sign of the pyroelectric coefficient is connected with the hydrogen bond system in this solid as well as in MNA.

Table 2.: Pyroelectric Coefficients of some Benzene Derivatives.

Compound	Space group	$\vec{p}^x/(\mu C m^{-2} K^{-1})$	Remarks	Ref.
1-Br-4-(CN)C$_6$H$_4$	C_s^3-Cm	24....170 100 ≤ T/K ≤ 370	order - disorder phase transition	/9/
1-NO$_2$-4-(CN)C$_6$H$_4$	C_2^2-P2$_1$	0.35....5.0 100 ≤ T/K ≤ 375	phase transition	/9/
1-Cl-3-(NO$_2$)C$_6$H$_4$	C_{2v}^9-Pna2$_1$	5.7.... 11.2 100 ≤ T/K ≤ 310		/9/
1,3-(NO$_2$)$_2$ C$_6$H$_4$	C_{2v}^9-Pna2$_1$	+4.....-13 120 ≤ T/K ≤ 320	sign reversal of $\vec{p}^x$	/14/
1-NH$_2$-3-(NO$_2$)C$_6$H$_4$	C_{2v}^5-Pbc2$_1$	-5.....+11 90 ≤ T/K ≤ 350	sign reversal of $\vec{p}^x$	/7/
1-NH$_2$-3-(OH)C$_6$H$_4$	C_{2v}^5-Pca2$_1$	24.....47 100 ≤ T/K ≤ 330		/7/
1,2-Cl$_2$-3-(OH)C$_6$H$_3$	$C_3^{2,3}$-P3$_{1,2}$	-11.....+0.3 100 ≤ T/K ≤ 270	sign reversal of $\vec{p}^{*x}$	/7/

Conclusion

Comparing the pyroelectric coefficients of the benzene derivatives studied, we find a wide spread of $p^x = f(T)$. In Table 2 some results are summarized.

The investigation of pyroelectricity is somewhat cumbersome since it starts with the growth of crystals of good size (1 cm^3 and more). Furthermore, the accuracy in measurement of $\vec{p}^x$ is limited by several facts, particularly by the quality of the crystal available. However, there is an interesting observation in the field of nonlinear optics which may give some useful link to the pyroelectricity in crystals of aromatic compounds. An exceptionally large optical second harmonic coefficient was observed in 1-NH$_2$-2-CH$_3$-4-(NO$_2$)C$_6$H$_3$ [4, 5]. The partial dipole moment of the electronegative NO$_2$-group points in the same direction as that of the electropositive groups in the 1-position (NH$_2$) and in the 2-position (CH$_3$). The space group in which 1-NH$_2$-2-CH$_3$-4-(NO$_2$)C$_6$H$_3$ crystallizes is C_s^4-Cc, $Z = 4$. It may be quite an interesting task to study both, the optical behaviour, such as second harmonic generation, and the pyroelectric coefficient. This would give some inside into the problem of

hyperpolarizability of aromatic compounds. Other possible candidates in this group of aromatic solids would be 1-Cl-3-NO$_2$-6-(NH$_2$)C$_6$H$_3$, space group C_{2v}^9-Pna2$_1$, $Z = 4$ [20] and the analogues Br-compounds.

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Preparation, Crystal Structure and Dielectric Properties of the New Unsymmetrically Substituted Diacetylenes NP/R₂

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Crystal Structure / Dielectrics / Dipole Moment / Electrical Properties

We report on the preparation, the crystal structure and the dielectric properties of several new unsymmetrically substituted diacetylenes $R_1 - C \equiv C - C \equiv C - R_2$ of the general constitution NP/R$_2$. They carry a polar nitrophenoxy-group on one side and different urethanes on the other.

1. Introduction

Substituted diacetylenes of the form $R_1 - C \equiv C - C \equiv C - R_2$ are very attractive systems for an attempt to taylor physical properties of crystalline organic materials at will. When appropriate substituents are chosen, macroscopic monomer single crystals can be grown. Via solid state polymerization, they can be converted into polymer single crystals of high perfection [1]. During the last decade, this topochemical reaction was studied by various groups with many different techniques [2]. Furthermore, different procedures of the preparation of thin films were reported. And in particular, the substituents R_1 and R_2 of the central diacetylene unit can be varied in a systematic manner.

Therefore, three years ago, we started a research project within the SFB 213, where chemists and physicists cooperate in exploring the potential of crystalline, substituted diacetylenes as monomeric and polymeric materials with interesting dielectric and pyroelectric properties. The basic idea is the incorporation of side-groups with large permanent electric dipole moments. For one series of compounds we use two identical polar side-groups. In these systems we analyse to what degree soft bending or twisting motions of the originally centrosymmetric molecular unit lead to large permittivities or pyroelectric canted low-temperature crystallographic structures. The second development line provides for the incorporation of two different side-groups with only one of them carrying a substantial electric dipole moment. But unfortunately also in this attempt only a systematic and time-consuming trial allows to identify those compounds exhibiting also a non-centrosymmetric crystalline structure.

