No. M32 $C_4[CH_2OC_6H_3(NO_2)_2]_2$, Disubstituted diacetylene 1,6-bis (2,4-dinitrophenoxy)-2,4-hexadiyne (DNP)

(M = 442.30)

1a Dielectric and pyroelectric properties of DNP single crystal were investigated by Lipscombe et al in 1980. Ferroelectric activity of DNP monomer crystal *) was discovered by Gruner-Bauer and Dormann in 1992. 80Lip 92Gru

b

phase	II	I	92Gru
state	F	P	
crystal system	monoclinic	monoclinic	a) 92Win
space group	$P2_1 - C_2^{2}$ a)	$P2_1/n - C_{2h}^{5}$ b)	b) 80Lip
Θ [K]	46 c)		c) 86Sch

$P_s \parallel b$. 86Sch

*) Thermal polymerization tends to occur in the crystal. Ferroelectric phase transition was supressed with increasing polymerization (cf. Fig. M32-006 in subsection 5a and Fig. M32-008 in subsection 5b). 80Lip

2a Crystal growth: DNP was dissolved in boiling acetone, then the solvent was evaporated from the solution by a slow stream of nitrogen. 86Sch

3a Unit cell parameters: Table M32-001.

b Z = 2. 92Win
Crystal structure: Fig. M32-001, Fig. M32-002, Fig. M32-003, Fig. M32-004.
Fractional coordinates and temperature parameters: Table M32-002, Table M32-003, Table M32-004.
Torsion angle: Table M32-005.

5a Dielectric constant: Fig. M32-005, Fig. M32-006; see also 80Lip

c Spontaneous polarization: Fig. M32-007, Fig. M32-008; see also 92Gru

6a Specific heat: Fig. M32-009.
Transition entropy: ΔS_m = 1.53(25) J mol^{-1} K^{-1}. 94Nem

13a NMR of proton: Fig. M32-010, Fig. M32-011.

Table M32-001. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). Lattice parameters and unit cell volume [92Win].

T [K]	a [Å]	b [Å]	c [Å]	β [deg]	V [Å^3]
296	5.189(5)	11.932(5)	14.729(5)	98.56(4)	901.7
145	5.126(5)	11.829(5)	14.698(5)	98.81(4)	880.7
70	5.082(10)	11.79(2)	14.66(2)	98.8(1)	866.5
5	5.036(10)	11.76(1)	14.66(2)	98.9(1)	857

Table M32-002. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). Fractional coordinates and equivalent isotropic temperature parameters B_{eq} at 296 K [92Win]. B_{eq} is defined as $B_{eq} = (4/3)(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab \cos\gamma \cdot B_{12} + ac \cos\beta \cdot B_{13} + bc \cos\alpha \cdot B_{23})$, where B_{ij} are defined by Eq. (a) in Introduction.

Atom	x	y	z	B_{eq} [Å^2]
O1	0.9315(3)	0.2173(2)	0.6693(1)	4.07(4)
O2	1.0270(4)	0.2446(2)	0.8442(1)	7.23(6)
O3	0.6992(4)	0.2908(2)	0.9076(1)	5.34(5)
O4	0.0817(4)	0.5526(2)	0.7611(2)	7.25(6)
O5	0.0119(5)	0.5601(2)	0.6131(2)	8.42(7)
N1	0.8088(4)	0.2834(2)	0.8411(1)	3.96(5)
N2	0.1288(5)	0.5258(2)	0.6857(2)	5.66(6)
C1	0.6018(5)	0.0352(2)	0.5166(2)	3.83(5)
C2	0.7747(5)	0.0964(2)	0.5443(2)	4.01(6)
C3	0.9788(5)	0.1743(3)	0.5822(2)	4.50(6)
C4	0.7363(5)	0.2918(2)	0.6692(2)	3.43(5)
C5	0.5904(5)	0.3355(2)	0.5897(2)	4.19(6)
C6	0.3962(5)	0.4122(2)	0.5954(2)	4.50(6)
C7	0.3432(5)	0.4451(2)	0.6798(2)	4.14(6)
C8	0.4767(5)	0.4028(2)	0.7597(2)	3.75(5)
C9	0.6737(4)	0.3267(2)	0.7536(2)	3.28(5)
H3A	0.993(4)	0.238(2)	0.540(1)	4*
H3B	1.136(4)	0.137(2)	0.593(2)	4*
H5	0.625(4)	0.314(2)	0.530(2)	4*
H6	0.316(4)	0.445(2)	0.541(2)	4*
H8	0.440(4)	0.422(2)	0.822(2)	4*

* Values fixed at the refinement.

