

Dielectric Properties of New Unsymmetrically Substituted Diacetylenes: DNP/R₂

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Z. Naturforsch. **42 a**, 413–420 (1987); received November 25, 1986

We report on the synthesis and the dielectric properties of four new unsymmetrically substituted diacetylenes: DNP/PU, DNP/4-MPU, DNP/DMPU and (+)-(R)- or (-)-(S)-DNP/MBU ((+)-/(-)- for dextro-/laevorotatory, (R)-/(S)-: Cahn-Ingold-Prelog notation for the asymmetric carbon atom). For (-)-(S)-DNP/MBU a pronounced temperature dependence of the permittivity is observed below the melting point. For thin polycrystalline pellets of (+)-(R)-DNP/MBU the poling characteristics are analysed in detail.

1. Introduction

The pioneering work of Wegner in 1969 [1] stimulated a series of investigations on the solid-state polymerization and related properties of substituted diacetylenes $R_1-C\equiv C-C\equiv C-R_2$, mostly the bis-p-toluene sulphonate of 2,4-hexadiyne-1,6-diol (pTS). For a recent summary of such results we refer to the reviews of Bässler, Sixl and Enkelmann [2]. No systematic analysis of the dielectric properties of such diacetylenes was reported until now, however. This is surprising, because it is well known that the side groups in these molecules must show large librational and vibrational amplitudes, which are necessary for the topochemical solid-state polymerization to occur. If polar side groups are attached to the diacetylene backbone, interesting dielectric properties may be expected for these materials. Indeed, a comparatively large permittivity of 7.7 was reported by Lipscomb et al. [3] for single crystals of 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP) at room temperature. DNP is a centrosymmetric diacetylene whose two side groups carry the same permanent electric dipole moment of about $1 \cdot 10^{-29}$ C m compensating each other for the static symmetry.

Recently we extended the study of the dielectric properties of DNP with the help of larger, more

perfect single crystals [4]. In contrast to the earlier report we only observed values of about 4.0 for the room temperature value of the permittivity. This is the same order of magnitude as for other diacetylenes like pTS [5, 6] or 3-BCMU [7]. In order to evaluate if unsymmetrically substituted, i.e. polar, diacetylenes give the same order of magnitude for the permittivities, we studied a series of compounds, abbreviated as DNP/R₂ in the following. At one side they carry a 2,4-dinitrophenoxy group, whereas on the other side different urethanes, including an optically active one, are added. None of these compounds polymerizes thermally or under UV irradiation. Thus they are especially well suited for investigations that require extended thermal cycling as we will report in this contribution. One of the newly synthesized compounds, the optically active DNP/MBU, melts below its decomposition temperature. Thus for (-)-(S)-DNP/MBU we were able to measure reliably the variation of the permittivity for temperatures approaching the melting point. For polycrystalline samples of (+)-(R)-DNP/MBU we furthermore analysed to what degree polycrystalline solid samples of this polar diacetylene can be poled in external electric fields.

Our report is organized as follows: in Sect. 2 we give the relevant experimental details, with the more "chemical" information collected in the appendix (Section 5). In Sect. 3 we present and discuss the experimental results on the permittivity, 3.1, and the electric polarization, 3.2, of the unsymmetrically substituted diacetylenes DNP/R₂. Our main conclusions are summarized in Section 4.

