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Structure of Ethyl 1-Cyano-1,2,3,4-tetrahydro-2-isoquinolinecarboxylate, $C_{13}H_{14}N_2O_2$

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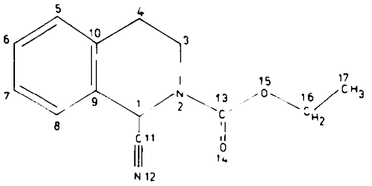
Abstract. $M_r = 230{\cdot}27$, triclinic, $P\bar{1}$, $a = 8{\cdot}868\,(1)$, $b = 10{\cdot}119\,(1)$, $c = 8{\cdot}2858\,(9)$ Å, $\alpha = 83{\cdot}624\,(8)$, $\beta = 119{\cdot}147\,(8)$, $\gamma = 111{\cdot}051\,(8)°$, $V = 604{\cdot}2\,(1)$ Å^3, $Z = 2$, $D_m = 1{\cdot}28$, $D_x = 1{\cdot}27$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}623$ mm^{-1}, $F(000) = 244$, room temperature, $R = 0{\cdot}053$ for 1361 observed reflexions. The hydrogenated heterocyclic ring has the conformation of a slightly deformed half-chair. The C(3)—N(2)—C(13)—O(14) torsion angle [−172·4 (4)°] characterizes the amide bond as *anti*. The NCOO group is exactly planar and makes an angle of 31·2 (4)° with the aromatic ring, minimizing steric interactions between the carbonyl group and neighboring H atoms.

Introduction. The present work is the second part of the investigation of a series of Reissert compounds. The structure investigation of the title compound has been undertaken to determine the effect of substituents on the molecular conformation and to facilitate interpretation of ^{13}C NMR data (Brózda, 1982).

Experimental. Elongated prismatic crystals from ethanol, D_m by flotation, crystal 0·3 × 0·3 × 0·2 mm, Syntex $P2_1$ diffractometer, cell parameters from least-squares treatment of setting angles of 15 reflections, profiles measured for 1717 reflexions with $2\theta \leq 115°$, range of *hkl*: h −9→7, k −10→11, l 0→9, profile analysis according to Lehmann & Larsen (1974), no significant intensity variation for two standard reflexions, no absorption correction, 1366 observed reflexions with $I \geq 1{\cdot}96\sigma(I)$; structure solved by direct methods using *SHELX*76 (Sheldrick, 1976), full-matrix least-squares refinement on F, $w^{-1} = \sigma^2(F)$, five extinction-affected reflexions excluded from final refinement, H atoms located in a ΔF map and included as fixed isotropic contributions to F_c, anisotropic thermal parameters for non-H atoms, $R = 0{\cdot}053$, $R_w = 0{\cdot}064$, $(\Delta/\sigma)_{\max} = 0{\cdot}05$, max. and min. height in final ΔF map 0·17 and −0·19 e Å^{-3}; computer programs: *SHELX*76 (Sheldrick, 1976) and local programs (Jaskólski, 1982), molecular illustrations drawn using *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates and bond lengths and angles are given in Table 1 and 2 respectively.† The labeling sequence is shown in the formula below.



The ethoxycarbonyl substituent is joined to the tetrahydroisoquinoline ring by a urethane bond. The cyano group is bonded to the C(1) asymmetric center. The N(2)—C(3) bond distance [1·463 (5) Å] agrees with the corresponding value characteristic of piperidine amides [1·464 (5) Å; Jaskólski, 1979], while

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† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39636 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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the N(2)—C(1) bond, adjacent to the —C≡N group, is somewhat shorter [1·452 (4) Å]. The C(9)—C(1)—N(2) and C(10)—C(4)—C(3) angles [both 112·3 (3)°] reflect the ring strain due to the neighboring sp^2 atoms.

A stereoview of the molecule is shown in Fig. 1, while Table 3 reports the torsion angles characterizing the molecular conformation. The heterocyclic ring has a half-chair conformation. The corresponding asymmetry parameter (Duax & Norton, 1975) $\Delta C_2^{2,3} = 5{\cdot}1°$. In our previous study of a similar molecule, 2-benzoyl-1,2,3,4-tetrahydro-1-isoquinolinecarbonitrile (Pływaczyk, Tykarska, Jaskólski & Kosturkiewicz, 1984) we reported the heterocyclic ring as having a sofa conformation. In both these structures the C=O group is disposed *anti* with respect to the C(3)—N(2) bond. The C(3)—N(2)—C(13)—O(14) torsion angle is −172·4 (4)°. This may be a consequence of steric hindrance between O(14) and the pseudo-equatorial H(C3) atom in the other possible rotational isomer. The ethoxycarbonyl group is nearly flat, while the NCOO group is exactly planar ($\chi^2 = 1{\cdot}4$). The sum of valency angles around N(2) is 359·1 (3)°. The twist angle τ around N(2)—C(13) equals 4·5 (4)°. The angle between the NCOO plane and the aromatic ring is 31·2 (4)°.

