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Quinoline-2-carboxamide Hemihydrate

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Abstract. $C_{10}H_8N_2O.\frac{1}{2}H_2O$, orthorhombic, *Pbca*, $a = 11 \cdot 885$ (2), $b = 39 \cdot 30$ (2), $c = 7 \cdot 6176$ (8) Å, $Z = 16$, $D_m = 1 \cdot 34$, $D_c = 1 \cdot 35$ g cm^{-3}, $R = 0 \cdot 052$. The planarity of the quinoline ring is different for the two independent molecules. Hydrogen bonding is discussed.

Introduction. Crystals suitable for single-crystal X-ray analysis were obtained by recrystallization from methanol–water solution. A crystal with the dimensions 0·1 × 0·1 × 0·07 mm was used for measurements on a Syntex $P2_1$ diffractometer. Cell dimensions were determined from a least-squares fit of 2θ, ω and χ values for 15 reflexions. Measurements of the intensities were carried out in the θ–2θ mode ($2\theta_{\max} = 115°$) with graphite-monochromated Cu radiation. A variable 2·95–29·3° min^{-1} scan rate was used. Application of the rejection criterion $I < 1 \cdot 96\sigma(I)$ yielded 1504 independent reflexions for use in the analysis.

The structure was solved by direct methods. 242 reflexions with $E \geq 1 \cdot 6$ were used as input to the program *MULTAN*. An E map calculated for the set with the highest absolute figure of merit gave the positions of all non-hydrogen atoms. Refinement of the structure was carried out by the full-matrix least-squares method. All H atoms, except those of the water molecule, were found from a difference Fourier synthesis and included in the refinement. The isotropic temperature factor assigned to a H atom was one unit greater than the isotropic temperature factor of the heavy atom to which it was bonded. The function minimized in full-matrix least-squares calculations was $\Sigma w(F_o - F_c)^2$. The weighting scheme was based on counting statistics, $w = (\sigma^2 + c^2F^2)^{-1}$; c was equal to zero until the refinement ceased. Least-squares analysis of the expression $\sigma^2 + c^2F^2 = (\Delta F)^2$ gave a value of $c = 0 \cdot 035$. This value was applied in three more cycles of least-squares refinement. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$ are 0·052 and 0·062 respectively; the goodness of fit, *i.e.* $[\Sigma w(F_o - F_c)^2/(N_o - N_v)]^{1/2}$, is 1·19, where N_o is the number of observations and N_v the number of variables.

Table 1. *Fractional coordinates of non-hydrogen atoms*

The coordinates are in fractions of unit-cell edges × 10^4.

	x	y	z
C(2)	1417 (3)	2100 (1)	1279 (5)
C(3)	347 (3)	2138 (1)	532 (5)
C(4)	−62 (4)	2458 (1)	289 (6)
C(5)	210 (4)	382 (1)	652 (6)
C(6)	863 (4)	3345 (1)	1203 (6)
C(7)	1948 (4)	3281 (1)	1889 (6)
C(8)	2336 (4)	2957 (1)	2022 (5)
C(9)	1649 (3)	2679 (1)	1502 (5)
C(10)	571 (3)	2742 (1)	789 (5)
C(11)	1880 (3)	1751 (1)	1619 (5)
N(1)	2063 (3)	2357 (1)	1753 (4)
N(2)	2856 (3)	1745 (1)	2483 (5)
O(1)	1383 (2)	1492 (1)	1158 (4)
C(2′)	3711 (3)	4530 (1)	3469 (5)
C(3′)	4715 (3)	4572 (1)	2511 (5)
C(4′)	5109 (3)	4892 (1)	2243 (5)
C(5′)	4856 (4)	5513 (1)	2715 (6)
C(6′)	4236 (4)	5770 (1)	3404 (6)
C(7′)	3246 (4)	5705 (1)	4312 (6)
C(8′)	2864 (4)	5379 (1)	4520 (5)
C(9′)	3499 (3)	5103 (1)	3829 (5)
C(10′)	4510 (3)	5172 (1)	2905 (5)
C(11′)	3282 (4)	4123 (1)	3808 (5)
O(1′)	3730 (3)	3925 (1)	3122 (4)
N(2′)	2412 (4)	4154 (1)	4897 (6)
N(1′)	3112 (3)	4781 (1)	4110 (4)
O(*W*)	4193 (2)	1259 (1)	4581 (4)

The calculations were performed on a NOVA minicomputer with Syntex *XTL* structure-determination programs [except for the program for the calculation of the *c* factor which was written by one of us (MJ)].