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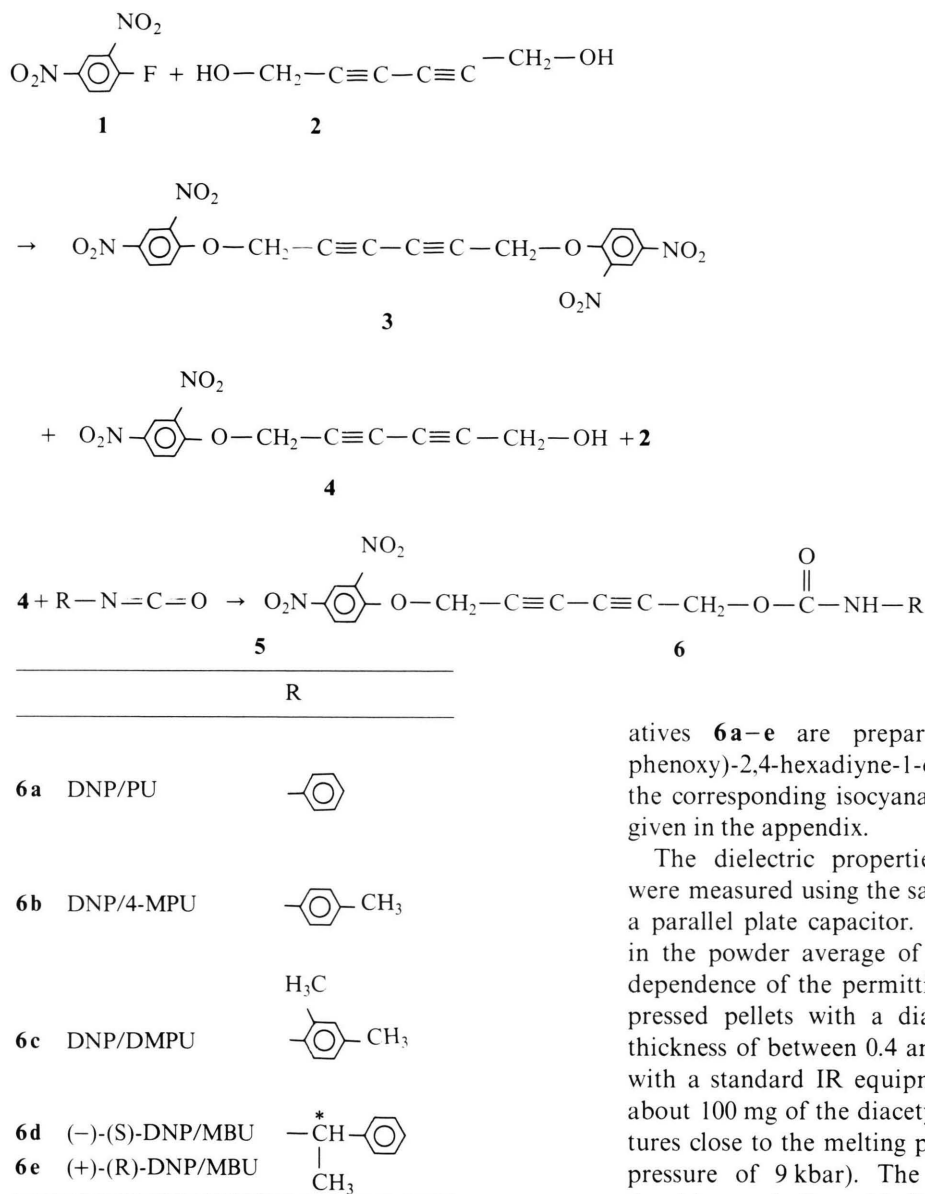
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Scheme 1.



2. Experimental Details

The synthesis of the diacetylenes with pendant polar groups is outlined in Scheme 1. 2,4-hexadiyne-1,6-diol (**2**) is reacted with one equivalent of 2,4-dinitrofluorobenzene (**1**) to yield a mixture of DNP (**3**), DNP/OH (**4**) and unreacted **2** which is separated by column chromatography [8]. The novel deriv-

atives **6a–e** are prepared from 6-(2,4-dinitrophenoxy)-2,4-hexadiyne-1-ol (DNP/OH) (**4**) and the corresponding isocyanates **5**. Further details are given in the appendix.

The dielectric properties of these diacetylenes were measured using the samples as the dielectric of a parallel plate capacitor. Since we were interested in the powder average of any possible orientation dependence of the permittivity only, polycrystalline pressed pellets with a diameter of 13 mm and a thickness of between 0.4 and 0.8 mm were prepared with a standard IR equipment (Pye Unicam) from about 100 mg of the diacetylenes **6a–e** (at temperatures close to the melting point and with an applied pressure of 9 kbar). The corresponding effective densities are indicated in Table 1. Different types of contacts were used, either silver-paste contacts (Ag in Table 1) or aluminum foils (Al) or evaporated gold films (Au). For repeated thermal cycles between room temperature and 4 K the silver contacts proved most reliable. The capacitances of the parallel-plate sample capacitors were measured either with a commercial RLC bridge or with a home-built, microprocessor-controlled setup using in- and out-of-phase lock-in detection at a fre-

