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

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Abstract. $C_{10}H_8N_2O$, monoclinic, $P2_1/a$, $a = 18\cdot128\,(6)$, $b = 11\cdot986\,(3)$, $c = 3\cdot9293\,(6)$ Å, $\beta = 90\cdot54\,(2)°$, $Z = 4$, $\mu(\text{Cu } K\alpha) = 7\cdot4$ cm^{-1}, $D_c = 1\cdot34$ g cm^{-3}, $R = 0\cdot044$ 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 θ–2θ mode on a Syntex $P2_1$ diffractometer using graphite-monochromated Cu radiation to $2\theta_{\max} = 120°$. 996 reflexions from the data set had $I > 1\cdot96\sigma(I)$ 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 $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0\cdot044$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{0\cdot5} = 0\cdot048$.

The calculations were performed on a Nova minicomputer 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

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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 32863 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. IR studies of quinoline-2-carboxamide and its derivatives (Dziembowska & Szafran, 1974) indicate that only one strong intermolecular hydrogen bond occurs in crystals of these compounds. However, two strong intermolecular hydrogen bonds exist in crystals of picolinamide (Takano, Sasada & Kakudo, 1966). Thus we undertook an X-ray analysis of quinoline-2-carboxamide (hereinafter QCA) to investigate the influence of the quinoline ring on hydrogen-bond formation.

An *ORTEP* drawing of the molecule and the atom numbering are shown in Fig. 1. The bond lengths and bond angles, given in Table 3, are very close to those found in QCA hemihydrate (Gdaniec, Jaskólski & Kosturkiewicz, 1977).

The deviations of atoms from the least-squares plane defined by the atoms of the quinoline ring are listed in Table 4. The quinoline ring does not deviate significantly from planarity, the maximum deviation being 0·015 Å. The least-squares plane defined by C(2), C(11), N(2) and O(1) shows that the carboxamide group is planar within experimental error. It is twisted about C(2)—C(11) by 1·5° relative to the quinoline ring. This twisting is considerably smaller than that observed in picolinamide (19°) (Takano *et al.*, 1966). The almost coplanar arrangement of the quinoline ring and carboxamide moiety can be attributed to the formation of an intramolecular N(2)···N(1) hydrogen bond. As can be seen from Table 5, the intramolecular N(2)···N(1) and N(1)···H(21) contacts in QCA are both shorter than the sums of the appropriate van der Waals radii [N: 1·50 Å, Pauling (1960); H: 1·0 Å, Baur (1972)]. The N···N intramolecular contact in QCA is longer than that found in *S*-methyldithizone (Preuss & Gieren, 1975) but shorter than the corresponding values in *β*- and *δ*-pyrazinecarboxamides (Rø & Sørum, 1972*a*,*b*) and 3,6-di-2-pyridyl-1,4-dihydro-1,2,4,5-tetrazine (Caira, Giles, Nassimbeni, Sheldrick & Hazell, 1976) where similar five-membered-ring hydrogen bridges can be postulated.

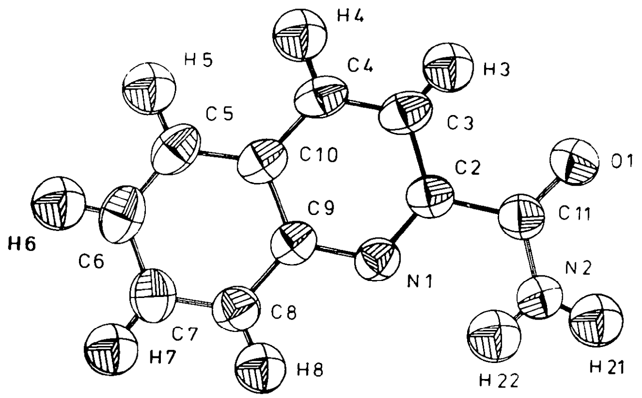

Fig. 1. *ORTEP* drawing and atom numbering of QCA.