The atomic coordinates and H atom thermal parameters, together with their e.s.d.'s, are given in Tables 1 and 2.*

Discussion. The present work was undertaken in connexion with spectroscopic investigations (Dziembowska & Szafran, 1974) in order to determine the geometry of the hydrogen bonding in 4-substituted quinoline-2-carboxamides.

There are two crystallographically independent molecules (*A* and *B*) in an asymmetric unit. Fig. 1 shows the scheme of atom numbering, and bond lengths and angles with their e.s.d.'s.

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

	x	y	z	B (Å^2)
H(3)	493 (3)	192 (1)	481 (5)	4·1
H(4)	425 (3)	249 (1)	21 (5)	4·6
H(5)	448 (3)	187 (1)	−12 (5)	4·6
H(6)	55 (3)	361 (1)	108 (5)	5·4
H(7)	242 (4)	348 (1)	230 (5)	5·6
H(8)	312 (3)	291 (1)	248 (5)	4·7
H(21)	312 (4)	195 (1)	280 (5)	4·9
H(22)	313 (3)	153 (1)	298 (5)	4·9
H(3′)	511 (3)	437 (1)	205 (5)	4·2
H(4′)	80 (3)	492 (1)	334 (5)	4·1
H(5′)	445 (3)	55 (1)	289 (5)	4·3
H(6′)	47 (3)	101 (1)	333 (5)	5·0
H(7′)	212 (4)	91 (1)	471 (5)	5·1
H(8′)	283 (3)	33 (1)	511 (5)	4·4
H(21′)	204 (3)	63 (1)	31 (5)	5·2
H(22′)	220 (4)	104 (1)	26 (6)	5·2

Table 3. *Equations of the least-squares planes and deviations of the atoms from the planes* (Å)

The equation of the planes is of the form: $AX + BY + CZ = D$.

	Molecule *A*	Molecule *B*
Plane 1		
A	0·4054	−0·5200
B	0·0247	0·0502
C	−0·9138	−0·8527
D	0·0016	−3·6496
N(1)	0·000	−0·001
C(2)	−0·006	−0·004
C(3)	0·003	0·006
C(4)	0·006	0·000
C(9)	0·007	0·006
C(10)	−0·010	−0·005
Plane 2		
A	0·3915	−0·5135
B	0·0591	0·0669
C	−0·9183	−0·8555
D	0·3479	−3·2838
C(5)	0·009	0·002
C(6)	−0·011	0·000
C(7)	−0·001	−0·005
C(8)	0·011	0·007
C(9)	−0·009	−0·003
C(10)	0·002	0·000
Plane 3		
A	0·4004	−0·5176
B	0·0394	0·0574
C	−0·9155	−0·8537
D	0·1300	−3·5049
N(1)	−0·006	−0·005
C(2)	−0·023	−0·013
C(3)	−0·005	0·002
C(4)	0·020	0·006
C(5)	−0·008	−0·005
C(6)	−0·040	−0·014
C(7)	−0·013	−0·010
C(8)	0·030	0·017
C(9)	0·022	0·013
C(10)	0·016	0·007

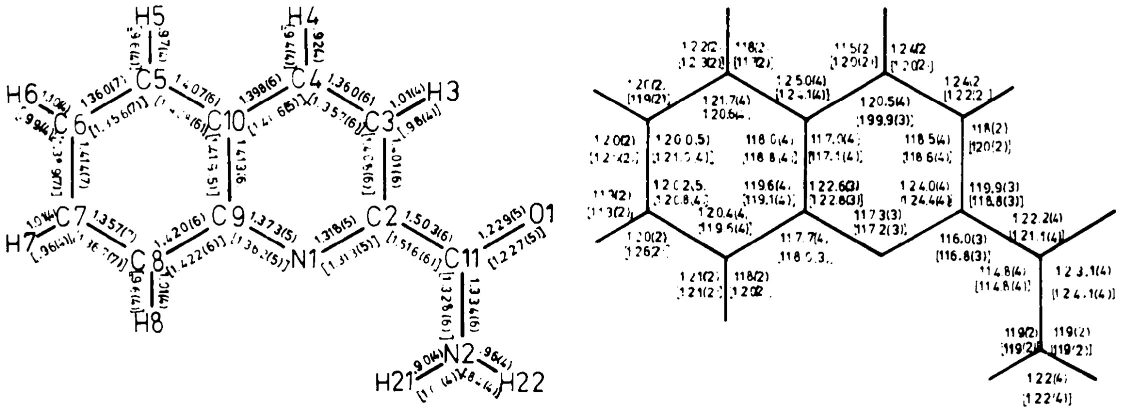

Fig. 1. The bond lengths (Å) and bond angles (°) of the two independent molecules. Numbers in square brackets refer to molecule *B*; e.s.d.'s are in parentheses.