Compound	Contact	Eff. dens. (g cm ⁻³)	ϵ'_r (293 K) (RLC-bridge)	ϵ'_r (293 K) (lock-in set up)	ϵ'_r (10 K)
DNP/PU	Ag	1.28	4.6 ± 0.8	4.55 ± 0.5	3.87 ± 0.5
	Au	1.29	4.14 ± 0.8	4.5 ± 0.5	4.0 ± 0.5
DNP/4-MPU	Ag	1.25	2.72 ± 1.0	3.05 ± 0.6	2.86 ± 0.6
	Au	1.29	2.79 ± 1.5	2.69 ± 0.9	2.45 ± 0.9
DNP/DMPU	Ag	1.09	3.24 ± 0.8	3.35 ± 0.3	3.14 ± 0.3
	Au	1.26	3.88 ± 0.8	3.7 ± 0.4	3.30 ± 0.4
(–)-(S)-DNP/MBU	Al	1.28	3.1 ± 0.8	3.03 ± 0.3	2.70 ± 0.3
	Al	1.45	3.1 ± 0.8	3.2 ± 0.3	2.8 ± 0.3
(+)-(R)-DNP/MBU	Ag	1.05	2.97 ± 0.7	3.09 ± 0.2	2.86 ± 0.2

Table 1. Dielectric properties for pressed pellets of unsymmetrically disubstituted diacetylenes DNP/R₂. The measuring frequency was 1 kHz.

quency of 1 kHz. The relatively large error bars of the permittivities given in Table 1 are due to the limited accuracy of the evaluation of the geometrical dimensions of the sample capacitors – the relative accuracy and the reproducibility were at least one order of magnitude better.

The electric polarization introduced by poling polycrystalline pressed-pellet samples of (+)-(R)-DNP/MBU close to the melting point was studied in two ways:

i) The poling-induced electric polarization was derived with the help of the charge-integration technique developed by Glass [9] as $\Delta P = \Delta Q/F$ (where F is the sample surface area) during warming-up of the sample in zero applied external field (i.e. thermally stimulated depolarization) after cool-down from high temperature with applied poling field, or

ii) after cool-down with poling field the thermally stimulated current $I(T, t)$ flowing from the electrode sample surfaces was measured during heating-up of the sample with an approximately constant rate dT/dt . Evidently

$$\Delta P = \Delta Q/F = (1/F) \int_{T_{\min}}^{T_{\max}} I(T, t) (dT/dt)^{-1} dT. \quad (1)$$

For more details of the experimental set-up used for the measurement of the dielectric and pyroelectric properties we refer to [4].

3. Experimental Results and Discussion

3.1. Permittivity

Figure 1 shows typical examples of the temperature dependence of the relative dielectric constant

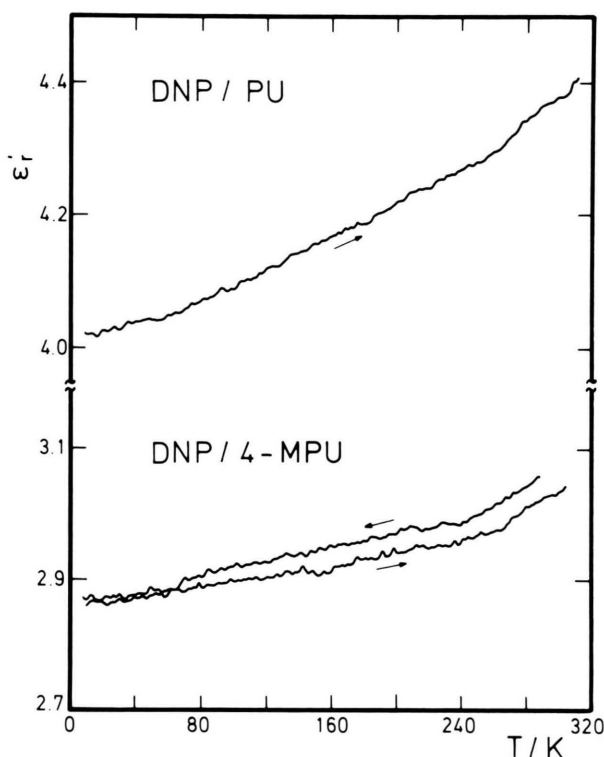


Fig. 1. Temperature dependence of the permittivity (relative dielectric constant, ϵ'_r) for polycrystalline pressed-pellet samples of DNP/PU (gold electrodes) and DNP/4-MPU (silver paste electrodes). The data were taken at 1 kHz measuring frequency during heating for DNP/PU and during cooling and heating for DNP/4-MPU.

for the unsymmetrically substituted diacetylenes DNP/R₂. In contrast to materials with only electronic polarizability, where the permittivity generally decreases with increasing temperature due to the diluting influence of the volume expansion, an increase of about 10% between 10 K and room

temperature is observed here (see also Table 1). This behaviour is characteristic for a dipolar polarizability [7]. For temperatures below 300 K, the relaxation time for dipole orientation of the whole polar molecule is infinite compared to the time scale of the measurement for the diacetylenes studied here. With increasing lattice expansion, the free volume left for a limited molecular reorientation increases, however, and likewise does the measured permittivity. The room temperature values of the relative dielectric constant reside in the range of 2.5 to 5, which can be considered typical for monomer crystals of disubstituted diacetylenes. DNP/PU, with the smallest side group R₂, shows the largest permittivity.

