

Hydrogen Bond Studies. CXIII.* The Crystal Structure of Ethanol at 87 K

BY PER-GUNNAR JÖNSSON

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

(Received 28 May 1975; accepted 3 June 1975)

C_2H_5OH , monoclinic, Pc , $a = 5.377$ (4), $b = 6.882$ (5), $c = 8.255$ (8) Å, $\beta = 102.2$ (1)°, $V = 298.6$ Å³ at 87 K, $Z = 4$, $D_x = 1.025$ g cm⁻³. Full-matrix least-squares refinement gave a final R value of 0.028 for 531 reflexions. The two crystallographically independent molecules are joined by H bonds [O...O distances 2.716 (3) and 2.730 (2) Å] to form infinite chains. The conformation about the C-C bond is staggered in both molecules, whereas the OH group is differently oriented so that one molecule has CCOH *gauche* and the other *trans*.

Introduction

Water-free ethanol was prepared according to Lund & Bjerrum (1931) and sealed in glass capillaries. Single crystals were very difficult to grow: ethanol supercools readily, and when crystallization starts the crystals grow quite fast but with a high degree of disorder. It was finally found that suitable single crystals could be grown at a temperature very close to the melting point (~156 K). Cell dimensions and intensities were measured with Ni-filtered Cu $K\alpha$ radiation on a paper-tape-controlled Stoe-Philips two-circle diffractometer modified for low-temperature work. a , b and c were obtained by a least-squares fit of 2θ values for 48 reflexions measured at 87 K using one crystal rotated about a and a second rotated about c . β was calculated from the setting angles for $h00$ and $00l$ reflexions by the method of level offsets (Buerger, 1942). Intensity data were collected at 87 K from a cylindrical crystal of radius 0.093 mm rotated about c . A moving-crystal moving detector technique as described by Jönsson (1972) was used in an equi-inclination geometry to record 551 independent reflexions (81% of the reflexions within the unique quadrant of the Cu $K\alpha$ sphere) for the layers $0 \leq l \leq 7$. Of these, 550 had $I > 3\sigma(I)$ where $\sigma(I)$ is based on counting statistics. Three standard reflexions monitored periodically during data collection decreased by 25% in intensity for which a correction was applied to all intensities.

Values of F^2 and $\sigma_{\text{count}}(F^2)$ were calculated by applying Lorentz, polarization and absorption corrections ($\mu = 661$ m⁻¹ for Cu $K\alpha$) to the values of I and $\sigma(I)$. The range of transmission factors was 0.87 to 0.90.

The systematic absences $h0l$ for l odd indicated the space groups Pc or $P2/c$. The former was assumed since the statistical averages and distribution of the normalized structure factor amplitudes suggested an acentric intensity distribution. With four ethanol molecules in the unit cell, Pc requires two independent

molecules in the asymmetric unit. The positions of the two O atoms and one methylene C atom were deduced from a Patterson map. A Fourier synthesis based on these atoms revealed the positions of the remaining C atoms. Full-matrix least-squares refinement on F with anisotropic thermal parameters for the non-hydrogen atoms resulted in an R value of 0.09. The 12 H atoms were revealed in subsequent difference maps based on reflexions with $(\sin \theta)/\lambda < 0.5$ Å⁻¹. In the final refinements an overall scale factor, positional parameters for all atoms, anisotropic thermal parameters for O and C atoms and isotropic thermal parameters for the H atoms were varied. The quantity minimized was $\sum w(F_o^2 - |F_c|^2)^2$ with the reflexions weighted according to the expression: $w = 1/\sigma^2(F^2)$, where $\sigma^2(F^2) = \sigma_{\text{count}}^2(F^2) + (0.05 F^2)^2$. Twenty reflexions in the upper layers with low detector angles were given zero weight. These reflexions were elongated in the ω scan and a simultaneous scan with the detector appears to truncate them. Later experience has shown that an ω scan mode is more satisfactory using a two-circle instrument. The final refinement converged with $R(F^2) = 0.051$ (0.076 for all reflexions) and $R_w(F^2) = 0.0727$. The corresponding $R(F)$ value was 0.028. The error in an observation of unit weight was 1.55. Atomic scattering factors for O and C were taken from Doyle & Turner (1968) and for H from Stewart, Davidson & Simpson (1965). Anomalous scattering correction was included for O and C atoms (Cromer & Liberman, 1970). A refinement of the structure with negative f'' values converged with $R(F^2) = 0.052$ (0.077), $R_w(F^2) = 0.0734$ indicating that the structural model used in the final refinement above should be preferred to the inverse model (the change of sign in f'' has the same effect as changing the sign of all the positional coordinates). The final atomic parameters are given in Table 1.† The

