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Intermolecular and intramolecular reorientations in nonchiral smectic liquid-crystalline phases studied by broadband dielectric spectroscopy

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Molecular dynamics has been studied by broadband dielectric relaxation spectroscopy in the Sm-*A*, Sm-*B*, and Sm-*E* phases (Sm denotes smectic) of a homologous series of nonchiral stilbenes. An assignment of modes is presented based on their dependence on temperature and molecular length, and, as far as they obey the Arrhenius law, their activation energy has been determined. In general, reorientations of entire molecules around their short axis are active, whereas reorientations of entire molecules around their long axis are locked out in the Sm-*E* phase of shorter homologs, yet intramolecular reorientations of polar sites have been established. Strong evidence is presented for an interdependence of reorientations of entire molecules around the short and long axes within the biaxial Sm-*E* phase of longer homologs.

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I. INTRODUCTION

Intramolecular reorientations as well as reorientations of entire molecules contribute to the molecular dynamics of liquid-crystalline phases. Reorientations of entire molecules around their short and long axes are characteristics that distinguish the liquid-crystalline state from crystalline phases where these reorientations as well as intramolecular reorientations are usually frozen and only vibrations of atoms around their equilibrium position still persist. The molecular dynamics of liquid crystals provides considerable insight into molecular interactions still representing a fundamental research target to improve theoretical models. Recently, the frequency range of dielectric relaxation spectroscopy has been increased dramatically and broadband dielectric relaxation measurements became an indispensable tool to characterize noncollective modes related to reorientations of nonchiral, dipolar low molecular mass liquid crystals.

In this work the temperature dependence and the influence of the molecular length on dipolar reorientations have been characterized in the frequency range 10 Hz to 1 GHz and in a homologous series of stilbenes, possessing orthogonal smectic liquid-crystalline phases (Sm-*A*, Sm-*B*), including the higher-ordered, almost crystallinelike, Sm-*E* phase. Reorientations of entire molecules around their short and long molecular axes are clearly distinguished from intramolecular reorientations of polar sites of the molecules.

Maier and Meier [1,2] observed a dielectric dispersion at surprisingly low frequencies in the oriented uniaxial nematic phase of *p*-azoxyanisole derivatives. This dispersion was assigned to reorientations of overall molecules around their short molecular axis connected to a reorientation of their parallel component of the average dipole moment. This average is taken with respect to faster reorientations, e.g., reorientations of entire molecules around their long molecular axis, intramolecular reorientations, and intramolecular vibrations. Additionally, Maier and Meier have attributed the decrease of the relaxation frequency f_1 of the low-frequency dispersion with temperature to the nematic potential barrier, a quantity which is, to some extent, interconnected with the nematic order parameter S commonly employed within the ‘‘Maier-Saupe’’ mean-field theory of the nematic phase [3]. Although nearest-neighbor interactions are supposed to play an important role [4], reorientations of entire molecules around their short molecular axis are biased or even hindered depending on the height of the nematic potential barrier. Subsequently, reorientations of whole molecules around the short molecular axis were described in terms of a molecular statistical approach by Maier and Saupe [5] who derived the temperature dependence of the corresponding relaxation frequency

$$\frac{f_1(T)}{f_0}=\frac{u}{kT\left[\exp\left(\frac{u}{kT}\right)-1\right]}, \tag{1}$$

where f_0 corresponds to the relaxation frequency measured in the isotropic phase near the isotropic to nematic phase transition, u is the height of the nematic potential barrier, and k is the Boltzmann constant. Equation (1) is in good agreement with measurements of the relaxation frequency f_1 in the nematic phase [6]. Martin, Meier, and Saupe [7] com-

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bined their approach with Debye's theory [8] describing the reorientation of dipolar molecules. A more general approach considering the effect of the nematic ordering was published by Nordio, Rigatti, and Segre [9] as well as by Luckhurst and Yeates [10]. Within their approach, the reorientation of entire molecules around the short molecular axis appears as a Debye mode in the dielectric spectrum at frequencies lower than f_0. The influence of the free volume, and the interdependence between f_1 and the nematic order parameter S was derived by Diogo and Martins [11]

$$f_1(T)=\frac{kT}{h}\exp\left(-a\frac{S(T)}{kT}-b\frac{S^2(T)}{T-T_V}\right), \tag{2}$$

where k and h are the Boltzmann and Planck's constant, respectively, $S(T)$ is the temperature-dependent nematic order parameter, T_V is the Vogel temperature at which f_1 diverges, and a and b represent individual material properties. Equation (2) reduces to the Arrhenius equation

$$f_1(T)=A_1\exp\left(-\frac{E_{\parallel}}{kT}\right) \tag{3}$$

if the b term in Eq. (2) is negligible compared to the a term, and the exponential dominates over the linear term. The a term describes the reorientation around the short molecular axis to be a thermally activated process with the activation energy $E_{\parallel}$ and a preexponential factor A_1.

Equation (2) reduces to the Vogel-Fulcher-Tammann law, if the b term dominates over the a term

$$f_1(T)=C_1\exp\left(-\frac{B_1}{T-T_V}\right) \tag{4}$$

with B_1 and C_1 representing material constants; hence, the reorientation around the short molecular axis depends on the free volume since the b term in Eq. (2) is related to the probability for a given molecule to flip around the short molecular axis. A wide distribution of jump angles may exist depending on the temperature and structure of the liquid-crystalline phase.

de Jeu [12] pointed out that interactions of permanent dipoles are neglected in any of the above theories. These interactions are usually considered as a minor contribution within the nematic phase, but in hexatic or higher-ordered liquid-crystalline phases this contribution may be important as expected from single-crystal structure analysis which shows that the sum of dipole moments in a unit cell is usually minimized. The sum of all dipole moments is exactly zero in centrosymmetric crystals, but even if molecular symmetry is incompatible with a centrosymmetric structure, an even number of molecules is usually packed in an antiparallel manner within the unit cell to minimize the sum of the dipole moments [13].

