BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 44, 2665—2670 (1968)

# The Crystal Structure of 3-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidene)-1-ethyl-2-methylpyrrolidine Hydrobromide

Yoji Tokuma, Hiroshi Nojima, and Yukiyoshi Morimoto

*Research Laboratories, Fujisawa Pharmaceutical Co., Ltd., Kashima-cho, Higashiyodogawa-ku, Osaka, Japan*

(Received April 26, 1971)

The crystal structure of 3-(10,11-dihydro-5H-dibenzo[*a*,*d*]cyclohepten-5-ylidene)-1-ethyl-2-methylpyrrolidine hydrobromide, $C_{22}H_{26}NBr$, has been determined. The crystal is monoclinic with space group $P2_1/a$; the unit-cell dimensions are: $a=30.16$, $b=18.78$, $c=7.048$ Å, $\beta=90.53°$. The asymmetric unit contains two molecules. The intensities were estimated visually from the multiple-film equi-inclination Weissenberg photographs. The structure was solved by the heavy atom method. The atomic parameters were refined by the block-diagonal least-squares method, and final $R$ index was reduced to 0.147. It is concluded that the overall geometry of the two independent molecules is similar in every detail The pyrrolidine ring is puckered. The 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidene part consists of three planes. The dihedral angles between the planes are 63° for the benzene planes I and II, 59° for the benzene plane I and the ylidene plane, and 76° for the benzene plane II and the ylidene plane.

3-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidene)-1-ethyl-2-methylpyrrolidine hydrochloride (piroheptine hydrochloride) has been found to show antagonism of tremorine tremor by S. Kumada *et al.*[1] S. Umio *et al.*[2] have suggested that both piroheptine hydrochloride and piroheptine hydrobromide seemed to have more than two conformations in the solution on the basis of interpretation of NMR spectra.

From our interest in the relation[3] between structure and drug action, we undertook X-ray determination of the crystal structure of piroheptine hydrobromide in order to obtain useful information on its conformation in the solution.

As a result, conformation in the crystal seems to correspond to the most stable conformation in the solution suggested by NMR study.

## Experimental

The crystal of piroheptine hydrobromide was obtained from a methanol-ether solution in the form of colorless prism elongated along the *c* axis.

Unit-cell dimensions were determined by the least-squares calculation, using 19 *hk*0 and 20 0*kl* reflections whose Bragg angles were measured on zero-layer Weissenberg photographs taken with Cu$K\alpha$ radiation and calibrated with aluminum powder lines. The density was measured by flotation in a benzene-carbon tetrachloride mixture.

Crystal data:

Piroheptine hydrobromide, $C_{22}H_{26}NBr$; M=384.4; mp=237—240°C

Monoclinic, $a=30.16\pm0.008$, $b=18.78\pm0.014$, $c=7.048\pm 0.003$ Å, $\beta=90.53\pm0.03°$, $V=3992.0$ Å$^3$

$D_m=1.28$, $Z=8$, $D_x=1.279$ g/cm$^3$

Absorption of X-ray, $\lambda=1.5418$ Å (Cu$K\alpha$); $\mu=31.3$ cm$^{-1}$. $F(000)=1608$

Absent spectra: *h*0*l* when *h* is odd, 0*k*0 when *k* is odd. Space group is $P2_1/a$.

Since a unit-cell contains eight molecules, an asymmetric unit contains two crystallographically independent molecules.

The three dimensional intensity data of nickel-filtered Cu$K\alpha$ radiation were collected from the multiple-film equi-inclination Weissenberg photographs for the layer line 0—5 about the *c* axis and 0—2 about the *b* axis. The intensities of reflections out to spacings of 1 Å were visually estimated by comparison with a standard scale. The values of intensity ranged from 1 to 10,000. They were corrected for Lorentz and polarization factors; no absorption or extinction corrections were applied. Corrections for variation in spot-size on higher-layer photographs were made by the method of Phillips.[4] The intensity data from the *b* axis photographs were used only for layer scale adjustment of the *a* axis photo-

---

[1] S. Kumada, M. Hitomi, and N. Kumadaki, private communication.

[2] S. Umio, H. Nojima, and Y. Morimoto, private communication.

[3] K. Larsson, *Acta Chem. Scard.*, **24**, 1503 (1970).

[4] D. C. Phillips, *Acta Crystallogr.*, **7**, 746 (1954).

graphs. 3797 intensity data were obtained of which 800 were too weak to be observed.

