈H₁₄N₂, monoclinic, $P2_1/a$, $a = 13.388$ (6), $b = 18.273$ (7), $c = 5.216$ (3) Å, $\beta = 95.72$ (2)°, $Z = 4$. The final R value was 0.04 including H atoms. The present study established the chemical structure of Lys-P-1 to be a derivative of pyridocarbazole.

Introduction. It has been shown that the pyrolysate of proteinous foods, proteins and amino acids exhibits high mutagenic activity (Nagao, Honda, Seino, Yahagi, Kawachi & Sugimura, 1977; Sugimura, Nagao, Kawachi, Honda, Yahagi, Seino, Matsushima, Shirai, Sawamura, Sato, Matsumoto & Matsukura, 1977). Since then, certain mutagenic principles have been extracted from the pyrolysis products of D,L-tryptophan, D,L-phenylalanine and L-glutamic acid (Sugimura, Kawachi, Nagao, Yahagi, Seino, Okamoto, Shudo, Kosuge, Tsuji, Wakabayashi, Iitaka & Itai, 1977; Kosuge *et al.*, 1978; Yamamoto *et al.*, 1978). A new potent mutagenic principle (Lys-P-1) has recently been isolated from the L-lysine pyrolysate. A preliminary paper describing the extraction, purification and the structure of this compound has been published (Wakabayashi *et al.*, 1978).

To elucidate the structure of Lys-P-1 and to obtain precise structural information, necessary for studying the mechanism of induction of mutation, we have undertaken the present X-ray crystallographic analysis.

The lattice constants and intensity data were obtained with a Philips PW 1100 diffractometer using Cu $K\alpha$ radiation monochromated by a graphite plate.

The θ - 2θ scan technique was employed for the whole angular range up to $2\theta = 130^\circ$. Background was measured at each end of the scan range for half the total scan time. 1556 reflexions were measured as being above the $2\sigma(I)$ level. Lorentz and polarization corrections were applied.

The crystal structure was determined by the direct method using *MULTAN* (Main, Woolfson & Germain, 1971) and refined by the block-diagonal least-squares method using the *HBL5* IV program (Okaya & Ashida, 1967).

The final R value was 0.043 including H atoms. Positional parameters are listed in Table 1.*

Discussion. The chemical structure of Lys-P-1 was determined as 5,6-cyclopentenopyrido[3,2- α]carbazole (Fig. 1). The bond lengths and valency angles are shown in Fig. 2. The standard deviations are estimated as $\sigma(C-C) = 0.004$, $\sigma(C-H) = 0.03$ Å, and $\sigma(C-C-C) = 0.2$, $\sigma(C-C-H) = 1.4$ and $\sigma(H-C-H) = 2.0^\circ$. In Table 2 the range of the bond lengths and their average values are listed for each kind of bond. The bond lengths and angles are compatible with the chemical structure.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34753 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.