system used here is shown in Fig. 1. The benzene ring, ethylene, carboxy and methoxy groups are planar. Dihedral angles are 2·2 (3)° between benzene ring and carboxy planes, 3·4 (3)° between benzene ring and ethylene planes, and 4·8 (3)° between benzene ring and methoxy planes. However, the dihedral angle between benzene and acetoxy planes is 77·7 (3)°.

Fig. 2 shows the molecular packing. A pair of acid molecules are associated through their carboxy groups by hydrogen bonds with distances of 1·80 Å in O(1)···H and 0·84 Å in O(2)−H. The reactive olefinic double bonds are inversion-related and stacked parallel and the centre-to-centre separation of such parallel bonds is 3·77 Å. The title compound therefore, has the α-structure and gives anti head–tail cyclobutane dimers on photoreaction as reported by Schmidt (1964). This indicates that the cyclobutane dimer obtained by the

mechanochemical reaction of 3,4-dimethoxycinnamyl alcohol has an anti head–tail structure.

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1-Phenyl-3-carbethoxy-4-hydroxypyrroline

BY E. F. PAULUS AND E. RIVO*

Hoechst AG, D-6230 Frankfurt 80, Federal Republic of Germany

Abstract. Ethyl 4-hydroxy-1-phenyl-2,5-dihydro-pyrrole-3-carboxylate, $C_{13}H_{15}NO_3$, $M_r = 233·27$, monoclinic, $C2/c$, $a = 23·000$ (8), $b = 4·993$ (4), $c = 21·14$ (1) Å, $\beta = 93·61$ (5)°, $V = 2422·4$ Å^3, $Z = 8$, $F(000) = 992$, $D_m = 1·27$ (flotation in aqueous K_2HgI_4 solution), $D_x = 1·279$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu = 0·084$ mm^{-1}, $T = 295$ K, $R = 0·087$, $wR = 0·048$ for 2314 unique diffractometer data $[F^2 > 1\sigma(F^2)]$. The five-membered ring has the enol form. The angle between the planes of the pyrroline and the phenyl ring is 2·5°, the angle between the carbethoxy (ethoxy-carbonyl) group and the pyrroline ring 33·7°. The pyrroline ring is planar; the deviation of the N atom is 0·020 (3) Å. There exists an intramolecular hydrogen bond between the hydroxyl and the carbonyl group. The same H atom is involved in an intermolecular bifurcated hydrogen bond (2·805 Å) to build a dimer. The intermolecular distance of the oxygens of the carbonyls is 2·838 Å. They are twice bonded by bifurcated hydrogen bonds.

Introduction. The Dieckmann condensation (see Scheme) may result in one of two different products. De

Mouilpied (1905) could not decide which of these two products is formed. IR and NMR spectroscopic investigations were unable definitely to prove which formula is correct, in terms of either the given keto or the enol tautomers (Southwick, Madhav & Fitzgerald, 1969; Bauer & Safir, 1971, 1972). Our own spectroscopic investigations were equally unsuccessful. We decided to perform an X-ray structure analysis.
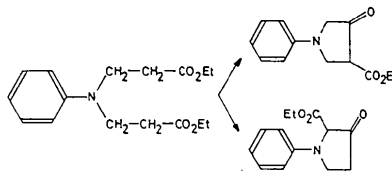
Experimental. Suitable crystals were obtained by recrystallization from a 2:1 mixture of ethanol and acetone. A crystal of dimensions 0·7 × 0·3 × 0·3 mm was sealed in a Lindemann-glass capillary; 25 reflections with $2\theta > 18°$ were used for the cell refinement; one standard reflection (512); 3829 measured reflections (h: −30 to 6; k: 0 to 6; l: −27 to 27; $R_{int} = 0·035$) resulted in 2314 of a total of 2949 unique reflections with an intensity $I > \sigma(I)$ which were used for the

* Present address: EGIS Pharmaceuticals, Budapest, Hungary.

Table 1. *The atomic coordinates and equivalent isotropic temperature coefficients*

The atomic coordinates are given in units of the lattice constants; the isotropic temperature coefficients (in $Å^2$) were calculated from the anisotropic ones after the last least-squares cycle. The e.s.d.'s are in parentheses.