The dielectric dispersion related to reorientations of the perpendicular component of the average dipole moment was first observed by Baessler, Beard, and Labes [14]. This dielectric dispersion has been ascribed to a reorientation around the long molecular axis with a relaxation frequency f_2 which is assumed to be almost independent of the nematic order parameter in a good agreement to experimental results. A continuous behavior of f_2 was found even in the vicinity of phase transitions into smectic phases as well as between various smectic phases [15], which proves that the impact of the smectic potential on reorientations around the long molecular axis may be small [16] in some cases. The relaxation frequency f_2 describing reorientations of entire molecules around the long axis commonly obeys the Arrhenius law

$$f_2(T)=A_2\exp\left(-\frac{E_{\perp}}{kT}\right), \tag{5}$$

with $E_{\perp}$ the activation energy related to reorientations around the long molecular axis and A_2 a preexponential factor. A comprehensive theory describing the reorientations of entire molecules in the nematic as well as in various smectic phases has not been developed yet.

The uniaxial Sm-*A* phase is often symbolized by a ''stack of layers'' of molecules oriented parallel to the smectic layer normal, although a very small and approximately sinusoidal modulation of the mass density exists [17] with a characteristic length usually correlated to the molecular length. The axis of macroscopic rotational symmetry coincides with the director, the smectic layer normal, and one principal direction of an anisotropic bulk material property described by a second rank tensor.

The hexatic smectic-*B* phase possesses a sixfold axis of symmetry which originates from the long-range orientational order of the center of mass of molecules within each particular smectic layer (bond orientational order). No quasi-long-range positional order within a smectic layer is present as was first demonstrated experimentally by x-ray diffraction on free-standing films [18]. Dielectric measurements performed by Benguigui [19] reveal that reorientations of entire molecules around their short molecular axis are active in the Sm-*A* and the Sm-*B* phase and a jump of the relaxation frequency f_1 at the phase transition between these smectic phases has been reported [20,21]. Reorientations of entire molecules around their short axis have been described in terms of a single-particle mechanism controlled by the free volume [19].

Three-dimensional long-range positional order is present in the Sm-*E* phase, but x-ray diffraction patterns usually exhibit only a few symmetry-independent reflections from which an orthogonal unit cell and a ''herringbone packing'' of molecules may be deduced. Therefore, the range of positional order is shorter compared to ordinary molecular crystals [22,23]. In fact, many properties of a Sm-*E* phase resemble those of plastic crystals. Using dielectric measurements Kresse *et al.* [24–26] and Buka *et al.* [27] established that reorientations of entire molecules around the short axis are active in the Sm-*E* phase. These reorientations are frozen in the ''crystalline'' smectic-*B* phase [15].

It is the purpose of the current paper to investigate intramolecular reorientations and to characterize reorientations of entire molecules around their short and long molecular axis depicted in Fig. 1, schematically, with emphasis on their temperature dependence and effect of the molecular length in orthogonal smectic phases of a homologous series of nonchiral stilbenes possessing the smectic-*A* (Sm-*A*), the hexatic smectic-*B* (Sm-*B*), and the ''crystalline like,'' higher-ordered smectic-*E* (Sm-*E*) phase. Our measurements show

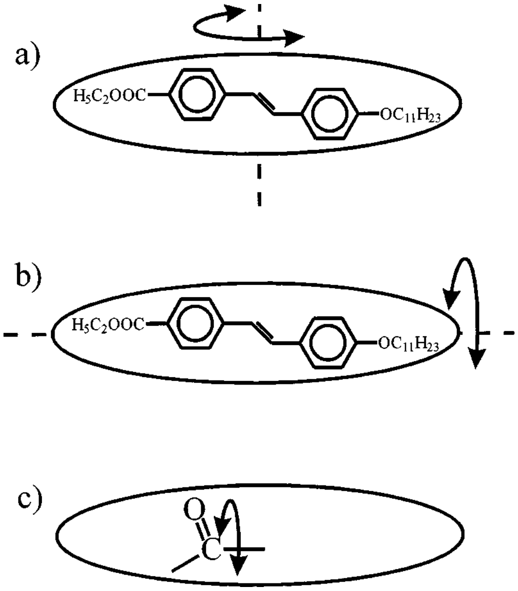


FIG. 1. Schematic representation of the dielectric dispersions in calamitic nonchiral liquid crystals (relaxation frequency f_k, dielectric increment $\Delta\varepsilon_k$, $k=1,2,3$): (a) reorientations of entire molecules around their short axis (f_1, $\Delta\varepsilon_1$), (b) reorientations of entire molecules around their long axis (f_2, $\Delta\varepsilon_2$), (c) intramolecular reorientations of polar sites (f_3, $\Delta\varepsilon_3$).

that the reorientations of entire molecules around their short and long axes do not necessarily obey the Arrhenius law in the Sm-*E* phase, and we present a strong evidence for an interdependence of reorientations of entire molecules around their short and long axes in the Sm-*E* phase. Intramolecular reorientations of polar sites are observed below 1 GHz in the Sm-*E* phase of some homologs.

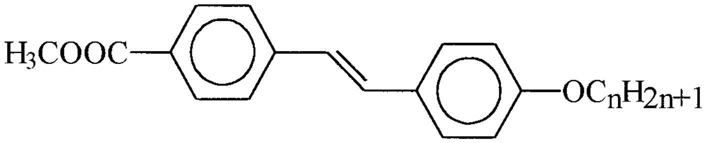
II. EXPERIMENT

The homologous series of liquid crystals, 4-(alkyloxy)-4′-(carboxymethyl)-*trans*-stilbene, abbreviated *n*Me with *n* the number of carbon atoms in the alkoxy chain (see Table I), possesses orthogonal smectic phases (Sm-*A*, Sm-*B*, and Sm-*E*) that have been characterized by differential scanning calorimetry and polarizing microscopy as well as small and wide angle x-ray diffraction methods [28]. Their chemical constitution, the sequence of their mesomorphic phases and the corresponding first-order phase transition temperatures are listed in Table I.