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

N(1)–C(2)	1·321 (3)	C(11)–O(1)	1·233 (3)
C(2)–C(3)	1·417 (3)	C(11)–N(2)	1·329 (3)
C(3)–C(4)	1·372 (4)	C(11)–C(2)	1·499 (4)
C(4)–C(10)	1·411 (4)	C(3)–H(3)	1·01
C(5)–C(10)	1·413 (4)	C(4)–H(4)	1·07
C(5)–C(6)	1·360 (4)	C(5)–H(5)	1·11
C(6)–C(7)	1·414 (4)	C(6)–H(6)	1·05
C(7)–C(8)	1·371 (4)	C(7)–H(7)	1·11
C(8)–C(9)	1·409 (4)	C(8)–H(8)	1·05
C(9)–C(10)	1·422 (3)	N(2)–H(21)	0·98
C(9)–N(1)	1·370 (3)	N(2)–H(22)	0·97
C(9)–N(1)–C(2)	118·1 (2)	O(1)–C(11)–N(2)	123·8 (2)
N(1)–C(2)–C(11)	116·5 (2)	C(2)–C(11)–N(2)	115·5 (2)
N(1)–C(2)–C(3)	124·4 (2)	H(22)–N(2)–H(21)	116
C(11)–C(2)–C(3)	119·1 (2)	H(22)–N(2)–C(11)	116
C(2)–C(3)–C(4)	117·4 (2)	H(21)–N(2)–C(11)	126
C(3)–C(4)–C(10)	120·8 (2)	C(2)–C(3)–H(3)	121
C(4)–C(10)–C(9)	117·3 (2)	H(3)–C(3)–C(4)	121
C(4)–C(10)–C(5)	124·1 (2)	C(3)–C(4)–H(4)	120
C(9)–C(10)–C(5)	118·7 (2)	H(4)–C(4)–C(10)	119
C(10)–C(5)–C(6)	121·0 (3)	C(10)–C(5)–H(5)	117
C(5)–C(6)–C(7)	120·5 (3)	H(5)–C(5)–C(6)	122
C(6)–C(7)–C(8)	120·0 (3)	C(5)–C(6)–H(6)	119
C(7)–C(8)–C(9)	120·6 (2)	H(6)–C(6)–C(7)	121
C(8)–C(9)–N(1)	118·7 (2)	C(6)–C(7)–H(7)	123
C(8)–C(9)–C(10)	119·3 (2)	H(7)–C(7)–C(8)	117
N(1)–C(9)–C(10)	122·0 (2)	C(7)–C(8)–H(8)	121
O(1)–C(11)–C(2)	120·7 (2)	H(8)–C(8)–C(9)	118

Table 4. *Deviations of atoms from the least-squares plane through the quinoline ring*

X,Y,Z are expressed in Å relative to orthogonal axes parallel to a, b and c^*. Asterisks indicate atoms not included in the calculations of the least-squares plane.

$$0{\cdot}2868X - 0{\cdot}3914Y - 0{\cdot}8744Z + 2{\cdot}5572 = 0$$

N(1)	0·004 Å	C(11)*	0·008 Å
C(2)	−0·007	N(2)*	−0·007
C(3)	−0·014	O(1)*	0·046
C(4)	0·006	H(3)*	0·022
C(5)	0·011	H(4)*	0·024
C(6)	−0·014	H(5)*	0·124
C(7)	−0·015	H(6)*	0·061
C(8)	0·005	H(7)*	−0·030
C(9)	0·008	H(8)*	−0·001
C(10)	0·007	H(21)*	−0·068
		H(22)*	−0·097

The packing mode of the molecules and the hydrogen-bond scheme are shown in Fig. 2. The feature common to crystals of various compounds containing a carboxamide group is the formation of dimers across centres of symmetry. This is also observed in the present case. Two molecules are joined by a pair of N—H···O hydrogen bonds. The distances and angles involved in these bonds are summarized in Table 6. The separation of the mean planes of the hydrogen-bonded amide groups is 0·33 Å. This is the

Table 5. *The geometric features of the* N—H···N *intramolecular hydrogen bond in some molecules with a five-membered-ring hydrogen bridge*

	N···N	N···H	N—H	∠N—H···N
QCA	2·66 Å	2·24 Å	0·97 Å	105°
QCA hemihydrate, molecule *A*	2·64	2·18	0·90	111
QCA hemihydrate, molecule *B*	2·67	2·25	1·01	103
β-Pyrazinecarboxamide	2·73	2·39	0·81	106
δ-Pyrazinecarboxamide	2·73	2·26	0·86	114
S-Methyldithizone	2·62	2·21	0·91	107
3,6-Di-2-pyridyl-1,4-dihydro-1,2,4,5-tetrazine	2·74	2·27	0·99	108
	2·72	2·13	0·99	116