$$U = (\text{trace } \tilde{U})/3.$$

	x	y	z	U_{eq}
C1	0·0368 (1)	0·6424 (5)	0·1497 (1)	0·068 (1)
C2	0·0344 (1)	0·4518 (5)	0·0963 (2)	0·063 (1)
C3	0·0816 (1)	0·4579 (5)	0·0636 (1)	0·058 (1)
C4	0·1241 (1)	0·6560 (5)	0·0929 (2)	0·063 (1)
C5	0·1167 (1)	0·9475 (5)	0·1873 (1)	0·062 (1)
C6	0·1716 (1)	1·0583 (5)	0·1800 (2)	0·069 (1)
C7	0·1943 (2)	1·2458 (5)	0·2221 (2)	0·077 (2)
C8	0·1639 (2)	1·3296 (5)	0·2724 (2)	0·084 (2)
C9	0·1102 (2)	1·2203 (5)	0·2805 (2)	0·086 (2)
C10	0·0867 (1)	1·0301 (5)	0·2390 (2)	0·074 (1)
C11	0·0892 (1)	0·2917 (4)	0·0095 (2)	0·068 (1)
C12	0·1501 (2)	0·1590 (7)	−0·0712 (2)	0·124 (2)
C13	0·2071 (2)	0·089 (1)	−0·0748 (2)	0·193 (4)
H1	−0·006 (1)	0·218 (6)	0·049 (1)	0·18 (1)
N1	0·0933 (1)	0·7642 (4)	0·1445 (1)	0·070 (1)
O1	−0·0138 (1)	0·3003 (4)	0·0873 (1)	0·080 (1)
O2	0·0522 (1)	0·1365 (3)	−0·0124 (1)	0·088 (1)
O3	0·1407 (1)	0·3202 (4)	−0·0149 (1)	0·086 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

The e.s.d.'s are given in parentheses. Symmetry transformation (i): −x, −y, −z.

C1−C2	1·474 (3)	C2−C1−N1	101·8 (2)
C1−N1	1·446 (2)	C1−C2−C3	113·1 (2)
C2−O1	1·345 (2)	C1−C2−O1	117·6 (2)
C2−C3	1·324 (3)	C3−C2−O1	129·3 (2)
C3−C4	1·499 (3)	C2−C3−C4	109·5 (2)
C3−C11	1·432 (3)	C2−C3−C11	123·4 (2)
C4−N1	1·442 (3)	C4−C3−C11	127·1 (2)
C5−N1	1·373 (3)	C3−C4−N1	102·7 (1)
C5−C6	1·396 (3)	C6−C5−C10	117·8 (2)
C5−C10	1·391 (3)	C6−C5−N1	120·7 (2)
C6−C7	1·371 (3)	C10−C5−N1	121·5 (2)
C7−C8	1·375 (4)	C5−C6−C7	120·6 (2)
C8−C9	1·370 (3)	C6−C7−C8	121·2 (2)
C9−C10	1·379 (3)	C7−C8−C9	118·8 (2)
C11−O2	1·220 (2)	C8−C9−C10	121·1 (2)
C11−O3	1·328 (2)	C5−C10−C9	120·6 (2)
C12−O3	1·465 (3)	C3−C11−O2	123·5 (2)
C12−C13	1·363 (4)	C3−C11−O3	113·8 (2)
H1−O1	0·94 (3)	O2−C11−O3	122·6 (2)
H1···O2	1·97 (3)	C13−C12−O3	112·2 (2)
H1···O2^i	2·18 (3)	C1−N1−C4	112·8 (2)
O1···O2	2·795 (3)	C1−N1−C5	123·1 (2)
O1···O2^i	2·805 (3)	C4−N1−C5	123·9 (2)
O2···O2^i	2·838 (3)	C2−O1−H1	100· (2)
		C11−O3−C12	115·9 (2)
		O1−H1···O2	146· (2)
		O1−H1···O2^i	123· (2)

structure analysis; Nicolet *R*3 computer-controlled diffractometer, $2\theta/\theta$ scan, $2\theta_{max} = 56°$; $3°$ min^{-1}; no correction for absorption or extinction. The phase problem was solved by direct methods quite easily: 32 phase sets were generated by systematic variation of the signs of five structure factors; the phase set with the best figures of merit (Sheldrick, 1983) resulted in a Fourier synthesis of the electron density (*E* map), which showed all the non-hydrogen atoms of the suggested

formula. The coordinates of the H atoms were found from a difference Fourier synthesis after a few cycles of least-squares refinement. The parameter refinement was performed by the cascade method (Sheldrick, 1983). Anisotropic temperature factors were refined for the non-hydrogen atoms, the H atoms were given isotropic temperature factors, which were also refined. The weighting scheme $w = 1/\sigma^2(F)$ was given by the counting statistics; 2314 unique reflections, 197 parameters, minimization of $\sum w(F_o - F_c)^2$, $R = 0·087$, $wR = 0·048$, $S = 2·47$; the ten largest peaks in a final difference electron density sysnthesis were between 0·16 and 0·33 e Å^{-3}; max. $\Delta/\sigma < 0·1$; all calculations and drawings were performed with a Nova 3/12 computer and *SHELXTL* (Sheldrick, 1983); scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic positions are given in Table 1 and bond lengths and angles in Table 2.*

Discussion. Fig. 1 shows that the Dieckmann condensation is accomplished in such a way that the product has the lowest steric hindrance. The molecule has the enol form. The two π systems of the molecule are separated from one other by methylene groups. The pyrroline ring is planar [the N is 0·020 (3) Å out of the plane] and coplanar with the phenyl ring [dihedral angle 2·5 (2)°]. The N atom is in optimal conjugation with the phenyl ring and is 0·036 (3) Å out of the plane of its ligands. The dihedral angle of the carboxyl group with the pyrroline ring is 1·8 (2)°. The reason for this coplanarity is not only the conjugation with the carbon−carbon double bond, but also the intramolecular hydrogen bond O1···O2 [2·795 (4) Å]. Only the ethoxy group lies out of the plane of the molecule; its