We reported before, that DNP (1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne) [3] is an example for a symmetrically substituted diacetylene, that shows a pyroelectric low-temperature phase of the monomer-crystal despite its originally centro-symmetric molecular unit. A well-defined phase transition was observed in the dielectric properties, with a pronounced maximum of the permittivity at about 46 K and spontaneous electric polarization in the direction of the two-fold b-axis below that temperature [4]. The direction of this polarization could not be inverted by means of an external electric field (< 7 kV/cm), as is typical for a pyro-, non-ferroelectric phase. The dielectric properties implied the loss of a mirror plane in the point symmetry of the low-temperature phase. Recently, this low-T crystal structure was solved by Bertault [5]. The space group was identified as $P2_1$ ($Z = 2$). The structural change corresponds to an intramolecular twisting of $5°$ between the planes of the aromatic groups, which is accompanied by a very weak reorientation of the NO_2-groups with respect to the benzene rings.

The symmetrically disubstituted diacetylene IPUDO (Isopropylurethane, dodecadiyne) is an example, where non-centrosymmetric crystal structures are observed for monomer as well as polymer crystals despite a centrosymmetric molecular building unit [6]. Since deviations from centro-symmetry were observed also in the most thoroughly studied diacetylene pTS (bis-p-toluene sulfonate of 2,4-hexadiyne-1,6-diol) [7] we conclude that distorted structures are evidently not exceedingly rare for disubstituted diacetylenes.

We also began to study different unsymmetrically substituted diacetylenes. A report on synthesis and dielectric properties of a series of diacetylenes with the general constitution DNP/R_2 is given in Ref. [8]; these diacetylenes carry a polar dinitrophenoxy-group on one side and different urethanes, including an optically active one, on the other side. The synthesis and a first characterization of the polar diacetylene TS/FBS will be published elsewhere [9]. In this report we will concentrate on the series of new unsymmetrically substituted diacetylenes with the polar nitrophenoxy-group on one side and different urethanes on the other, abbreviated as NP/R_2.

2. Experimental Details

2.1. Synthesis and Chemical Characterization

4-Nitrophenyl-2-propynyl ether (1)

The product was obtained by a method similar to that described by Appriou et al. [10].

To a solution of 1-bromo-2-propyne (34.5 g) and 4-nitro-phenol (41.7 g) in dry acetone (150 ml), K_2CO_3 (49.8 g) was added and the mixture was refluxed for 20 hours. After cooling the mixture was filtered and the residue washed with acetone. Evaporation of the acetone and recrystallization from ethanol yielded 32.4 g (63%) yellow needles; m.p. 113°C.

3-Bromo-2-propynyl-4-nitrophenyl ether (2)

The product was obtained according to the method of Garito [11].

To a solution of KOBr in water (22.4 g KOH, 5 ml Br_2 and 100 ml H_2O) 8.86 g of 1 in 1,4-dioxane (100 ml) were added dropwise at 5°C. After additional stirring for 1 hour at room temperature the solution was poured into 400 ml of ice/water, the precipitate filtered off and washed neutral with water. Drying over P_2O_5 yielded 12.4 g (97%) of a white powder; m.p. 158°C.

6-(4-Nitrophenoxy)-2,4-hexadiyne-1-ol (3, NP/OH)

The product was prepared by modification of the method of Garito [11].

To a suspension of cuprous chloride (200 mg), ethylamine (70%, 8 ml) and hydroxylamine hydrochloride (1.0 g) in water (40 ml), a solution of 2-propyne-1-ol (3.88 g) in N,N-dimethyl-acetamide (40 ml) was added dropwise. Afterwards 10.24 g of 2 in 80 ml of N,N-dimethyl-acetamide were added at 30°C. After stirring for 1 hour at 30°C, the mixture was treated with 400 ml ice/water, the precipitate filtered off and recrystallized from methanol to yield 6.67 g (72%) of short yellow needles; m.p. 172°C.

NP/PU (4a)

To a solution of phenylisocyanate (3.08 g) and 5.0 g of 3 in 50 ml dry THF 5 drops of dibutyltin-dilaurate and 5 drops of triethylamine were added. The mixture was kept at 50°C for 3 hours and then poured into 100 ml of ice-cold hexane with vigorous stirring. The precipitate was filtered off and washed with hexane (60 ml). The material was purified by recrystallization from toluene. Yield 5.60 g (74%); m.p. 128°C.

IR (KBr): 3320, 1700, 1540, 1340 cm^{-1}.

^{1}H-NMR (acetone-d$_6$): $\delta = 8.2 - 8.3$ (m, 2H); 7.0 - 7.6 (m, 7H); 5.14 (s, 2H); 4.88 (s, 2H).

The diacetylenes 4b and 4c were prepared by the same method. Melting points: 4b: 119°C (dec.); 4c: 102°C.

The elemental analyses of the diacetylenes NP/R_2 are given in Table 1.