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31180 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* Part CXII: *Acta Univ. Ups.* (1975). In the press.

programs used in the calculations have been described by Lundgren (1975).

Discussion

The two independent ethanol molecules are illustrated in Fig. 1 together with the atoms of neighbouring molecules to which they are hydrogen bonded. The two molecules have different conformations: CCOH is *gauche* in molecule 1 and *trans* in molecule 2. The torsion angles at the C–O bond are $\tau[\text{C}(2)\text{--C}(1)\text{--O}(1)\text{--H}(1)] = -63(2)^\circ$ and $\tau[\text{C}(12)\text{--C}(11)\text{--O}(11)\text{--H}(11)] = 179(2)^\circ$. The conformation about the C–C bond is staggered in both molecules; none of the O–C–H

torsion angles deviates by more than 4σ from the value required for a perfectly staggered conformation.

It has been shown from microwave spectra that ethanol in the gas phase contains both the *trans* and the *gauche* conformers (Michielsen-Effinger, 1969; Sasada, Takano & Satoh, 1971). *Ab initio* calculations by Radom, Hehre & Pople (1971) have shown that the *trans* form is the most stable of the rotational isomers. The energy difference between the *gauche* and the *trans* conformer was calculated to be 2.8 kJ mol^{-1} . An experimental determination by Kolbe (1972) from measurements of the splitting of the free OH-stretching vibration in carbon tetrachloride solution gave an energy difference of 6.3 kJ mol^{-1} .

Table 1. Final fractional coordinates and thermal parameters

The parameter values for the non-hydrogen atoms are multiplied by 10^4 and the hydrogen atom coordinates by 10^3 . The anisotropic thermal parameters are defined as $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0	1349 (2)	2500	218 (3)	105 (2)	43 (2)	-35 (2)	49 (2)	-9 (2)
C(1)	85 (3)	2987 (2)	1462 (3)	193 (5)	97 (3)	50 (3)	6 (3)	37 (3)	8 (2)
C(2)	2106 (4)	2771 (2)	448 (3)	235 (6)	124 (3)	57 (3)	-59 (3)	62 (3)	-2 (2)
O(11)	-1330 (2)	1785 (1)	5475 (2)	146 (3)	114 (2)	44 (3)	24 (2)	37 (2)	7 (1)
C(11)	-3959 (3)	2313 (2)	5217 (3)	132 (5)	102 (3)	46 (3)	11 (3)	11 (2)	0 (2)
C(12)	-4665 (4)	2534 (2)	6869 (3)	169 (5)	113 (3)	58 (4)	14 (3)	43 (3)	5 (2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
H(1)	-43 (5)	44 (4)	179 (4)	3.0 (5)	H(11)	-101 (5)	166 (4)	459 (4)	1.9 (5)
H(2)	20 (5)	404 (4)	217 (4)	2.6 (5)	H(12)	-502 (5)	143 (4)	447 (4)	3.0 (5)
H(3)	-164 (6)	315 (4)	63 (4)	3.6 (6)	H(13)	-428 (5)	342 (4)	447 (4)	3.0 (5)
H(4)	175 (4)	159 (3)	-39 (4)	2.2 (5)	H(14)	-370 (6)	356 (4)	746 (4)	3.4 (6)
H(5)	379 (6)	247 (4)	121 (4)	2.8 (5)	H(15)	-442 (5)	131 (4)	757 (4)	2.6 (5)
H(6)	235 (7)	390 (6)	-18 (5)	5.2 (8)	H(16)	-639 (6)	281 (4)	678 (4)	2.8 (5)