## Structure Determination

The coordinates of two bromine ions in an asymmetric unit were deduced from the Patterson function. A Fourier synthesis based on the coordinates of the two bromine ions clearly revealed all 46 light atoms. Succesive Fourier synthesis showed no spurious peak except for a few peaks about the bromine ions.

The positional and thermal parameters of the atoms were refined by the block-diagonal least-squares method minimizing $\sum w(|F_o|-|F_c|)^2$. The weighting scheme

Table 1. Final atomic coordinates (fractional), isotropic temperature factors (Å$^2$) and their standard deviations (Å, Å$^2$)

| Atom | $x$ ($x$) | $y$ ($y$) | $z$ ($z$) | $B$ ($B$) |
|---|---|---|---|---|
| Br(A) | 0.2057(0.002) | 0.1038(0.002) | −0.1446(0.002) | |
| N(A1) | 0.1914(0.012) | 0.0982(0.012) | 0.2925(0.012) | 1.74(0.24) |
| C(A2) | 0.1857(0.015) | 0.1759(0.015) | 0.3794(0.016) | 2.10(0.31) |
| C(A3) | 0.2324(0.016) | 0.2033(0.016) | 0.3762(0.017) | 2.34(0.33) |
| C(A4) | 0.2656(0.018) | 0.1426(0.018) | 0.3123(0.019) | 3.30(0.39) |
| C(A5) | 0.2350(0.017) | 0.0748(0.017) | 0.3580(0.018) | 2.86(0.36) |
| C(A6) | 0.1537(0.016) | 0.0511(0.017) | 0.3731(0.017) | 2.82(0.35) |
| C(A7) | 0.1592(0.022) | −0.0214(0.022) | 2.2718(0.023) | 5.32(0.51) |
| C(A8) | 0.1516(0.017) | 0.2164(0.017) | 0.2519(0.018) | 2.87(0.36) |
| C(A9) | 0.1879(0.023) | 0.4495(0.023) | 0.4303(0.023) | 5.56(0.52) |
| C(A10) | 0.1648(0.023) | 0.4428(0.024) | 0.5911(0.024) | 5.99(0.54) |
| C(A11) | 0.1647(0.023) | 0.3817(0.024) | 0.7038(0.024) | 5.94(0.55) |
| C(A12) | 0.1940(0.021) | 0.3213(0.022) | 0.6308(0.022) | 4.93(0.49) |
| C(A13) | 0.2159(0.017) | 0.3280(0.017) | 0.4633(0.018) | 3.07(0.36) |
| C(A14) | 0.2461(0.016) | 0.2699(0.016) | 0.4152(0.017) | 2.51(0.34) |
| C(A15) | 0.2926(0.016) | 0.2889(0.016) | 0.3969(0.017) | 2.62(0.34) |
| C(A16) | 0.3237(0.019) | 0.2693(0.019) | 0.5338(0.020) | 4.01(0.42) |
| C(A17) | 0.3689(0.019) | 0.2900(0.019) | 0.5100(0.020) | 4.19(0.43) |
| C(A18) | 0.3810(0.023) | 0.3271(0.023) | 0.3542(0.024) | 5.74(0.54) |
| C(A19) | 0.3496(0.023) | 0.3479(0.023) | 0·2069(0.024) | 5.82(0.54) |
| C(A20) | 0.3062(0.019) | 0.3288(0.019) | 0.2360(0.019) | 3.96(0.41) |
| C(A21) | 0.2694(0.021) | 0.3478(0.022) | 0.0879(0.022) | 5.29(0.49) |
| C(A22) | 0.2396(0.023) | 0.4073(0.023) | 0.1680(0.024) | 5.66(0.54) |
| C(A23) | 0.2155(0.020) | 0.3935(0.021) | 0.3403(0.021) | 4.67(0.45) |
| Br(B) | 0.0288(0.002) | 0.1225(0.003) | 0.3356(0.002) | |
| N(B1) | 0.0421(0.011) | 0.1212(0.011) | 0.7763(0.012) | 1.38(0.23) |
| C(B2) | 0.0478(0.016) | 0.1970(0.016) | 0.8692(0.016) | 2.22(0.33) |
| C(B3) | 0.0026(0.016) | 0.2269(0.016) | 0.8593(0.016) | 2.38(0.33) |
| C(B4) | −0.0320(0.017) | 0.1677(0.018) | 0.8049(0.018) | 3.09(0.37) |
| C(B5) | −0.0032(0.018) | 0.0991(0.018) | 0.8323(0.018) | 3.31(0.38) |
| C(B6) | 0.0795(0.018) | 0.0708(0.019) | 0.8551(0.019) | 3.46(0.40) |
| C(B7) | 0.0745(0.020) | −0.0004(0.021) | 0.7517(0.021) | 4.46(0.45) |
| C(B8) | 0.0833(0.018) | 0.2351(0.018) | 0.7325(0.018) | 3.30(0.38) |
| C(B9) | 0.0633(0.025) | 0.4628(0.026) | 0.9316(0.026) | 6.42(0.61) |
| C(B10) | 0.0853(0.025) | 0.4456(0.025) | 1.0980(0.026) | 6.79(0.61) |
| C(B11) | 0.0811(0.027) | 0.3838(0.028) | 1.2043(0.028) | 7.67(0.67) |
| C(B12) | 0.0485(0.020) | 0.3338(0.021) | 1.1252(0.021) | 4.47(0.45) |
| C(B13) | 0.0248(0.017) | 0.3477(0.017) | 0.9642(0.018) | 3.18(0.37) |
| C(B14) | −0.0089(0.016) | 0.2927(0.016) | 0.9037(0.017) | 2.53(0.34) |
| C(B15) | −0.0552(0.018) | 0.3179(0.018) | 0.8818(0.018) | 3.34(0.38) |
| C(B16) | −0.0855(0.022) | 0.3014(0.022) | 1.0301(0.023) | 5.23(0.51) |
| C(B17) | −0.1308(0.027) | 0.3304(0.027) | 0.9990(0.027) | 7.61(0.65) |
| C(B18) | −0.1390(0.026) | 0.3673(0.027) | 0.8481(0.027) | 7.36(0.64) |
| C(B19) | −0.1114(0.025) | 0.3881(0.025) | 0.6974(0.026) | 6.62(0.59) |
| C(B20) | −0.0642(0.021) | 0.3616(0.021) | 0.7184(0.021) | 4.84(0.47) |
| C(B21) | −0.0288(0.026) | 0.3812(0.027) | 0.5730(0.027) | 7.11(0.65) |
| C(B22) | 0.0049(0.023) | 0.4330(0.023) | 0.6805(0.023) | 5.59(0.52) |
| C(B23) | 0.0303(0.019) | 0.4110(0.019) | 0.8620(0.019) | 3.83(0.40) |

