X-Ray and ^{35}Cl NQR Studies on the Trichloroacetyl Group in Covalent and Ionic Compounds of L-Valine and DL-Valine

A. R. Ofial[a], S.-q. Dou, V. G. Krishnan[b], H. Paulus, H. Fuess, and Al. Weiss[†]

Fachbereich Materialwissenschaft, Fachgebiet Strukturforschung,
Technische Hochschule Darmstadt, Petersenstraße 23, D-64287 Darmstadt, Germany

[a] Institut für Organische Chemie, Technische Hochschule Darmstadt, Petersenstraße 22, D-64287 Darmstadt, Germany
[b] Department of Physics, Osmania University, Hyderabad-500007, India
[†] Deceased.

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The crystal structures and ^{35}Cl NQR of trichloroacetyl-DL-valine (**1**), trichloroacetyl-L-valine (**2**), as well as the salts of trichloroacetic acid with DL-valine (**3**) and L-valine (**4**) have been investigated. Crystal data are for (**1**): Monoclinic, C2/c, $a = 15.835(4)$ Å, $b = 10.481(3)$ Å, $c = 14.046(4)$ Å, $\beta = 103.28(1)$, $Z = 8$; (**2**): Orthorhombic, $P2_12_12_1$, $a = 12.117(3)$ Å, $b = 10.896(3)$ Å, $c = 8.718(2)$ Å, $Z = 4$; (**3**): Triclinic, $P\bar{1}$, $a = 17.269(3)$ Å, $b = 8.504(3)$ Å, $c = 10.427(4)$ Å, $\alpha = 105.38(2)$, $\beta = 96.98(2)$, $\gamma = 96.24(2)$, $Z = 2$; (**4**): Monoclinic, $P2_1$, $a = 10.378(4)$ Å, $b = 20.349(8)$ Å, $c = 11.890(5)$ Å, $\beta = 95.28(2)$, $Z = 8$. The onset of rotational motion within the trichloroacetyl groups bleaches out ^{35}Cl NQR lines between 115 K and 185 K for (**1**)–(**4**). While TCA-L-valine (**1**), TCA-DL-valine (**2**), and $TCA^{(-)} \cdot$ DL-$valine^{(+)}$ (**3**) do not show any phase transition in the temperature range 77 K to 295 K, $TCA^{(-)} \cdot$ L-$valine^{(+)}$ (**4**) shows more than one phase transition above 77 K before the three NQR signals bleach out at 164 K.

Key words: ^{35}Cl NQR study, trichloroacetyl, valine, crystal and molecular structure.

Introduction

Librational motions of CH_2Cl, $CHCl_2$, and CCl_3 groups are often found in chlorinated organic compounds even far below the melting point, in some cases just above 77 K. This leads to a dynamic or static disorder which is associated with a broadening of the ^{35}Cl NQR lines and a decrease in their signal-to-noise ratio. Sometimes the increasing disorder is also accompanied with phase transitions [1, 2]. Recently we reported on the X-ray structures and ^{35}Cl NQR spectra of N-trichloroacetyl and N-dichloroacetyl amino acids and salts of amino acids with trichloroacetic acid [3]. These compounds showed a bleachout of reasonances at temperatures below the melting points, but none of them exhibited a phase transition between 77 K and room temperature.

It was pointed out that molecules with one or more optically active centers offer an interesting possibility for the study of van der Waals interactions in molecular solids. By crystallizing the pure enantiomers or their racemic mixtures one can investigate the same molecules in different crystallographic environments which in turn alters the electric field gradient (EFG) at the site of the ^{35}Cl nuclei. To extend these investigations, we now report on further X-ray and ^{35}Cl NQR studies on the trichloroacetylated amino acid valine as well as on salts of this amino acid with trichloroacetic acid.

Reprint requests to Prof. Dr. Hartmut Fuess.

Experimental

(**1**) and (**2**) were synthesized following the method reported in [4]. The salts of L-valine and DL-valine were prepared by mixing stoichiometric amounts of trichloroacetic acid and the respective amino acids. X-ray diffraction intensities for (**1**)–(**4**) were collected on a four-circle goniometer and were corrected for absorption as well as the Lorentz-polarization factor. The structures were determined by direct methods [5] and least squares refinement [6]. The atomic positions of all hydrogen atoms were fixed isotropically. The results of the crystal structure determinations as well as the crystallographic data for the four compounds are given in Table 1. The relative atomic positions and the mean thermal parameters are reported in Table 2, the intramolecular bond lengths in Table 3. Bond an-

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Table 1. X-ray diffraction results. Experimental conditions and crystallographic data for the compounds (**1**)–(**4**); Diffractometer: Stoe Stadi-4; wavelength MoK_α, 0.71069 Å; monochromator Graphite (002); scan $\omega/2\Theta$.

Compound	TCA-DL-valine (**1**)	TCA-L-valine (**2**)	$TCA^{(-)} \cdot$ DL-$valine^{(+)}$ (**3**)	$TCA^{(-)} \cdot$ L-$valine^{(+)}$ (**4**)
Empirical formula	$C_7H_{10}Cl_3NO_3$	$C_7H_{10}Cl_3NO_3$	$C_7H_{12}Cl_3NO_4$	$C_7H_{12}Cl_3NO_4$
Formula weight	262.53	262.53	280.55	280.55
Habitus	irregular	irregular	prism	prism
Dimensions/mm	0.45 × 0.45 × 0.75	0.3 × 0.35 × 0.5	0.22 × 0.5 × 1.7	0.19 × 0.36 × 0.76
T/K	296	298	298	300
Abs.coeff. μ/m^{-1}	720	707	675	659
$(\sin\Theta/\lambda)_{max}/Å^{-1}$	0.650	0.595	0.595	0.538
Reflexions: measured	4572	3150	3508	7596
considered ($F > 2\sigma(F)$)	2596	2040	2133	6518
Free parameters	136	181	141	546
$F(000)$	1072	536	292	1152
Θ range for data collection/°	2.35 to 27.48	2.51 to 25.02	2.05 to 24.97	1.72 to 22.49
Index ranges	$-20 \le h \le 20$, $0 \le k \le 13$, $-18 \le l \le 2$	$-14 \le h \le 14$, $-12 \le k \le 4$, $0 \le l \le 10$	$-8 \le h \le 4$, $-10 \le k \le 0$, $-12 \le l \le 12$	$-11 \le h \le 11$, $-21 \le k \le 21$, $-12 \le l \le 1$
Final R indices ($I \ge 2\sigma(I)$)	0.048 wR_2 0.126	0.032 wR_2 0.078	0.044 wR_2 0.107	0.069 wR_2 0.179
indices (all data)	0.052 wR_2 0.133	0.035 wR_2 0.082	0.048 wR_2 0.112	0.086 wR_2 0.205
Lattice constants/Å a/Å	15.835(4)	12.117(3)	17.269(3)	10.378(4)
b/Å	10.481(3)	10.896(3)	8.504(3)	20.349(8)
c/Å	14.046(4)	8.718(2)	10.427(4)	11.890(5)
α/°	90.0	90.0	105.38(2)	90.0
β/°	103.28(1)	90.0	96.89(2)	95.28(2)
γ/°	90.0	90.0	96.24(2)	90.0
Unit cell V/Å^3	2268.8(11)	1151.0(5)	610.1(4)	2500(2)
Space group	$C_{2h}^6 - C2/c$	$D_2^4 - P2_12_12_1$	$C_1^1 - P\bar{1}$	$C_2^2 - P2_1$
Molecules/cell Z	8	4	2	8
D_X/Mg · m^{-3}	1.537(2)	1.515(2)	1.538(2)	1.491(1)
Point positions	All atoms in (8f)	All atoms in (4a)	All atoms in (2i)	All atoms in (2a)

gles, hydrogen bond distances and a full list of structure factors F_c, F_o can be obtained [7]. The procedure adopted for the variable temperature NQR measurements was the same as that outlined earlier [3].

