

Nachbarschichten nach Art einer hexagonal dichtesten Kugelpackung jeweils auf Lücke liegen. Daher gibt es in **b**-Richtung kaum Überlappungen der parallelen Molekülteile, so dass eine π -Wechselwirkung bzw. eine Ladungsübertragung (CT-Wechselwirkung) nicht gegeben ist. Nur der Stickstoff der Cyanogruppen schiebt sich jeweils zwischen zwei heterocyclische Ringe. Die kürzesten zwischenmolekularen Kontakt-abstände sind $N(3)\cdots H(4')$ ($x + 0,5, \bar{y}, z + 0,5$) und $O\cdots H(5')$ ($x + 0,5, y, \bar{z} + 0,5$) = 2,42 Å. Alle übrigen zwischenmolekularen Atomabstände liegen in der Nähe der Summe der van-der-Waals-Radien oder sind grösser als diese.

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A Reinvestigation of the Structure of Formic Acid (at 98 K)*

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Abstract. HCOOH, orthorhombic, space group $Pna2_1$, $a = 10.241$ (1), $b = 3.544$ (1), $c = 5.356$ (1) Å, $Z = 4$, $D_c = 1.573$ g cm⁻³. Three-dimensional single-crystal X-ray data were collected on a semi-automatic Stoe-Philips Weissenberg diffractometer modified for low-temperature work. The overall structure is the same as that previously reported [Holtzberg, Post & Fankuchen, *Acta Cryst.* (1953), **6**, 127–130]. The formic acid molecules are connected by hydrogen bonds (2.624 Å) to form infinite planar chains. The two C–O distances are significantly different: C=O 1.222 (2) and C–O(H) 1.308 (2) Å. The O=C–O(H) angle is 123.9 (0.2)°. The hydroxyl H is in the *cis* position with respect to the carbonyl O.

Introduction. Formic acid (*pro analysi*) was purified by fractional distillation and subsequently sealed in glass capillary tubes with a diameter of 0.25 mm and a wall thickness of 0.02 mm. The water content was less than 0.2%, as verified by NMR measurements. Single crystals were grown by zone melting at a temperature near their melting point (281.5 K).

In order to confirm and study the polymorphism of formic acid as postulated by several authors (Mikawa, Jakobsen & Brasch, 1966; Jakobsen, Mikawa & Brasch, 1967; Zelsmann, Bellon, Marechal & Bullemer, 1970) several crystals were subjected to a preliminary X-ray investigation above and below the proposed transition temperature (207–218 K). The only differences between two complete three-dimensional sets of Weissenberg film data collected at 278 and 98 K, respectively, could be ascribed to differences in thermal motion. A careful analysis of several rotation and zero-layer Weissenberg photographs taken at 278, 248, 223

* Hydrogen Bond Studies. CXXVII. Part CXXVI: Berglund & Tegenfeldt (1977).

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and 98 K using different crystals also failed to reveal any phase transition.

The intensities and unit-cell dimensions were measured at 98 K with a Stoe-Philips semi-automatic two-circle diffractometer (Cu $K\alpha$, Ni-filtered radiation, moving-crystal moving-detector scan technique) modified for low-temperature studies.

Two crystals grown along the c and b axes, respectively, were used to obtain the cell dimensions. The parameters were calculated from 2θ values of axial reflections and agreed satisfactorily with values previously determined from quartz-calibrated zero-layer oscillation Weissenberg photographs. The space group $Pna2_1$, previously assigned by Holtzberg, Post & Fankuchen (1953), was also confirmed.

A cylindrical crystal (diameter 0.25 mm, length 0.45 mm) grown along the c axis was used to record intensities from layers $0 \leq l \leq 5$. 519 reflections were measured. Three standard reflections were monitored periodically in each layer, and their intensities showed only minor statistical fluctuations.

After corrections for Lorentz, polarization and absorption effects had been made (transmission factors 0.658–0.736, $\mu = 14.5 \text{ cm}^{-1}$ for Cu $K\alpha$), the F_o^2 values for equivalent reflections were averaged together and an appropriately reduced $\sigma_c(F_o^2)$ was calculated based on Poisson counting statistics. 204 independent reflections remained, of which 202 were greater than $2\sigma_c(F_o^2)$ and were used in the refinements.

Atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms, and an overall scale factor were refined by full-matrix least-squares techniques with the program *UPALS* (Lundgren, 1974). The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$, where $w^{-1} = \sigma^2(F^2) = \sigma_c^2(F_o^2) + (0.012F_o^2)^2$. The two reflections with $F_o^2 < 2\sigma_c^2(F_o^2)$ were assigned zero weight. Trial atomic coordinates were those of Holtzberg, Post & Fankuchen (1953). A difference synthesis revealed the positions of the two H atoms. Coordinates and isotropic temperature factors for the H atoms were allowed to vary in a subsequent refinement. An isotropic extinction parameter g (Coppens & Hamilton, 1970) was also included in a final refinement: the final value of g was 1836 (355). The refinement converged at $R(F^2) = \sum ||F_o|^2 - |F_c|^2| / \sum |F_o|^2 = 0.049$ [equivalent to $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.027$]. The atomic scattering factors for

Table 1. *Non-hydrogen* ($\times 10^5$) *and hydrogen* ($\times 10^4$) *atom coordinates*

	x	y	z
C	15837 (13)	31087 (32)	16555 (45)
O(1)	8342 (8)	14230 (26)	226 (0)
O(2)	27660 (9)	34238 (23)	14304 (45)
H(1)	1331 (17)	535 (46)	-1137 (40)
H(2)	1109 (17)	4139 (45)	2955 (49)

Table 2. *Anisotropic thermal parameters* ($\times 10^4$)

The form of the anisotropic thermal factor is $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$. The r.m.s. components (R_i) ($\times 10^3 \text{ \AA}$) of thermal displacement of the atoms along the ellipsoid axes are included. Isotropic thermal parameters (B , \AA^2) are given for the H atoms.

	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
C	27 (1)	188 (11)	75 (7)	7 (2)	6 (2)	18 (5)	98	109	127
O(1)	27 (1)	314 (10)	109 (6)	-5 (1)	1 (2)	-39 (4)	116	120	149
O(2)	26 (1)	283 (9)	117 (7)	-2 (1)	4 (2)	-13 (5)	116	128	139
H(1)	1.13 (0.35)								
H(2)	0.72 (0.32)								

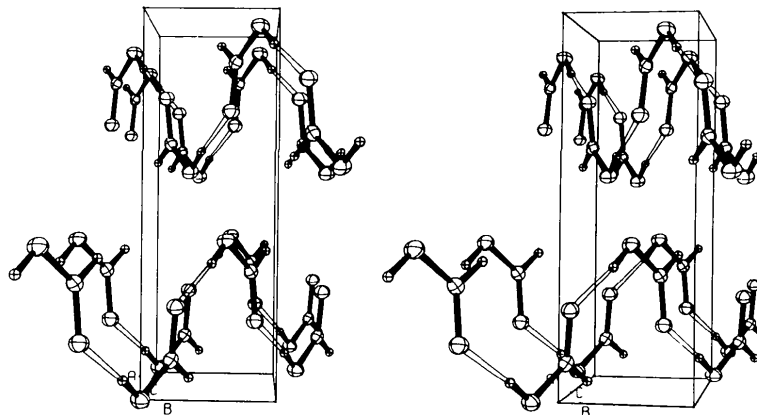


Fig. 1. A general stereoscopic view of the structure.

C and O were those suggested by Hanson, Herman, Lea & Skillman (1964). For H, the spherical scattering factors proposed by Stewart, Davidson & Simpson (1965) were used (positional and thermal). The final parameters are given in Tables 1 and 2.*

Discussion. The overall structure is as reported by Holtzberg, Post & Fankuchen (1953). As illustrated in Fig. 1, the formic acid molecules are hydrogen bonded together to form planar chains. The maximum deviation of the atoms from the least-squares plane is 0.1 Å. The hydrogen-bonded chains are tightly packed in layers parallel to (100). The directions of the chains in adjacent close-packed layers alternate between being parallel to [011] and [01 $\bar{1}$].

The angle between successive planes is 77.7°. A very similar packing situation is found for acetic acid (Nahringbauer, 1970a). The carbon-bonded H atom is not involved in any hydrogen bond and the interaction between the chains is apparently of a van der Waals type.

The aim of the present investigation has been primarily to arrive at a more accurately determined geometry for the formic acid molecule. According to Holtzberg *et al.* (1953), the C=O and C—O(H) distances are not significantly different ($\Delta = 0.03$ Å, $\sigma = 0.03$ Å). More recent studies of compounds containing formic acid (*e.g.* Nahringbauer & Larsson, 1968) have shown, however, that this difference is usually at least 0.1 Å.

Of particular interest is the suggestion (*e.g.* see Zelsmann *et al.*, 1970) that polymorphism occurs in formic acid. IR spectra and DTA measurements indicated a first-order phase transition with hysteresis between 207 and 218 K. The same authors proposed a coexistence of two polymorphic forms with the hydroxyl H *cis* or *trans* with respect to the carbonyl O (*cf.* Fig. 2, the β_1 and β_2 forms respectively). They also suggested that the X-ray observed positions were averaged values from an overlapping disorder situation, thus explaining the insignificant difference in the C—O distances observed by Holtzberg *et al.*

As seen from Fig. 3, the present work involves the *cis* modification (Fig. 2, β_1 form) which might even be the most stable form. According to theoretical calculations on the formic acid monomer, using INDO localized molecular orbitals (Gordon & Tallman, 1972; Köhler, 1972), as well as calculations made on the basis of experimental measurements of IR spectra (Miyazawa & Pitzer, 1959), the *cis* conformation for the hydroxyl H with respect to the carbonyl O is more stable than the *trans* by approximately 2 kcal mol⁻¹.