Table M32-003. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). Fractional coordinates and equivalent isotropic temperature parameters B_{eq} at 145 K [92Win]. See the caption of Table M32-002 for definition of B_{eq}.

Atom	*x*	*y*	*z*	B_{eq} [Å^2]
O1	0.9379(2)	0.2201(1)	0.66989(8)	2.16(3)
O2	1.0373(3)	0.2464(2)	0.8457(1)	3.62(3)
O3	0.7031(3)	0.2940(1)	0.90973(9)	2.70(3)
O4	0.0770(3)	0.5575(1)	0.7626(1)	3.91(4)
O5	0.0026(3)	0.5655(2)	0.6138(1)	4.57(4)
N1	0.8155(3)	0.2863(1)	0.8427(1)	2.05(3)
N2	0.1249(3)	0.5305(2)	0.6868(1)	3.08(4)
C1	0.6025(4)	0.0359(2)	0.5163(1)	2.05(4)
C2	0.7788(4)	0.0987(2)	0.5438(1)	2.15(4)
C3	0.9856(4)	0.1778(2)	0.5820(1)	2.45(4)
C4	0.7399(4)	0.2951(2)	0.6702(1)	1.85(3)
C5	0.5907(4)	0.3390(2)	0.5903(1)	2.31(4)
C6	0.3933(4)	0.4169(2)	0.5959(1)	2.48(4)
C7	0.3409(4)	0.4501(2)	0.6810(1)	2.25(4)
C8	0.4775(4)	0.4072(2)	0.7612(1)	2.06(4)
C9	0.6774(3)	0.3303(2)	0.7552(1)	1.74(3)
H3A	1.001(5)	0.243(2)	0.539(2)	4*
H3B	1.147(5)	0.139(2)	0.593(2)	4*
H5	0.625(4)	0.320(2)	0.531(2)	4*
H6	0.304(4)	0.451(2)	0.541(2)	4*
H8	0.440(4)	0.429(2)	0.821(2)	4*

* Values fixed at the refinement.

Table M32-004. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). Fractional coordinates and equivalent isotropic temperature parameters B_{eq} at 5 K [92Win]. See the caption of Table M32-002 for definition of B_{eq}.

Atom	*x*	*y*	*z*	B_{eq} [Å^2]
O1	0.281(1)	0.357	0.0726(3)	0.6(1)
O2	0.229(1)	0.3309(4)	–0.1027(3)	1.1(1)
O3	0.585(1)	0.2766(4)	–0.1551(3)	0.9(1)
O4	1.184(1)	0.0154(4)	0.0122(3)	0.7(1)
O5	1.219(1)	0.0056(4)	0.1599(3)	0.9(1)
O11	1.173(1)	0.7956(3)	0.4183(2)	0.72(9)
O12	1.308(1)	0.8172(4)	0.5936(3)	0.89(9)
O13	0.987(1)	0.8692(4)	0.6663(2)	0.9(1)
O14	0.333(1)	1.1346(4)	0.5330(3)	1.1(1)
O15	0.225(1)	1.1446(4)	0.3845(3)	1.0(1)
N1	0.451(1)	0.2887(4)	–0.0933(3)	0.6(1)
N2	1.117(1)	0.0417(4)	0.0846(3)	0.5(1)
N11	1.087(1)	0.8600(4)	0.5964(3)	0.8(1)
N12	0.368(1)	1.1074(4)	0.4541(3)	0.6(1)
C1	0.617(2)	0.5414(6)	0.2284(4)	1.3(2)
C2	0.432(2)	0.4791(5)	0.1995(4)	0.4(1)
C3	0.219(2)	0.4037(5)	0.1567(4)	0.9(1)
C4	0.483(1)	0.2812(5)	0.0795(4)	0.3(1)
C5	0.619(2)	0.2365(5)	0.1630(4)	0.6(1)
C6	0.819(2)	0.1575(5)	0.1630(4)	0.7(1)
C7	0.892(2)	0.1234(5)	0.0836(4)	0.5(1)
C8	0.774(1)	0.1668(5)	–0.0018(4)	0.3(1)
C9	0.570(1)	0.2451(5)	–0.0016(4)	0.3(1)
C11	0.826(2)	0.6128(5)	0.2631(4)	0.5(1)
C12	1.002(2)	0.6782(5)	0.2903(4)	0.8(1)
C13	1.210(2)	0.7566(5)	0.3273(4)	0.7(1)
C14	0.976(2)	0.8708(5)	0.4243(4)	0.4(1)
C15	0.808(2)	0.9172(5)	0.3473(4)	1.0(1)
C16	0.620(1)	0.9950(5)	0.3561(4)	0.4(1)
C17	0.579(2)	1.0279(5)	0.4450(4)	1.0(1)
C18	0.736(2)	0.9822(5)	0.5216(4)	0.6(1)
C19	0.930(2)	0.9043(5)	0.5102(4)	1.2(2)
H3A	0.16(3)	0.349(9)	0.193(6)	2.0*
H3B	0.06(3)	0.461(8)	0.133(6)	2.0*
H5	0.57(2)	0.261(8)	0.204(6)	2.0*
H6	0.90(2)	0.131(8)	0.211(6)	2.0*
H8	0.82(2)	0.150(9)	–0.052(6)	2.0*
H13A	1.21(2)	0.820(8)	0.296(6)	2.0*
H13B	1.40(3)	0.704(8)	0.351(6)	2.0*
H15	0.80(2)	0.897(8)	0.278(6)	2.0*
H16	0.52(2)	1.020(8)	0.307(6)	2.0*
H18	0.66(2)	0.993(8)	0.568(6)	2.0*