Results and Discussion

N-Trichloroacetyl-DL-valine (**1**):

Compound **1** crystallizes in a centrosymmetric monoclinic space group (C2/c) with one molecule in the asymmetric unit. Figure 1 shows the molecular arrangement with the atom numbering, and Fig. 2 the projection on the ac plane. In accordance with the crystallographic data, three ^{35}Cl NQR lines were obtained in the temperature range between 77 K and the bleachout temperature $T_b = 133$ K (Fig. 3, see also Table 4 for NQR frequencies at certain temperatures).

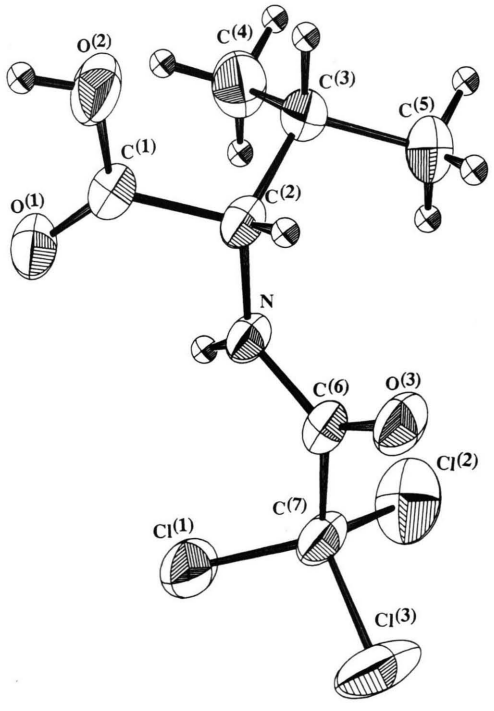

Fig. 1. Molecular arrangement of N-TCA-DL-valine (**1**) and thermal ellipsoids (50% probability level).