As stated earlier, Weissenberg photographic data collected at different temperatures using several crystals grown under different conditions showed no polymorphism. A coexistence of the *cis* and the *trans* forms seems unlikely since the rearrangement between the two forms involves not only the displacement of the protons within the hydrogen bonds but also a considerable rearrangement of the atoms as a whole.

The formic acid molecules are approximately planar. The H atoms deviate only 0.04 Å from the plane through C, O(1) and O(2). The angle between the planes through O(2), C, H(2) and C, O(1), H(1) is only 0.2°. The bond lengths and angles found for the

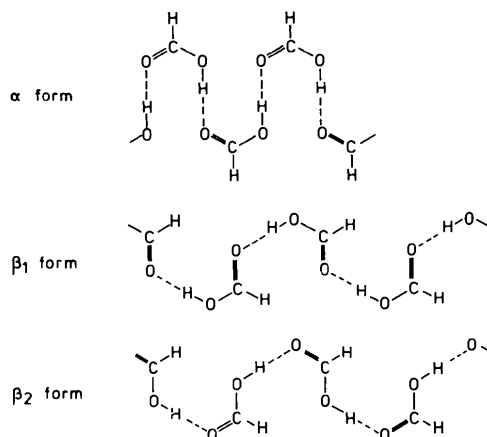


Fig. 2. Proposed polymorphic forms of crystalline formic acid.

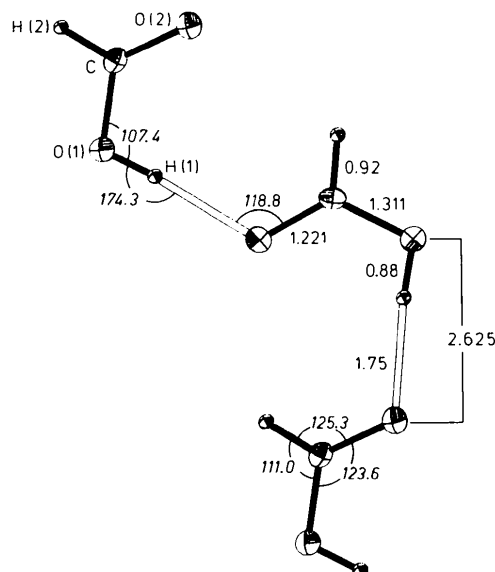


Fig. 3. Bond distances (Å) and angles (°) in the structure. The average standard deviations are: X—X 0.002 Å, X—H 0.02 Å; $\angle X-X-X$ 0.2°, $\angle X-X-H$ (or $\angle X-H-X$) 1.2°. Thermal ellipsoids for the non-hydrogen atoms are drawn to include 50% probability.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32958 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

molecule are given in Fig. 3. There are some notable differences between the values obtained here and those obtained previously. The C—O distances are now significantly different: C=O 1.222 (2) and C—O(H) 1.308 (2) Å, compared with 1.23 (3) and 1.26 (3) Å respectively (Holtzberg *et al.*, 1953). The new dimensions are also in closer agreement with those obtained for other carboxyl compounds (Nahringbauer, 1970*b*).

The length of the hydrogen bond is 2.624 (2) Å. The previously reported value of 2.58 (3) Å is shorter, but not significantly so. The present hydrogen-bond distance is similar to that found in acetic acid: 2.626 (6) and 2.625 (4) Å at 278 and 83 K respectively (Nahringbauer, 1970*a*). Replacement of CH₃ by only a slightly more electronegative H atom would not be expected to cause a significant change in the hydrogen bond, as seen from a comparison of the hydrogen-bond situations in ammonium acetate and ammonium formate (Nahringbauer, 1967, 1968).

In the case of acetic acid, the hydrogen bond is accepted in the *trans* position with respect to the hydroxyl group. The same is also true of the formic acid molecules in HCOOH.HCONH₂ (Nahringbauer & Larsson, 1968). A molecular-orbital treatment by EHT and CNDO/2 methods (Murthy, Davis & Rao, 1969) suggests that the β form is more stable than the α form. *Ab initio* LCAO—MO—SCF calculations of the conformation of protonated formic acid made by Hopkinson, Yates & Csizamadia (1970) also indicate that a similar arrangement of the two protons is the most stable.

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3-Methyl-8-azaguanine Hydrobromide Monohydrate

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Abstract. C₃H₇N₆OBr.H₂O, monoclinic, *P*2₁/*m*, *a* = 10.120 (6), *b* = 6.654 (4), *c* = 7.508 (4) Å, β = 109.91 (4)°, *U* = 475.4 Å³, *Z* = 2, *D_c* = 1.85, *D_m* = 1.82 g cm⁻³ (by flotation in CHBr₃/CCl₄), μ (Mo *K* α) =

42.6 cm⁻¹. The crystal has a layer structure with the cations, anions and water molecules all lying on crystallographic mirror planes perpendicular to the *b* axis, the distance between the layers being 3.327 Å.