Figure 2 shows the temperature dependence of the permittivity for a pressed-pellet sample of (–)-(S)-DNP/MBU at temperatures close to its melting point. In this temperature range, the relaxation frequency (rate) for dipolar orientation increases strongly, approaching finally the measuring frequency of 1 kHz and leading to typical paraelectric behaviour. For these measurements, (–)-(S)-DNP/MBU was especially appropriate, since it melts before any detectable decomposition takes place. Furthermore, the transition region is more extended than in the lower-melting (+)-(R)-DNP/MBU (possibly caused by the limited isomeric purity of about 98%). We restrict our discussion here to the high temperature asymptotic behaviour – a more detailed analysis of the frequency dependence of the real and imaginary part of the permittivity will be reported elsewhere, with special emphasis also on the related diacetylene (–)-(S)-NP/MBU, which polymerizes thermally or under UV irradiation at least partially. If we assume, that at the highest temperature shown in Fig. 2 the isotropical average of a liquid for the molecular positions is already reached, we can use the Clausius-Mosotti relation [10]

$$(\epsilon_r - 1)/(\epsilon_r + 2) = (3\epsilon_0)^{-1}(N/V)p^2/(3k_B T) \quad (2)$$

in order to estimate the molecular dipole moment p from $\epsilon_r(340\text{ K}) = 20$ and the approximate density taken from Table 1. The resulting value of $p = 1.3 \cdot 10^{-29}\text{ C m}$ for the molecular electric dipole moment of DNP/MBU compares favourably with that of the DNP side group, i.e. $p(\text{DNP}) = 1 \cdot 10^{-29}\text{ C m}$ [3]. These experimental results demonstrate, that large permittivities can be obtained with di-

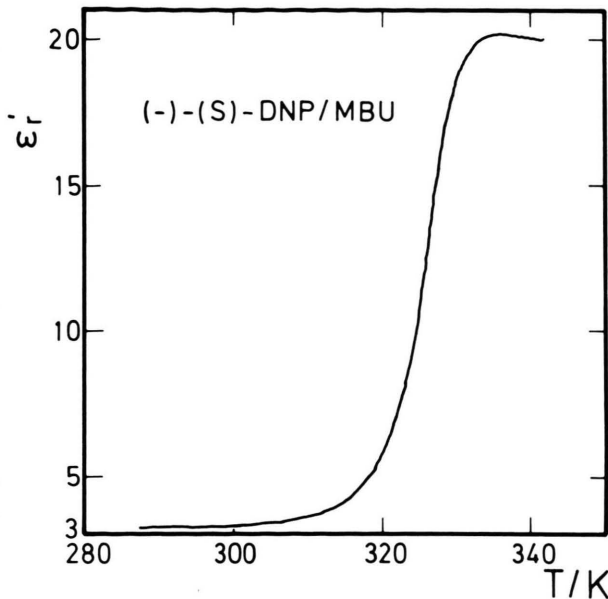


Fig. 2. Temperature dependence of the real part (ϵ'_r) of the permittivity for a pressed-pellet sample of (–)-(S)-DNP/MBU for temperatures approaching the melting point, measured at a frequency of 1 kHz.

acetylene monomers of polar molecular structure, even in the case that cooperative effects [6] play no important role, provided, however, that the free volume is sufficiently large.

3.2. Electric Polarization

Since both enantiomers of the optically active diacetylene DNP/MBU melt before any appreciable decomposition takes place, highly compact thin-parallel-plate samples can easily be prepared. These poly- or microcrystalline plates can be poled in an electric field at elevated temperature. Figure 3 shows the thermally stimulated depolarization of (+)-(R)- and (–)-(S)-DNP/MBU after poling with about 1 MV/m field strength. The total electric polarization derived is of the order of $0.5 \cdot 10^{-8}\text{ C cm}^{-2}$. This value lies in the range typical for electrets [11]. The electric field strength required to obtain such polarization is, however, too small for appreciable charge carrier injection; thus we can exclude that we are producing standard space-charge or surface-charge electrets. However, we could not discriminate between dipole alignment and charge separation as potential polarization mechanisms without a detailed analysis. Indeed, the Maxwell-