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters U_{eq} ($Å^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
– TCA-DL-valine (**1**)				
$Cl^{(1)}$	1464(1)	2339(1)	7446(1)	66(1)
$Cl^{(2)}$	2794(1)	1087(1)	6707(1)	74(1)
$Cl^{(3)}$	2088(1)	3474(1)	5892(1)	80(1)
$N^{(1)}$	3217(1)	3029(2)	8636(1)	31(1)
$O^{(1)}$	2809(1)	3858(2)	10285(1)	43(1)
$O^{(2)}$	4086(1)	4824(2)	10808(1)	50(1)
$O^{(3)}$	3625(1)	3966(2)	7362(1)	42(1)
$C^{(3)}$	4665(1)	2643(2)	9768(2)	36(1)
$C^{(2)}$	3915(1)	3591(2)	9379(1)	30(1)
$C^{(1)}$	3526(1)	4102(2)	10197(1)	32(1)
$C^{(5)}$	5024(2)	2125(2)	8926(2)	49(1)
$C^{(4)}$	4403(2)	1567(3)	10365(2)	52(1)
$C^{(6)}$	3140(1)	3285(2)	7692(2)	32(1)
$C^{(7)}$	2387(2)	2591(2)	6973(2)	42(1)
– TCA-L-valine (**2**)				
$Cl^{(1)}$	8669(2)	8479(1)	2114(2)	93(1)
$Cl^{(2)}$	9481(1)	10822(1)	1217(1)	84(1)
$Cl^{(3)}$	7422(2)	10642(8)	2731(6)	129(2)
$O^{(2)}$	9860(2)	7360(2)	6573(2)	66(1)
$C^{(2)}$	10444(2)	9455(2)	6281(2)	46(1)
$O^{(3)}$	9248(2)	11329(2)	4699(2)	75(1)
$O^{(1)}$	10626(2)	8336(2)	8551(2)	74(1)
$C^{(1)}$	10269(2)	8256(2)	7125(3)	49(1)
$C^{(6)}$	9303(2)	10291(2)	4203(3)	49(1)
$N^{(1)}$	9841(2)	9367(2)	4829(2)	48(1)
$C^{(3)}$	11689(2)	9696(2)	6046(3)	59(1)
$C^{(7)}$	8724(2)	10032(2)	2654(3)	55(1)
$C^{(4)}$	12225(2)	8721(3)	5043(5)	86(1)
$C^{(5)}$	11897(2)	10971(3)	5412(3)	80(1)
$Cl^{(1A)}$	9306(2)	8599(3)	1942(3)	81(6)
$Cl^{(1B)}$	8195(2)	8573(3)	2706(3)	87(5)
$Cl^{(2A)}$	8792(2)	11123(3)	1453(3)	95(5)
$Cl^{(2B)}$	9666(2)	10258(3)	1250(3)	75(4)
$Cl^{(3A)}$	7348(2)	9898(3)	3058(3)	102(4)
$Cl^{(3B)}$	7361(2)	10947(3)	2533(3)	51(5)
– $TCA^{(-)}$ · DL-$valine^{(+)}$ (**3**)				
$Cl^{(1)}$	3021(1)	3637(1)	8210(1)	66(1)
$Cl^{(2)}$	5502(1)	5764(2)	7286(2)	116(1)
$Cl^{(3)}$	4818(2)	2262(2)	5968(1)	113(1)
$O^{(11)}$	8325(3)	4305(2)	8546(2)	60(1)
$O^{(12)}$	6470(3)	2293(2)	8922(2)	54(1)
$C^{(11)}$	5116(4)	3801(4)	7529(3)	50(1)
$C^{(12)}$	6807(3)	3455(3)	8426(3)	41(1)
$N^{(11)}$	10301(3)	7465(2)	9159(2)	43(1)
$O^{(21)}$	12295(3)	10475(2)	9672(2)	49(1)
$O^{(22)}$	14027(3)	9590(3)	8074(2)	55(1)
$C^{(21)}$	11342(3)	7804(3)	8100(3)	42(1)
$C^{(22)}$	12612(3)	9445(3)	8715(3)	40(1)
$C^{(23)}$	9986(4)	7788(4)	6839(3)	54(1)
$C^{(24)}$	8930(5)	9258(4)	7066(4)	71(1)
$C^{(25)}$	10979(6)	7607(6)	5620(4)	95(1)
– $TCA^{(-)}$ · L-$valine^{(+)}$ (**4**)				
$Cl^{(11)}$	541(3)	946(1)	2647(2)	83(1)
$Cl^{(12)}$	167(3)	–442(1)	2704(2)	91(1)
$Cl^{(13)}$	2730(3)	97(2)	2766(2)	122(1)
$O^{(11)}$	1912(5)	–40(3)	393(4)	56(1)
$O^{(12)}$	–123(4)	282(3)	425(4)	49(1)
$C^{(11)}$	1113(7)	176(4)	2203(6)	50(2)
$C^{(12)}$	968(6)	150(3)	863(6)	42(2)
$Cl^{(21)}$	3167(5)	5977(2)	4512(3)	152(2)
$Cl^{(22)}$	572(5)	4637(2)	4594(2)	142(2)
$Cl^{(23)}$	5153(4)	5011(4)	4601(3)	220(4)
$O^{(22)}$	2363(4)	5324(3)	2306(4)	50(1)
$O^{(21)}$	4375(4)	4970(3)	2243(4)	55(1)
$C^{(22)}$	3632(7)	5215(5)	4060(6)	61(2)
$C^{(21)}$	3436(7)	5171(4)	2745(6)	48(2)
$Cl^{(31)}$	2820(2)	3037(2)	–3157(2)	106(1)
$Cl^{(32)}$	5490(3)	3370(2)	–2721(2)	129(2)
$Cl^{(33)}$	4615(5)	2084(2)	–2207(4)	159(2)
$O^{(31)}$	3012(4)	3424(3)	–827(5)	58(1)
$O^{(32)}$	5011(5)	3041(3)	–309(4)	54(1)
$C^{(31)}$	4067(7)	3145(4)	–997(6)	49(2)
$C^{(32)}$	4212(8)	2907(5)	–2215(8)	70(2)
$Cl^{(41)}$	1617(9)	7143(2)	5768(4)	284(5)
$Cl^{(42)}$	2926(3)	8301(5)	5260(3)	272(5)
$Cl^{(43)}$	253(3)	8208(2)	4828(2)	103(1)
$O^{(41)}$	484(5)	8495(3)	7206(5)	66(2)
$O^{(42)}$	2475(5)	8078(3)	7644(4)	54(1)
$C^{(41)}$	1512(7)	8201(4)	7001(7)	51(2)
$C^{(42)}$	1574(8)	7980(5)	5767(7)	64(2)
$N^{(51)}$	–2373(5)	3514(3)	0(5)	44(1)
$O^{(51)}$	139(5)	3825(3)	50(5)	55(1)
$O^{(52)}$	546(5)	3085(3)	–1273(5)	62(2)
$C^{(51)}$	–188 (6)	3394(4)	–587 (6)	44(2)
$C^{(52)}$	–1582 (6)	3140(4)	–774 (6)	45(2)
$C^{(53)}$	–1741 (8)	2396(4)	–620 (9)	71(3)
$C^{(54)}$	–1514(10)	2020(5)	–1742(11)	101(4)
$C^{(55)}$	–903(11)	2129(5)	377(10)	95(3)
$N^{(61)}$	–206 (5)	4826(3)	1914 (5)	47(1)
$O^{(61)}$	–2659 (5)	4495(3)	2057 (5)	57(1)
$O^{(62)}$	–3325 (5)	5529(3)	2213 (6)	66(2)
$C^{(61)}$	–2436 (6)	5067(4)	2160 (6)	47(2)
$C^{(62)}$	–1098 (6)	5353(4)	2224 (6)	45(2)
$C^{(63)}$	–639 (8)	5641(4)	3406 (7)	63(2)
$C^{(64)}$	–1248(10)	6311(6)	3606(11)	103(4)
$C^{(65)}$	–848(10)	5152(7)	4336 (7)	95(3)
$N^{(71)}$	4890 (5)	3519(3)	2004 (5)	44(1)
$O^{(71)}$	2380 (5)	3850(3)	1898 (4)	51(1)
$O^{(72)}$	1961 (5)	3171(3)	3290 (5)	69(2)
$C^{(71)}$	2701 (6)	3434(4)	2600 (6)	45(2)
$C^{(72)}$	4081 (6)	3173(3)	2782 (6)	44(2)
$C^{(73)}$	4173 (7)	2433(4)	2648 (8)	59(2)
$C^{(74)}$	3921(10)	2054(5)	3708 (9)	87(3)
$C^{(75)}$	3311 (9)	2180(5)	1645 (9)	79(3)
$N^{(81)}$	2680 (5)	4752(3)	1 (5)	43(1)
$O^{(81)}$	5150 (5)	4452(3)	–114 (5)	4(1)
$O^{(82)}$	5727 (5)	5484(3)	–421 (6)	65(2)
$C^{(81)}$	4900 (6)	5017(4)	–275 (6)	45(2)
$C^{(82)}$	3512 (6)	5276(4)	–353 (6)	43(2)
$C^{(83)}$	3035 (7)	5519(5)	–1551 (7)	63(2)
$C^{(84)}$	3276(10)	5007(7)	–2442 (7)	102(4)
$C^{(85)}$	3568(10)	6169(6)	–1826(11)	108(5)

Table 3. Bond lengths of compounds (**1**)–(**4**).