Table 1
Elemental analysis

	C	H	N	O
4a: $C_{19}H_{14}N_2O_5$ (350.26)				
calc.	65.14	4.03	8.00	22.83
found	64.52	4.10	8.18	21.5
4b: $C_{20}H_{16}N_2O_5$ (364.26)				
calc.	65.93	4.43	7.69	21.96
found	65.95	4.47	7.81	21.8
4c: $C_{21}H_{18}N_2O_5$ (378.37)				
calc.	66.66	4.80	7.40	21.14
found	66.54	4.98	7.83	19.3

2.2. Crystal Growth

NP/4-MPU (4b)

a) from 2-propanol (NP/4-MPU(p))

NP/4-MPU (1.0 g) was dissolved in 50 ml of hot 2-propanol. The solution was filtered and then cooled from 65°C to 25°C with a rate of 1°C per hour; small light yellow plates. Size $15 \times 2 \times 1$ mm³.

b) from methanol (NP/4-MPU(m))

NP/4-MPU (1.0 g) was dissolved in 70 ml of hot methanol. The solution was filtered and then cooled from 65°C tö 25°C with a rate of 0.5°C per hour; small colourless needles, which rapidly turned blue on exposure to light.

2.3. UV-Polymerization

The finely powdered diacetylenes (100 mg) were suspended in 150 ml of water and irradiated under vigorous stirring in a quartz Erlenmeyer-flask with a 200 W UV-lamp.

The suspension was filtered through a 0.45 µm filter, the residue washed with acetone (30 ml) to dissolve unpolymerized material. The polymer remaining in the filter was weighed after drying. To prove the correctness of the analysis, the amount of residual monomer was determined after evaporation of the solvent.

Table 2
Polymerizability of diacetylenes NP/R_2

NP/R_2	thermal	UV
NP/PU	—	(+)
NP/4-MPU	—	(+)
(+)-(R)-NP/MBU	(+)	(+)

2.4. Measurement of the Dielectric Properties

The dielectric properties of the different diacetylenes NP/R_2 were characterized for temperatures between 4 K and room-temperature using the samples in the form of thin parallel-plate capacitors. The surfaces of either single crystals (naturally or appropriately cut) or of polycrystalline thin pressed (9 kbar) pellets were electroded with silver paint. Due to the low melting point of the optically active diacetylene NP/MBU, no pronounced decomposition took place during the pellet preparation close to the melting point and compact, homogeneous, polycrystalline thin plates could be obtained. We determined real and imaginary part of the frequency-dependent dielectric constant, the pyroelectric coefficient and the electric polarization and we evaluated possible electret-properties (poling with electric field and thermally stimulated depolarization, [12]), all in dependence of the temperature. For details of the experimental setup we refer to [4, 6].

2.5. Crystal Structure Analyses

Crystallization of NP/4-MPU from 2-propanol gave crystals of two different modifications. The majority (<95%) are slightly yellow plates with dimensions up to $10 \times 3 \times 1$ mm³. These crystals which will be referred to as Modification I belong to the polar space group Fdd2. The polar c axis corresponds to the longest dimensions of the plates with crystals faces {100} and {110}. Modification I is not reactive in the X-ray beam. The second modification (II) are small platelets adhering to the larger crystals of modification I. They show low reactivity and slowly turn red under ambient conditions and thus can be easily detected.

Preliminary lattice parameters and systematic absences were obtained from Weissenberg and Buerger photographs. Crystals of the size $0.6 \times 0.2 \times 0.1$ mm³ and $0.4 \times 0.1 \times 0.06$ mm³ were used for the data collection of modifications I and II, respectively. Accurate cell dimensions were obtained from least-squares fits of the setting angles of 25 reflections with high scattering angle.

Table 3
Crystallographic data of NP/4-MPU. E.s.d.'s are given in parentheses

	Mod. I	Mod. II
$a/\text{Å}$	77.649(12)	16.124(6)
$b/\text{Å}$	19.687(2)	23.606(8)
$c/\text{Å}$	4.608(1)	10.190(5)
$\beta/°$		114.45
$V/\text{Å}^3$	7043.9	3530.7
Z	16	8
$D_x/\text{g cm}^{-3}$	1.37	1.37
space group	Fdd2	C2/c

Crystals of NP/4-MPU grown from methanol (NP/4-MPU(m), Mod. III) apparently contain methanol as a solvate which is slowly lost under ambient conditions. As a consequence single crystals become opaque and decompose leaving a fibrillar texture. The crystal structure analysis of this modification at low temperatures is in progress. Pertinent crystallographic data are summarized in Table 3. Intensity data were collected with a four circle diffractometer CAD4 (Enraf-Nonius) with graphite monochromated Mo K_α radiation using the $2\vartheta - \vartheta$ scan mode. Three monitor reflections were measured at regular intervals and showed no significant decrease. Polymerization of modification II in the X-ray beam during the data collection was negligible. Of the 2364 (4456) unique reflections ($\vartheta \leqslant 25°$) significant counts ($I > 3\sigma(I)$) were collected for 1293 (1253). (Values for Mod. II in parentheses).

The structures were solved by direct methods using MULTAN 84. The refinement was done by full matrix least-squares analyses with unit weights. No absorption corrections were applied. The programs used in the calculation were those of the SDP system (13).

The positions of the H atoms belonging to the methyl (H1 – H3) and urethane groups (H8) were found in difference maps. The others were given reasonable parameters. All H atoms were refined in the riding mode, i.e. with parameter shifts equal to those of the C and N atoms they are bound to with fixed isotropic temperature factors ($B = 5$ Å²). All other atoms were refined with anisotropic temperature factors. The final R and R_w values were 0.049 and 0.051 for Mod. I and 0.057 and 0.055 for Mod. II, respectively.

