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Acta Cryst. (1991). **C47**, 2400–2402

Structure and ³⁵Cl NQR of (±)-Methyl 4,4,4-Trichloro-3-hydroxybutyrate

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(Received 20 January 1991; accepted 15 May 1991)

Abstract. C₅H₇Cl₃O₃, *M_r* = 221.47, triclinic, *P* $\bar{1}$, *a* = 10.214 (3), *b* = 9.865 (3), *c* = 9.375 (3) Å, α = 93.21 (1), β = 98.76 (1), γ = 97.38 (1)°, *V* = 923.13 Å³, *Z* = 4, *D_m* = 1.57 Mg m⁻³, *D_x* = 1.593 Mg m⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.955 mm⁻¹, *F*(000) = 448, *T* = 296 K, final *R* = 0.041 for 2398 unique reflexions. The title compound crystallizes with two molecules [(I) and (II)] in the asymmetric unit; two molecules of (I) and two molecules of (II), respectively, are connected by hydrogen bonds to form pairs. The ³⁵Cl nuclear quadrupole resonance shows a six-line spectrum with two distinct triplets, differentiated by the temperature behavior of the ³⁵Cl frequencies, $\nu(^{35}\text{Cl}) = f(T)$, 77 ≤ *T* ≤ 330 K.

Introduction. CCl₃ groups have a tendency to undergo an order–disorder transition far below the melting point of the compound considered. This transition can be observed by ³⁵Cl nuclear quadrupole resonance, NQR, but no decision can be made concerning its nature. The freely rotating state has not been observed, either by NQR or by diffraction methods [for a recent discussion of the problem, see Basaran, Dou & Weiss (1991)].

Experimental. Colorless plates of the title compound (Aldrich) were obtained by slow evaporation from an ethanolic solution. *D_m* measured pycnometrically with water as liquid. [For the synthesis and the optical properties of the compound, see Ross (1936).] Crystal size 0.25 × 0.4 × 0.5 mm, Stoe Stadi-4 four-circle diffractometer, graphite(002)-monochromated Mo *K*α radiation, lattice parameters from setting 50 reflexions with 35.0 ≤ 2θ ≤ 38.6°, ω–2θ scan.

Lorentz–polarization corrections, empirical absorption correction, min., max. transmission factors 0.674, 0.765; (sinθ/λ)_{max} = 0.5384 Å⁻¹, –10 ≤ *h* ≤ 10, –10 ≤ *k* ≤ 10, –10 ≤ *l* ≤ 1. Three standard reflexions (222, $\bar{2}\bar{1}3$, $\bar{2}11$) measured every 120 min to monitor the crystal showed about 30% decrease in intensity. 3130 reflexions measured, 2218 independent (unique) reflexions with *F* ≥ 2σ(*F*), *R*_{int} = 0.011. Structure solved by direct methods using *SHELXS86* (Sheldrick, 1986) refined by full-matrix least squares (on *F*) with minimization of $\sum w(|F_o| - |F_c|)^2$, *w* = 1/σ²(*F_o*) (*SHELX76*; Sheldrick, 1976). All H atoms except those from the methyl group of molecule (II) and H(O¹), H(C¹) of molecule (I) were assigned from difference Fourier maps and refined with fixed isotropic temperature factors. 233 free parameters, final *R* = 0.041, *wR* = 0.037 for 2218 reflexions with *F* ≥ 2σ(*F*), (Δ/σ)_{max} = 0.016, (Δ/σ)_{mean} = 0.004, (Δρ)_{max} = +0.32, (Δρ)_{min} = –0.26 e Å⁻³ in the final difference Fourier synthesis. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1* contains the atomic coordinates and the equivalent isotropic thermal parameters *U*_{eq}. Bond lengths and bond angles are given in Table 2.

