*Acta Cryst.* (1977). B**33**, 3555–3558

# 2,6-Dicarboxypyridine *N*-Oxide

By Urszula Rychlewska and Maria Gdaniec

*Laboratory of X-ray Crystallography, Institute of Chemistry, A. Mickiewicz University, ul. Grunwaldzka* 6,
60-780 *Poznań, Poland*

(*Received* 14 *April* 1977; *accepted* 20 *June* 1977)

**Abstract.** $C_7H_5NO_5$, monoclinic, $P2_1/c$, $a = 9{\cdot}825$ (1), $b = 6{\cdot}1868$ (8), $c = 24{\cdot}596$ (4) Å, $\beta = 93{\cdot}36$ (1)°, $V = 1492{\cdot}5$ (4) Å$^3$, $Z = 8$, $D_c = 1{\cdot}63$, $D_m = 1{\cdot}60$ g cm$^{-3}$, $\mu = 12{\cdot}6$ cm$^{-1}$. The final $R$ was 0·049 for 1665 reflexions. Each carboxyl H atom in the molecule is bonded to an O atom of the *N*-oxide group *via* a short intramolecular hydrogen bond.

**Introduction.** Previously reported structures of 2-carboxypyridine *N*-oxide (Laing & Nicholson, 1971), 2-carboxy-6-methylpyridine *N*-oxide (Dideberg & Dupont, 1975) and 2-carboxy-4-chloroquinoline *N*-oxide (Rychlewska & Kosturkiewicz, 1973) revealed that between the *N*-oxide group and the carboxyl group in the $\alpha$ position, a short intramolecular hydrogen bond is formed. From our point of view, it was interesting to study the geometry of the hydrogen bonding between two carboxyl groups in close proximity to the *N*-oxide group.

Needle-shaped single crystals were obtained by recrystallization from methyl cyanide. The crystal for investigation was cut to dimensions of 0·20 × 0·15 × 0·10 mm. Least-squares fitting of $2\theta$, $\omega$ and $\chi$ for 15 intense reflexions centred on a Syntex $P2_1$ diffractometer gave accurate cell constants. X-ray diffraction data were measured with graphite-monochromated Cu $K\alpha$ radiation. A variable-speed (1·5 to 29·3° min$^{-1}$) $\theta$–$2\theta$ scan technique was used in measuring 2021 independent reflexions to a maximum $2\theta$ of 114°. Of these, 1656 had intensities greater than $1{\cdot}96\sigma(I)$ and were used in all calculations. The intensities were reduced to a set of structure amplitudes by application of the Lorentz–polarization corrections. No absorption or extinction corrections were applied, though the most intense reflexions were judged to suffer from extinction. The strongest of these, 004, was excluded from the final stages of least-squares refinement.

*MULTAN* was used to determine the phases of 226 reflexions with $|E| > 1{\cdot}6$. An $E$ map based on the set of phases with the highest figure of merit revealed the positions of all non-hydrogen atoms. Two cycles of block-diagonal least-squares refinement followed by six cycles of full-matrix least-squares calculations with isotropic thermal parameters reduced $R$ to 0·136, and with anisotropic thermal parameters to 0·082. All the H atoms were located on two successive difference Fourier syntheses by means of 19-point electron-density interpolation. The H atom contributions were included in the structure factor calculations with an isotropic thermal parameter for each H atom one unit greater than the isotropic parameter of the atom to which it is bonded. The H parameters were not varied during subsequent refinement. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{0\cdot5}$ values are 0·049 and 0·051 respectively. The quantity minimized in the least-squares calculations was $\Sigma w(F_o - F_c)^2$. The weighting scheme was based on counting statistics; $w = 1/\sigma^2(F_o)$.