ORTEP plots of the monomer molecules in the two modifications with the atomic labelling scheme are shown in Fig. 2. The final atomic parameters for the C, N and O atoms are given in Table 4*).

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*) Further information concerning the X-ray structure analysis, including the coordinates of the H atoms, anisotropic temperature factors, bond lengths and angles and lists of observed and calculated structure factors may be requested from Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein, Leopoldshafen 2, with the indication of the registry number CSD, the author's names and the reference to this publication.
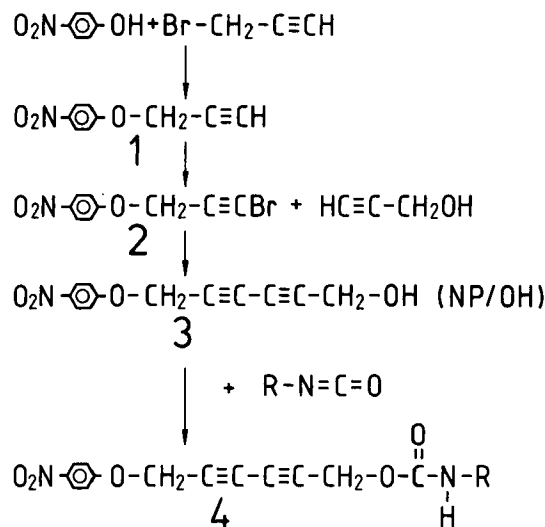
Table 4a
Atomic coordinates and equivalent isotropic temperature factors for
NP/4-MPU Mod. I

Atom	x	y	z	B(Å^2)
O1	0.05210(4)	0.5746(2)	0.166	5.5(1)
O2	0.04770(5)	0.4866(2)	0.470(1)	4.8(1)
O3	−0.02487(5)	0.2312(2)	0.986(1)	4.7(1)
O4	−0.08928(6)	0.2574(3)	0.172(1)	6.8(1)
O5	−0.07976(6)	0.1571(2)	0.054(1)	6.0(1)
N1	0.07243(5)	0.4918(2)	0.237(1)	4.0(1)
N2	−0.07906(6)	0.2092(3)	0.196(1)	5.1(1)
C1	0.12657(8)	0.5597(4)	−0.552(2)	6.2(2)
C2	0.11197(7)	0.5412(4)	−0.347(2)	4.6(1)
C3	0.10994(4)	0.4755(2)	−0.242(2)	4.7(1)
C4	0.09677(7)	0.4603(3)	−0.049(2)	4.2(1)
C5	0.08544(7)	0.5115(3)	0.035(1)	3.5(1)
C6	0.08740(7)	0.5768(3)	−0.064(2)	4.1(1)
C7	0.10066(7)	0.5911(3)	−0.261(2)	4.6(1)
C8	0.05714(7)	0.5239(3)	0.277(2)	3.8(1)
C9	0.03106(8)	0.5157(3)	0.535(2)	5.3(2)
C10	0.02019(7)	0.4621(3)	0.662(2)	4.4(1)
C11	0.01055(7)	0.4219(3)	0.759(2)	4.4(1)
C12	−0.00068(7)	0.3771(3)	0.881(2)	4.2(1)
C13	−0.01034(7)	0.3393(3)	0.996(2)	4.0(1)
C14	−0.02129(7)	0.2912(3)	1.150(2)	4.7(1)
C15	−0.03853(7)	0.2307(3)	0.798(1)	3.6(1)
C16	−0.04096(7)	0.1694(3)	0.653(2)	4.2(1)
C17	−0.05407(7)	0.1623(3)	0.452(2)	4.2(1)
C18	−0.06504(7)	0.2171(3)	0.410(2)	3.8(1)
C19	−0.06293(7)	0.2778(3)	0.554(2)	4.1(1)
C20	−0.04967(7)	0.2860(3)	0.752(2)	4.0(1)