* Values fixed at the refinement.

Table M32-005. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). Torsion angles at the joint of the diacetylene rod and the benzene rings [92Win].

Torsion angle [°]	296 K	145 K	5 K *
C5-C4-O1-C3	–4.8	–4.2	–2.4 (6.2)
C9-C4-O1-C3	174.5	175.1	176.9 (–172.1)
C4-O1-C3-C2	–72.5	–72.9	–74.0 (69.6)

* Values in parentheses correspond to the right half of the molecule in Fig. M32-001.

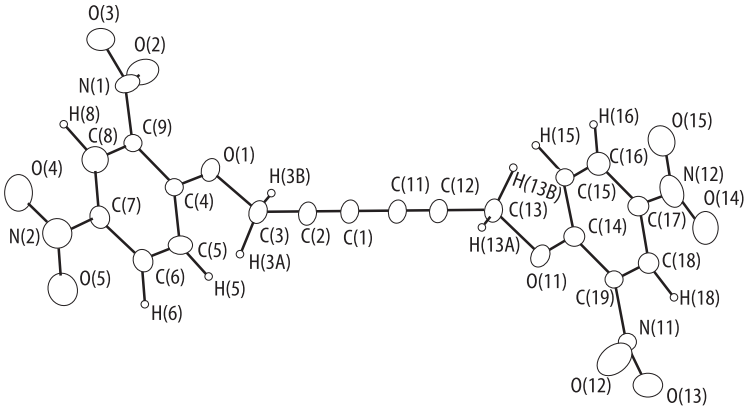

Fig. M32-001. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). DNP molecule viewed along the *a* axis in the low temperature phase [92Win].

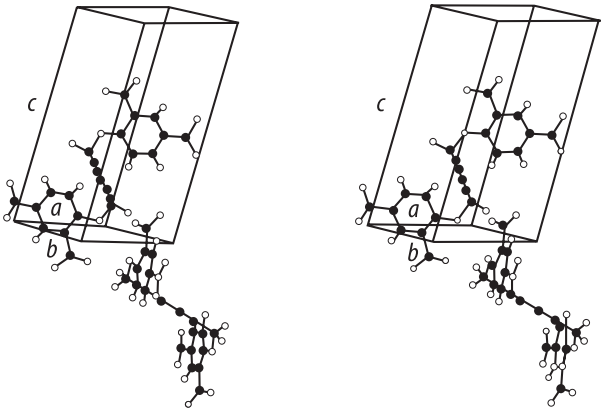

Fig. M32-002. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). Stereoscopic view of the unit cell with two molecules [92Win]. $T = 5$ K.