The molecular packing is shown in Fig. 2.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å²)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
C(1)	0·6769 (4)	0·1630 (3)	0·3682 (4)	0·060 (1)
N(2)	0·5717 (3)	0·2573 (2)	0·3068 (3)	0·0661 (9)
C(3)	0·6327 (4)	0·3770 (3)	0·2099 (5)	0·071 (1)
C(4)	0·6095 (4)	0·3227 (3)	0·0341 (4)	0·073 (1)
C(5)	0·7248 (4)	0·1687 (3)	−0·0634 (4)	0·069 (1)
C(6)	0·7916 (5)	0·0609 (4)	−0·0363 (5)	0·074 (1)
C(7)	0·8197 (4)	−0·0148 (3)	0·1160 (5)	0·070 (1)
C(8)	0·7810 (4)	0·0190 (3)	0·2460 (4)	0·063 (1)
C(9)	0·7146 (4)	0·1286 (3)	0·2212 (4)	0·052 (1)
C(10)	0·6850 (4)	0·2052 (3)	0·0653 (4)	0·058 (1)
C(11)	0·8552 (5)	0·2291 (3)	0·5388 (5)	0·072 (1)
N(12)	0·9933 (5)	0·2827 (3)	0·6651 (4)	0·087 (1)
C(13)	0·4492 (4)	0·2409 (3)	0·3675 (4)	0·054 (1)
O(14)	0·4151 (3)	0·1482 (2)	0·4629 (3)	0·0716 (8)
O(15)	0·3700 (3)	0·3396 (2)	0·3069 (3)	0·0672 (8)
C(16)	0·2378 (4)	0·3310 (3)	0·3674 (5)	0·079 (1)
C(17)	0·1696 (5)	0·4477 (4)	0·2882 (6)	0·092 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *and their standard deviations*

C(1)—N(2)	1·452 (4)	C(9)—C(10)	1·391 (5)
N(2)—C(3)	1·463 (5)	C(9)—C(1)	1·513 (5)
C(3)—C(4)	1·507 (6)	C(1)—C(11)	1·489 (5)
C(4)—C(10)	1·504 (5)	C(11)—N(12)	1·136 (5)
C(5)—C(10)	1·395 (5)	N(2)—C(13)	1·358 (4)
C(5)—C(6)	1·368 (5)	C(13)—O(14)	1·209 (4)
C(6)—C(7)	1·363 (6)	C(13)—O(15)	1·338 (4)
C(7)—C(8)	1·385 (6)	O(15)—C(16)	1·457 (5)
C(8)—C(9)	1·386 (4)	C(16)—C(17)	1·465 (5)
C(1)—N(2)—C(3)	114·9 (2)	C(5)—C(10)—C(9)	118·1 (3)
N(2)—C(3)—C(4)	109·8 (3)	C(4)—C(10)—C(5)	120·8 (3)
C(3)—C(4)—C(10)	112·3 (3)	C(9)—C(1)—C(11)	109·3 (3)
C(4)—C(10)—C(9)	121·2 (3)	N(2)—C(1)—C(11)	109·7 (3)
N(2)—C(1)—C(9)	112·3 (3)	C(1)—C(11)—N(12)	177·6 (4)
C(1)—C(9)—C(10)	121·2 (3)	O(1)—N(2)—C(13)	118·4 (2)
C(5)—C(6)—C(7)	121·2 (3)	C(3)—N(2)—C(13)	125·8 (3)
C(6)—C(7)—C(8)	119·3 (3)	N(2)—C(13)—O(14)	124·2 (3)
C(7)—C(8)—C(9)	120·3 (3)	N(2)—C(13)—O(15)	111·4 (2)
C(8)—C(9)—C(10)	120·4 (3)	O(14)—C(13)—O(15)	124·4 (2)
C(1)—C(9)—C(8)	118·4 (3)	C(13)—O(15)—C(16)	115·2 (2)
C(6)—C(5)—C(10)	120·8 (3)	O(15)—C(16)—C(17)	106·4 (3)

Table 3. *Torsion angles* (°) *characterizing the molecular conformation*

C(9)—C(1)—N(2)—C(3)	−44·1 (3)	C(1)—N(2)—C(13)—O(14)	−3·7 (4)
C(1)—N(2)—C(3)—C(4)	62·8 (3)	C(1)—N(2)—C(13)—O(15)	176·9 (3)
N(2)—C(3)—C(4)—C(10)	−47·6 (4)	C(3)—N(2)—C(13)—O(14)	−172·4 (4)
C(3)—C(4)—C(10)—C(9)	19·3 (3)	C(3)—N(2)—C(13)—O(15)	8·2 (3)
C(4)—C(10)—C(9)—C(1)	−1·7 (3)	N(2)—C(13)—O(15)—C(16)	−179·3 (3)
C(10)—C(9)—C(1)—N(2)	13·0 (3)	O(14)—C(13)—O(15)—C(16)	1·3 (4)
C(11)—C(1)—N(2)—C(13)	92·3 (3)	C(13)—O(15)—C(16)—C(17)	179·5 (3)
C(9)—C(1)—N(2)—C(13)	145·9 (3)		