Table 4b
Atomic coordinates and equivalent isotropic temperature factors for
NP/4-MPU Mod. II
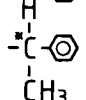
Atom	x	y	z	B(Å^2)
C1	1.1338(3)	0.1159(2)	−0.5917(5)	5.7(2)
C2	1.0579(4)	0.1282(3)	−0.5382(7)	3.9(2)
C3	1.0128(3)	0.0851(2)	−0.4989(5)	5.0(2)
C4	0.9509(4)	0.0974(3)	−0.4442(7)	4.7(2)
C5	0.9267(4)	0.1526(3)	−0.4346(7)	3.7(2)
C6	0.9675(4)	0.1954(3)	−0.4764(7)	4.6(2)
C7	1.0319(4)	0.1826(3)	−0.5305(7)	4.8(2)
N1	0.8595(3)	0.1616(2)	−0.3800(6)	4.3(1)
C8	0.8341(4)	0.2112(3)	−0.3472(7)	4.1(2)
O1	0.8564(3)	0.2583(2)	−0.3576(5)	4.8(1)
O2	0.7706(3)	0.1988(2)	−0.2923(4)	4.6(1)
C9	0.7406(4)	0.2452(3)	−0.2356(7)	4.6(2)
C10	0.6804(4)	0.2200(3)	−0.1743(7)	4.2(2)
C11	0.6329(4)	0.1972(3)	−0.1285(7)	4.1(2)
C12	0.5754(4)	0.1732(3)	−0.0736(7)	4.0(2)
C13	0.5238(4)	0.1556(3)	−0.0290(7)	4.1(2)
C14	0.4546(4)	0.1392(3)	0.0234(7)	4.6(2)
O3	0.4576(3)	0.0801(2)	0.0412(4)	4.3(1)
C15	0.3998(4)	0.0569(3)	0.0929(7)	3.6(2)
C16	0.4022(4)	−0.0012(3)	0.1011(7)	3.9(2)
C17	0.3483(4)	−0.0289(3)	0.1552(7)	3.9(2)
C18	0.2918(4)	0.0022(3)	0.1997(7)	3.6(1)
C19	0.2889(4)	0.0596(3)	0.1911(7)	4.1(2)
C20	0.3433(4)	0.0882(3)	0.1378(7)	4.1(2)
N2	0.2345(3)	−0.0277(2)	0.2569(5)	4.6(1)
O4	0.2447(3)	−0.0788(2)	0.2757(5)	5.5(1)
O5	0.1789(3)	−0.0009(2)	0.2817(5)	7.4(1)

3. Results

3.1. New Unsymmetrically Substituted Diacetylenes NP/R$_2$

The synthesis of the diacetylenes with pendant polar groups is outlined in scheme 1. In the first step 4-nitrophenyl-2-propynyl ether 1 is prepared from 4-nitrophenol and 1-bromo-2-propyne [10] and subsequently brominated to yield 3-bromo-2-propynyl-(4-nitrophenyl) ether 2 [11]. A Cadiot-Chodkiewicz coupling of 2 with 2-propyne-1-ol yields 6-(4-nitrophenoxy)-2,4-hexadiyne-1-ol 3 [11]. In the last step the novel diacetylenes 4a−c were prepared from NP/OH and the corresponding isocyanates.

O_2N-◎-OH + Br-CH_2-$C\equiv CH$

O_2N-◎-O-CH_2-$C\equiv CH$
1

O_2N-◎-O-CH_2-$C\equiv CBr$ + $HC\equiv C$-CH_2OH
2

O_2N-◎-O-CH_2-$C\equiv C$-$C\equiv C$-CH_2-OH (NP/OH)
3

+ R-$N=C=O$

O_2N-◎-O-CH_2-$C\equiv C$-$C\equiv C$-CH_2-O-$\overset{O}{\overset{\|}{C}}$-$\overset{}{\underset{H}{N}}$-$R$
4

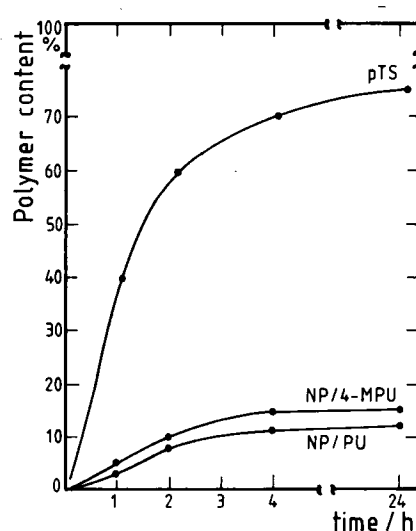| Abbreviation		R
4a	NP/PU	◎
4b	NP/4-MPU	◎-CH$_3$
4c	(+)-(R)-NP/MBU	-C-◎ / CH$_3$

Abb. 1
UV-polymerization of unsymmetrically substituted diacetylenes NP/R$_2$ in comparison with pTS

All the compounds 4a−c get coloured on exposure to visible light. To get an impression of the polymerization behaviour, we suspended the finely powdered compounds in water, irradiated

them with UV-light and determined the amount of polymerized material gravimetrically. The results of the measurements are shown in Fig. 1. NP/4-MPU polymerizes with a yield of 15% within 24 hours; the irradiation of NP/PU yields 12% of polymer. TS, which was measured for comparison, polymerizes to 75% within the same time. It should be added that this method is only semi-quantitative because of the limited penetration depth of UV-light, which is strongly absorbed by the diacetylenes. For a quantitive analysis, irradiation with X-rays is necessary. But nevertheless this simple method gives an impression about the polymerizability of a novel diacetylene. From our measurements we conclude that NP/PU as well as NP/4-MPU are only partially polymerizable (Table 2).