Table 1. *Final coordinates* (× $10^4$) *of non-hydrogen atoms*

| | $x$ | $y$ | $z$ | | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| C(2) | 688 (3) | 7074 (6) | 1493 (1) | C(2′) | 3272 (3) | 7853 (6) | 3693 (1) |
| C(3) | 1033 (3) | 6489 (7) | 2024 (1) | C(3′) | 2834 (4) | 8118 (7) | 4206 (1) |
| C(4) | 1756 (4) | 4630 (7) | 2143 (1) | C(4′) | 3113 (4) | 6560 (7) | 4600 (1) |
| C(5) | 2149 (3) | 3382 (6) | 1719 (1) | C(5′) | 3847 (4) | 4768 (7) | 4473 (2) |
| C(6) | 1803 (3) | 3930 (6) | 1185 (1) | C(6′) | 4326 (3) | 4534 (6) | 3965 (1) |
| C(7) | 2227 (4) | 2497 (7) | 730 (1) | C(7′) | 5213 (4) | 2619 (7) | 3840 (2) |
| C(8) | −81 (4) | 9152 (6) | 1376 (2) | C(8′) | 2913 (4) | 9554 (7) | 3264 (2) |
| O(1) | 683 (3) | 6265 (4) | 566 (1) | O(1′) | 4467 (3) | 5855 (4) | 3080 (1) |
| O(2) | 1847 (3) | 3059 (5) | 230 (1) | O(2′) | 5651 (3) | 2463 (5) | 3352 (1) |
| O(3) | 2876 (3) | 895 (5) | 840 (1) | O(3′) | 5476 (3) | 1309 (5) | 4197 (1) |
| O(4) | -383 (3) | 9662 (4) | 867 (1) | O(4′) | 3304 (3) | 9182 (5) | 2771 (1) |
| O(5) | −375 (3) | 10293 (4) | 1745 (1) | O(5′) | 2301 (3) | 11130 (5) | 3387 (1) |
| N(1) | 1066 (3) | 5760 (5) | 1081 (1) | N(1′) | 4019 (3) | 6075 (5) | 3581 (1) |

Table 2. *Final coordinates* ($\times 10^3$) *and isotropic thermal parameters for the hydrogen atoms*

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| H(3) | 69 | 753 | 235 | 4·9 |
| H(4) | 208 | 426 | 257 | 4·4 |
| H(5) | 278 | 200 | 180 | 5·5 |
| H(O2) | 114 | 448 | 26 | 6·7 |
| H(O4) | −3 | 847 | 61 | 5·8 |
| H(3′) | 228 | 958 | 430 | 5·9 |
| H(4′) | 291 | 681 | 499 | 5·8 |
| H(5′) | 410 | 359 | 481 | 5·5 |
| H(O2′) | 517 | 403 | 309 | 6·9 |
| H(O4′) | 395 | 766 | 277 | 7·0 |

All calculations were performed on a Nova minicomputer with the Syntex *XTL* programs for structure determination (*Syntex XTL Operation Manual*, 1973). The final parameters for the non-hydrogen atoms are given in Table 1 and for the H atoms in Table 2.*

**Discussion.** There are two crystallographically independent molecules in an asymmetric unit. Fig. 1 shows the numbering scheme, bond lengths and bond angles for the molecules. Each molecule consists of two chemically equivalent moieties. The chemically equivalent bond lengths and angles of these moieties are in good agreement with each other. The corresponding values of bond lengths and angles for molecules $M$ and $M'$ do not differ significantly and are in reasonable agreement with those found recently in 2-carboxy-6-methylpyridine $N$-oxide (Dideberg & Dupont, 1975). The C–C average bond length for both pyridine rings is 1·374 Å with a spread of −0·007 to +0·009 Å. The C–N distances in pyridine systems are relatively longer (average value of 1·362 Å with a spread of −0·003 to +0·005 Å) than in 2,6-dicarboxypyridine [1·338 (5) and 1·336 (5) Å] (Takusagawa, Hirotsu & Shimada, 1973). Similarly, the C–N bond length in pyridine $N$-oxide is longer than in pyridine (Snerling, Nielsen, Nygaard, Pedersen & Sørensen, 1975). These effects are consistent with the observations made by Desiderato, Terry & Freeman (1971) for 8-hydroxyquinoline $N$-oxide and with their suggestion that it is the $N$-oxide group which may be responsible for the C–N lengthening. The values characteristic of the geometric features of the carboxyl group agree with those given by Leiserowitz (1976).