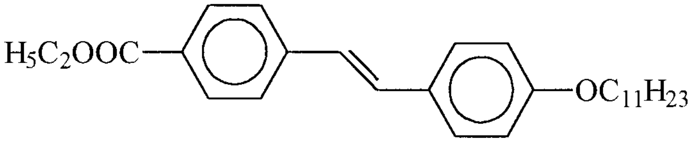
Dielectric spectra in the low-frequency range (LF) between 10 Hz and 13 MHz were carried out using an impedance analyzer (Hewlett-Packard, HP 4192A) equipped with a Linkham hot stage and Linkham temperature controlling unit (TMS 600). An oscillating electric field of an amplitude of 0.1 $\mathrm{MV\,m^{-1}}$ has been used for all measurements, and no bias electric field has been applied. On a logarithmic scale ten measurement points per frequency decade have been collected. For each distinct frequency 64 transient measurements have been averaged at frequencies below 10 kHz and 16 transient measurements at higher frequencies. Liquid-crystal (LC) cells, built in-house, have been employed which were composed of glass plates with copper electrodes evaporated on. Any charge injection into the liquid-crystalline material has been prevented by a blocking SiO layer on top of the copper electrodes. The active electrode area of the LC

TABLE I. Phase transition temperatures of the homologous series *n*Me (*n*, number of carbon atoms in the alkoxy chain) and compound 11Et (see Fig. 9) all of which possessing the same sequence of enantiotropic phases: smectic *A* (Sm-*A*), hexatic smectic *B* (Sm-*B*), and higher-ordered smectic *E* (Sm-*E*).

Phase transition temperatures



	Cryst$_1$		Cryst$_2$		Sm-E		Sm-B		Sm-A		I
4Me	●	157			●	187					●
5Me	●	91	●	146	●	171	●	175	●	182	●
7Me	●	122	●	136	●	160	●	168	●	177	●
8Me	●	123	●	135	●	157	●	166	●	175	●
9Me	●	133			●	157	●	165	●	173	●
12Me	●	132			●	154	●	161	●	166	●



	Cryst$_1$		Cryst$_2$		Sm-E		Sm-B		Sm-A		I
11Et	●	92	●	108	●	119	●	132	●	144	●

cells was 15 mm^2, and a cell thickness of approximately 10 μm was fixed by polymer spacers. A precise capacitance measurement of the empty LC cell and its stray capacitance (determined after filling with *n*-hexane) is necessary for the calibration of each individual LC cell which were filled subsequently by capillary action at high temperature near the isotropic to Sm-*A* phase transition, and the exposure time of the samples to high temperatures has been minimized to sustain a sufficiently low static conductivity. The homologs investigated exhibit an almost planar smectic layer alignment (director **n** approximately parallel to the substrates) within these LC cells. However, no surfactant has been used to generate a perfect homeotropic smectic layer alignment, but moderate mechanical shear produces a texture that differs remarkably from the planar alignment. The evaporated copper metal on the glass plates prevents the texture from being observed in detail within the active volume of the LC cell.

In the low-frequency regime a single Debye relaxation has been observed for the smectic phases of a 12Me (see Table I) compound. This mode is connected to reorientations around the short molecular axis [28]. The frequency and temperature-dependent complex dielectric permittivity $\varepsilon^*(\omega,T)$ is described by Eq. (6) which includes contributions related to charge carriers and the finite resistivity of the metal electrodes leading to a cutoff at high frequencies

$$\varepsilon^*(\omega,T)=\frac{\sigma}{i\varepsilon_0\omega}+\frac{\Delta\varepsilon_1}{1+i\omega\tau_1}+\frac{\varepsilon_h}{1+i\omega\tau_{RC}}, \tag{6}$$

with σ the static conductivity related to charge carriers, $\Delta\varepsilon_1$ the dielectric increment, $\tau_1=1/(2\pi f_1)$ the relaxation time of a Debye mode describing reorientations of molecules around the short molecular axis, ε_h the dielectric constant containing all contributions from processes exceeding the upper frequency limit of the LF bridge (13 MHz), $f_{RC}=1/(2\pi\tau_{RC})$ the cutoff frequency of the measurement cell, ε_0 the vacuum permittivity, and $i=\sqrt{-1}$ the imaginary unit.

The high-frequency (HF) reflectometer (Hewlett-Packard HP 4191) has been employed for dielectric measurements in the frequency range between 1 MHz and 1 GHz. The sample was placed in a capacitor which consists of two copper plates directly inserted into the reflectometer. A heating system, built in-house, has been used for temperature control. The long-time stability of the relative temperature was within 0.1 K, and the absolute temperature calibration due to standard materials was better than ±1 K.

The HF dielectric spectra measured at various temperatures for each homolog have been analyzed by fitting the Cole-Cole equation (7) to the experimental data

$$\varepsilon^*(\omega,T)=\frac{\Delta\varepsilon_k}{1+(i\omega\tau_k)^{1-\alpha_k}},\quad k=2,3. \tag{7}$$

Equation (7) describes reorientations of entire molecules around the long axis ($k=2$) or intramolecular reorientations of polar sites ($k=3$), with α_k the symmetric distribution parameter of relaxation times, $\Delta\varepsilon_k$ the dielectric increment, and $f_k=1/(2\pi\tau_k)$ the relaxation frequency.