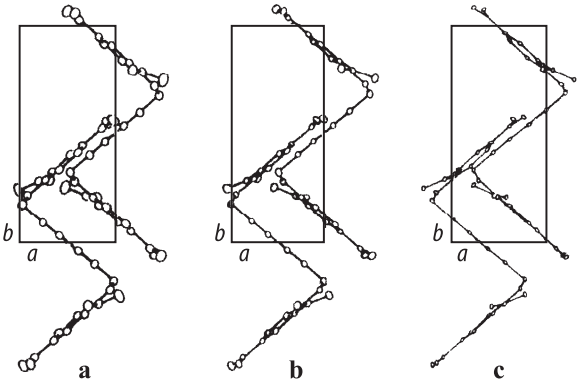

Fig. M32-003. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). Packing of the molecules viewed along the *c* axis [92Win]. (**a**) $T = 296$ K. (**b**) $T = 145$ K. (**c**) $T = 5$ K.

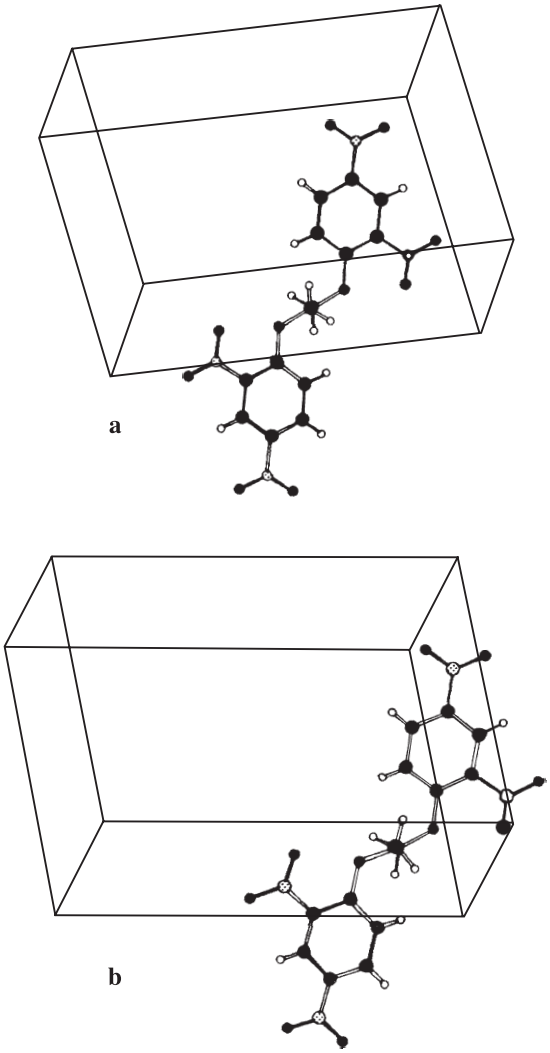

Fig. M32-004. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). Projection of a molecule along the C3–C13 chain [92Win]. (**a**) T = 145 K. (**b**) T = 5 K. For numbering of the atoms, see Fig. M32-001.

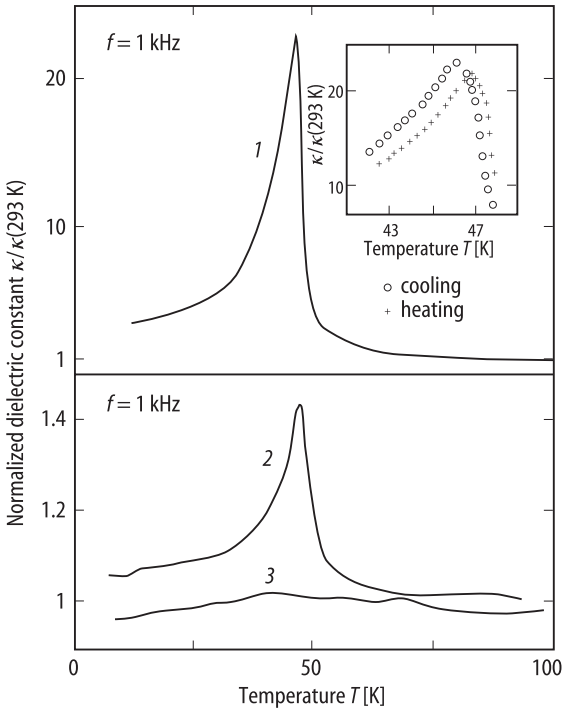

Fig. M32-005. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). $\kappa/\kappa(293\ K)$ vs. T [86Sch]. $\kappa(293\ K)$: κ at $T = 293$ K. $\kappa(293\ K) = 4(1)$. *1*: (010) plane. *2*: (001) plane. *3*: (101) plane.