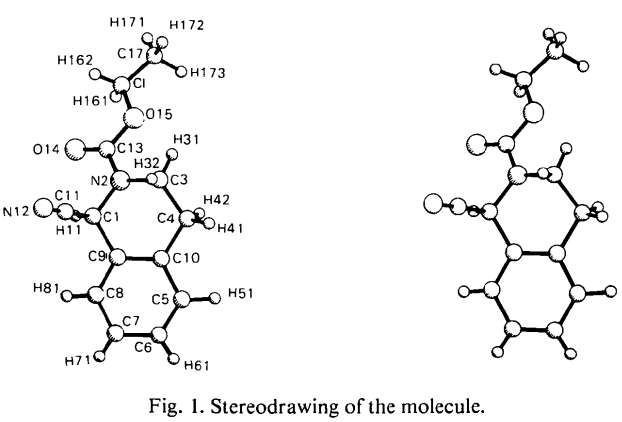

Fig. 1. Stereodrawing of the molecule.

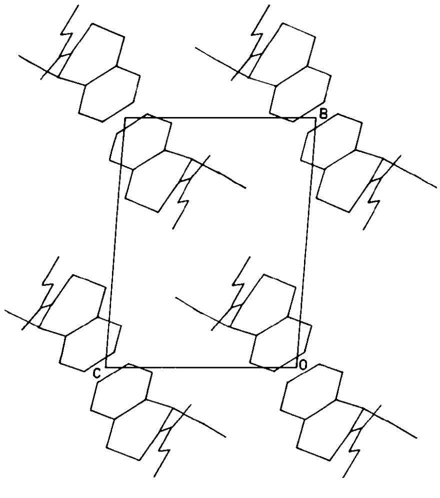

Fig. 2. Projection of the structure down **a**.

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The Structure of a Citric Anhydride Derivative, $C_8H_6O_7$*†

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Abstract. $M_r = 214\cdot13$, orthorhombic, $P2_12_12_1$, $a = 9\cdot495\ (2)$, $b = 16\cdot286\ (3)$, $c = 5\cdot841\ (1)$ Å, $V = 903\cdot2\ (3)$ Å^3, $Z = 4$, $D_x = 1\cdot575$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 11\cdot4$ cm^{-1}, $F(000) = 440$, $T = 293$ K, $R = 0\cdot036$ ($wR = 0\cdot053$) for 999 reflections. The structure is of interest because the compound is a derivative of citric anhydride and consists of two fused five-membered rings, one of which is an anhydride and the other a γ-lactone, with one carbon of the fusion bearing an acetoxy group. The molecule has bond lengths and angles comparable with those of other anhydrides. The packing is determined by interaction between carbonyl and ether oxygen atoms.

Introduction. Citric anhydride, derived from the α-hydroxycarboxylic acid citric acid, has been invoked in the reaction catalyzed by the enzyme citrate synthase so that the reversibility of the conversion of low-energy citrate into high-energy acetyl-CoA may be accounted for (Spector, 1972; Eggerer & Remberger, 1963; Eggerer, Remberger & Grünewälder, 1964; Wunderwald & Eggerer, 1969; Buckel & Eggerer, 1969; Buckel, 1976); however, detailed high-resolution X-ray crystallographic studies of citrate bound to the enzyme citrate synthase (Remington, Wiegand & Huber, 1982) suggest that there is not room in the active site for such an anhydride to be formed.

The existence of citric anhydride as a well-defined molecule has been reported by Repta (Repta, Robinson & Higuchi, 1966; Repta, 1969; Repta & Higuchi, 1969), who prepared solid citric anhydride. His preparation has been repeated, and the infrared spectrum of the solid was consistent with citric anhydride (Smart, 1984) but we have not been able to obtain crystals of the product (only very small amounts of crystalline anhydrous citric acid when the crystallization medium is not sufficiently dry). A report that citric acid exists in aqueous solution in equilibrium with its anhydride is really an extrapolation from the existence of anhydrides of acids such as succinic acid (Higuchi, Miki, Shah & Herd, 1963; Higuchi, McRae & Shah, 1966; Higuchi, Eberson & McRae, 1967) and no firm evidence for the existence of citric anhydride in aqueous solutions is available.

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† (2*S*,3*S*)-Tetrahydro-3-acetoxy-5-oxo-2,3-furandicarboxylic anhydride.

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