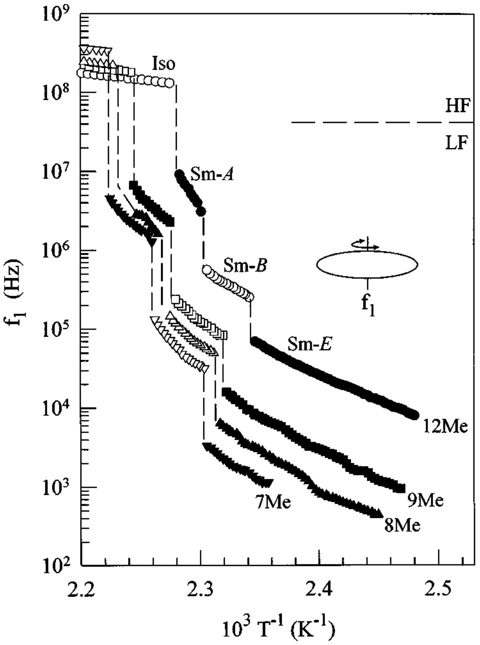


FIG. 2. Relaxation frequency f_1 (reorientation of entire molecules around their short axis; LF, low-frequency regime; HF, high-frequency regime) as a function of the reciprocal temperature $1/T$ for the higher-ordered Sm-*E*, the hexatic Sm-*B*, and the Sm-*A* phases of the homologous series *n*Me. The integer *n* defines the number of carbon atoms within the alkoxy chain. The dashed lines indicate first-order phase transitions.

III. RESULTS AND DISCUSSION

Reorientations of entire molecules around their short axis are influenced by the nematic potential barrier which depends on temperature and molecular length. In general, the nematic potential barrier increases with decreasing temperature or elongation of molecules. As a homologous series is ascended, the width of the nematic phase is commonly reduced and smectic polymorphism occurs or is extended. In contrast, reorientations of entire molecules around their long axis are almost independent of the molecular length. Therefore, both reorientations of entire molecules may be distinguished from each other unambiguously. The molecular length is invariant due to a shift of one methylene group from the alkoxy chain to the opposite side of the molecule, transforming the carboxymethyl derivative into its carboxyethyl isomer. Reorientations of entire molecules are supposed to remain approximately unchanged, whereas intramolecular reorientations of polar sites are supposed to be affected significantly.

A. Molecular length dependence

The temperature dependence of the relaxation frequency f_1 related to the overall molecular reorientations around the short axis is depicted in Fig. 2. In general, each first-order phase transition is accompanied by a discontinuity in the $f_1(T)$ curve (steps) in accordance with the results reported previously [19]. These steps decrease as the homologous series is ascended, therefore, the range of frequencies occupied by the Sm-*E* phase of all homologs is significantly larger than the corresponding range of the Sm-*A* phase. The impact

TABLE II. Activation energies ($\mathrm{kJ\,mol^{-1}}$) of the reorientation around the short molecular axis and the long molecular axis of the homologous series *n* Me and compound 11Et within their isotropic (Iso), smectic-*A* (Sm-*A*), hexatic smectic-*B* (Sm-*B*), and higher-ordered smectic-*E* (Sm-*E*) phase.

	Reorientation of entire molecules around the long molecular axis				Reorientations of entire molecules around the short molecular axis		
	Sm-*E*	Sm-*B*	Sm-*A*	Iso	Sm-*E*	Sm-*B*	Sm-*A*
4Me	[a]	[b]	[b]	15.0	[c]	[b]	[b]
7Me	[a]	10.6	12.6	13.6	76.7	122.0	116.8
8Me	[a]	20.8	18.1	21.1	75.3	102.1	121.3
9Me	16.4	14.6	20.1	16.0	68.2	96.0	121.6
12Me	[d]	17.2	17.0	13.6	[d]	74.6	[c]
11Et	[a]	[a]	15.0	13.8	77.8	73.8	71.8

[a] Reorientation is locked out.

[b] Nonexistent phase (see Table I).

[c] Not determined.

[d] Temperature dependence does not obey the Arrhenius law (see Fig. 3).

of the molecular length on the relaxation frequency f_1 increases from Sm-*A* to Sm-*E*. The nematic order parameter *S* is not an appropriate quantity to be solely correlated with the relaxation frequency f_1 connected to reorientations of entire molecules around the short axis, since *S* closely approaches unity within the Sm-*E* phase of the homologous series irrespective of the molecular length. Although the temperature dependence of f_1 is described satisfactorily by the theory of Diogo and Martin [cf. Eq. (2)] for the individual homologs, a decrease of f_1 with increasing molecular length may be expected since the nematic potential barrier increases with decreasing temperature and increasing molecular length because a longer molecule experiences a larger orienting force due to the nematic potential. The opposite behavior is observed: f_1 increases as the homologous series is ascended starting from the heptyloxy derivative 7Me to the dodecyloxy derivative 12Me. These results support the conclusion drawn by Benguigui: The reorientation of entire molecules around the short molecular axis in orthogonal smectic phases is dominated by the anisotropic free volume. In the biaxial Sm-*E* phase reorientations of entire molecules around their short axis are, to a lesser extent, controlled by the nematic order parameter *S*, but predominantly to the density and the packing of molecules. In contrast, the long-range orientational order may be considered to affect f_1 predominately in a nematic phase.

Generally, the relaxation frequency f_1 describing molecular reorientation around the short axis of the molecule obeys an Arrhenius law within the orthogonal smectic phases irrespective of the molecular length with the exception of the Sm-*E* phase of compound 12Me. The activation energies are listed in Table II. For each homolog, the activation energy $E_\parallel$ decreases in the following order of smectic mesophases: Sm-*A*, Sm-*B*, to Sm-*E*. Furthermore, $E_\parallel$ decreases as the homologous series is ascended as it can be deduced from Fig. 2 and Table II. In many cases, a reasonable fit of an Arrhenius equation to the experimental data is obtained taking into account experimental limitations and the commonly small temperature range of the mesomorphic phases.

