51 CCl_3CONH_2

51A Pure compound

No. 51A-1 CCl_3CONH_2, Trichloroacetamide

(M = 162.402)

1a Dielectric anomaly in CCl_3CONH_2 was observed at about 355 K by Hashimoto et al. [a]) in 1990. Ferroelectricity was confirmed by Kamishima et al. [b]) in 1991. [a]) 90Has [b]) 91Kam

b

phase	III	II	I	
state	F		P	
crystal system	monoclinic		monoclinic	90Has
space group	$P2_1 - C_2^2$			
Θ [K]	354.6		356.9	91Kam

For Θ see also 90Has
$P_s \parallel b$. 91Kam
$\rho = 1.82 \cdot 10^3$ kg m^{-3} at RT. 87Has
Colorless. 87Has
Cleavage plane: bc plane. 91Kam
Sublimation occurs appreciably around the transition temperatures. 90Has

2a Crystal growth: cooling method from ethanol solution or ethyl ether solution. 87Has

3a Unit cell parameter at RT: a = 10.415(2) Å, b = 5.785(1) Å, c = 10.182(2) Å, β = 107.61°. 87Has

b Z = 4. 87Has
Crystal structure of phase III determined at RT: Table 51A-1-001, Table 51A-1-002; Fig. 51A-1-001, Fig. 51A-1-002.

5a Dielectric constant vs. temperature along b: Fig. 51A-1-003, Fig. 51A-1-004.
Curie-Weiss law $\kappa_b = \kappa_\infty + C/(T - \Theta_p)$ is hold in phase I: κ_∞ = 4.0, Θ_p = 353.9 K, C = 5.6 K. 91Kam
Dielectric constant vs. temperature along a^*: Fig. 51A-1-005.
Dielectric constant vs. temperature along c: Fig. 51A-1-006.

6a Transition heat: Fig. 51A-1-007.
Enthalpy changes for transition and fusion: 0.5 K J mol^{-1} and 22 K J mol^{-1}, respectively. 90Has

10a Raman scattering in the low wave number region: Fig. 51A-1-008.

13a ^{35}Cl NQR frequency and the line widths: Table 51A-1-003.
Vibration of NH_2: see 90Has

Table 51A-1-001. CCl_3CONH_2. Fractional coordinates *x, y, z* [$\cdot 10^{-4}$] and *B* [$Å^2$] in phase III [87Has]. *T* = RT. *B* is defined by Eq. (e) in Introduction.

	x	*y*	*z*	*B*
Molecule A				
Cl(1)	9099(2)	492(4)	4132(2)	4.56(5)
Cl(2)	7538(2)	3985(4)	2342(2)	4.13(6)
Cl(3)	7462(2)	3642(4)	5122(2)	4.05(6)
C(1)	7576(6)	2056(12)	3670(6)	2.7(1)
C(2)	6447(6)	221(13)	3187(6)	2.8(2)
N	5925(6)	–649(12)	4120(5)	3.3(2)
O	6139(5)	–401(10)	1976(4)	3.6(1)
H(1)	6080(90)	40(200)	4940(90)	4.8(25)
H(2)	5180(70)	–1830(160)	3830(70)	2.2(16)
Molecule B				
Cl(1)	2759(2)	764(5)	1200(4)	9.45(14)
Cl(2)	1283(3)	3814(8)	2388(3)	7.31(12)
Cl(3)	1251(2)	4410(6)	–379(2)	7.57(9)
C(1)	2240(6)	3617(13)	1270(6)	2.8(2)
C(2)	3545(5)	5112(11)	1795(6)	2.5(2)
N	4068(5)	5873(12)	850(5)	3.3(2)
O	4014(5)	5472(11)	3029(4)	3.8(1)
H(1)	3670(90)	5680(22)	–150(90)	4.4(23)
H(2)	4840(70)	6600(170)	1170(70)	2.5(18)

Table 51A-1-002. CCl_3CONH_2. Interatomic distances and bond angles in phase III [87Has]. *T* = RT.