³⁵Cl NQR spectra were registered with a super-regenerative oscillator-type spectrometer; 2 cm³ sample of polycrystalline material of the title compound. At a few temperatures the ³⁷Cl NQR spec-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54266 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and equivalent isotropic thermal parameters for the non-H atoms ($\text{\AA}^2 \times 10^3$) with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cl(1 ^l)	0.7275 (1)	0.4536 (1)	0.0876 (1)	79 (1)
Cl(2 ^l)	0.8479 (1)	0.4882 (1)	0.3844 (1)	83 (1)
Cl(3 ^l)	0.7294 (1)	0.2206 (1)	0.2574 (1)	97 (1)
O(1 ^l)	0.5686 (2)	0.5599 (3)	0.3157 (3)	66 (2)
O(2 ^l)	0.3267 (2)	0.3576 (2)	0.3921 (3)	73 (2)
O(3 ^l)	0.2278 (2)	0.3271 (2)	0.1623 (3)	71 (2)
C(1 ^l)	0.3341 (3)	0.3470 (3)	0.2658 (4)	54 (2)
C(2 ^l)	0.4601 (3)	0.3483 (4)	0.2032 (4)	57 (2)
C(3 ^l)	0.5801 (3)	0.4202 (3)	0.3078 (3)	50 (2)
C(4 ^l)	0.7135 (3)	0.3969 (3)	0.2605 (3)	57 (2)
C(5 ^l)	0.0997 (5)	0.3119 (6)	0.2078 (5)	95 (3)
Cl(1 ^{ll})	0.8656 (1)	0.0694 (1)	0.8962 (1)	95 (1)
Cl(2 ^{ll})	0.8876 (1)	0.0620 (1)	0.5955 (1)	97 (1)
Cl(3 ^{ll})	0.8484 (1)	0.3110 (1)	0.7442 (1)	116 (1)
O(1 ^{ll})	0.6209 (3)	-0.0491 (2)	0.6693 (3)	69 (2)
O(2 ^{ll})	0.3807 (2)	0.1221 (2)	0.6237 (3)	73 (2)
O(3 ^{ll})	0.3658 (2)	0.1490 (2)	0.8575 (2)	68 (2)
C(1 ^{ll})	0.4324 (3)	0.1359 (3)	0.7478 (4)	55 (2)
C(2 ^{ll})	0.5795 (4)	0.1449 (4)	0.8018 (4)	61 (3)
C(3 ^{ll})	0.6539 (3)	0.0935 (3)	0.6862 (3)	51 (2)
C(4 ^{ll})	0.8062 (3)	0.1321 (3)	0.7293 (4)	63 (2)
C(5 ^{ll})	0.2243 (3)	0.1534 (4)	0.8180 (4)	77 (3)
H(O1 ^l)†	0.6006 (31)	0.5916 (33)	0.3896 (34)	
H(O1 ^{ll})†	0.6271 (31)	-0.0826 (32)	0.5908 (33)	

† H atoms were given fixed isotropic temperature factors of 0.06 \AA^2 .

Table 2. Intramolecular and intermolecular distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

The intermolecular distances given are the sum of van der Waals radii (O 1.4, Cl 1.8, CH₃ 2.0, H 1.2 \AA).

	(I)	(II)
Cl(1)—C(4)	1.764 (3)	1.765 (3)
Cl(2)—C(4)	1.768 (3)	1.764 (3)
Cl(3)—C(4)	1.766 (3)	1.755 (3)
C(4)—C(3)	1.536 (4)	1.539 (4)
C(3)—C(2)	1.516 (4)	1.514 (4)
C(3)—O(1)	1.397 (4)	1.398 (4)
C(2)—C(1)	1.493 (5)	1.502 (4)
C(1)—O(2)	1.198 (4)	1.195 (4)
C(1)—O(3)	1.327 (4)	1.326 (4)
O(3)—C(5)	1.430 (5)	1.443 (3)
O(1)···O(2)	2.818 (3)	2.797 (3)
O(2)···H(O1)	2.077 (31)	2.014 (30)
Cl(2)···Cl(2)	3.480 (2)	3.421 (2)
Cl(1)···C(5)	4.232 (5)	3.707 (4)
Cl(2)···C(5)	3.808 (5)	3.715 (3)
Cl(3)···C(5)	3.878 (5)	4.299 (3)
Cl(1 ^l)···C(5 ^{ll})	3.879 (4)	
Cl(3 ^l)···C(5 ^{ll})	3.821 (4)	
Cl(1 ^{ll})···C(5 ^l)	3.907 (5)	
Cl(3 ^{ll})···C(5 ^l)	3.681 (5)	
Cl(1)—C(4)—Cl(12)	107.5 (2)	108.2 (2)
Cl(2)—C(4)—Cl(13)	108.7 (2)	108.7 (2)
Cl(3)—C(4)—Cl(1)	108.7 (2)	108.5 (2)
Cl(1)—C(4)—C(3)	112.3 (2)	111.8 (2)
Cl(2)—C(4)—C(3)	109.8 (2)	109.5 (2)
Cl(3)—C(4)—C(3)	109.8 (2)	110.0 (2)
O(1)—C(3)—C(4)	110.2 (3)	109.9 (3)
O(1)—C(3)—C(2)	107.2 (3)	107.0 (3)
C(4)—C(3)—C(2)	112.6 (3)	111.5 (3)
C(3)—C(2)—C(1)	111.6 (3)	111.8 (3)
C(2)—C(1)—O(2)	125.7 (3)	125.7 (3)
C(2)—C(1)—O(3)	111.0 (3)	110.6 (3)
O(3)—C(1)—O(2)	123.3 (3)	123.8 (3)
C(1)—O(3)—C(5)	116.8 (3)	115.5 (3)
O(1)—H(O1)···O(2)	168.5 (35)	164.5 (31)