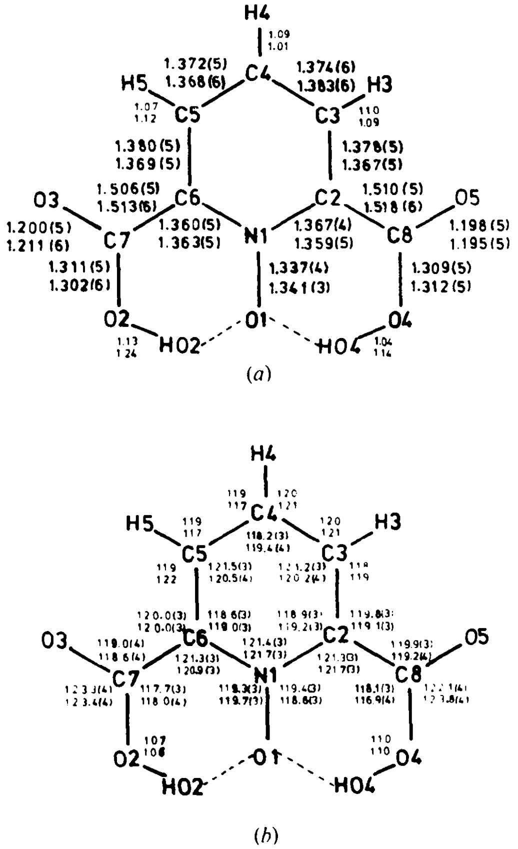

Fig. 1. (*a*) Bond lengths (Å), (*b*) bond angles (°) of the two independent molecules. Upper numbers refer to molecule $M$, the lower to molecule $M'$: e.s.d.'s are in parentheses.

Table 3. *Hydrogen-bond lengths* (Å) *and angles* (°)

| $D$–H···$A$ | $D$–H | H···$A$ | $D$···$A$ | ∠$D$–H···$A$ |
|---|---|---|---|---|
| O(2)–H(O2)···O(1) | 1·13 | 1·43 | 2·457 (4) | 149 |
| O(4)–H(O4)···O(1) | 1·04 | 1·54 | 2·480 (4) | 147 |
| O(2′)–H(O2′)···O(1′) | 1·24 | 1·32 | 2·473 (4) | 150 |
| O(4′)–H(O4′)···O(1′) | 1·14 | 1·43 | 2·453 (4) | 142 |

In both molecules, $M$ and $M'$, each carboxyl group is hydrogen bonded to the $N$-oxide O atom and this is the only type of intramolecular hydrogen bond in the structure. The hydrogen-bond distances and angles are given in Table 3. O···O contacts range from 2·453 (4) to 2·480 (4) Å, fulfilling the criterion for very short hydrogen bonds (Catti & Ferraris, 1976). There seems to be conclusive evidence that the O–H distance increases regularly as O···O decreases (Hamilton & Ibers, 1968). We observed this effect for three of the O–H···O bonds. However, the longest distance, O(2′)–H(O2′) of 1·24 Å, does not correspond to the shortest O···O contact, but to one of 2·473 (4) Å.

Least-squares planes calculated for the two different pyridine rings show that these are nearly planar, though it cannot be proved so according to the $\chi^2$ test. Table 4 gives the deviations of individual atoms from these planes. The dihedral angles between the least-squares best planes of the carboxyl groups and that of the pyridine ring of molecule $M$ are 1·3° for the C(7)

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32855 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Deviations of the atoms from the least-squares planes of the pyridine rings* (Å)

The planes are expressed as $AX + BY + CZ = D$ where $X$, $Y$ and $Z$ are in Å relative to the axes $a$, $b$ and $c^*$. The atoms indicated with asterisks were omitted from the calculations of the least-squares planes.