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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 32543 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

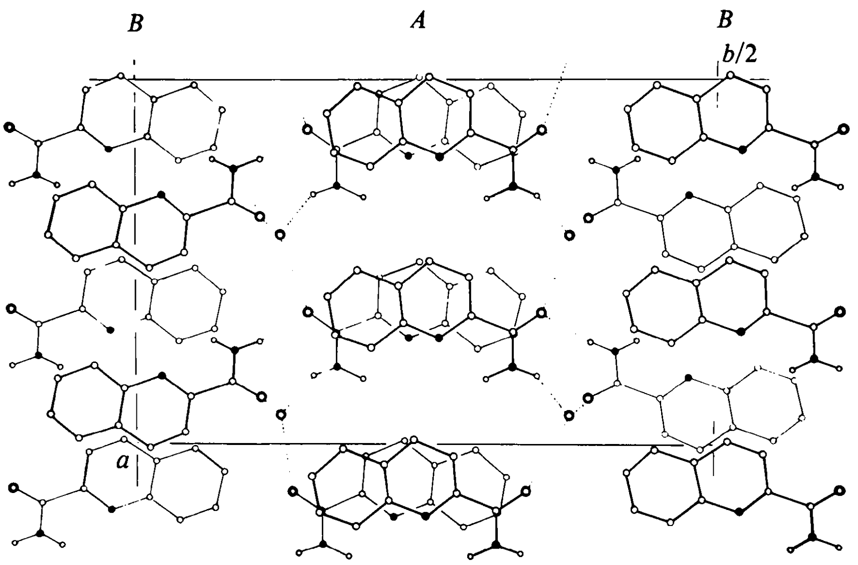

Fig. 2. The arrangement of the molecules viewed along [001].

The corresponding values in molecules *A* and *B* agree with each other within three e.s.d.'s. Bond lengths and angles are found to be in reasonable agreement with values reported previously [quinoline ring: Harlow, Simonsen & Sammes (1976), Lenner & Lindgren (1976); carboxamide moiety: Calleri, Chiari, Villa, Manfredotti, Guastini & Viterbo (1975), Takano, Sadada & Kakudo (1966), Rø & Sørum (1972)].

Table 3 lists deviations of the atoms from the least-squares planes calculated through the quinoline ring, and the pyridine and benzenoid moieties. The quinoline ring of molecule *B* is planar, deviations being within 0·017 Å. The quinoline ring of molecule *A* shows surprisingly large deviations from planarity. They arise from folding about the C(9)–C(10) bond axis and twisting around the C(3)–C(7) axis – similar to 8-quinolyl cyanomethyl sulphone (Harlow *et al.*, 1976).

In molecules *A* and *B* the length of the C(11)–C(6) bond corresponds to a C_{sp^2}–C_{sp^2} single-bond length and indicates that there is little or no conjugation between the carboxamide substituent and the quinoline ring. Carboxamide groups are twisted by 5·7 and 7·7° out of the plane of the pyridine moiety in molecules *A* and *B* respectively.

The projection of the structure of quinoline-2-carboxamide hemihydrate along the *c* axis is shown in Fig. 2. Molecules of type *A* lie near $y = \frac{1}{4}$ and $\frac{3}{4}$ while those of type *B* lie near $y = 0$ and $\frac{1}{2}$. The water molecules lie between them occupying *y* positions approximately equal to $\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$ and $\frac{7}{8}$. Molecules of type *A* are stacked in columns parallel to the *c* axis, the distance between columns being *a*/2. In each column the molecules overlap, the dihedral angle between the least-squares planes of two adjacent molecules being about 4°. Molecules of type *B* do not overlap, but, as can be easily seen from Fig. 2, are shifted from the overlap position obeyed by *A* molecules.

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

X···H–*Y*		H···*X*		∠*X*···H–*Y*
O(1)···N(2′)	2·977	H(22′)···O(1)	2·15	170
O(*W*)···N(2)	2·953	H(22)···O(*W*)	2·06	152
O(1)···O(*W*)	2·847			
O(1′)···O(*W*)	2·814			

Molecules *A* and *B* are involved in different types of hydrogen bonding. The O atom of the carbonyl group of molecule *A* is hydrogen bonded to a water molecule and to the carboxamide N atom of one *B* molecule. The carbonyl O atom of molecule *B*, on the other hand, accepts only one H atom of the water molecule. The water molecule takes part in three hydrogen bonds: two with molecule *A* and one with molecule *B*. The hydrogen-bond distances and angles are given in Table 4.

The difference in planarity of the two independent molecules seems to be mainly due to their different arrangement in the structure.

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