trum of the compound was also investigated ($(\nu(^{35}\text{Cl})/\nu(^{37}\text{Cl}))_{\text{found}} = 1.269$). The spectra were measured with a lock-in technique, recorder and time constant 10 s. The temperature at the probe was

obtained by liquid nitrogen, a nitrogen gas-flow thermostat and by a methanol cryostat, respectively. The temperature was measured to ± 0.5 K, the ^{35}Cl NQR frequencies given are accurate to ± 5 kHz, the error being due to the line width. In Table 3 the results of the ^{35}Cl NQR measurements are given for two temperatures (77 and 300.3 K). The frequencies $\nu(^{35}\text{Cl}) = f(T)$ are parameterized according to $\nu(^{35}\text{Cl}) = \sum_i^2 -_1 a_i T^i$ and the coefficients are included in Table 3 as are the bleaching-out temperatures.

Discussion. In Fig. 1, a projection of the unit cell onto the *ab* plane is given along with the numbering scheme of molecule (I). Hydrogen bonds connect molecules of (I) [O(1^l)—H(O1^l)···O(2^l)] as pairs as well as molecules of (II) [O(1^{ll})—H(O1^{ll})···O(2^{ll})]. The $d[\text{O}(1^{\text{l}})\cdots\text{O}(2^{\text{l}})]$ distance 2.818 \AA is somewhat longer than the $d[\text{O}(1^{\text{ll}})\cdots\text{O}(2^{\text{ll}})]$ distance 2.797 \AA . No influence of the hydrogen bond on the C(1)=O(2) bond is reflected in different C=O bond lengths. There are only minor differences in geometry between molecules (I) and (II). The mean C—Cl bond distances are 1.766 (3) and 1.761 (6) \AA for molecules (I) and (II), respectively. The van der Waals interactions within the hydrogen-bonded dimers seem to be stronger than the interaction between the dimers (I) and (II).

The results of the ^{35}Cl NQR experiments are presented graphically in Fig. 2. The six lines observed at room temperature confirm the structure. There are six independent positions for the Cl atoms within the unit cell and at each of these sites an individual

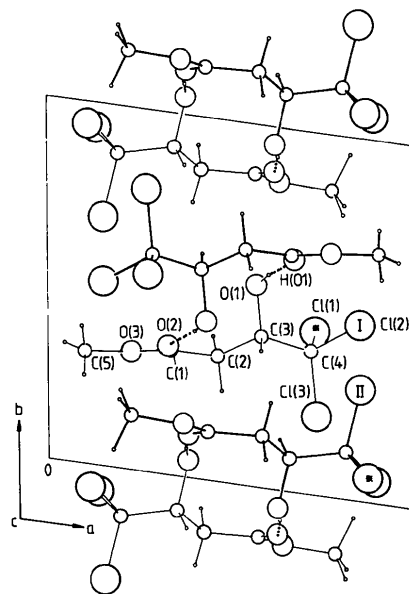


Fig. 1. Projection of the unit cell along [001] onto the *ab* plane. The positional parameters for molecules marked with an asterisk are given in Table 1.