TABLE 2. ANISOTROPIC TEMPERATURE FACTORS FOR BROMIDE IONS (THEIR STANDARD DEVIATIONS)

The anisotropic temperature factors are expressed in the from
$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Br(A) | 0.0017 | 0.0043 | 0.0199 | 0.0007 | 0.0004 | 0.0003 |
| | (0.00003) | (0.00009) | (0.00062) | (0.00005) | (0.00011) | (0.00018) |
| Br(B) | 0.0014 | 0.0052 | 0.0187 | −0.0009 | −0.0004 | 0.0005 |
| | (0.00003) | (0.00010) | (0.00061) | (0.00005) | (0.00010) | (0.00019) |

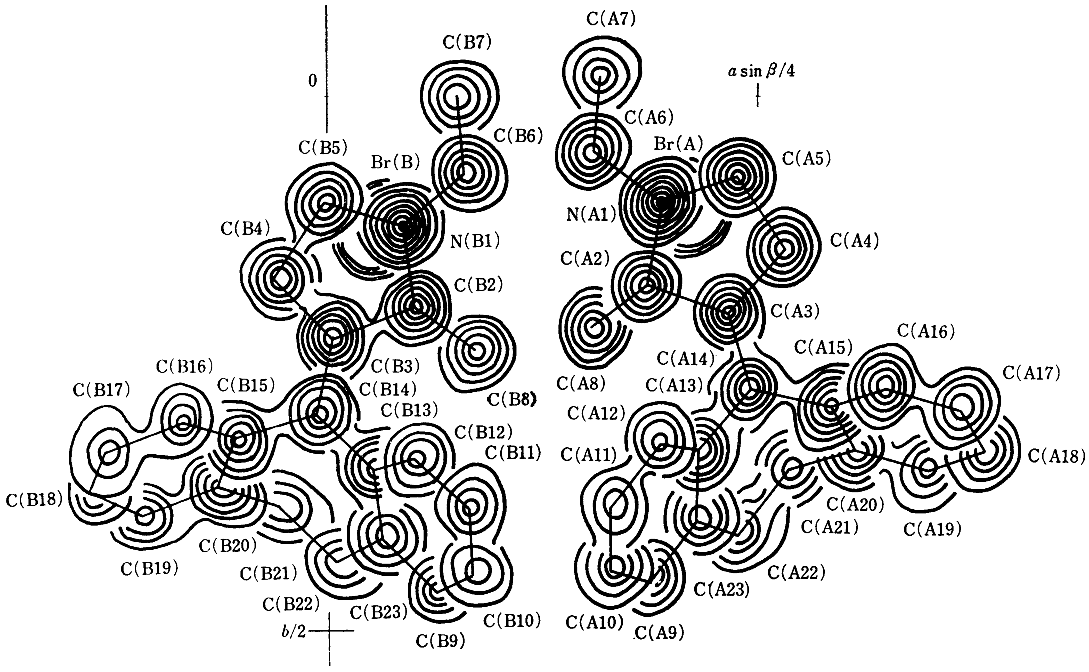

Fig. 1. A composite drawing of the final electron density map, viewed along the $c$ axis. Contours are drawn at 1.5, 2.5, 3.5 e.Å$^{-3}$…for the light atoms. Contours for the bromide ions are omitted.

was; $w=0.3$ when $|F_o|=0$ and $w=1$ when $|F_o|\neq 0$. The scattering factors for H, C, N, and Br$^-$ were taken from International Tables.[5] Two cycles of the least-squares refinement were carried out, assigning isotropic temperature factors to all atoms and ions. These two cycles decreased the reliability index $R$ to 0.192. Four more cycles of the refinement were performed, assigning anisotropic temperature factors to two bromine ions. The $R$ index was reduced to 0.147, excluding non-observed reflections ($R=0.188$, for all 3797 reflections).

The final atomic coordinates and isotropic temperature factors are given in Table 1, and the anisotropic temperature factors for the bromine ions in Table 2. The two independent molecules are denoted by symbols A and B. A composite drawing of the final electron density map is shown in Fig. 1.

All the numerical computations were carried out on a CDC 3600, C. Itoh Electronic Computing Service Co., Ltd. and a HITAC 8400, Fujisawa Pharmaceutical Co., Ltd. Most computing programs used were the application programs of C. Itoh Electronic Computing Service Co., Ltd.

## Discussion

*Geometry of the molecule.* Comparison of the corresponding bond lengths and angles in the two independent molecules are given in Table 3 and 4, and the average values of the corresponding bond lengths and angles in the two independent molecules are shown in Fig. 2. The bond lesgths and angles in the two molecules agree closely with each other, with a few exceptions. The root mean square deviations between the two molecules are 0.052 Å for the bond lengths and 4.0° for the bond angles. The C(3)–C(14) bond length 1.33 Å agrees with the standard C–C double bond length 1.34 Å.

The conformation of the pyrrolidine rings is shown in Fig. 3. Arabic numerals denote the displacements (in Å) of the atoms from the best plane of the pyrrolidine ring. The pyrrolidine rings are puckered. The conformation about the C(2)–N(1) bond by stereographic projection is shown in Fig. 4.

The 10,11-dihydro-5H-dibenzo[*a*,*d*]cyclohepten-5-ylidene part consists of the three planes. The first is benzene plane I through the C(9), C(10), C(11), C(12), C(13), C(23), C(14), and C(22) atom. The second is benzene plane II through the C(15), C(16),

---

[5] "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.