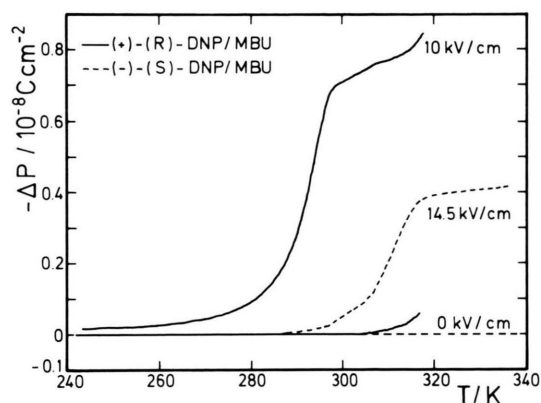
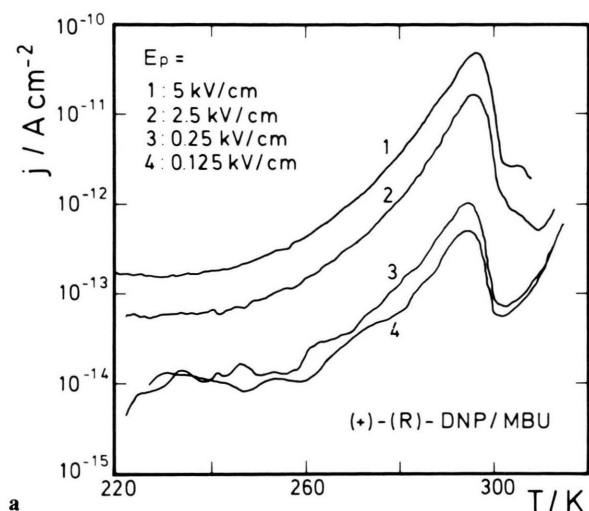


Fig. 3. Thermally stimulated depolarization of a polycrystalline thin-parallel-plate sample of (+)-(R)-DNP/MBU ((-)-(S)-DNP/MBU) with a sample thickness of 0.40 mm (0.55 mm). Prior to the measurement, the sample was polarized by applying an electric field of the strength E_p indicated in the figure at $T_p = 310$ K (340 K) for $t_p = 45$ min (30 min) and during cool-down to $T_{\min} = 200$ K (260 K).

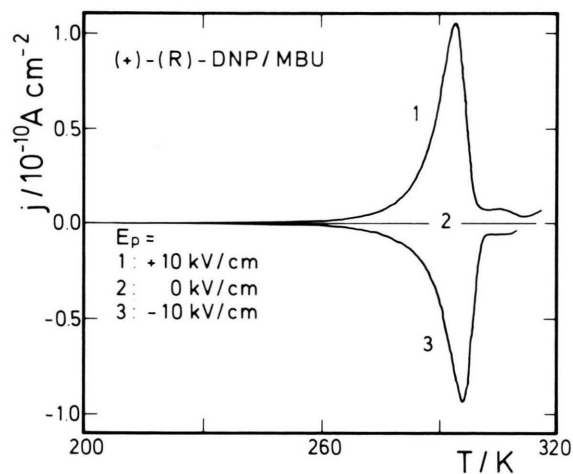
Wagner effect, where during poling the charges are separated and accumulated near interfaces, is a well-known origin of polarization in polycrystalline samples [11]. But such charge build-up is usually slow, whereas relatively fast poling was observed here.

In order to delineate the origin of the polarization obtained, we studied the thermally stimulated current (TSC) and depolarization in dependence of sample preparation, poling field strength E_p , poling temperature T_p , poling duration t_p , heating rate dT/dt and discharge time – see Figs. 4, 5, and 6 for examples. A weak dependence of the effective sample permittivity on previous poling history was detected too, but will not be discussed here. (+)-(R)-DNP/MBU was used for these detailed investigations, since it could easily be poled close to room temperature. Furthermore, no measurable decay of its poling-induced electric polarization could be observed, even when the poled sample was stored in zero applied field at a temperature below 220 K for more than 4 days.