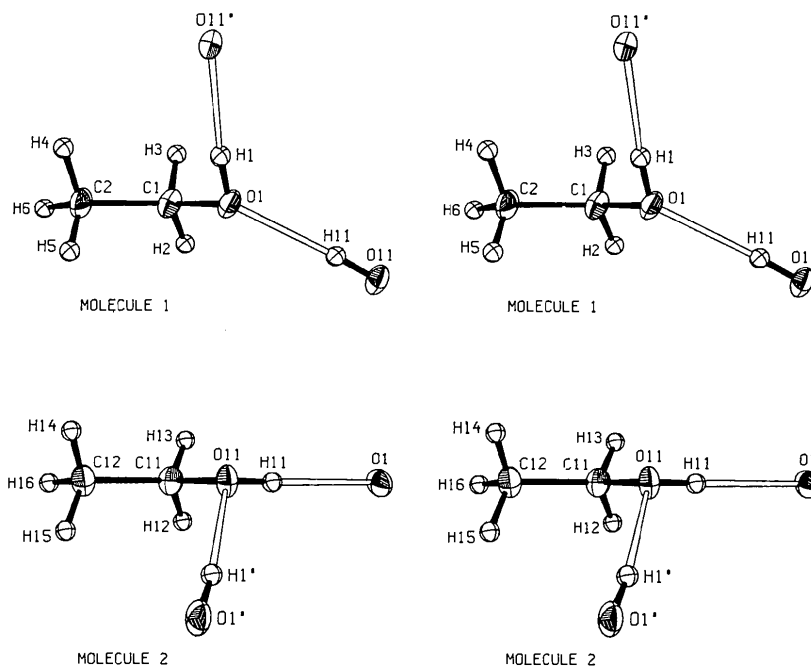


Fig. 1. Stereoscopic drawings of the two crystallographically independent ethanol molecules. Thermal ellipsoids for carbon and oxygen atoms are scaled to include 50% probability.

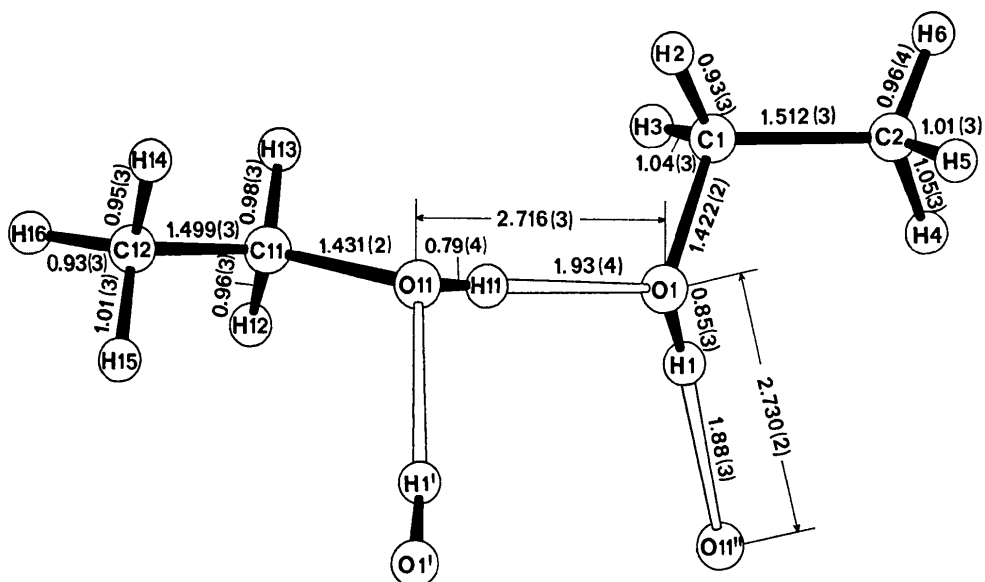


Fig. 2. Bond distances (Å).