Atoms	Bond length [Å]	Atoms	Bond length [Å]	Atoms	Bond length [Å]
– TCA-DL-valine (**1**)		– $TCA^{(-)}$ · DL-$valinie^{(+)}$ (**3**)			
$Cl^{(1)}-C^{(7)}$	1.759(2)	$Cl^{(1)}-C^{(11)}$	1.764(3)	$Cl^{(42)}-C^{(42)}$	1.708(10)
$Cl^{(2)}-C^{(7)}$	1.755(3)	$Cl^{(3)}-C^{(11)}$	1.770(3)	$Cl^{(43)}-C^{(42)}$	1.749 (8)
$Cl^{(3)}-C^{(7)}$	1.748(2)	$N^{(11)}-C^{(21)}$	1.483(3)	$O^{(41)}-C^{(41)}$	1.266 (9)
$N^{(1)}-C^{(6)}$	1.331(2)	$O^{(11)}-C^{(12)}$	1.225(3)	$O^{(42)}-C^{(41)}$	1.227 (9)
$N^{(1)}-C^{(2)}$	1.458(2)	$O^{(12)}-C^{(12)}$	1.246(3)	$C^{(41)}-C^{(42)}$	1.541(11)
$O^{(1)}-C^{(1)}$	1.198(3)	$C^{(11)}-C^{(12)}$	1.555(4)	$N^{(51)}-C^{(52)}$	1.497 (9)
$O^{(2)}-C^{(1)}$	1.322(3)	$O^{(21)}-C^{(22)}$	1.205(3)	$O^{(51)}-C^{(51)}$	1.188 (8)
$O^{(3)}-C^{(6)}$	1.215(3)	$O^{(22)}-C^{(22)}$	1.305(3)	$O^{(52)}-C^{(51)}$	1.325 (8)
$C^{(3)}-C^{(4)}$	1.519(3)	$C^{(21)}-C^{(22)}$	1.521(3)	$C^{(51)}-C^{(52)}$	1.533 (9)
$C^{(3)}-C^{(5)}$	1.525(3)	$C^{(21)}-C^{(23)}$	1.540(4)	$C^{(52)}-C^{(53)}$	1.536(11)
$C^{(3)}-C^{(2)}$	1.548(3)	$C^{(23)}-C^{(24)}$	1.518(5)	$C^{(53)}-C^{(55)}$	1.51 (2)
$C^{(2)}-C^{(1)}$	1.520(3)	$C^{(23)}-C^{(25)}$	1.518(5)	$C^{(53)}-C^{(54)}$	1.573(14)
$C^{(6)}-C^{(7)}$	1.556(3)			$N^{(61)}-C^{(62)}$	1.485 (9)
				$O^{(61)}-C^{(61)}$	1.192 (9)
– TCA-L-valine (**2**)		– $TCA^{(-)}$ · L-$valine^{(+)}$ (**4**)		$O^{(62)}-C^{(61)}$	1.323 (9)
$Cl^{(1)}-C^{(7)}$	1.758(3)	$Cl^{(11)}-C^{(11)}$	1.772 (8)	$C^{(61)}-C^{(62)}$	1.500(10)
$Cl^{(2)}-C^{(7)}$	1.775(3)	$Cl^{(12)}-C^{(11)}$	1.735 (8)	$C^{(62)}-C^{(63)}$	1.557(10)
$Cl^{(3)}-C^{(7)}$	1.713(5)	$Cl^{(13)}-C^{(11)}$	1.756 (7)	$C^{(63)}-C^{(65)}$	1.518(14)
$N^{(1)}-C^{(2)}$	1.464(3)	$O^{(11)}-C^{(12)}$	1.233 (8)	$C^{(63)}-C^{(64)}$	1.531(13)
$N^{(1)}-C^{(6)}$	1.318(3)	$O^{(12)}-C^{(12)}$	1.231 (8)	$N^{(71)}-C^{(72)}$	1.483 (9)
$O^{(2)}-C^{(1)}$	1.195(3)	$C^{(11)}-C^{(12)}$	1.588(10)	$O^{(71)}-C^{(71)}$	1.213 (8)
$C^{(2)}-C^{(1)}$	1.516(3)	$Cl^{(21)}-C^{(22)}$	1.726(10)	$O^{(72)}-C^{(71)}$	1.291 (8)
$C^{(2)}-C^{(3)}$	1.545(3)	$Cl^{(22)}-C^{(22)}$	1.768(10)	$C^{(71)}-C^{(72)}$	1.524 (9)
$O^{(3)}-C^{(6)}$	1.213(3)	$Cl^{(23)}-C^{(22)}$	1.700 (8)	$C^{(72)}-C^{(73)}$	1.519(10)
$O^{(1)}-C^{(1)}$	1.319(3)	$O^{(22)}-C^{(21)}$	1.226 (8)	$C^{(73)}-C^{(75)}$	1.513(13)
$C^{(6)}-C^{(7)}$	1.547(3)	$O^{(21)}-C^{(21)}$	1.258 (8)	$C^{(73)}-C^{(74)}$	1.521(12)
$C^{(3)}-C^{(5)}$	1.517(4)	$C^{(22)}-C^{(21)}$	1.560(10)	$N^{(81)}-C^{(82)}$	1.458 (9)
$C^{(3)}-C^{(4)}$	1.522(4)	$Cl^{(31)}-C^{(32)}$	1.765 (9)	$O^{(81)}-C^{(81)}$	1.189 (9)
$Cl^{(1A)}-C^{(7)}$	1.822(4)	$Cl^{(32)}-C^{(32)}$	1.777(10)	$O^{(82)}-C^{(81)}$	1.303 (9)
$Cl^{(1B)}-C^{(7)}$	1.716(4)	$Cl^{(33)}-C^{(32)}$	1.726(10)	$C^{(81)}-C^{(82)}$	1.529 (9)
$Cl^{(2A)}-C^{(7)}$	1.587(4)	$O^{(31)}-C^{(31)}$	1.265 (9)	$C^{(82)}-C^{(83)}$	1.546(10)
$Cl^{(2B)}-C^{(7)}$	1.692(4)	$O^{(32)}-C^{(31)}$	1.236 (9)	$C^{(83)}-C^{(85)}$	1.480(13)
$Cl^{(3A)}-C^{(7)}$	1.710(4)	$C^{(31)}-C^{(32)}$	1.549(11)	$C^{(83)}-C^{(84)}$	1.524(13)
$Cl^{(3B)}-C^{(7)}$	1.933(4)	$Cl^{(41)}-C^{(42)}$	1.704(10)		

Table 4. ^{35}Cl NQR frequencies (in MHz) at selected temperatures for compounds (**1**)–(**4**).

T/K	(**1**) $T_b = 133$ K	(**2**) $T_b = 114$ K	(**3**) $T_b = 183$ K	(**4**) $T_b = 163$ K	
77	40.295	39.876	38.985	39.088	
	39.284	39.804	38.566	38.804	
	39.199	38.827	38.422	38.422	
110	40.168	39.626	38.860	39.187	38.745
	39.164	39.485	38.394	39.058	38.383
	39.096	38.629	38.245	39.004	38.329
132	40.062	–	38.787	38.783	
	39.064	–	38.292	38.349	
	39.010	–	38.122	38.256	
183	–	–	38.500	–	
	–	–	37.887	–	
	–	–	37.642	–	

Two different types of hydrogen bonds were found. The first one is located between the amido NH and the carboxylic oxygen which leads to the formation of dimers, each consisting of one molecule with D- and one with L-configuration, respectively. These dimers are connected with each other via hydrogen bonds between the amido CO and the carboxylic OH groups.