We were able to grow single crystals from two of the novel diacetylenes, namely NP/PU and NP/4-MPU. NP/4-MPU crystallizes in two modifications. Small needles, which rapidly turn blue on exposure to visible light, are obtained from methanol solution (NP/4-MPU(m)), whereas crystallization from 2-propanole yields slightly yellow plates (NP/4-MPU(p)), which are inactive.
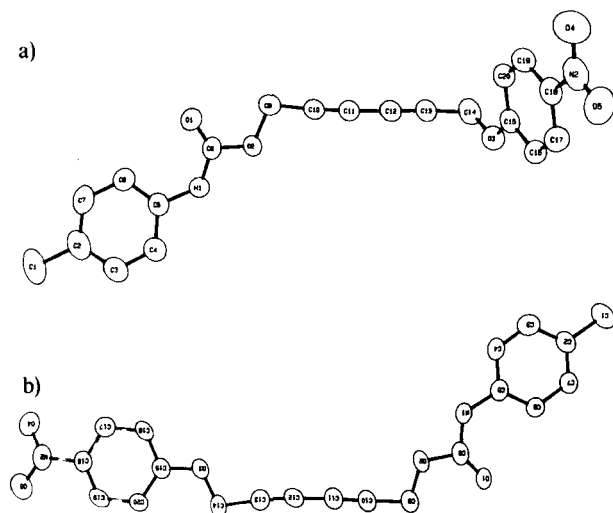
Fig. 2
ORTEP plots of the NP/4-MPU molecules.
a) Mod. I, b) Mod. II

3.2. Crystal Structures

As it is shown in Fig. 2 the monomer molecules exhibit different conformations in both modifications. No unusual bond lengths and angles are observed and within the experimental error equivalent values are identical in both crystal forms.

In Mod. II the phenyl rings, the urethane and the nitro groups are nearly coplanar whereas in Mod. I the phenyl rings at the ends of the molecule are nearly oriented perpendicular to each other. In both structures hydrogen bonds are formed between the urethane group (H8) and the nitro group of a neighbor monomer unit. Stereoscopic projections of both structures are shown in Fig. 3.

In the highly reactive diacetylenes translationally related monomer units form continuous stacks in a way that only small rotational motions are necessary to bring about the reaction [2]. The lack of reactivity in both structures can be understood by the monomer packing. In Mod. I the molecules form stacks along the polar c axis. However, the packing is in the range which is unfavourable for the polymerization. The stacking distance is $d = 4.61$ Å and the diacetylene rods make an angle $\varphi = 67°$ with c. In Mod. II no continuous stacks are observed. Here dimers are formed with an internal stacking distance of 3.47 Å and a separation of 5.26 Å between dimers which are arranged in a zigzag fashion. In addition the diacetylene groups are not coplanar but form an angle of approximately 45°. This packing arrangement in crossed dimers has been previously found in other diacetylenes, e.g. HDU-2 [2] and requires large translational and rotational motions in the reaction and thus explains the small reactivity of Mod. II. Plots of the monomer packing in both modifications are shown in Fig. 4.
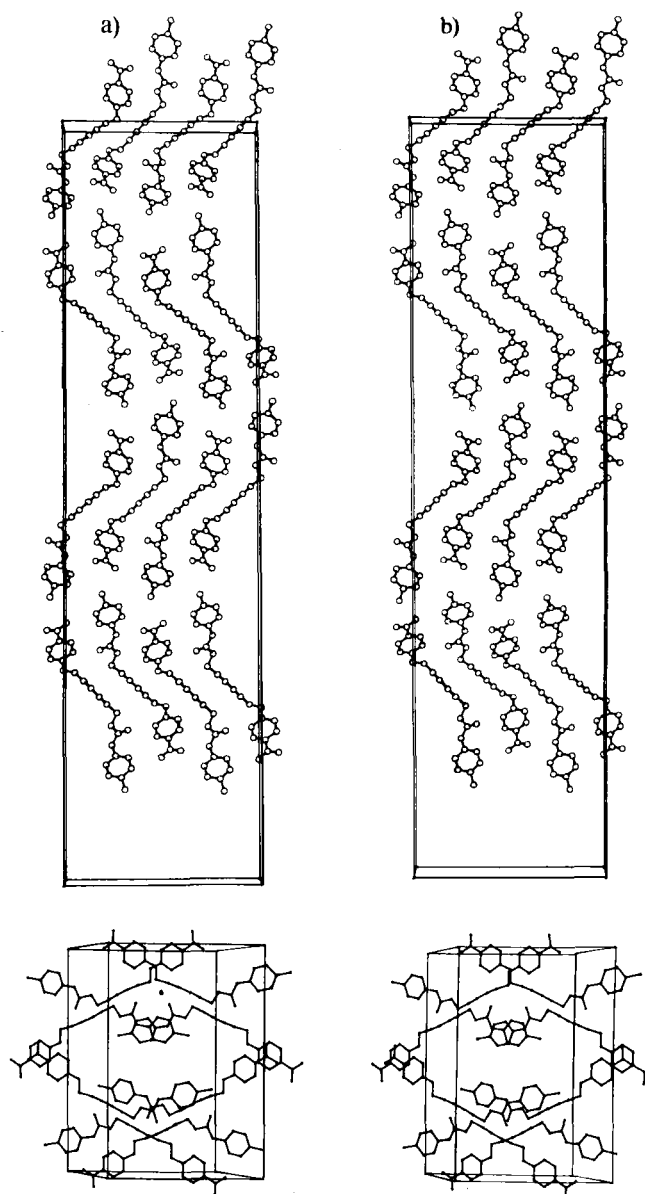
Fig. 3
Stereoscopic projections of the structures.
a) Modification I, b) Modification II

3.3. Dielectric Properties

The dielectric properties of NP/4-MPU(p) were measured on single crystals in different directions. We derived values of the permittivity ε_r at room-temperature ranging between $\varepsilon_r(E \perp S) = 7 \pm 2$ for electric field perpendicular to the large natural planes of the crystals and $\varepsilon_r(E \parallel S) = 13.4 \pm 2.3$ for electric field in the plane, normal to the natural long, narrow sides of the crystal plates. The capacitance of the single-crystal parallel-plate capacitors decreased by 8% (4%) for $E \parallel S$ ($E \perp S$), if the temperature was changed from room-temperature to 10 K.