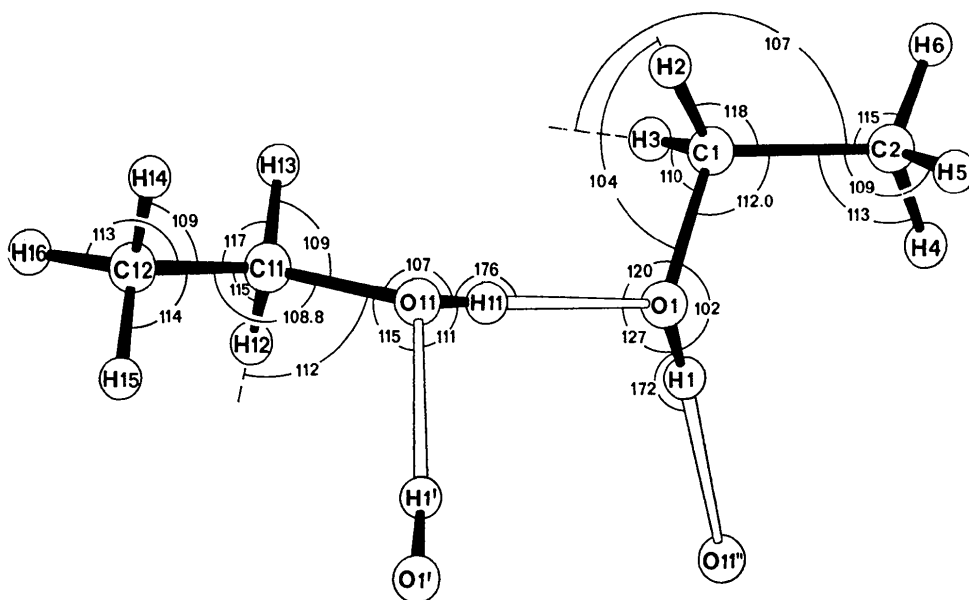


Fig. 3. Bond angles. The estimated standard deviations are 0.2° for the C-C-O angles and 1 to 3° for other angles.

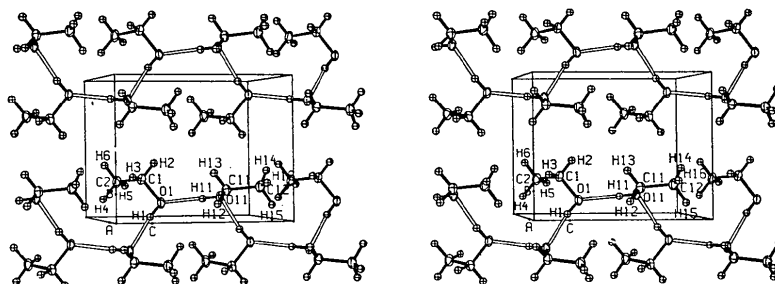


Fig. 4. Stereoscopic drawing of the crystal structure of ethanol. The atoms of the asymmetric unit are labelled.

The dimensions of the two molecules are similar (Figs. 2 and 3); the most significant difference occurs for the C–C–O angles. This angle is 3.1 (2)° larger for the *gauche* compared to the *trans* form. A similar difference of about 5° was observed in the molecular structure derived from the microwave spectrum of CH₃CHDOH by Sasada *et al.* (1971). This was attributed to the electronic repulsion between the hydroxyl hydrogen and the methylene hydrogens. Structural parameters determined by Sasada *et al.* for the *trans* form in the gas phase are C–C, 1.5297 (20); C–O, 1.4247 (25) Å and C–C–O angle, 107.33 (23)°. Large differences compared to the present results are found for all bond lengths involving hydrogen. It is well known that X–H bond lengths determined by least-squares procedures from X-ray data are appreciably contracted compared to those obtained by other techniques.