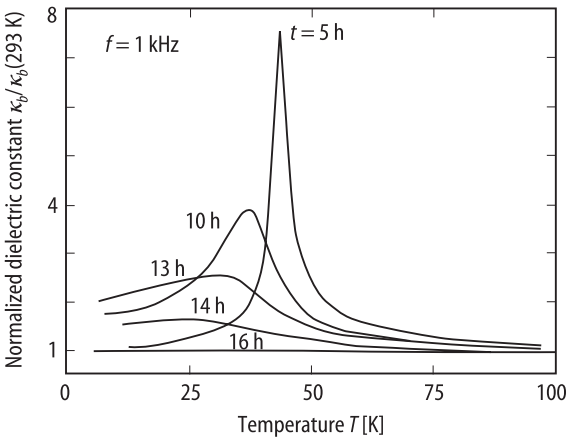

Fig. M32-006. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). $\kappa_b/\kappa_b(293\ K)$ vs. T [86Sch]. Parameter: t. t: duration of thermal polymerization at 130 °C. $\kappa_b(293\ K)$: κ_b at $T = 293$ K.

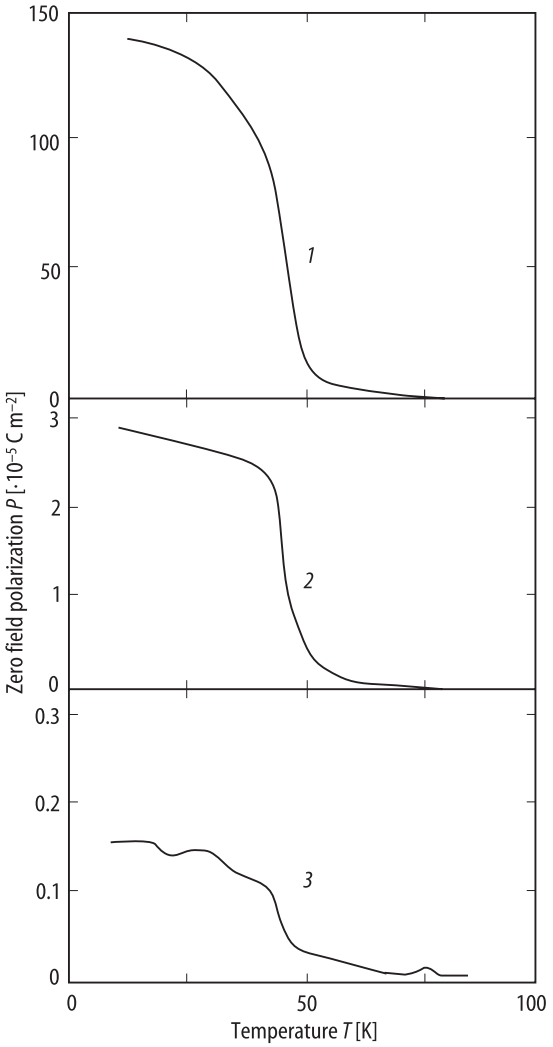

Fig. M32-007. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). *P* vs. *T* [86Sch]. *P*: zero field polarization. *1*: (010) plane. *2*: (001) plane. *3*: (101) plane.

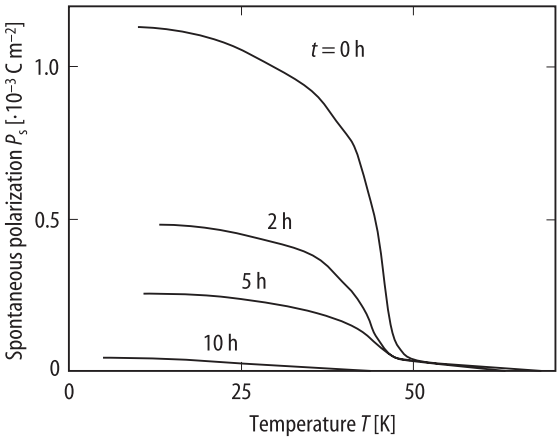

Fig. M32-008. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). P_s vs. *T* [86Sch]. Parameter: *t*. *t*: duration of thermal polymerization at 130 °C.