Dielectric relaxations with a relaxation frequency near the upper frequency limit of the LF bridge (13 MHz) are partially overlapped by the *RC* relaxation of the LC cell originating from the finite resistivity *R* of the copper electrodes. The accuracy of the fitting parameter f_1 is limited in this frequency range, and the corresponding error of $\ln f_1$ is estimated to be of the order of 10% in this case. Subsequently, the determination of the activation energy within the Sm-*A* phase is hampered or even impossible. At particularly low frequencies ($f_1 < 3$ kHz) the measurement error increases with decreasing frequency which requires extensive data accumulation and averaging. The accuracy of the dielectric measurements in the LF regime approaches an optimum within the range of frequencies between 3 and 300 kHz, hence, the measurement error (ε', ε'') falls short of 1% leading to an uncertainty of the fitting parameter $\ln f_1$ less

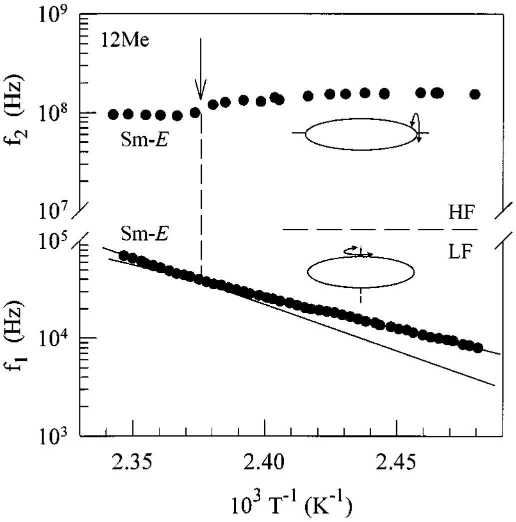


FIG. 3. Relaxation frequency f_1 (reorientation of entire molecules around their short axis; LF, low-frequency regime) as a function of the reciprocal temperature $1/T$ compared with the relaxation frequency f_2 (reorientation of entire molecules around their long axis; HF, high-frequency regime) for the higher-ordered Sm-*E* phase of the homolog 12Me. Note the change of the activation energy describing the temperature dependence of f_1 (solid lines) and the increase of f_2 with decreasing temperature (arrow). The dashed lines are for guidance.

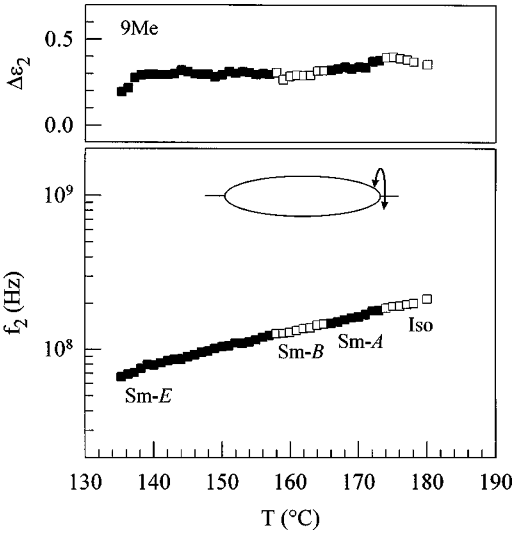


FIG. 4. Dielectric increment $\Delta\varepsilon_2$ and relaxation frequency f_2 (reorientation of entire molecules around their long axis) versus temperature T for the higher-ordered Sm-*E*, the hexatic Sm-*B*, the Sm-*A* phase, and the isotropic melt (Iso) of the nonyloxy derivative 9Me.

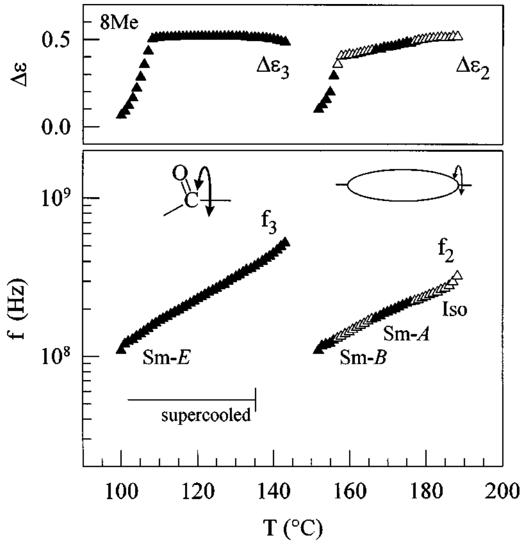


FIG. 5. Dielectric increment $\Delta\varepsilon_2$ and relaxation frequency f_2 (reorientation of entire molecules around the long axis in the Sm-*B*, Sm-*A*, and isotropic phases of compound 8Me) as well as dielectric increment $\Delta\varepsilon_3$ and relaxation frequency f_3 (intramolecular reorientation in the Sm-*E* phase) versus temperature T (cooling trace). The supercooled region of the Sm-*E* phase is included.

than 1%. Since the relaxation frequency f_1 characterizing reorientations of entire molecules around the short axis is located within the range of high accuracy of the LF dielectric measurements, the temperature dependence of f_1 is determined most precisely within the Sm-*E* phase of compound 12Me. An Arrhenius-like temperature dependence of f_1 within the temperature range of the Sm-*E* phase depicted in Fig. 3 has to be excluded. Nevertheless, the f_1 data in the high-temperature region and the low-temperature region of the Sm-*E* phase may be independently fitted to Arrhenius equations with activation energies of 73 and 53 $\mathrm{kJ\,mol^{-1}}$, respectively. The decrease of the activation energy at $T = 238\,°\mathrm{C}$ is accompanied by a steplike increase of the relaxation frequency f_2 describing reorientations of entire molecules around their long molecular axis which do not obey an Arrhenius-like temperature dependence. The mutual incidence of the change of the activation energy assigned to reorientations around the short molecular axis and the discontinuity in the temperature dependence of reorientations around the long molecular axis compel a strong evidence for an interdependence of both reorientations in the higher-ordered Sm-*E* phase of compound 12Me.

The increase of f_1 with increasing molecular length (cf. Fig. 2) is at variance with a ‘‘free’’ reorientation of entire molecules around their short molecular axis within the orthogonal smectic phases, and the results are also compatible with a rotational diffusion or a rotational jump model. Both of these models depend on the free volume, a quantity that is supposed to increase with increasing length of the alkoxy chain of molecules.