The geometry of the ethanol molecule in the solid state has previously been determined by Liminga (1967) in hydrazine bisethanol, N₂H₄·2C₂H₅OH. The torsion angle $\tau[C(2)-C(1)-O(1)-H(1)]$ is 88° in this compound. The C–C–O angle is 113.0 (2)° and the C–C and C–O bond lengths are 1.487 (4) and 1.424 (3) Å, respectively.

The hydrogen bonding and packing of the molecules is shown in Fig. 4. The ethanol molecules are joined by O–H...O hydrogen bonds of length 2.716 (3) and 2.730 (2) Å to form infinite zigzag chains. The orthorhombic high-temperature modification of solid methanol also contains infinite hydrogen-bonded chains of alcohol molecules (Tauer & Lipscomb, 1952). The O...O distance in this structure is 2.66 (3) Å, a hydrogen-bond length very similar to those occurring in the

present structure. With the exception of the hydrogen bonds, no intermolecular contacts exist which are significantly shorter than the expected van der Waals contacts. The shortest approach between methyl carbon atoms is 3.73 Å.

I would like to thank Professor Ivar Olovsson for the facilities placed at my disposal. I am also indebted to Hilding Karlsson for his highly skilled technical assistance.

References

- BUERGER, M. J. (1942). *X-ray Crystallography*, pp. 375–377. New York: John Wiley.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- JÖNSSON, P.-G. (1972). *Acta Chem. Scand.* **26**, 1599–1619.
- KOLBE, A. (1972). *Z. phys. Chem. Leipzig*, **250**, 183–194.
- LIMINGA, R. (1967). *Acta Chem. Scand.* **21**, 1206–1216.
- LUND, H. & BJERRUM, J. (1931). *Ber. dtsh. chem. Gesell.* **64B**, 210–213.
- LUNDGREN, J.-O. (1975). *Crystallographic Computer Programs*. Report UUIC-B13-04-02, Institute of Chemistry, Univ. of Uppsala.
- MICHELSEN-EFFINGER, J. (1969). *J. Mol. Spectrosc.* **29**, 489–491.
- RADOM, L., HEHRE, W. J. & POPLE, J. A. (1971). *J. Amer. Chem. Soc.* **93**, 289–300.
- SASADA, Y., TAKANO, M. & SATOH, T. (1971). *J. Mol. Spectrosc.* **38**, 33–42.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TAUER, K. J. & LIPSCOMB, W. N. (1952). *Acta Cryst.* **5**, 606–612.

Acta Cryst. (1976). **B32**, 235

Structure Cristalline du Nitrate de Calcium Trihydraté

PAR ANDRÉ LECLAIRE

Laboratoire de Cristallographie Minéralogie, Groupe de Cristallographie et Chimie du Solide,
U.E.R. des Sciences, Université, 14032 Caen, France*

(Reçu le 12 mai 1975, accepté le 23 mai 1975)

Crystals of calcium nitrate trihydrate are monoclinic, space group $P2_1/n$, with $a = 12.250(7)$, $b = 20.359(9)$, $c = 13.517(7)$ Å, $\beta = 114.89(8)^\circ$, $Z = 16$. The material was crystallized from a supersaturated aqueous solution. The crystal structure has been determined by direct methods from 2382 reflexions collected with a single-crystal diffractometer. The final R value is 0.040. The structure consists of layers of $[Ca(NO_3)_2 \cdot 3H_2O]_4$ units parallel to the ab plane, held together by hydrogen bonds. The Ca coordination is 9.

Introduction

En étudiant la cristallisation du nitrate de calcium à partir d'une solution aqueuse, Millon (1842) obtint un

composé auquel il attribua, après analyse, la composition $Ca(NO_3)_2 \cdot 3,5H_2O$. Gernez (1878) d'abord et Lescoeur (1890) ensuite, obtinrent le composé isolé par Millon et, en l'analysant avec beaucoup de soins, furent conduits à lui donner la formule $Ca(NO_3)_2 \cdot 3H_2O$. Plus tard, en étudiant le diagramme

* Equipe de Recherche Associée au CNRS n° 305.