TABLE 3. BOND LENGTHS AND THEIR STANDARD DEVIATIONS

| | A (σ) | B (σ) | Average | | A (σ) | B (σ) | Average |
|---|---|---|---|---|---|---|---|
| N(1)-C(2) | 1.59 (0.019) | 1.57 (0.019) | 1.58 Å | C(12)-C(13) | 1.36 (0.028) | 1.36 (0.027) | 1.36 Å |
| N(1)-C(5) | 1.46 (0.021) | 1.49 (0.021) | 1.47 | C(13)-C(14) | 1.46 (0.024) | 1.51 (0.024) | 1.49 |
| N(1)-C(6) | 1.55 (0.020) | 1.57 (0.022) | 1.56 | C(13)-C(23) | 1.50 (0.027) | 1.40 (0.026) | 1.45 |
| C(2)-C(3) | 1.50 (0.022) | 1.48 (0.022) | 1.49 | C(14)-C(15) | 1.45 (0.023) | 1.48 (0.024) | 1.47 |
| C(2)-C(8) | 1.56 (0.023) | 1.61 (0.024) | 1.59 | C(15)-C(16) | 1.39 (0.025) | 1.43 (0.029) | 1.41 |
| C(3)-C(4) | 1.59 (0.024) | 1.57 (0.024) | 1.58 | C(15)-C(20) | 1.42 (0.026) | 1.44 (0.028) | 1.43 |
| C(3)-C(14) | 1.34 (0.023) | 1.32 (0.023) | 1.33 | C(16)-C(17) | 1.43 (0.027) | 1.48 (0.035) | 1.46 |
| C(4)-C(5) | 1.61 (0.025) | 1.57 (0.025) | 1.59 | C(17)-C(18) | 1.35 (0.031) | 1.29 (0.038) | 1.32 |
| C(6)-C(7) | 1.55 (0.027) | 1.53 (0.028) | 1.54 | C(18)-C(19) | 1.45 (0.033) | 1.41 (0.037) | 1.43 |
| C(9)-C(10) | 1.34 (0.033) | 1.38 (0.036) | 1.36 | C(19)-C(20) | 1.38 (0.030) | 1.51 (0.032) | 1.45 |
| C(9)-C(23) | 1.49 (0.031) | 1.47 (0.032) | 1.48 | C(20)-C(21) | 1.56 (0.029) | 1.53 (0.034) | 1.54 |
| C(10)-C(11) | 1.40 (0.034) | 1.39 (0.038) | 1.39 | C(21)-C(22) | 1.55 (0.032) | 1.59 (0.035) | 1.57 |
| C(11)-C(12) | 1.53 (0.032) | 1.47 (0.034) | 1.50 | C(22)-C(23) | 1.44 (0.032) | 1.54 (0.030) | 1.49 |

TABLE 4. BOND ANGLES AND THEIR STANDARD DEVIATIONS

| | A (σ) | B (σ) | Average | | A (σ) | B (σ) | Average |
|---|---|---|---|---|---|---|---|
| C(2)-N(1)-C(5) | 105° (1.1°) | 104° (1.1°) | 104° | C(3)-C(14)-C(13) | 123° (1.5°) | 122° (1.5°) | 123° |