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* Lists of structure factors, anisotropic temperature factors, H-atom coordinates and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44827 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
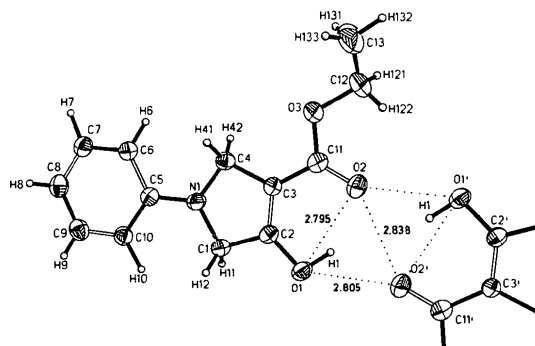

Fig. 1. Molecular structure, showing 30% probability thermal ellipsoids, the atom-numbering scheme and part of another molecule, connected by hydrogen bonding. Symmetry transformation (i): −x, −y, −z. The hydrogen-bond lengths are in Å.
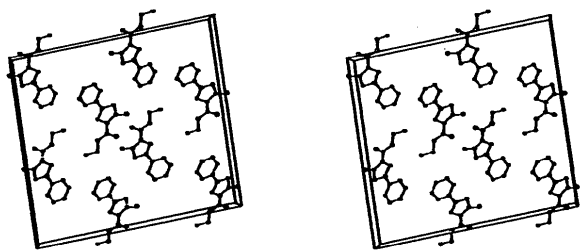
$C_{13}H_{15}NO_3$

Fig. 2. Stereoscopic projection of the crystal structure along the b axis.

dihedral angle with the pyrroline ring is 33·7 (2)°. Fig. 2 shows the crystal structure. There are dimers on centres of symmetry and these dimers build columns, which in turn form sheets of molecules parallel to (100). The distance separating two parallel dimers in the column is 3·480 (4) Å. The intermolecular hydrogen bonds in the dimer are bifurcated ones [2·805 (4) Å]. The distance O2···O2' is also relatively short [2·838 (4) Å; sum of the van der Waals radii: 2·80 Å].

These two atoms are twice bonded by bifurcated hydrogen bonds.

One may conclude that the enol form is also found in solution, because we have an intramolecular hydrogen bond between the hydroxyl and the carbonyl groups, which will stabilize the tautomer found in solution also.

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A Neutron Diffraction Study of Deuterated Semicarbazide Hydrochloride

BY B. K. ROUL AND R. N. P. CHOUDHARY

Department of Physics, Indian Institute of Technology, Kharagpur 721 302, India

AND H. RAJAGOPAL AND A. SEQUEIRA

Neutron Physics Division, Bhaba Atomic Research Centre, Trombay, Bombay 400 085, India

Abstract. $CD_6N_3O^+.Cl^-$, $M_r = 117·5$, orthorhombic, $P2_12_12_1$, $a = 7·55$ (1), $b = 13·21$ (2), $c = 4·68$ (1) Å, $V = 466·8$ Å^3, $Z = 4$, $D_x = 1·699$ g cm^{-3}, $\lambda = 1·036$ Å, $\mu_c = 0·45$ cm^{-1}, $T = 298$ K, final $R = 0·033$ (on F) for 321 independent reflections. The unit-cell volume of deuterated semicarbazide hydrochloride (SEM-DCl) is 466·8 Å^3 compared with 463·5 Å^3 for semicarbazide hydrochloride (SEM-HCl). The crystal structure is stabilized by a three-dimensional network of N–D···Cl and N–D···O bonds. The present analysis, together with electrical, optical and spectroscopic studies, does not show a ferroelectric phase transition in SEM-DCl and SEM-HCl crystals.

Introduction. Semicarbazide hydrochloride, CH_6N_3-$O^+.Cl^-$ (SEM-HCl), containing protonated semicarbazide cations and chloride anions, is reported to undergo two unusually close second-order ferroelectric phase transitions at 292 and 294 K (Rocaries & Boldrini, 1971). The structure of SEM-HCl has been solved (Nardelli, Fava & Geraldi, 1965) at 294 K, but the H atoms were derived geometrically. No change in crystal symmetry was observed in their X-ray photographic studies at 273 and 294 K. However, the above transitions were supported by marked room-temperature X-ray diffuse scattering. Since the accurate crystal structure and the existence and explanation of the above phase transitions were not clear, we have carried out a thorough study of the structure (Roul, Choudhary, Rajagopal & Sequeira, 1987) and of the optical, spectroscopic and electrical properties (Roul, Choudhary & Rao, 1987) of SEM-HCl. The isotope effect has a major effect on transition temperature (T_c), structural parameters and other properties of some hydrogen-bonded ferroelectrics. We have now carried out these studies on the deuterated species SEM-DCl to gain a better understanding of these phenomena.

Experimental. SEM-DCl crystals were grown by slow evaporation of a supersaturated solution of SEM-HCl

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