N-Trichloroacetyl-L-valine (**2**):

The pure enantiomer **2** crystallizes in an orthorhombic space group ($P2_12_12_1$) with one molecule in the asymmetric unit. Figure 4a shows the projection on the ab plane with the mean positions of the three

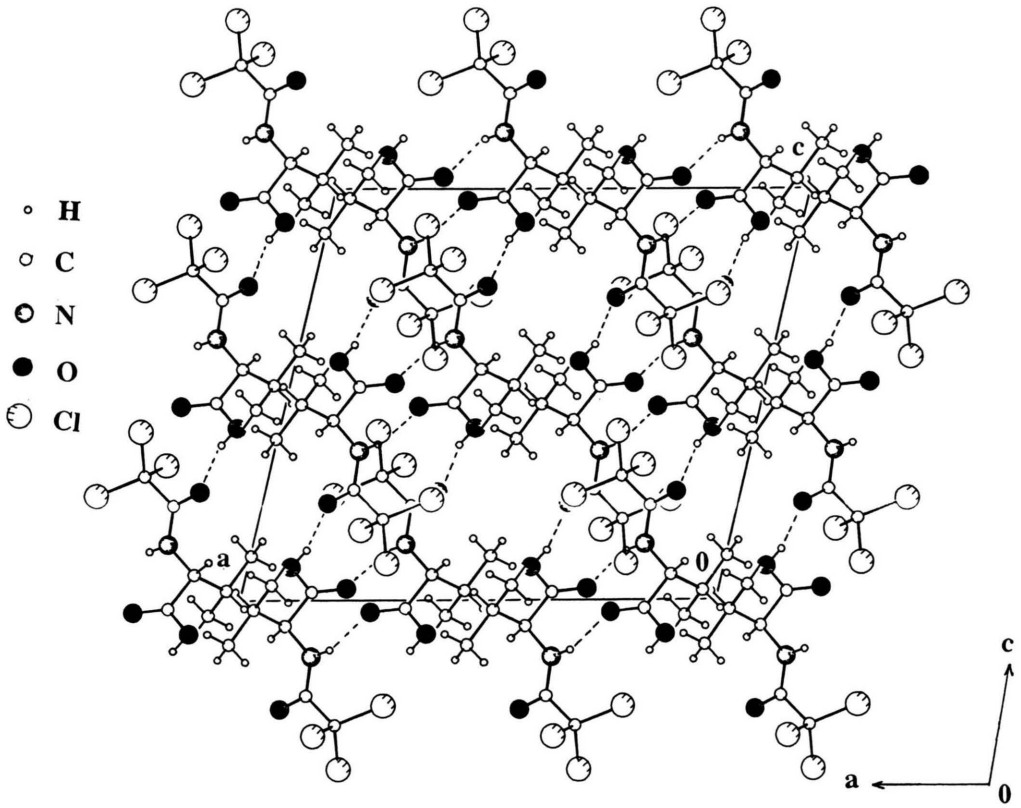

Fig. 2. Projection of N-TCA-DL-valine (**1**) on the ac plane.

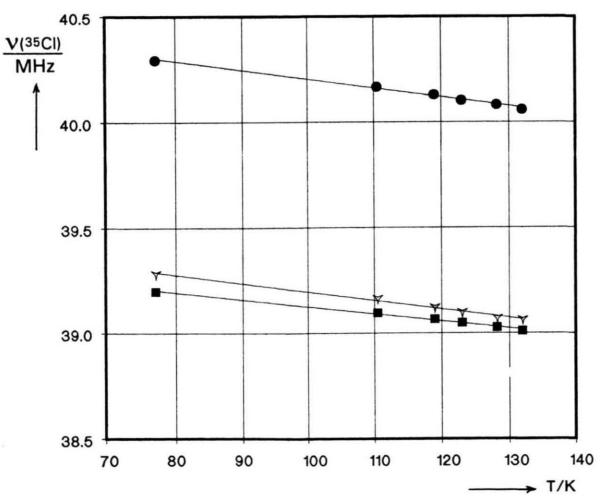

Fig. 3. Temperature dependence of ^{35}C NQR lines between 77 K and 133 K for N-TCA-DL-valine (**1**).

chlorine atoms. In contrast to **1** only one type of hydrogen bond is found for the TCA-L-valine (**2**) which connects the carboxylic OH with the amido oxygen. The nitrogen-bonded hydrogens do not seem to be involved in the formation of any hydrogen bonds. The weaker intermolecular interactions in **2** compared to **1** are also reflected by the lower bleachout temperature of the three NQR resonances of **2** (Fig. 5, $T_b = 114$ K) and the difficulty to fix the atomic positions of the CCl_3 group in the X-ray investigations at room temperature (Figure 4). Figure 4b shows the nine probable positions of the three chlorines of the CCl_3 group fixed with the help of a Fourier map. The occupancy factor for the three positions of each Cl, viz., $Cl^{(1)}$, $Cl^{(2)}$, and $Cl^{(3)}$ is nearly 0.8 : 0.1 : 0.1, respectively.

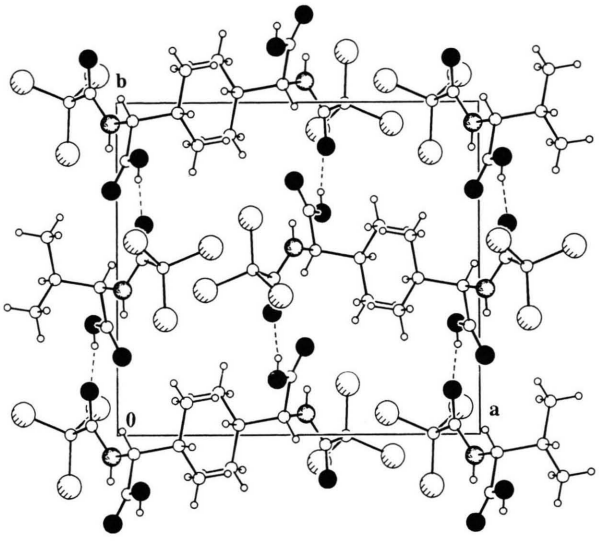

Fig. 4. Projection of N-TCA-L-valine (**2**) on the ab-plane a) only the most probable positions of the Cl atoms are shown, b) all positions of Cl atoms, which have been obtained with the help of the Fourier map, are shown.

Fig. 4a

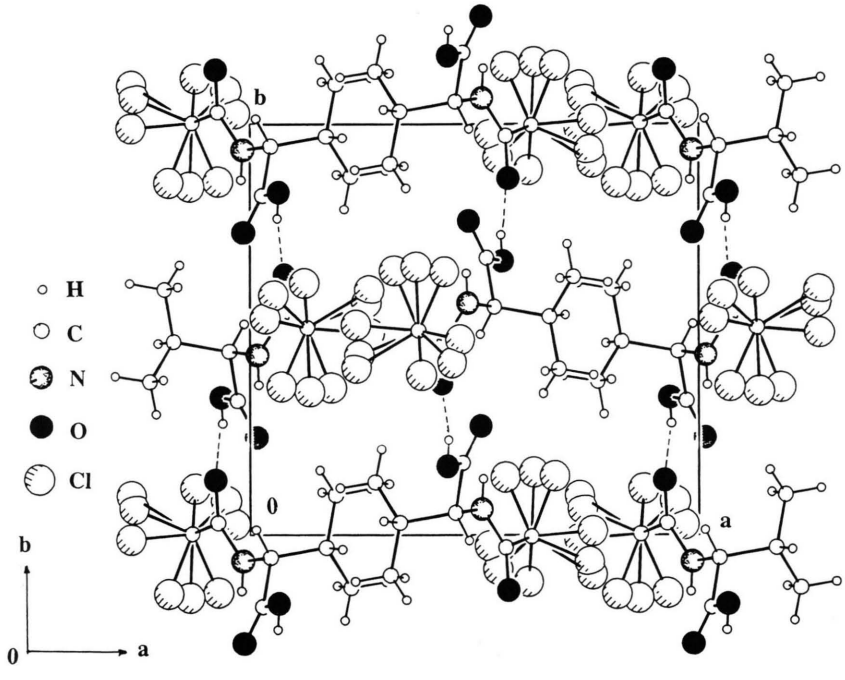

Fig. 4b

DL-Valinium Trichloroacetate (**3**):