As it can be realized from an inspection of the spurious depolarization visible in Fig. 3 (which was observed without earlier application of a poling field, $E_p = 0$), for (+)-(R)-DNP/MBU (ohmic) conduction becomes significant only at temperatures above 305 K on the time scale of the measurement. Two different processes must be considered accord-



a



b

Fig. 4. Thermally stimulated current $j(T) = I(T, t)/F$ for a polycrystalline thin-parallel-plate sample of (+)-(R)-DNP/MBU (thickness 0.40 mm). After poling at $T_p = 310$ K for $t_p = 45$ min and cool-down to $T_{\min} = 200$ K, the sample was heated (Fig. 4a) with a constant rate of $dT/dt = 5.2$ K/min (3.4 K/min) at temperatures above (below) 260–265 K, while the depolarization current was measured under short-circuit conditions. For the linear scale examples (Fig. 4b) the heating rate was constant at $dT/dt = 5.3$ K/min.

ing to our experimental observations – there are two peaks in the TSC-curves (Fig. 4) and two time constants of the polarization decay, depending differently on temperature, as it can be discerned in Figure 5. Our experimental results are in keeping with the interpretation, that the dominating low-temperature TSC-peak ($T_m = 296$ K in Fig. 4)

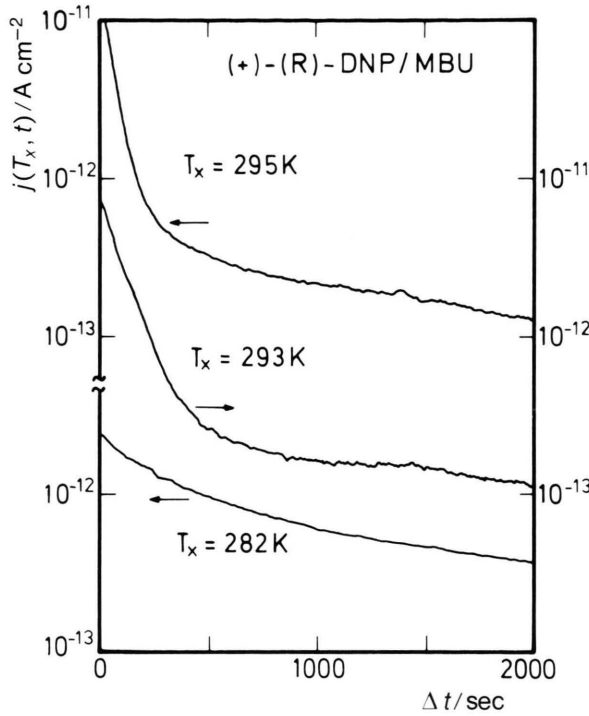


Fig. 5. Time dependence of the thermally stimulated current $j(T_x, t) = I(T_x, t)/F$ at fixed temperature $T_x = 295$ K and 282 K (left hand scale) and 293 K (right hand scale). After poling with $E_p = 10$ kV/cm at $T_p = 310$ K for $t_p = 60$ min and during cool-down to $T_{\min} = 220$ K, the temperature was raised under short-circuit conditions to the measurement-temperature T_x in a time interval being short compared to that for complete thermally stimulated discharge.

originates from the disorientation of dipoles; the weak high-temperature structure ($T_h = 305$ K) might be due to a space charge effect – for example its dependence on poling field E_p seems to be non-linear –, but here a reliable analysis is prohibited by non-negligible sample conduction and proximity of the melting point.

The linear dependence on poling field strength – see Fig. 6 – for the TSC-maximum $j_m(T_m)$ or for the total depolarization ΔP (for $T_{\max} = 300$ K in (1)) support our conclusion. A further support stems from the independence of the TSC-peak temperature T_m on polarization temperature T_p or from the variation of the TSC-maximum $j_m(T_m)$ with the heating rate dT/dt [11].

In the temperature range shown in Fig. 5, the decay of the dipole polarization with the dipole-relaxation frequency (rate) R_d dominates the short