| C(2)-N(1)-C(6) | 107 (1.1 ) | 109 (1.1 ) | 108 | C(3)-C(14)-C(15) | 120 (1.5 ) | 122 (1.5 ) | 121 |
| C(5)-N(1)-C(6) | 112 (1.2 ) | 113 (1.2 ) | 113 | C(13)-C(14)-C(15) | 116 (1.4 ) | 116 (1.4 ) | 116 |
| N(1)-C(2)-C(3) | 102 (1.1 ) | 103 (1.2 ) | 102 | C(14)-C(15)-C(16) | 121 (1.6 ) | 118 (1.6 ) | 119 |
| N(1)-C(2)-C(8) | 107 (1.2 ) | 103 (1.2 ) | 105 | C(14)-C(15)-C(20) | 119 (1.5 ) | 116 (1.6 ) | 117 |
| C(3)-C(2)-C(8) | 116 (1.3 ) | 115 (1.3 ) | 115 | C(16)-C(15)-C(20) | 120 (1.6 ) | 126 (1.8 ) | 123 |
| C(2)-C(3)-C(4) | 111 (1.3 ) | 111 (1.3 ) | 111 | C(15)-C(16)-C(17) | 119 (1.7 ) | 114 (2.0 ) | 116 |
| C(2)-C(3)-C(14) | 127 (1.5 ) | 126 (1.5 ) | 127 | C(16)-C(17)-C(18) | 120 (1.9 ) | 119 (2.4 ) | 120 |
| C(4)-C(3)-C(14) | 122 (1.4 ) | 123 (1.5 ) | 123 | C(17)-C(18)-C(19) | 123 (2.1 ) | 131 (2.6 ) | 127 |
| C(3)-C(4)-C(5) | 98 (1.3 ) | 101 (1.3 ) | 99 | C(18)-C(19)-C(20) | 116 (2.0 ) | 113 (2.1 ) | 115 |
| N(1)-C(5)-C(4) | 103 (1.2 ) | 104 (1.3 ) | 103 | C(15)-C(20)-C(19) | 123 (1.8 ) | 116 (1.8 ) | 119 |
| N(1)-C(6)-C(7) | 105 (1.4 ) | 107 (1.4 ) | 106 | C(15)-C(20)-C(21) | 117 (1.6 ) | 123 (1.9 ) | 120 |
| C(10)-C(9)-C(23) | 126 (2.1 ) | 117 (2.2 ) | 121 | C(19)-C(20)-C(21) | 121 (1.8 ) | 121 (2.0 ) | 121 |
| C(9)-C(10)-C(11) | 124 (2.2 ) | 127 (2.4 ) | 126 | C(20)-C(21)-C(22) | 110 (1.7 ) | 106 (1.9 ) | 108 |
| C(10)-C(11)-C(12) | 114 (2.0 ) | 113 (2.3 ) | 114 | C(21)-C(22)-C(23) | 118 (1.9 ) | 123 (1.9 ) | 121 |
| C(11)-C(12)-C(13) | 121 (1.9 ) | 123 (2.0 ) | 122 | C(9)-C(23)-C(13) | 109 (1.7 ) | 118 (1.8 ) | 114 |
| C(12)-C(13)-C(14) | 116 (1.6 ) | 117 (1.6 ) | 116 | C(9)-C(23)-C(22) | 121 (1.9 ) | 115 (1.8 ) | 118 |
| C(12)-C(13)-C(23) | 125 (1.7 ) | 122 (1.7 ) | 123 | C(13)-C(23)-C(22) | 129 (1.8 ) | 126 (1.7 ) | 128 |
| C(14)-C(13)-C(23) | 119 (1.5 ) | 121 (1.6 ) | 120 | | | | |