The salt of the racemic amino acid DL-valine with trichloroacetic acid crystallized in a triclinic space group ($P\bar{1}$) with one molecule in the asymmetric unit. A plot of the unit cell on the bc plane is sketched in Figure 6. As discussed for compound **1**, the structure of the salt of trichloroacetic acid with DL-valine (**3**) is also dominated by the formation of dimers consisting of protonated D- and L-valine. The connection of these two molecules is made possible by the hydrogen bonds between the ammonium group and the carboxylic oxygens. Each of these dimers is linked with the next unit via two trichloroacetates that interact with the amino acids by three further hydrogen bonds. Since no phase transition was found between 77 K

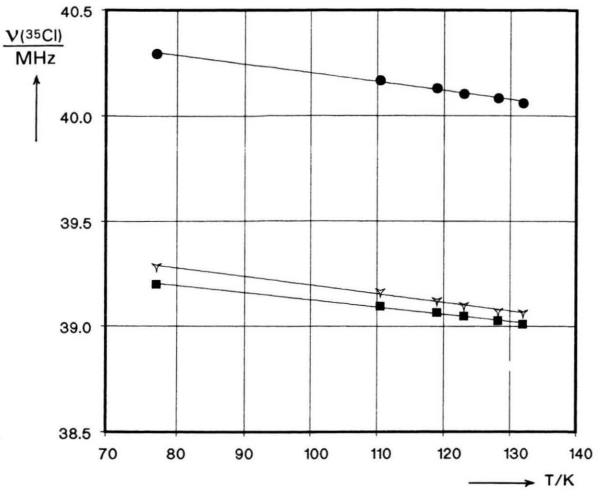

Fig. 5. Variation of ^{35}Cl resonances with temperature for N-TCA-L-valine (**2**).

and room temperature, the number of crystallographically independent chlorine atoms, viz., three, in the unit cell deduced from the NQR spectroscopy (Fig. 7, $T_b = 183$ K) is in agreement with the results of the X-ray structure determination.

L-Valinium Trichloroacetate (**4**):

The behavior of L-valinium trichloroacetate (**4**) in the solid state seems to be more complicated. The NQR measurements show evidence for two phase transitions between 77 K and $T_b = 163$ K (Figure 8). While only three resonance lines were detected at 77 K, six signals were observed in the temperature range 103 to 128 K. A more detailed NQR investigation was hindered due to lack of precise temperature control between 77 and 103 K. After the disappearance of six signals at 128 K, only three reappeared at 132 K. The

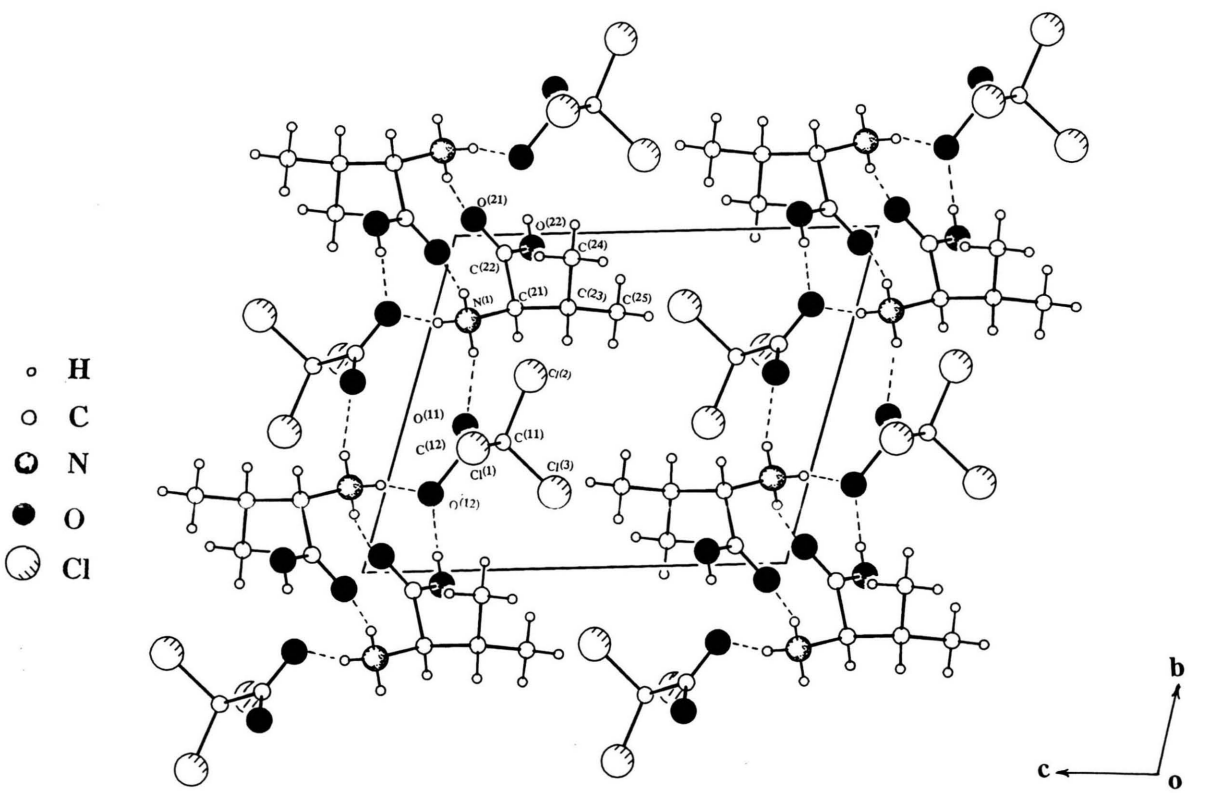

Fig. 6. Projection of the unit cell of DL-valinium trichloroacetate (**3**) on the *bc* plane.