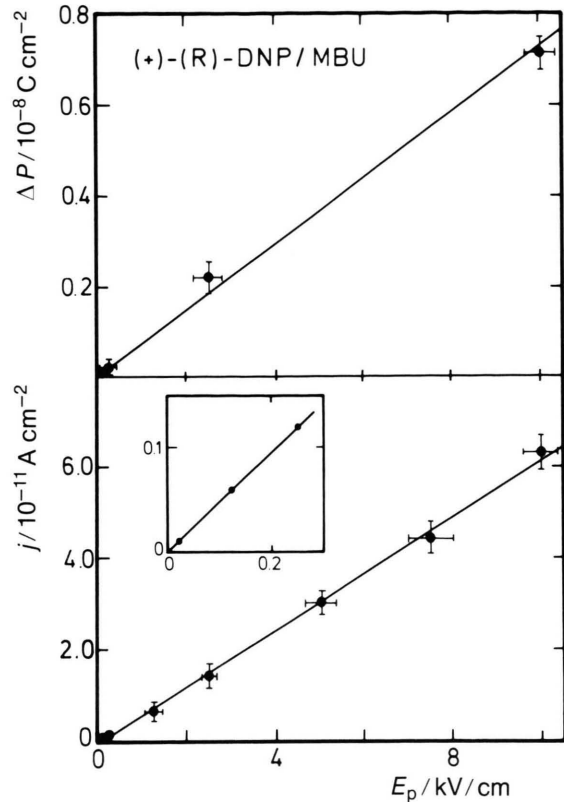


Fig. 6. Dependence of the total thermally stimulated depolarization $\Delta P(T_{\max} = 300$ K) (Fig. 3) and of the maximum thermally stimulated current $j_m(T_m = 295$ K) (Fig. 4, for heating rate $dT/dt = 3.4$ K/min) on field strength E_p of poling electric field ($T_p = 310$ K, $t_p = 45$ min). The insert shows the current- versus low-field data on a extended scale.

time behaviour of the current $j(T_x, t)$:

$$j(T_x, t) = d/dt P(T_x, t), \quad (3a)$$

$$P(T_x, t) = \Delta P_d \exp[-R_d(T_x) t] + \Delta P_h \exp[-R_h(T_x) t]. \quad (3b)$$

The temperature dependence of the dipole relaxation rate $R_d(T_x)$ can reasonably be described by

$$R_d(T) = R_{0,d} \exp(-W_d/k_B T) \quad (4)$$

with an activation energy of $W_d = 1.5$ eV and a preexponential factor $R_{0,d} = 8.5 \cdot 10^{23} \text{ s}^{-1}$. (In contrast, for the second, smaller decay rate $R_h(T)$ we derive an activation energy of $W_h = 0.19$ eV and $R_{0,h} = 1.2 \text{ s}^{-1}$.) At temperatures below 270 K, the dipole relaxation ($R_d(T)$) is slower than the other depolarization process with the smaller activation energy. In agreement with this, from the low-

temperature TSC initial slope we estimate with [11]

$$d/d(1/T) \ln j(T) = -W_{\text{in}}/k_B \quad (5)$$

poorly defined values W_{in} that lie at about 150 meV or even up to an order of magnitude lower.

The temperature of the TSC-peak (Fig. 4) and its shift with variation of the heating rate was compared with the relation appropriate for a pure dipole peak [11]

$$T_m^2 = (dT/dt) (W_m/k_B) R_d^{-1} (T_m). \quad (6)$$

Here we found values of $2.37 \text{ eV} < W_m < 2.54 \text{ eV}$ for heating rates of $3.3 \text{ K/s} \leq (dT/dt) \leq 5.4 \text{ K/s}$. Finally, from the widths at half height, ΔT , of the TSC peaks (see e.g. Fig. 4b), we derived with the relation [11]

$$\Delta T/T_m \cong 2.47 k_B T_m / W_w \quad (7)$$

values of $2.0 \text{ eV} < W_w < 2.6 \text{ eV}$ for the corresponding activation energy. Thus we conclude that the activation energy for the dominating dipole orientation process is relatively well defined with $W_d \cong W_m \cong W_w \cong 2 \text{ eV}$ (or 190 kJ/mole). This value seems reasonable for the barrier height of a side group reorientation in the solid. In contrast, the origin of the weak additional polarization and depolarization (with $T_h \cong 305 \text{ K}$, $W_h \cong 0.19 \text{ eV}$, $0.005 \text{ eV} < W_{\text{in}} < 0.15 \text{ eV}$) could not be definitively elucidated here. The differences in the smaller activation energies ($W_h \neq W_{\text{in}}$) may point to a distribution of activation energies (trap depths?) or to a temperature dependence of the prefactor in an equation analogous to (4). Under our presented experimental conditions, this additional contribution always was below 10% of the total polarization, anyhow.