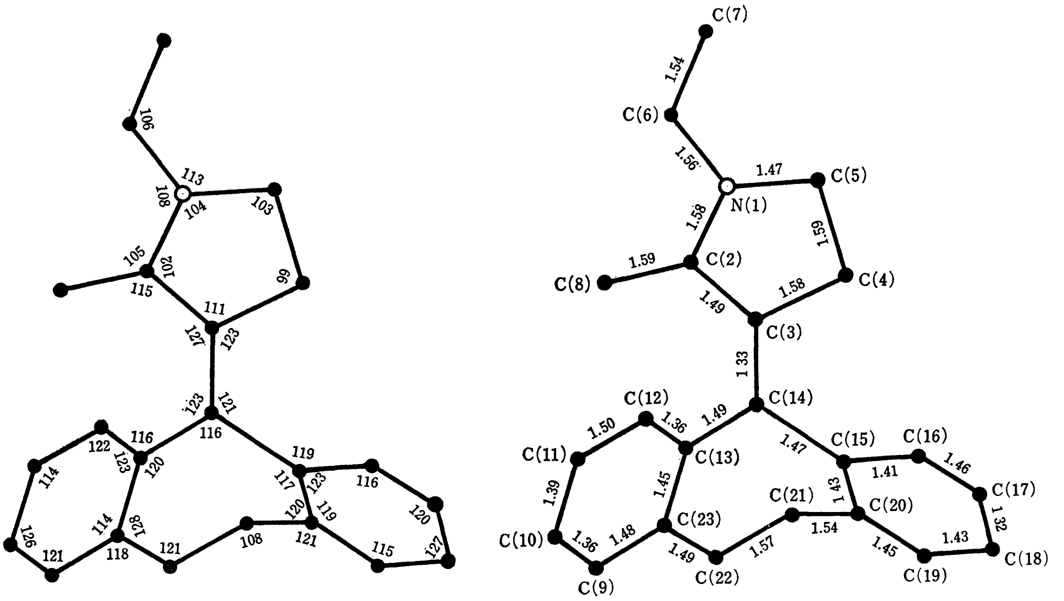

Fig. 2. Average values of the corresponding bond lengths and angles in the two independent molecules.

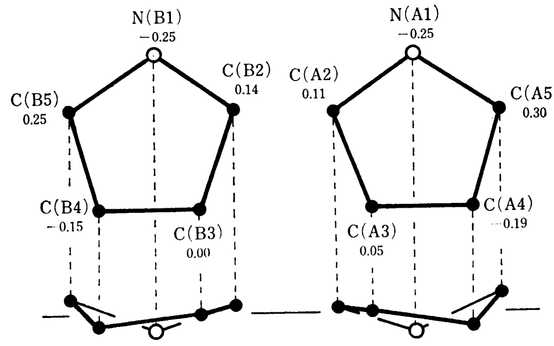

Fig. 3. Conformation of the pyrrolidine rings. Arabic numerals show the displacements (in Å) of the atoms from the best plane of the pyrrolidine rings.