	Molecule A	Molecule B
C(1)–Cl(1)	1.762(8) Å	1.745(9) Å
C(1)–Cl(2)	1.745(7)	1.729(9)
C(1)–Cl(3)	1.775(7)	1.745(8)
C(1)–C(2)	1.550(10)	1.563(10)
C(2)–N	1.328(10)	1.316(10)
C(2)–O	1.230(9)	1.220(9)
Cl(1)–C(1)–Cl(2)	110.1(4)°	109.7(4)°
Cl(1)–C(1)–Cl(3)	109.0(4)	108.0(4)
Cl(2)–C(1)–Cl(3)	108.9(4)	109.0(4)
Cl(1)–C(1)–C(2)	105.6(5)	106.8(5)
Cl(2)–C(1)–C(2)	110.8(5)	110.7(5)
Cl(3)–C(1)–C(2)	112.5(5)	112.5(5)
C(1)–C(2)–O	117.5(6)	118.8(6)
C(1)–C(2)–N	117.9(6)	116.4(6)
N–C(2)–O	124.5(7)	124.8(7)

Table 51A-1-003. CCl_3CONH_2. ^{35}Cl NQR frequencies and the line width before and after annealing for two kinds of samples R and S [90Has]. ν_0: ^{35}Cl NQR frequency. $\Delta\nu$: line with. T = 77 K. $A_{1–3}$ and $B_{1–3}$ correspond to CCl_3 of molecule A and B, respectively.

Line no.	Initial		Annealed	
	ν_0 [MHz]	$\Delta\nu$ [kHz]	ν_0 [MHz]	$\Delta\nu$ [kHz]
Crystal R				
A_1	39.4795	5.0	39.4806	3.2
A_2	39.6685	5.5	39.6680	4.1
A_3	40.0069	4.8	40.0082	3.1
B_1	38.8588	6.8	38.8567	4.4
B_2	39.6046	5.6	39.6051	4.9
B_3	39.8176	5.6	39.8182	4.4
Crystal S				
A_1	39.4805	2.1	39.4807	1.7
A_2	39.6684	2.4	39.6682	1.8
A_3	40.0081	1.9	40.0083	1.6
B_1	38.8576	2.4	38.8573	1.8
B_2	39.6055	2.6	39.6056	2.1
B_3	39.8185	2.3	39.8185	1.8

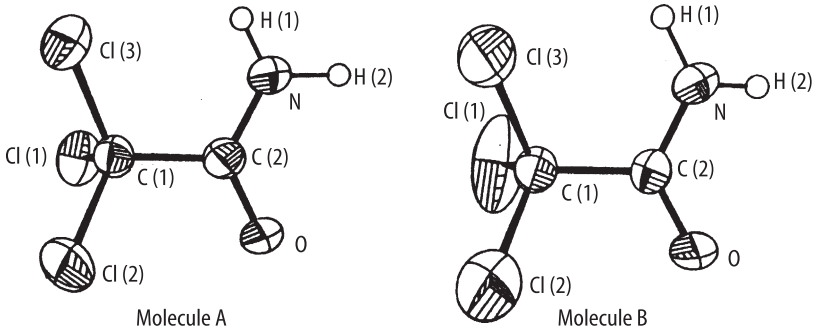

Fig. 51A-1-001. CCl_3CONH_2. View of two kinds of trichloroacetamide in phase III [87Has].

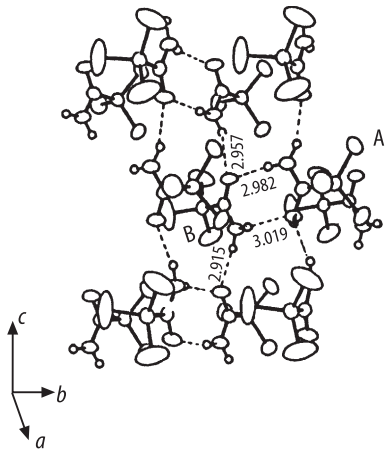

Fig. 51A-1-002. CCl_3CONH_2. Crystal structure viewed along a^* axis in phase III [87Has].