Table 3. Power series expansion of $\nu = f(T)$

$f(T) = \sum_{i=-1}^z a_i T^i$; ν_b = bleaching out frequency; T_b = bleaching out temperature; the temperature range in which the least-squares adjustment is valid is for ν_1, ν_4, ν_5 : 77–310.4 K, for ν_2, ν_3, ν_6 : 77–330.1 K; z = number of data; σ = standard deviation.

Sign	$\nu(^{35}\text{Cl})^*$ (MHz)	T (K)	$\nu(^{35}\text{Cl})$ (MHz)	T (K)	$\nu_b(^{35}\text{Cl})^\dagger$ (MHz)	T_b (K)	z	σ (kHz)	a_{-1} (MHz K)	a_0 (MHz)	$a_1 \times 10^{-3}$ (MHz K ⁻¹)	$a_2 \times 10^{-6}$ (MHz K ⁻²)
ν_1	38.786	(77)	37.681	(300.3)	37.623	(310.4)	10	3.6	-1.394	39.076	-3.170	-4.848
ν_2	38.626	(77)	37.745	(300.3)	—	—	12	2.2	4.246	38.718	-1.415	-6.259
ν_3	38.285	(77)	37.247	(300.3)	—	—	12	2.8	2.484	38.522	-3.199	-3.605
ν_4	38.196	(77)	36.532	(300.3)	36.440	(310.4)	13	3.2	-20.442	39.053	-7.523	-2.168
ν_5	38.116	(77)	36.761	(300.3)	36.685	(310.4)	13	2.5	-13.600	38.749	-5.739	-2.448
ν_6	38.058	(77)	36.888	(300.3)	—	—	15	4.7	3.593	38.341	-4.030	-2.892

* The signal to noise ratio (lock-in technique, recorder and time constant 10 s) is 20 to 25.

† The signal to noise ratio is 2–3 near the bleaching out temperature.

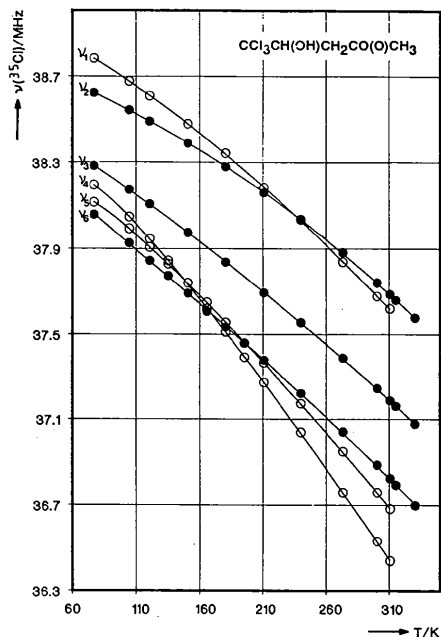


Fig. 2. ³⁵Cl nuclear quadrupole resonance frequencies as a function of temperature.

electric field gradient exists; this in turn leads to six different resonance frequencies at constant temperature. We find two groups of frequencies: the signals of one group bleach out at 310.4 K (above this temperature they become unobservable owing to line broadening) and the signals of the other group are observable nearly up to the melting point of the title compound (331.8 K; Ross, 1936). According to the NQR results, there is no phase transition between 77 K and the melting point.

One of us (RB) is indebted to the Physics Department, Faculty of Science, University of Istanbul, for permitting leave of absence.

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Acta Cryst. (1991). C47, 2402–2406

Absolute Structures of (–)-(S_S,S_C)-1-Phenylethyl 2-Pyridyl Sulfoxide and (–)-(R)-1-Methyl-2-(1-phenylethyl)pyridinium Perchlorate

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(Received 28 December 1990; accepted 22 May 1991)

Abstract. (I) C₁₃H₁₃NOS, $M_r = 231.31$, monoclinic, $P2_1$, $a = 14.0654$ (8), $b = 7.7361$ (6), $c = 5.7751$ (3) Å,

$\beta = 94.892$ (6)°, $V = 626.11$ (5) Å³, $Z = 2$, $D_x = 1.227$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 2.073$ mm⁻¹, $F(000) = 244$, $T = 295$ K, $R = 0.029$ for 2064 observed reflections. (II) C₁₄H₁₆N⁺.ClO₄⁻, M_r ,

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