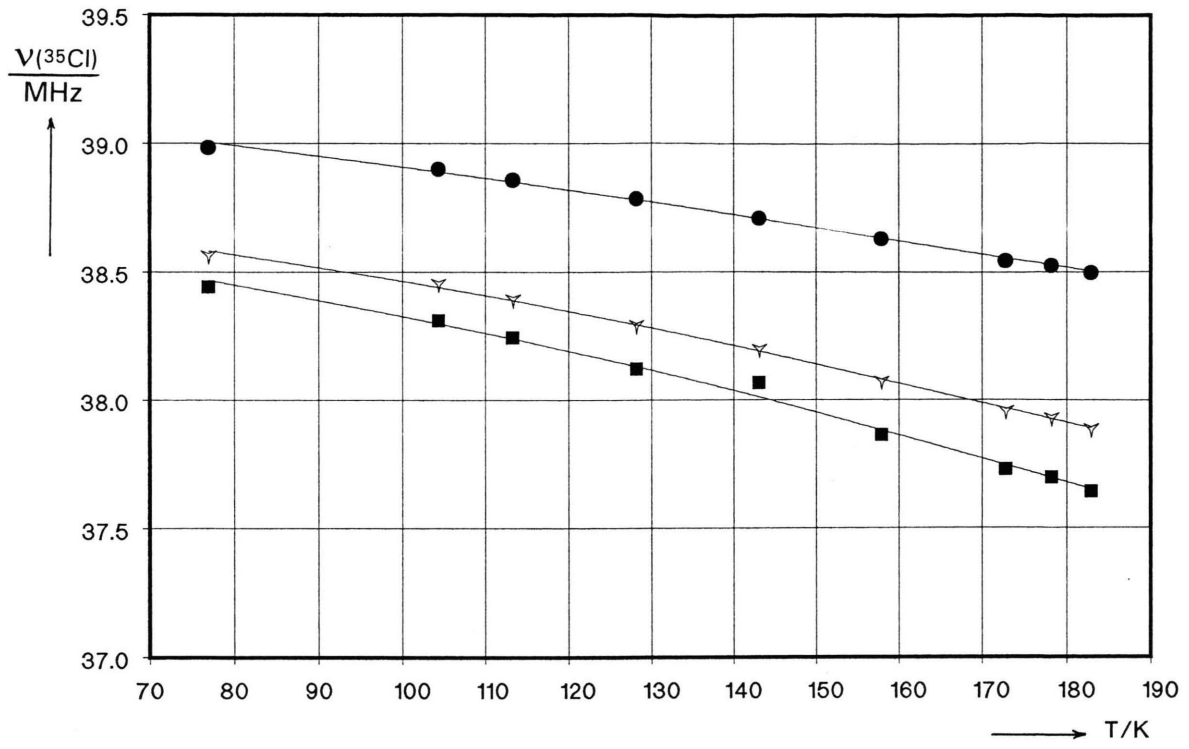

Fig. 7. Temperature dependence of the ^{35}Cl NQR signals between 77 K and T_b for the trichloroacetate of DL-valine (**3**).

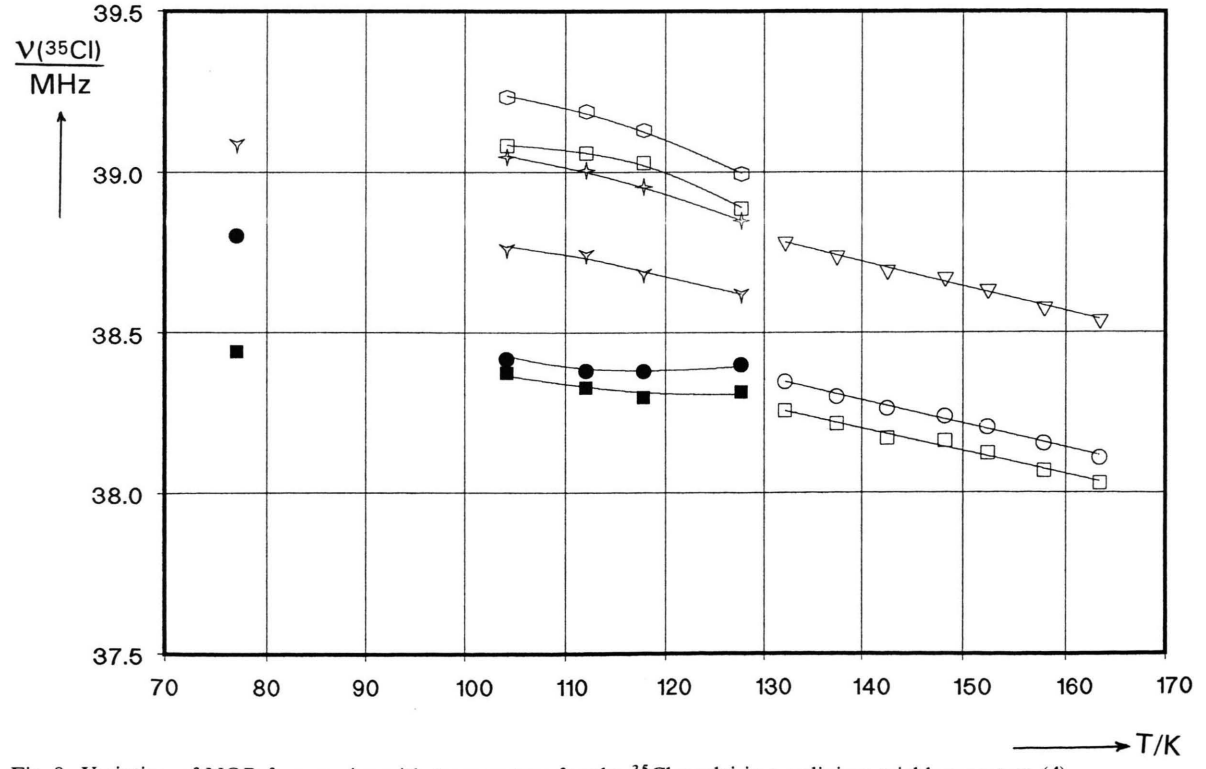

Fig. 8. Variation of NQR frequencies with temperature for the ^{35}Cl nuclei in L-valinium trichloroacetate (**4**).