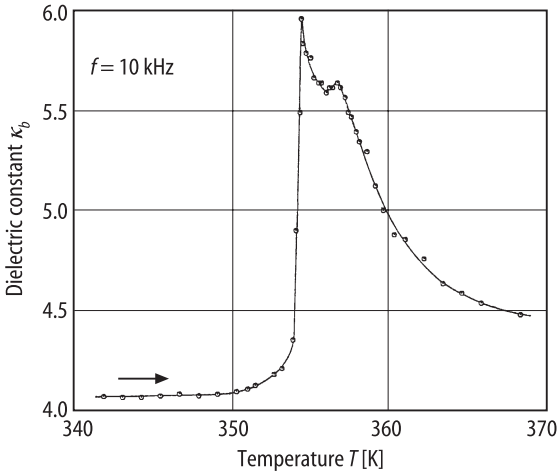

Fig. 51A-1-003. CCl_3CONH_2. κ_b vs. T [91Kam].

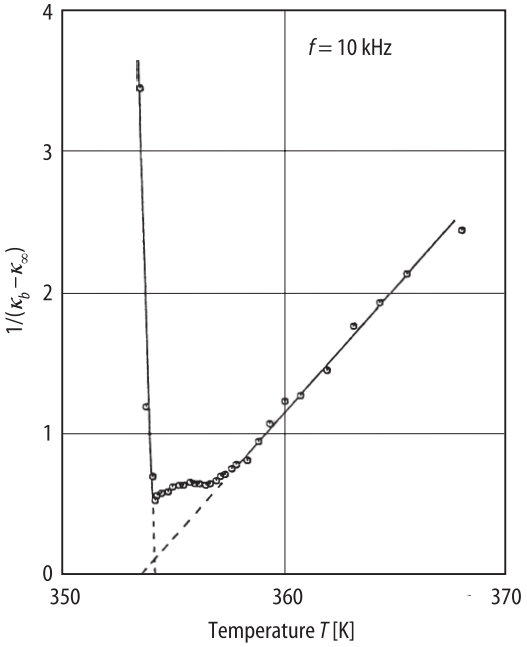

Fig. 51A-1-004. CCl_3CONH_2. $1/(\kappa_b - \kappa_\infty)$ vs. T [91Kam].

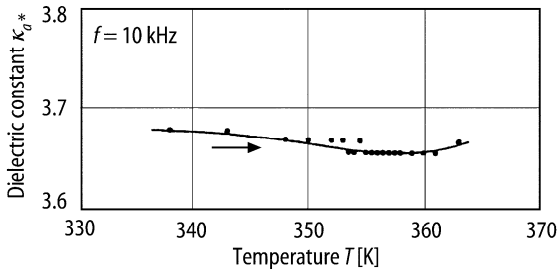

Fig. 51A-1-005. CCl_3CONH_2. κ_{a^*} vs. T [91Kam].

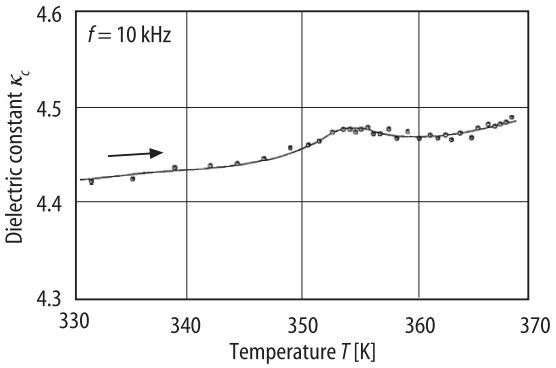

Fig. 51A-1-006. CCl_3CONH_2. κ_c vs. T [91Kam].