| | Molecule $M$ | Molecule $M'$ |
|---|---|---|
| N(1) | −0·009 | 0·000 |
| C(2) | 0·010 | 0·010 |
| C(3) | 0·001 | −0·012 |
| C(4) | −0·011 | 0·000 |
| C(5) | 0·007 | 0·012 |
| C(6) | 0·004 | −0·011 |
| *C(7) | −0·003 | −0·087 |
| *O(2) | −0·038 | −0·123 |
| *O(3) | 0·006 | −0·116 |
| *C(8) | 0·053 | 0·042 |
| *O(4) | 0·069 | 0·122 |
| *O(5) | 0·094 | −0·004 |
| $A$ | 0·8550 | 0·8274 |
| $B$ | 0·5174 | 0·4839 |
| $C$ | −0·0350 | 0·2851 |
| $D$ | 2·5209 | 7·1659 |
| $\chi^2$ | 31 | 39 |

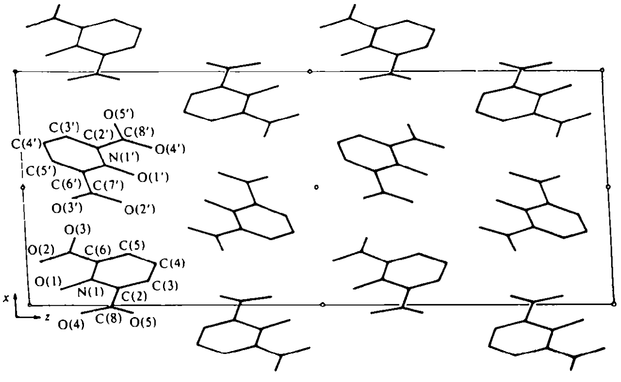

Fig. 2. The molecular packing diagram, excluding hydrogen atoms, viewed down **b**.

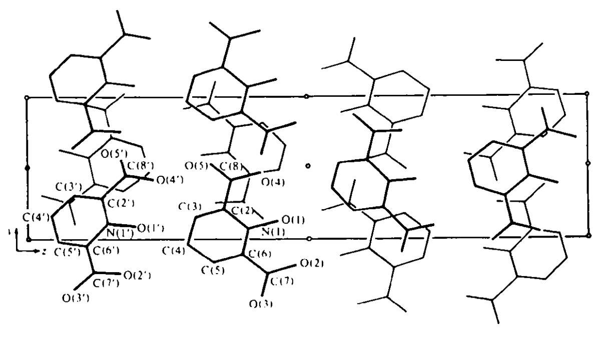

Fig. 3. The molecular packing diagram, excluding hydrogen atoms, viewed down **a**.

Table 5. *Intermolecular distances* (Å) *less than* 3·45 Å *between non-hydrogen atoms*

Estimated standard deviations are given in parentheses.

Symmetry code

| | | | |
|---|---|---|---|
| none | $x,y,z$ | (iv) | $-x, 1-y, -z$ |
| (i) | $x, 1+y, z$ | (v) | $1-x, 1-y, 1-z$ |
| (ii) | $-x, \frac{1}{2}+y, \frac{1}{2}-z$ | (vi) | $x, \frac{1}{2}-y, -\frac{1}{2}+z$ |
| (iii) | $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ | | |

| | | | |
|---|---|---|---|
| N(1')–O($3^{\mathrm{iii}}$) | 3·293 (4) | C(3')–O($3'^{\mathrm{i}}$) | 3·263 (5) |
| O(5')–C($2^{\mathrm{ii}}$) | 3·025 (4) | C(2')–O($3'^{\mathrm{i}}$) | 3·238 (5) |
| O(5')–C($3^{\mathrm{ii}}$) | 3·379 (5) | O(5)–C($3^{\mathrm{ii}}$) | 3·219 (4) |
| O(5')–C($8^{\mathrm{ii}}$) | 2·956 (5) | O(5)–C($4^{\mathrm{ii}}$) | 3·149 (4) |
| O(5')–O($5^{\mathrm{ii}}$) | 3·201 (4) | O(5)–C($5^{\mathrm{i}}$) | 3·134 (4) |
| O(5')–C($6'^{\mathrm{i}}$) | 3·175 (5) | O(5)–C($6^{\mathrm{i}}$) | 3·447 (4) |
| O(5')–C($7'^{\mathrm{i}}$) | 3·147 (5) | O(5)–C($2'^{\mathrm{ii}}$) | 3·377 (4) |
| O(5')–O($2'^{\mathrm{i}}$) | 3·399 (4) | O(4)–C($7^{\mathrm{i}}$) | 3·141 (5) |
| O(4')–C(3) | 3·263 (5) | O(4)–O($2^{\mathrm{iv}}$) | 3·424 (4) |
| O(4')–O($1'^{\mathrm{iii}}$) | 3·284 (4) | O(4)–O($3^{\mathrm{i}}$) | 3·296 (4) |
| O(4')–O($2'^{\mathrm{i}}$) | 3·331 (4) | O(4)–C($3'^{\mathrm{ii}}$) | 3·217 (5) |
| O(4')–O($2'^{\mathrm{iii}}$) | 3·187 (4) | O(4)–C($4'^{\mathrm{ii}}$) | 3·087 (5) |
| O(3')–O($3^{\mathrm{iii}}$) | 3·271 (4) | O(3)–C($4'^{\mathrm{vi}}$) | 3·427 (5) |
| O(2')–O($3^{\mathrm{iii}}$) | 3·197 (4) | O(2)–O($1^{\mathrm{iv}}$) | 3·101 (4) |
| C(8')–C($7'^{\mathrm{i}}$) | 3·216 (6) | O(2)–C($5'^{\mathrm{vi}}$) | 3·288 (5) |
| C(8')–O($2'^{\mathrm{i}}$) | 3·233 (5) | O(1)–O($1^{\mathrm{iv}}$) | 3·403 (3) |
| C(7')–O($3^{\mathrm{iii}}$) | 2·843 (5) | C(8)–O($3^{\mathrm{i}}$) | 3·434 (5) |
| C(6')–O($3^{\mathrm{iii}}$) | 2·889 (5) | C(7)–O($3'^{\mathrm{iii}}$) | 3·262 (5) |
| C(5')–O($3^{\mathrm{iii}}$) | 3·426 (4) | C(6)–O($3'^{\mathrm{iii}}$) | 3·239 (5) |
| C(5')–C($5'^{\mathrm{v}}$) | 3·352 (5) | C(5)–O($2'^{\mathrm{iii}}$) | 3·335 (5) |
| C(4')–O($3'^{\mathrm{v}}$) | 3·455 (5) | C(4)–O($2'^{\mathrm{iii}}$) | 3·378 (5) |

carboxyl group, achieved mostly by twisting, and 2·1° for the C(8) carboxyl group, achieved mostly by bending. In molecule $M'$ the C(7') carboxyl group is inclined to the pyridine ring by 2·8° (simple bending) while the C(8') carboxyl group is twisted by 3·5°.

The molecular-packing projections down **b** and **a** are shown in Figs. 2 and 3 respectively. Many short intermolecular interatomic distances were found of which those less than 3·45 Å between non-hydrogen atoms are listed in Table 5.

The authors are grateful to Professor M. Szafran and Dr B. Brzeziński for suggesting the problem and for providing the compound for investigation.

## References

Catti, M. & Ferraris, G. (1976). *Acta Cryst.* B**32**, 2754–2756.

Desiderato, R., Terry, J. C. & Freeman, G. R. (1971). *Acta Cryst.* B**27**, 2443–2447.

Dideberg, P. O. & Dupont, L. (1975). *Acta Cryst.* B**31**, 2719–2720.

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids*, p. 52. New York: Benjamin.

Laing, M. & Nicholson, C. (1971). *J. S. Afr. Chem. Inst.* **24**, 186–195.

Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.

RYCHLEWSKA, U. & KOSTURKIEWICZ, Z. (1973). *Rocz. Chem.* **47**, 1917–1926.

SNERLING, O., NIELSEN, C. J., NYGAARD, L., PEDERSEN, E. J. & SØRENSEN, G. O. (1975). *J. Mol. Struct.* **27**, 205–211.

*Syntex XTL Operation Manual* (1973). Cupertino: Syntex Analytical Instruments.

TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2020–2027.