Furthermore, we analysed the complex dielectric constant $\varepsilon_r(T, \omega) = \varepsilon_r' + i \cdot \varepsilon_r''$ for pressed pellet samples of the optically active $(+)$-(R)-NP/MBU, applying an alternating electric field strength of 200 V_{pp}/cm. Figs. 5 and 6 illustrate, that for temperatures below 260 K the losses are negligible and at the error limit of our set-up, whilst the real part of the dielectric constant decreases weakly from 3.4 to 3.1 with increasing frequency.

Between 260 and 290 K the real part $\varepsilon_r'(T)$ of the dielectric constant increases almost step-like by a small amount (Fig. 5a). The position of these "steps" depends on frequency and shifts from (273 ± 3) K to (296 ± 5) K, if the measuring frequency is increased

from 500 Hz to 25 kHz. At the temperatures of the ε_r'-steps a small maximum of the losses is observed as can be seen in the inset to Fig. 5b. Since these anomalies are weak and sample-dependent, we
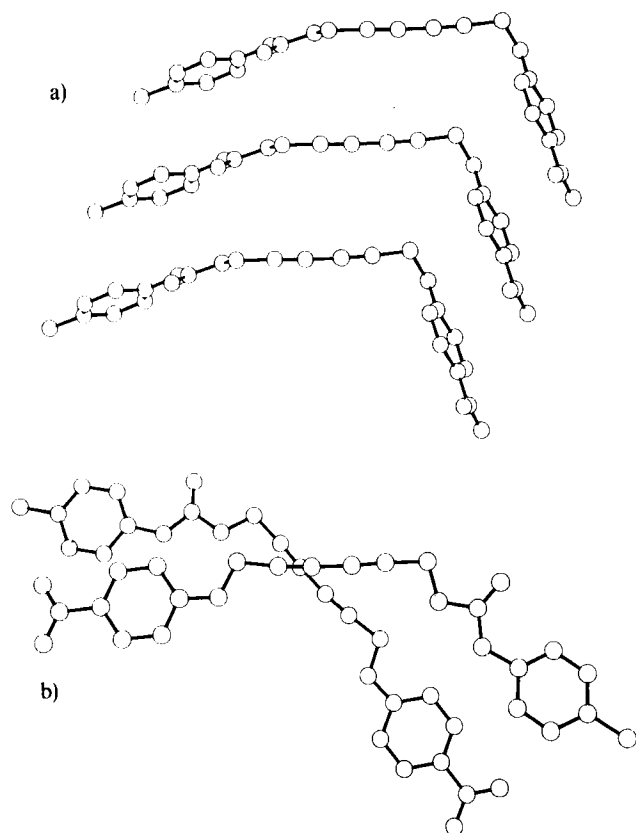
a)

b)

Fig. 4
Monomer packing.
a) Projection of the crystal structure of Mod. I on the plane of the monomer stacks.
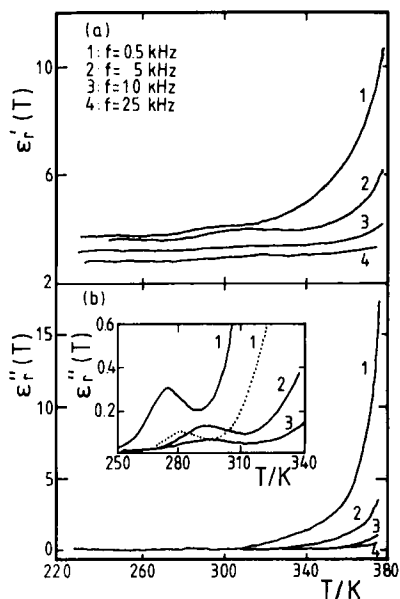b) Crossed dimer in Modification II.

Fig. 6
Frequency-dependence of real and imaginary part of the relative dielectric constant of a (+)-(R)-NP/MBU pressed-pellet sample

assume that they originate from impurities of very low concentration, giving rise to a typical dipole relaxation process. From the frequency-dependence of the temperature of the loss maxima (i.e. via $\omega \cdot \tau(T_{max}) = 1$) we estimated an upper limit of the effective activation energy for the relaxation time-constant τ of the dipole orientation of 1 eV.

At temperatures above 290 K, the losses caused by electrical conductivity dominate the dielectric behaviour. Their influence decreases with increasing frequency. Real and imaginary part of the dielectric constant reach very large values. We believe, that impurities and solvent inclusions at grain boundaries dominate the observed properties in this higher temperature range.