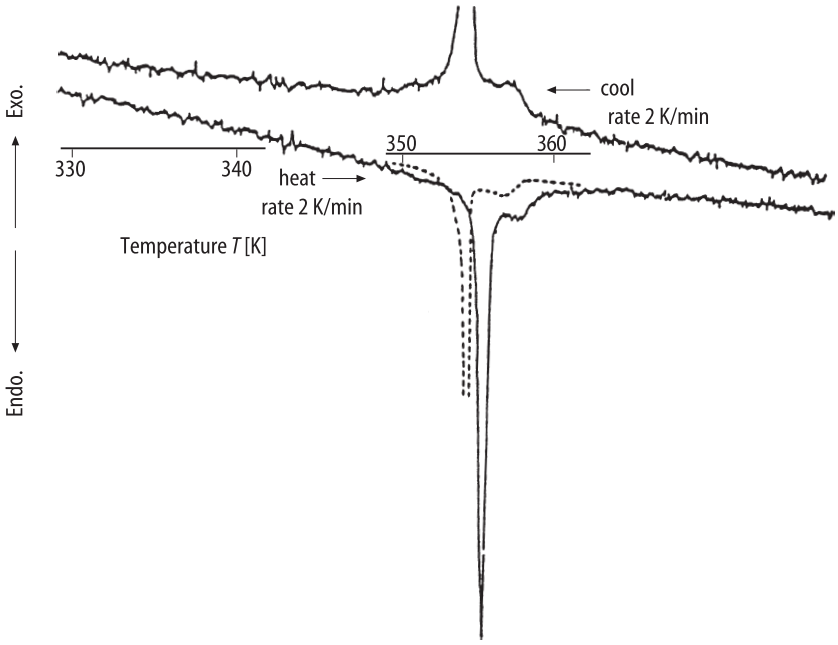

Fig. 51A-1-007. CCl_3CONH_2. Transition heat measured by DSC [90Has]. Endo.: endothermic. Exo.: exothermic. Broken line: for deuterated crystal.

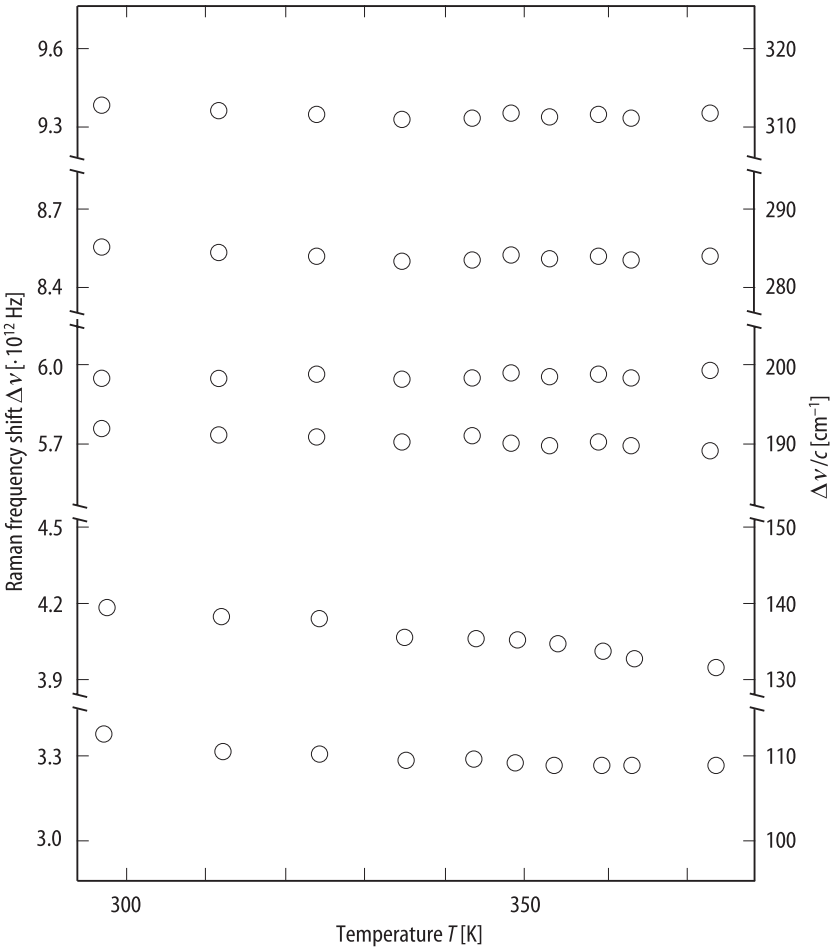

Fig. 51A-1-008. CCl_3CONH_2. $\Delta\nu$ vs. T in the low wave number region [90Has]. $\Delta\nu$: shift of Raman frequency.

References

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