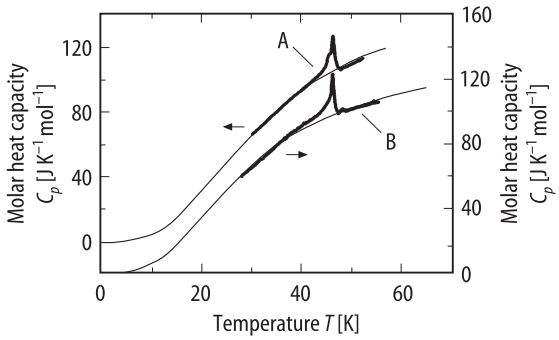

Fig. M32-009. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). C_p vs. T [94Nem]. C_p: molar heat capacity at constant pressure. Thin lines: Debye fit. The behavior A is typical for most DNP crystals, whereas B is rather an exception.

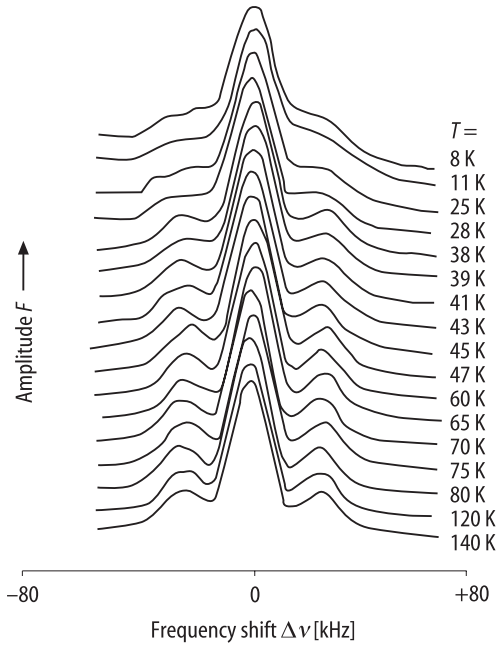

Fig. M32-010. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). F vs. $\Delta\nu$ of proton NMR spectra [92Win]. Parameter: T. F: amplitude of Fourier-transformed spectra. $\Delta\nu$: frequency shift from ν_L = 200 MHz. ν_L: proton Larmor frequency. $\boldsymbol{H} \perp \boldsymbol{a}$.

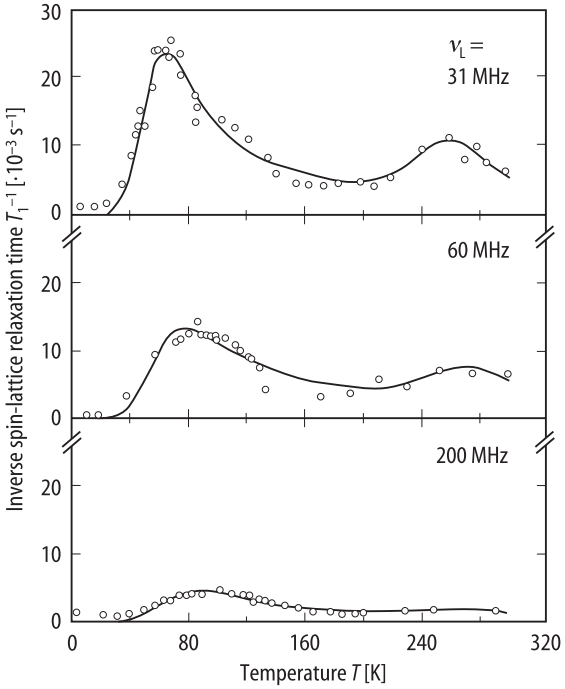

Fig. M32-011. $C_4[CH_2OC_6H_3(NO_2)_2]_2$ (DNP). T_1^{-1} vs. T for different Larmor frequencies ν_L [92Win]. T_1: spin-lattice relaxation time.

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