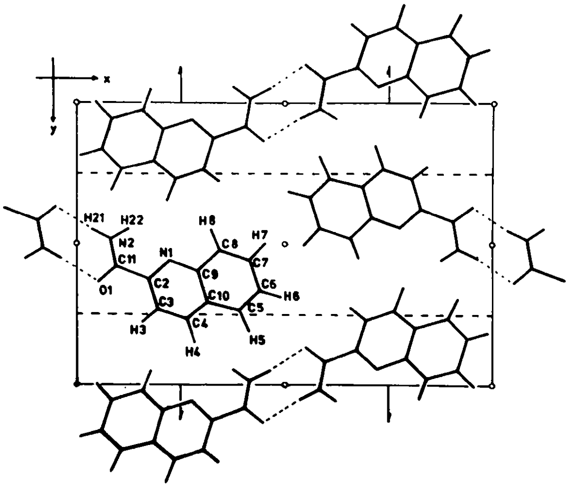

Fig. 2. Packing of the molecules viewed along the *c* axis.

Table 6. *Hydrogen-bond distances* (Å) *and angles* (°)

N(2)···O(1)	2·897 (3)	H(21)···O(1)	1·95
N(2)—H(21)···O(1)	162	C(11)—O(1)···H(21)	117

Table 7. *Intermolecular contacts less than* 3·5 Å

Symmetry code

(i)	$-x$,	$1-y$,	$-z$
(ii)	x,	y,	$1+z$
(iii)	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$1-z$

Molecules within a stack are related by symmetry operation ii.

N(2)—O(1^{i})	2·897 (3) Å	C(6)—C(5^{ii})	3·472 (4) Å
N(2)—O(1^{ii})	3·459 (3)	C(8)—C(9^{ii})	3·488 (4)
O(1)—C(11^{ii})	3·490 (3)	N(2)—C(5^{iii})	3·470 (4)
C(4)—C(10^{ii})	3·498 (4)		

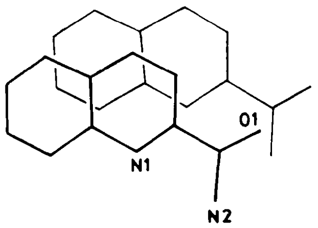

Fig. 3. Stacking pattern viewed perpendicular to the quinoline ring.

only intermolecular hydrogen bond in the crystal structure. In crystal structures of similar amides containing six-membered rings instead of a quinoline moiety, however, not only are the molecules hydrogen-bonded to form centrosymmetric dimers, but there also exist hydrogen bonds of another type interlinking adjacent dimers (Takano *et al.*, 1966; Rø & Sørum, 1972*a*; Blake & Small, 1972; Takaki, Sasada & Watanabé, 1960). It seems that it is the increase in size of the cyclic moiety of the molecule that precludes formation of hydrogen bonds between dimers. This is confirmed by the results obtained for 4-chloroquinoline-2-carboxamide (Gdaniec & Kosturkiewicz, 1975).

Table 7 lists intermolecular distances less than 3·5 Å. Almost all are between molecules stacked in columns parallel to the *c* axis. The distance between least-squares planes of two adjacent molecules within a stack is 3·44 Å. The stacking pattern, viewed perpendicular to the quinoline ring, is shown in Fig. 3.

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References

Baur, W. H. (1972). *Acta Cryst.* **B28**, 1456–1465.

Blake, C. C. F. & Small, R. W. H. (1972). *Acta Cryst.* **B28**, 2201–2206.

Caira, M. R., Giles, R. G. F., Nassimbeni, L. R., Sheldrick, G. M. & Hazell, R. G. (1976). *Acta Cryst.* **B32**, 1467–1469.

Dziembowska, T. & Szafran, M. (1974). *Rocz. Chem.* **48**, 1001–1012.

Gdaniec, M., Jaskólski, M. & Kosturkiewicz, Z. (1977). *Acta Cryst.* **B33**, 2284–2286.