Reorientations of entire molecules around their long molecular axis are usually observed in the high-frequency regime (HF) of the dielectric spectrum (10 MHz to 1 GHz). For the nonyloxy derivative of the homologous series, the temperature dependence of the dielectric increment $\Delta\varepsilon_2$ and the relaxation frequency f_2 of this mode are depicted in Fig. 4. No discontinuity of either $f_2(T)$ or $\Delta\varepsilon_2(T)$ at the first-order phase transitions between the orthogonal smectic phases is observed, within the experimental error, in contrast to the temperature dependence of f_1 describing reorientations of entire molecules around the short molecular axis (cf. Fig. 2). The relaxation frequency of entire molecules around the long axis f_2 obeys an Arrhenius law within the entire temperature range of all smectic phases of compound 9Me, and this observation agrees with the results of measurements reported previously [16]. Within the measurement limitations, the smectic potential forming the long-range orientational order and the quasi-long-range positional order in smectic materials does not affect the reorientations of entire molecules around the long molecular axis.

The high-frequency dielectric behavior of the octyloxy homolog, 8Me, is depicted in Fig. 5. In analogy to the homolog 9Me, the relaxation frequency $f_2(T)$ obeys an Arrhenius law within the entire temperature range of the isotropic, the Sm-*A*, and the Sm-*B* phases of compound 8Me. Within the accuracy of the dielectric measurements and the fitting of the dielectric spectra, no discontinuities of $f_2(T)$ or $\Delta\varepsilon_2(T)$ are observed at the first-order phase transitions separating the isotropic, the Sm-*A*, and the Sm-*B* phase. In contrast to the behavior of compound 9Me, the dielectric increment $\Delta\varepsilon_2$ related to reorientations of entire 8Me molecules around their long axis vanishes in the vicinity of the Sm-*B* to Sm-*E* phase transition, a strong argument for reorientations around the long molecular axis being at least partially locked out in the Sm-*E* phase of compound 8Me.

At low temperatures in the Sm-*E* phase of compound 8Me, a new dielectric dispersion of the Cole-Cole-type enters the dielectric spectrum at the upper frequency limit of the HF reflectometer. Its dielectric increment $\Delta\varepsilon_3$ is comparable to the dielectric increment $\Delta\varepsilon_2$ of the reorientation of entire molecules around their long axis but its relaxation frequency f_3 exceeds f_2 measured at approximately 50 °C higher temperature in the isotropic phase of this compound.

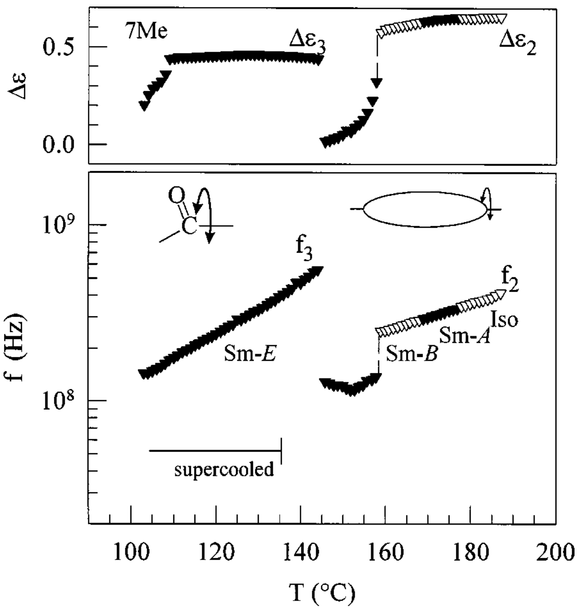


FIG. 6. Dielectric increment $\Delta\varepsilon_2$ and relaxation frequency f_2 (reorientation of entire molecules around the long axis in the Sm-*B*, Sm-*A*, and the isotropic phase of compound 7Me) as well as dielectric increment $\Delta\varepsilon_3$ and relaxation frequency f_3 (intramolecular reorientation in the Sm-*E* phase) versus temperature *T* (cooling trace).

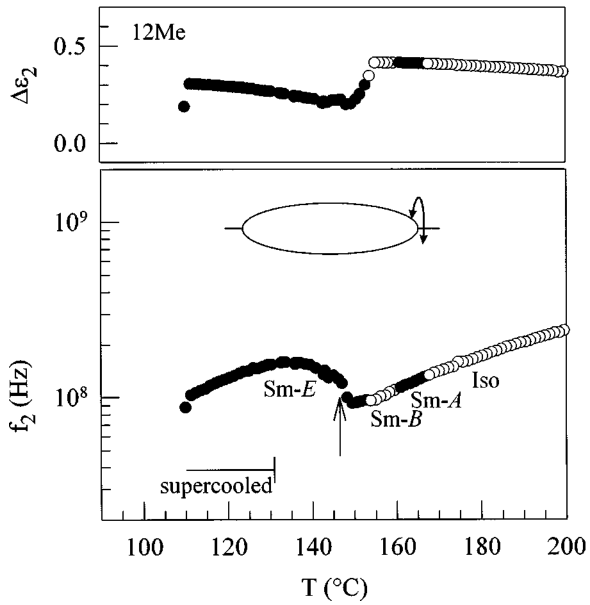


FIG. 7. Dielectric increment $\Delta\varepsilon_2$ and relaxation frequency f_2 (reorientation of entire molecules around their long axis) as a function of temperature *T* for the Sm-*E*, Sm-*B*, Sm-*A* phases and the isotropic melt (Iso) of the homolog 12Me. $f_2(T)$ shows a jump (arrow) and a maximum within the Sm-*E* phase of compound 12Me (cooling trace). The supercooled region of the Sm-*E* is included.

Therefore, this dielectric dispersion should *not* be assigned to a reorientation of the entire 8Me molecule around its long axis. This dispersion is assigned and further addressed to an intramolecular reorientation of a polar site within the 8Me molecule. Usually, these reorientations are located in the microwave region of the dielectric spectrum. However, in a higher-ordered, almost crystallinelike smectic phase as the Sm-*E*, such an intramolecular reorientation may slow down considerably and may enter the frequency range of our dielectric measurements. The temperature dependence is appropriately described by the Arrhenius equation even in the supercooled regime of the Sm-*E* phase of compound 8Me. Its dielectric increment $\Delta\varepsilon_3$ is approximately constant and it decreases upon crystallization. Hence, this mode is locked out in the crystalline state of compound 8Me. In consequence, reorientations of entire molecules around their short molecular axis and intramolecular reorientations of polar sites of the molecule are active in the Sm-*E* phase of compound 8Me, while reorientations of entire molecules around their long molecular axis are, within our experimental accuracy, strongly hindered or even locked out.