Fig. 5
Temperature-dependence of the complex dielectric constant — $\varepsilon_r'(T)$ in a) and $\varepsilon_r''(T)$ in b) — for polycrystalline pressed-pellet samples of (+)-(R)-NP/MBU at different measuring frequencies. The inset shows the resonance structure of the dielectric losses for two different samples on a blown-up scale
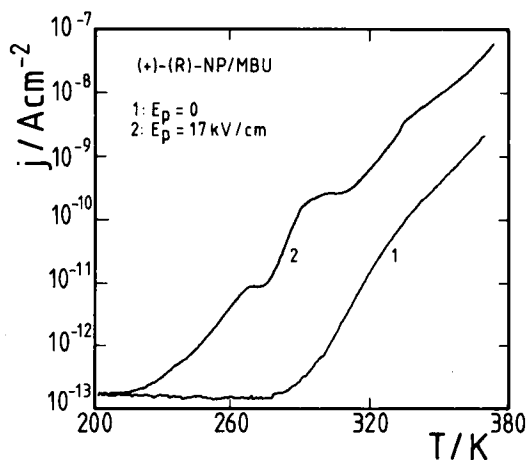
Fig. 7
Thermally stimulated depolarization current of a polycrystalline pressed-pellet sample of (+)-(R)-NP/MBU. For curve 1, prior to the measurement the sample was heated with shorted electrodes up to the melting point and then cooled to 200 K. For curve 2, instead, an electric poling field of $E_p = 17$ kV/cm was applied for 1 hour at $T_p = 370$ K and during cool-down to 200 K. During the subsequent slow heating with $h = 4.4$ K/min (3.6 K/min) for curve 1 (2) the short-circuit current j was measured. The two TSC peaks depend on E_p and h

3.4. Poling of Polycrystalline Samples of NP/MBU

We reported before, that polycrystalline pressed pellets of the optically active diacetylenes (+)-(R)- and (−)-(S)-DNP/MBU can easily be poled, if electric fields are applied close to their melting point. Dipole orientation was suggested as the polarization mechanism: the dinitrophenoxy-group possesses a permanent electric dipole moment of about $1 \cdot 10^{-29}$ C·m that points at an angle of about 60° away from the axis of the single bond between the benzenic ring and the rest of the substituted diacetylene. Thus by thermally activated rotation of the side-group around the single bond direction a resulting polarization may be established with a poling field.

The nitrophenoxy-group of NP/MBU carries an electric dipole moment of exactly the same size that points, however, just in the direction of the single bond rotation axis of the benzenic ring. Thus we expected and observed much less pronounced poling effects for NP/MBU. The extent of the poling-induced thermally stimulated depolarization current (TSC) is illustrated in Fig. 7. It is indeed of minor importance then for DNP/MBU − comparing e.g. Fig. 7 with the Figs. 3 and 4 in Ref. [8]. Two ill-defined TSC peaks can be discriminated. The lower TSC-peak at about 268 K occurs at the same temperature as the weak anomaly of the permittivity (low-frequency limit) mentioned above. Thus we may reasonably assume, that it has the same origin.

Our NP/MBU samples had a larger electrical conductivity than the DNP/MBU samples investigated earlier − as was found in the analysis of the complex dielectric constant, above, and explained with the influence of impurities (ions) or solvent inclusions at grain boundaries. This leads to a measurable increase of the current density for an un-poled sample (curve 1 in Fig. 7) beginning already at 270 K, i.e. 100 K below the melting point. At room-temperature (290 K), we derived for pressed pellet samples the dc-electrical conductivity $\sigma_{NP/MBU} = (2.0 \pm 0.6) \cdot 10^{-12}$ S/cm, that is to be compared with $\sigma_{DNP/MBU} = 6 \cdot 10^{-15}$ S/cm and $\sigma_{PVDF} = 10^{-14}$ S/cm for the standard organic polymer electret and ferroelectricum polyvinylidenefluoride.

4. Conclusions

We are currently engaged in a screening research, where we investigate, whether non-centrosymmetric crystal structures and interesting dielectric properties can be realized for monomer and/or polymer crystals of appropriately substituted diacetylenes. Here we reported the synthesis and characterization of different non-centrosymmetric diacetylenes $R_1 - C \equiv C - C \equiv C - R_2$, that carry a polar nitrophenoxy-group on one side. We introduced the abbreviation NP/R_2 for them. In contrast to the DNP/R_2-series analysed before [8], these new diacetylenes polymerize under UV-light at least partially. For the optically active (+)-(R)-NP/MBU also thermal polymerization was observed. These compounds are, however, by far less polymerization-active then the best known symmetric diacetylene pTS [1,2] or the newly synthesized polar diacetylene TS/FBS [9].

Comparable to what we observed in the DNP/R_2-series before [8], despite the non-centrosymmetric molecular units generally a centrosymmetrical crystal structure seems to be realized and consequently the permittivity of the NP/R_2-diacetylenes is not remarkably large. Restricted free volume and lack of cooperative effects are evidently further obstacles for more interesting dielectric properties. NP/4-MPU(p) is an exception with a clearly anisotropic room-temperature permittivity and with ε_r-values of partly above 10.

We presented one example of a diacetylene monomer single crystal in the NP/R_2-series, the NP/4-MPU(p), that has also a non-centrosymmetric crystal structure. This proves, that the employment of unsymmetrically substituted diacetylenes is indeed a promising approach for a systematic tayloring of polar diacetylene crystals.

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