GDANIEC, M. & KOSTURKIEWICZ, Z. (1975). *Rocz. Chem.* **49**, 2039–2046.
PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 260. New York: Cornell Univ. Press.
PREUSS, J. & GIEREN, A. (1975). *Acta Cryst.* B**31**, 1276–1282.
RØ, G. & SØRUM, H. (1972*a*). *Acta Cryst.* B**28**, 991–1002.
RØ, G. & SØRUM, H. (1972*b*). *Acta Cryst.* B**28**, 1677–1684.
TAKAKI, Y., SASADA, Y. & WATANABÉ, T. (1960). *Acta Cryst.* **13**, 693–702.
TAKANO, T., SASADA, Y. & KAKUDO, M. (1966). *Acta Cryst.* **21**, 514–522.

Acta Cryst. (1977). B**33**, 3561–3564

tert-Butyloxycarbonyl-L-cysteinyl-L-cysteine Disulfide Methyl Ester

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Abstract. $C_{12}H_{20}N_2O_5S_2$, orthorhombic, $P2_12_12_1$, $a = 17{\cdot}404$ (1), $b = 10{\cdot}565$ (2), $c = 9{\cdot}137$ (5) Å, $D_m = 1{\cdot}328$ (by flotation in CCl_4–*n*-hexane), $D_x = 1{\cdot}330$ g cm^{-3} for $Z = 4$. The title compound is a cyclo cystine compound. The structure was solved by direct methods and refined by the block-diagonal least-squares technique to a final R of 0·078 ($R_w = 0{\cdot}065$). The peptide group has a *cis* conformation. The torsion angle about the S–S bond is 95·7° and those about the two S–C bonds are −76·8 and −48·6°.

Introduction. Colorless, transparent, needle-shaped single crystals elongated along **c** were obtained by slow evaporation from a mixture of ethyl acetate and chloroform. A crystal with dimensions 0·2 × 0·3 × 0·5 mm was used for the X-ray analysis. The unit-cell dimensions were obtained by least-squares refinement of the settings of 13 reflections measured on a diffractometer. Intensity data were measured on an automatic Rigaku four-circle diffractometer, equipped with a rotating anode, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) and a monitor-counting technique. The θ–2θ scan mode with a scan rate of 16° min^{-1} in 2θ was employed. The θ scan range was calculated as $(1{\cdot}2 + 0{\cdot}35 \tan\theta)°$. Intensity data of 2314 independent reflections were collected with $(\sin\theta)/\lambda \le 0{\cdot}66$ Å^{-1}; of these, 200 were measured with $|F_o| = 0{\cdot}0$. No absorption correction was applied [μ(Mo $K\alpha$) = 3·32 cm^{-1}]. The structure was solved by direct methods, using the symbolic addition method for noncentrosymmetric crystals (Karle & Karle, 1966) and the weighted tangent-formula technique (Germain, Main & Woolfson, 1971). All nonhydrogen atoms were located from the E map based on the phases of 281 reflections with $|E| \ge 1{\cdot}2$. The parameters were refined by block-diagonal least-squares calculations with *HBLS*-5 (Ashida, 1973), first using isotropic temperature factors and then anisotropic. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. A difference map revealed the positions of all but two of the H atoms. The contributions of the H atoms to the structure factors were included in further refinement, but their parameters were not refined; their thermal parameters were assumed to be isotropic ($B = 3{\cdot}8$ Å^2). The final R is 0·078 for 2114 non-zero reflections and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ was 0·065 for all reflections. The weighting scheme finally adopted was $w = 0{\cdot}2$ for $|F_o| = 0{\cdot}0$ and $w = [\sigma^2(F_o) + 0{\cdot}001|F_o|^2]^{-1/2}$ for $|F_o| > 0{\cdot}0$. The atomic coordinates are given in Table 1.†

Discussion. Structures of various cystine compounds have been determined by X-ray or neutron diffraction methods to study the conformation of the disulfide bridge. The title compound is a cyclo cystine compound, which contains an eight-membered disulfide ring. Thus it is of interest to compare the conformation of this compound with those of other cystine compounds and/or proteins.

Bond lengths and angles in the molecule are listed in Table 2; they lie within the normal range found in other cystine compounds. In the crystal structure, as shown in Fig. 1, each molecule is linked by intermolecular hydrogen bonds [O(2)···H–N(1) 2·894 (5) Å] to

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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 32824 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.