Figure 6 depicts the dielectric behavior of the homolog shortened by one methylene unit, compound 7Me. Again, the dielectric dispersion addressed to reorientations of entire molecules around their long molecular axis slows down and ceases at the Sm-*B* to Sm-*E* phase transition. Owing to the fact that the dielectric increment $\Delta\varepsilon_2$ becomes very small in the vicinity of the Sm-*B* to Sm-*E* phase transition the accuracy related to the fitting parameter f_2 is limited due to the small temperature range. The dielectric dispersion assigned to intramolecular reorientations is clearly observed at lower temperatures within the Sm-*E* phase of compound 7Me and it obeys the Arrhenius law.

The high-frequency dielectric behavior of the dodecyloxy derivative, 12Me, is shown in Fig. 7. The relaxation frequency f_2 characterizing the reorientation of entire molecules around their long molecular axis decreases continuously obeying an Arrhenius law within the entire temperature range of the isotropic, Sm-*A*, and Sm-*B* phases. The corresponding dielectric increment $\Delta\varepsilon_2$ decreases slightly at the vicinity of the Sm-*B* to Sm-*E* first-order phase transition, but this mode does not vanish as it is observed for the 7Me and 8Me derivatives. The relaxation frequency f_2 continuously decreases with decreasing temperature in the Sm-*E* phase until a small jump of f_2 to larger frequencies is observed (see Fig. 2). At further cooling f_2 increases continuously, passes through a broad maximum and decreases in the supercooled Sm-*E* phase of compound 12Me. As concluded from Fig. 2, the dielectric dispersion observed in the Sm-*E* phase of compound 12Me is assigned to reorientations of entire molecules around their long axis. Its usual temperature dependence is related to an interdependence between reorientations of entire molecules around their long and their short molecular axes. Intramolecular reorientations within the Sm-*E* phases of the ‘‘longer homologs,’’ 9Me and 12Me, exceed the measurement range of our HF reflectometer and are not observed.

Figure 8 depicts the relaxation frequency f_2 addressed to reorientations of entire molecules around their long axis for different homologs. In contrast to the reorientations of entire molecules around their short molecular axis (cf. Fig. 1), f_2 increases with increasing molecular length and weight. An activation energy of $16\pm5\ \mathrm{kJ\,mol^{-1}}$ is determined for this relaxation within the isotropic, the Sm-*A*, and the Sm-*B* phase irrespective of the molecular length (cf. Table II). The data in the Sm-*E* phase of the homologs 7Me and 8Me are omitted in Fig. 8 since a completely different temperature dependence is observed. Therefore, these dielectric dispersions have been assigned to intramolecular reorientations of

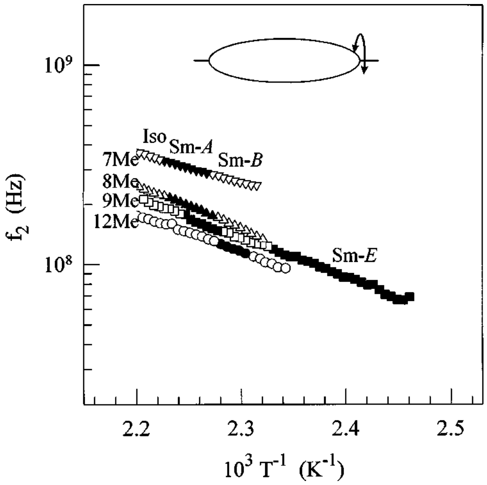


FIG. 8. Relaxation frequency f_2 (reorientation of entire molecules around their long axis) versus the reciprocal temperature $1/T$ within the Sm-*B* and the Sm-*A* phases of the homologous series *n*Me. An Arrhenius-like temperature dependence is observed in the Sm-*E* phase of compound 9Me, but this dispersion was not observed in the Sm-*E* phase of the shorter homologs 7Me and 8Me. The f_2 data measured in the Sm-*E* phase of homolog 12Me has been omitted since it does not obey an Arrhenius law (see Figs. 3 and 7).

polar sites in the molecule. A comparison of the dielectric behavior of isomers possessing almost identical molecular length and weight will underpin this assignment of bands. Following the idea of Martin *et al.*, reorientations of entire molecules around the long and the short molecular axes of these isomers are almost unaffected, in contrast to intramolecular reorientations which depend significantly on the molecular constitution.

B. Intramolecular reorientations within isomeric compounds of equal molecular length

One methylene unit of the dodecyloxy chain of the carboxymethyl compound 12Me is shifted to the opposite side of the molecule. The new isomeric compound (see Table I) comprises an undecyloxy chain and an carboxyethyl function attached to the stilbenic core. This is schematically shown in Fig. 9. The mesomorphic properties of both isomers have been described in a previous work [28]. The molecular length and width of both isomers are approximately equivalent, and they exhibit the same sequence of smectic mesophases but the clearing point of compound 11Et is located 22 °C below the clearing temperature of the 12Me isomer.

For comparison, the relaxation frequency of reorientations of entire molecules around the short f_1 and the long f_2 molecular axes of both isomeric compounds are depicted in Fig. 10. Within the low-frequency regime (LF), the temperature dependence of f_1 of the 11Et isomer corresponds with an extrapolation (solid lines) from the $f_1(T)$ curve of the 12Me homolog towards lower temperatures. This is observed in either the Sm-*A*, the Sm-*B*, or the Sm-*E* phase. This finding ensures that the mechanism of reorientations of entire molecules around their short molecular axis is very similar in the smectic phases of both isomers, and they are not affected by the shift of one methylene unit (see Fig. 9) within the accuracy of our measurements.