*Acta Cryst.* (1977). B**33**, 3558–3561

# Quinoline-2-carboxamide

BY MARIA GDANIEC, MARIUSZ JASKÓLSKI AND ZOFIA KOSTURKIEWICZ

*Laboratory of X-ray Crystallography, Institute of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland*

(*Received* 30 *June* 1977; *accepted* 12 *July* 1977)

**Abstract.** $C_{10}H_8N_2O$, monoclinic, $P2_1/a$, $a$ = 18·128 (6), $b$ = 11·986 (3), $c$ = 3·9293 (6) Å, $\beta$ = 90·54 (2)°, $Z$ = 4, $\mu$(Cu $K\alpha$) = 7·4 cm$^{-1}$, $D_c$ = 1·34 g cm$^{-3}$, $R$ = 0·044 for 994 reflexions. The molecules are joined by N—H···O hydrogen bonds of length 2·897 (3) Å to form dimers across the centres of symmetry.

**Introduction.** A single crystal of quinoline-2-carboxamide of dimensions 0·25 × 0·3 × 0·4 mm was obtained by recrystallization from $CHCl_3$–$CCl_4$. Intensity measurements were carried out in the $\theta$–$2\theta$ mode on a Syntex $P2_1$ diffractometer using graphite-monochromated Cu radiation to $2\theta_{max}$ = 120°. 996 reflexions from the data set had $I > 1·96\sigma(I)$ and were used in the analysis. No absorption correction was applied.

The structure was solved by *MULTAN*. An $E$ map calculated for the set of phases with the highest absolute figure-of-merit revealed the positions of all the non-hydrogen atoms. Structure refinement was carried out by full-matrix least-squares calculations with weights based on counting statistics. The positional parameters of the H atoms were found from a difference electron-density map. The H atoms were given isotropic temperature factors one unit greater than the isotropic temperature factors of the heavy atoms to which they were bonded. They were included in the structure factor calculations but their positions and temperature factors were not refined. Inspection of the strongest reflexions indicated that 11$\bar{1}$ and 21$\bar{1}$ were seriously affected by extinction and they were therefore removed from the data set. Three subsequent cycles of refinement gave agreement indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ = 0·044 and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{0·5}$ = 0·048.

The calculations were performed on a Nova mini-computer with Syntex *XTL* structure-determination programs.

The atomic coordinates and (for H only) thermal parameters with their e.s.d.'s are given in Tables 1 and 2.*

Table 1. *Fractional coordinates of the non-hydrogen atoms* (× $10^4$)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| C(2) | 1745 (1) | 6236 (2) | 1584 (6) |
| C(3) | 1925 (2) | 7318 (2) | 405 (7) |
| C(4) | 2636 (2) | 7679 (2) | 928 (7) |
| C(5) | 3894 (2) | 7319 (2) | 3302 (7) |
| C(6) | 4364 (2) | 6631 (3) | 5018 (8) |
| C(7) | 4126 (2) | 5567 (3) | 6111 (7) |
| C(8) | 3417 (2) | 5224 (2) | 5451 (7) |
| C(9) | 2917 (1) | 5930 (2) | 3726 (6) |
| C(10) | 3157 (2) | 7000 (2) | 2634 (6) |
| C(11) | 980 (1) | 5798 (2) | 984 (7) |
| N(1) | 2211 (1) | 5562 (2) | 3172 (5) |
| N(2) | 849 (1) | 4784 (2) | 2209 (6) |
| O(1) | 518 (1) | 6358 (2) | −585 (5) |

Table 2. *Fractional coordinates* (× $10^3$) *and isotropic thermal parameters* (Å$^2$) *of the hydrogen atoms*

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| H(21) | 37 | 440 | 218 | 5·9 |
| H(22) | 123 | 442 | 354 | 5·9 |
| H(3) | 155 | 779 | −90 | 5·5 |
| H(4) | 280 | 849 | 3 | 5·8 |
| H(5) | 413 | 810 | 226 | 5·9 |
| H(6) | 492 | 687 | 531 | 6·5 |
| H(7) | 449 | 497 | 751 | 6·2 |
| H(8) | 323 | 444 | 625 | 5·5 |

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32863 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.