C(17), C(18), C(19), C(20), C(14), and C(21) atom. The third is the ylidene plane through the C(2), C(3), C(4), C(13), C(14), and C(15) atom. The equations for these planes, displacements of the individual atoms from the planes and the dihedral angles between the planes are given in Table 5.

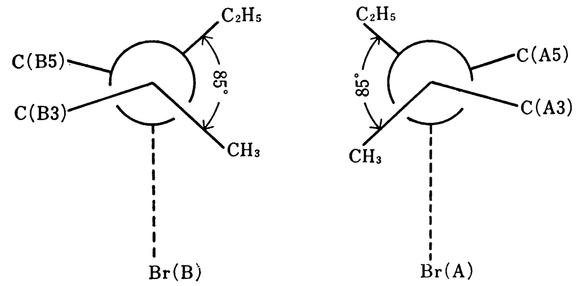

Fig. 4. Stereographic projection of the conformation about the C(2)-N(1) bond.

It is concluded that the overall geometry of the two independent molecules is similar in every detail.

*Packing of the Molecules.* The drawing of the structure viewed along the *c* axis and the *b* axis are shown in Figs. 5 and 6, respectively. The N(1)···

Table 5. Best planes

(a) Equations[a)]

| | |
|---|---|
| A molecule | |
| Benzene plane I | $0.7702X + 0.3770Y + 0.5073Z = 9.051$ |
| Benzene plane II | $-0.1738X + 0.8552Y + 0.4898Z = 4.478$ |
| Ylidene plane | $0.1221X - 0.2424Y + 0.9612Z = 2.460$ |
| B molecule | |
| Benzene plane I | $-0.7118X + 0.4413Y + 0.5530Z = 6.124$ |
| Benzene plane II | $0.2438X + 0.8247Y + 0.5081Z = 7.710$ |
| Ylidene plane | $-0.1490X - 0.2461Y + 0.9591Z = 4.773$ |

a) *X*, *Y*, and *Z* in Å units.

(b) Displacements of atoms from the planes

| Benzene plane I | | Benzene plane II | | Ylidene plane | |
|---|---|---|---|---|---|
| A molecule | | | | | |
| C(A9) | 0.034 Å | C(A15) | −0.001 Å | C(A2) | −0.006 Å |
| C(A10) | 0.025 | C(A16) | −0.007 | C(A3) | 0.019 |
| C(A11) | −0.007 | C(A17) | 0.006 | C(A4) | −0.015 |
| C(A12) | −0.013 | C(A18) | 0.001 | C(A13) | −0.020 |
| C(A13) | −0.057 | C(A19) | −0.010 | C(A14) | 0.031 |
| C(A23) | −0.041 | C(A20) | 0.013 | C(A15) | −0.009 |
| C(A14) | 0.062 | C(A14) | −0.001 | | |
| C(A22) | −0.002 | C(A21) | −0.001 | | |
| B molecule | | | | | |
| C(B9) | −0.017 | C(B15) | −0.034 | C(B2) | −0.023 |
| C(B10) | 0.018 | C(B16) | 0.018 | C(B3) | −0.025 |
| C(B11) | 0.010 | C(B17) | 0.024 | C(B4) | 0.036 |
| C(B12) | −0.012 | C(B18) | −0.006 | C(B13) | 0.025 |
| C(B13) | −0.017 | C(B19) | −0.021 | C(B14) | 0.022 |
| C(B23) | −0.009 | C(B20) | −0.008 | C(B15) | −0.034 |
| C(B14) | 0.015 | C(B14) | −0.006 | | |
| C(B22) | 0.012 | C(B21) | 0.034 | | |

(c) Dihedral angles between the planes

| | | | A | B | Average |
|---|---|---|---|---|---|
| Benzene plane I | and | Benzene plane II | 64° | 62° | 63° |
| Benzene plane I | | Ylidene plane | 60 | 59 | 59 |
| Benzene plane II | | Ylidene plane | 76 | 76 | 76 |