Let us finally discuss the absolute value of the poling-induced electric polarization. The maximum depolarization detected (Fig. 6) is several hundred times smaller than the polarization which would be obtained, if all DNP molecular dipoles of the complete sample would be aligned by cooperative effects. It might thus stem from small orientable pyroelectric portions of the sample, only. On the other hand, the polarization observed compares favourably with the equilibrium polarization resulting from orientation of all dipoles of the sample, if these are considered to be independent,

$$\Delta P = \frac{\varepsilon_r + 2}{3} \frac{(N/V) (p^2/3 \varepsilon_0 k_B T_p)}{1 - (1/3) (N/V) (p^2/3 \varepsilon_0 k_B T_p)} \varepsilon_0 E_p. \quad (8)$$

The calculated value of $p = 1.2 \cdot 10^{-29} \text{ C m}$ is quite reasonable for a DNP side group (or also for a polarizable $\text{C}=\text{O} \cdots \text{H}-\text{N}$ hydrogen bridge bonding). Our discussion has thus shown, that the pressed-pellet samples of the optically active diacetylene (+)-(R)-DNP/MBU behave very similar to amorphous solids, when their poling characteristics are considered.

4. Concluding Remarks

In the investigation of the dielectric properties of the polar, unsymmetrically substituted diacetylenes DNP/R₂ we found room-temperature permittivities of monomers in the range of about 2.5 to 5. Thus the permittivity of crystalline diacetylenes with polar side groups is comparable to that of many other organic solids. The permittivity increases with increasing temperature. This can be understood as the consequence of the lack of mobility of the polar side groups due to restricted free volume in the low-temperature solid. High values of the permittivity for the polar monomeric diacetylenes DNP/R₂ are found, if the temperature approaches the melting point. However, the permittivity is not as high as in the case of the transition to the pyroelectric low temperature phase in DNP [4], where cooperative effects play an important role.

Both enantiomers of the newly synthesized optically active diacetylene DNP/MBU have properties that may be interesting for different kinds of applications. Since they melt without decomposition at 45 °C and 74 °C, polycrystalline samples of arbitrary shape can easily be prepared. Pronounced temperature dependence of the permittivity just above room temperature and storage of the polarization obtained by poling little above room temperature with weak electric fields have been shown for (-)-(S)- and (+)-(R)-DNP/MBU, respectively.

Acknowledgements

D. Heindl, J. Gmeiner, and I. Müller helped in the sample preparation and G. Denninger in the data analysis. We thank M. Schwoerer, M. Schott, and G. Wegner for discussions. This work was supported by the Emil-Warburg-Stiftung and by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 213, Universität Bayreuth).

5. Appendix

DNP/OH (**4**) was synthesized similar to a method described by Kalyanaraman *et al.* [8].

DNP/PU (**6a**): In a 100 ml three necked flask 1.38 g (5 mmol) of DNP/OH (**4**) and 0.71 g (6 mmol) of phenylisocyanate were dissolved in 40 ml of dry tetrahydrofuran. Five drops of dibutyltindilaurate and triethylamine were added as catalysts and the mixture was heated to 50 °C for three hours. After cooling, the mixture was poured into cold hexane. The solid residue was filtered off and recrystallized from ethanol to yield 1.49 g (75%) of yellow crystals.

All the diacetylenes **6b–e** were prepared by the same method. For the synthesis of **6d** and **6e**, the optically active isocyanates **5** (about 98% isomeric purity) were used. **6d** and **6e** were purified by column chromatography on silica gel with dichloromethane as eluent.

Analytical Data

Melting points: **6a**: 165 °C, **6b**: 146 °C, **6c**: 133 °C, **6d**: 74 °C, **6e**: 45 °C.

IR (KBr): 3390 (s; NH), 1740 (s; C=O), 1535, 1350 cm⁻¹ (s; NO₂).

6a :	C ₁₉ H ₁₃ N ₃ O ₇	(395.32)			
	calc.	C 57.73	H 3.31	N 10.62	O 28.33
	found	C 57.85	H 3.36	N 10.5	O 27.7
6b :	C ₂₀ H ₁₅ N ₃ O ₇	(409.35)			
	calc.	C 58.68	H 3.69	N 10.27	O 27.36
	found	C 59.28	H 3.79	N 10.1	O 27.6
6c :	C ₂₁ H ₁₇ N ₃ O ₇	(423.37)			
	calc.	C 59.58	H 4.05	N 9.93	O 26.45
	found	C 60.44	H 4.10	N 9.9	O 25.4
6d :	C ₂₁ H ₁₇ N ₃ O ₇	(423.37)			
	calc.	C 59.58	H 4.05	N 9.93	O 26.45
	found	C 58.85	H 4.10	N 9.9	O 27.2
6e :	C ₂₁ H ₁₇ N ₃ O ₇	(423.37)			
	calc.	C 59.58	H 4.05	N 9.93	O 26.45
	found	C 60.06	H 4.30	N 9.59	O 25.5

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