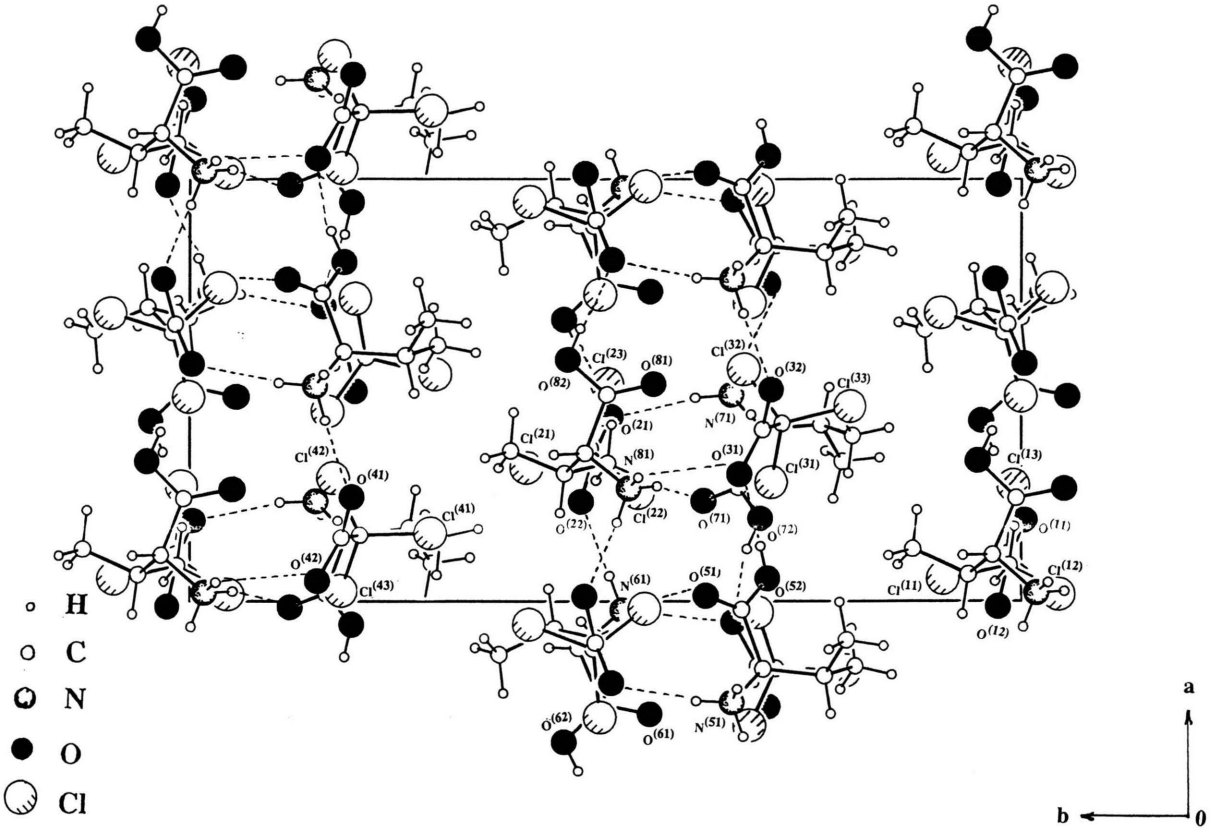

Fig. 9. Unit cell projection for L-valinium trichloroacetate (**4**) onto the *ab* plane.

definite bleachout temperature was reached at 163 K. Additional DSC investigations confirmed the phase transitions at 88 K and 128 K. The structure refinement for this compound was made difficult by the rotational motions of the CCl_3 group which resulted in high temperature factors for atoms $Cl^{(13)}$, $Cl^{(23)}$, $Cl^{(33)}$, $Cl^{(41)}$, and $Cl^{(42)}$. A plot of the unit cell projection on the ab plane is given in Figure 9. Despite the fact that no phase transition was detected between 163 K and room temperature by DSC technique, the crystallographic data show four independent molecules in the unit cell (Fig. 10) which should result in twelve NQR lines. The disagreement between the results of the NQR and the X-ray measurements cannot be explained in a straightforward manner. Further investigations including low temperature X-ray are in progress to elucidate the temperature dependence of the molecular arrangements in the solid state of **4**.

Acknowledgement

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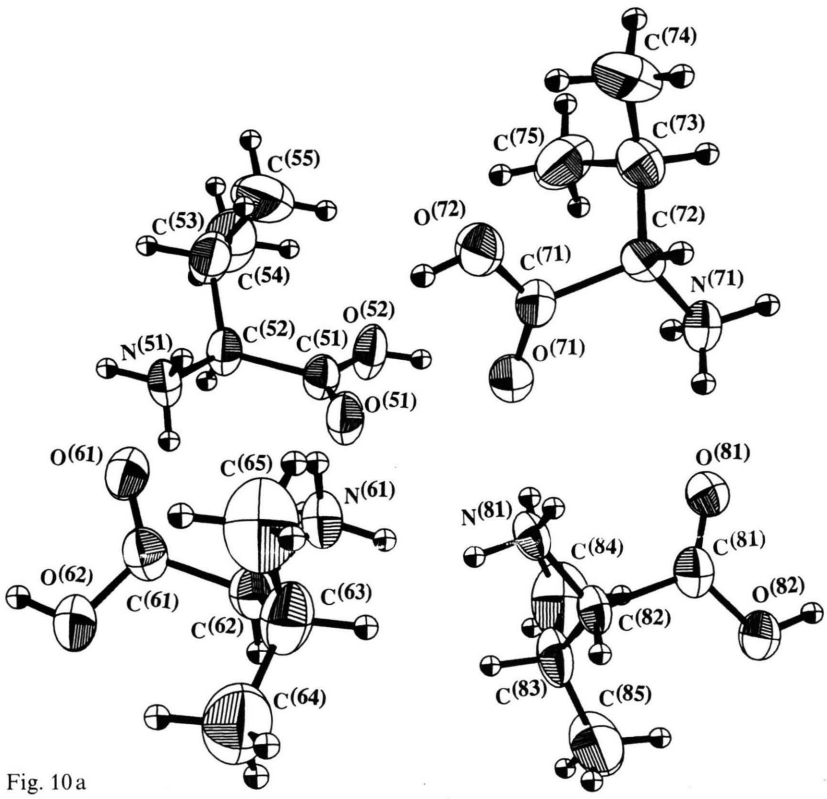


Fig. 10a

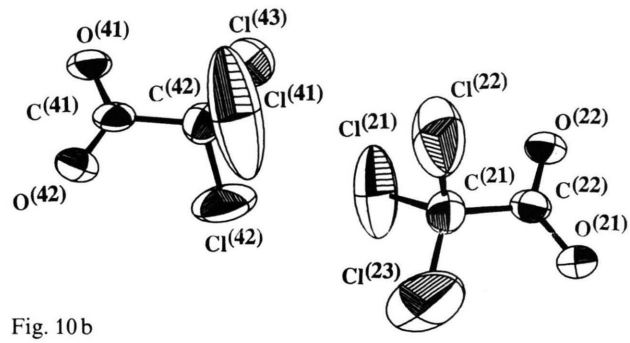
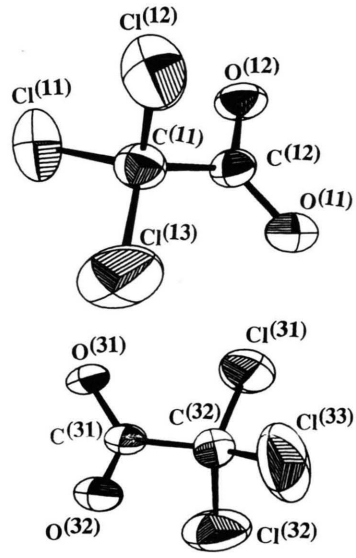


Fig. 10b

Fig. 10. Crystallographic structure of L-valinium trichloroacetate (**4**), determined at room temperature, with the numbering of atoms for the four independent molecules in the asymmetric unit and thermal ellipsoids (50% probability level). a) cationic part and b) anionic part.



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[7] Further information on the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Inquiries should be accompanied by the depository number CSD-59340, the names of the authors and the full literature reference.