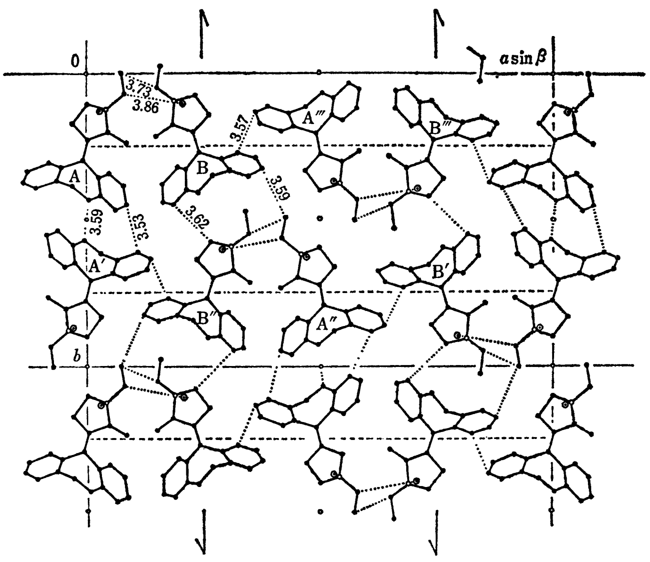

Fig. 5. A drawing of the structure viewed along the *c* axis. Some of the van der Waals contacts are indicated by dotted lines.

Br⁻ distances are 3.12 Å in the A molecule and 3.13 Å in the B molecule. In both A and B molecules, the C(2), C(5), C(6) atom, and the Br⁻ ion are approximately on the four vertices of a tetrahedron centered at the N(1) atom. The bond angles involving the N(1) atom and the Br⁻ ion are:

| | A molecule | B molecule |
|---|---|---|
| Br⁻···N(1)-C(2) | 111° | 115° |
| Br⁻···N(1)-C(5) | 101 | 99 |
| Br⁻···N(1)-C(6) | 119 | 116 |

The evidence thus obtained suggests that N(1)···Br⁻ form N-H···Br⁻ hydrogen bondings. They are indicated by the broken lines in Fig. 6.

Some shorter intermolecular distances are indicated by dotted lines in Figs. 5 and 6. No unusually short contact is found in this crystal structure.

The complete data of the $F_o$-$F_c$ table are kept at the office of the Bulletin of the Chemical Society of Japan.[6]

The authors thank Miss Kazuko Nakayama for her assistance in the intensity measurement. They are also indebted to Professor Masao Kakudo and Dr. Tamaichi Ashida for discussions and suggestions.

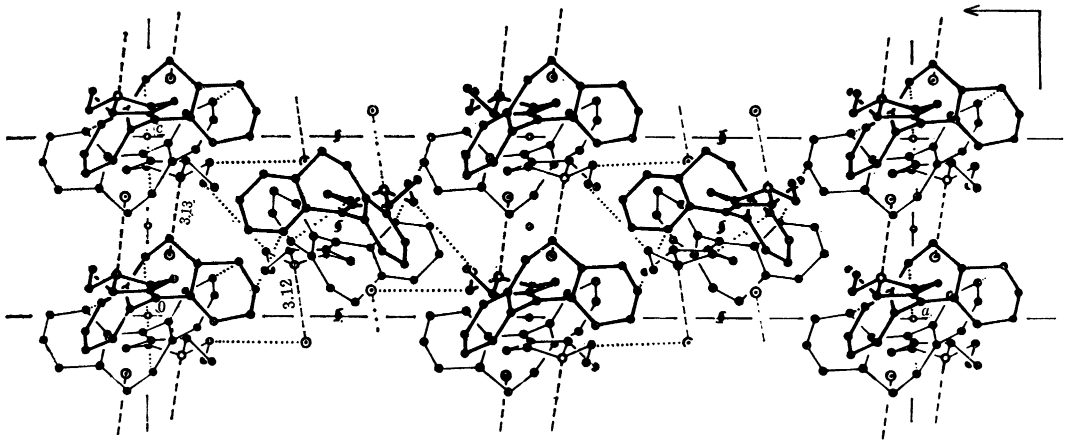

Fig. 6. A drawing of the structure viewed along the *b* axis. The hydrogen bonds and van der Waals contacts are indicated by broken and dotted lines, respectively.

---

[6] Document No. 7115. A copy may be secured by citing the document number and remitting, in advance, ¥500 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.