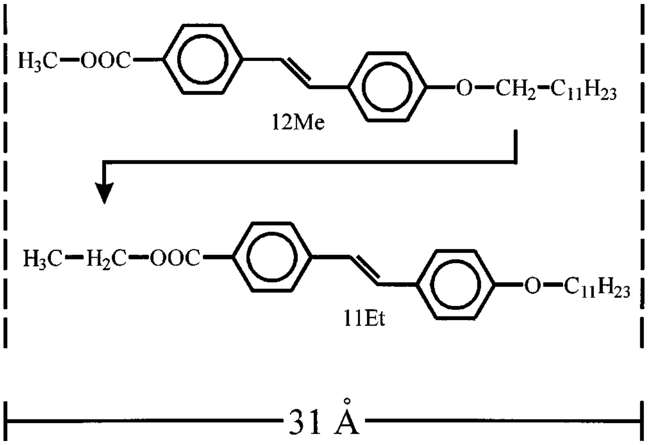


FIG. 9. A pair of isomeric compounds is formed by a shift of one methylene unit of the alkoxy group of compound 12Me to the opposite side of the molecule. The new compound (11Et) exhibits an undecyloxy and a carboxyethyl unit attached to the mesogenic core (*trans*-stilbene). Both isomeric compounds exhibit a molecular length of 31 Å and an equivalent sequence of mesomorphic phases [28].

The temperature dependences of the relaxation frequency f_2 of both isomers are very close to each other, although a small but significant shift of the $f_2(T)$ curve of the 11Et isomer to higher frequencies is observed. We address this small shift to a slightly different average conformation of the isomers. Likewise, the $f_1(T)$ curves of the isomers follow one Arrhenius equation which means that the frequency

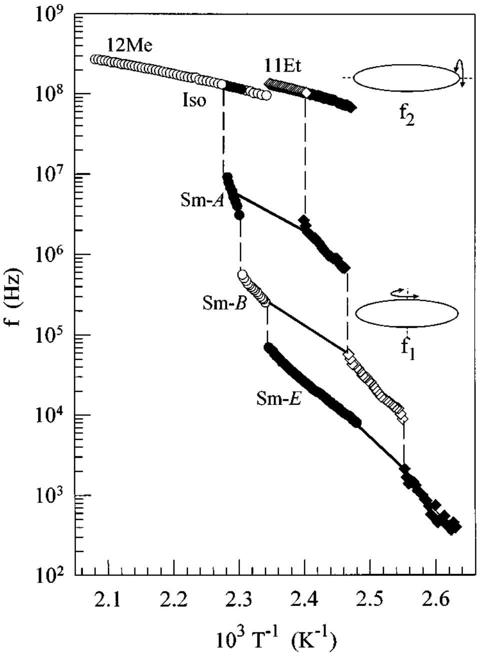


FIG. 10. Relaxation frequency f_1 (reorientation of entire molecules around their short axis) versus the reciprocal temperature $1/T$ compared to the relaxation frequency f_2 (reorientation of entire molecules around their long axis) for the Sm-*E*, Sm-*B*, Sm-*A*, and the isotropic phase of the homolog 12Me (○, ●) and the isomeric compound 11Et (□, ■). The thick almost parallel solid lines indicate that the low-frequency shift of f_1 is predominately caused by the lower clearing temperature of the isomer 11Et. The dashed lines indicate first-order phase transitions.

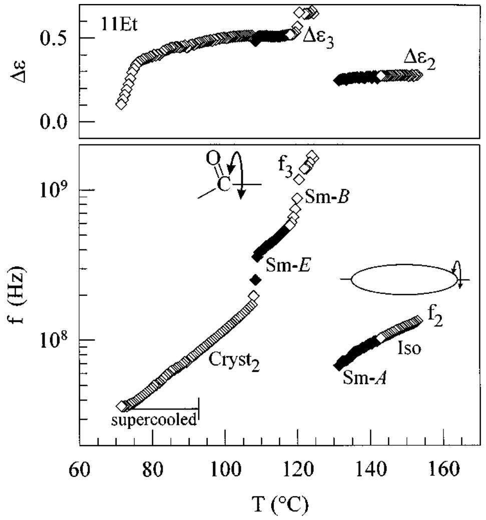


FIG. 11. Dielectric increment $\Delta\varepsilon_2$ and relaxation frequency f_2 (reorientation of entire molecules around the long axis observed in the Sm-*A* and isotropic phase of compound 11Et) as well as dielectric increment $\Delta\varepsilon_3$ and relaxation frequency f_3 (intramolecular reorientation observed in the Sm-*E* and the Sm-*B* phases of compound 11Et) as a function temperature T (cooling trace). In the vicinity of the Sm-*A* to Sm-*B* phase transition (dashed line) reorientations of entire molecules around the long axis are not observed, and the relaxation frequency f_2 related to intramolecular reorientations exceeds the upper frequency limit of our measurement window. Intramolecular reorientations are active in the high-temperature crystalline phase (Cryst$_2$).

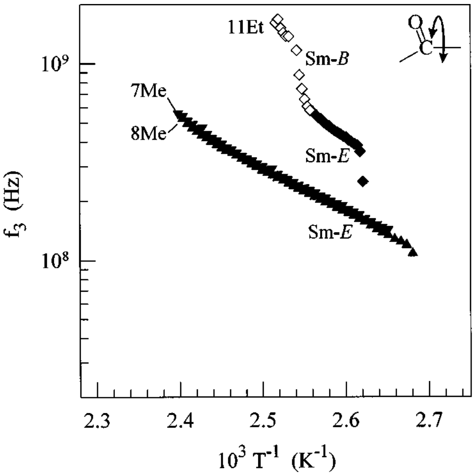


FIG. 12. Dielectric increment $\Delta\varepsilon_3$ and relaxation frequency f_3 (intramolecular reorientations) in the Sm-*E* of homologs 7Me (▼), 8Me (▲), and the Sm-*B* and Sm-*E* of compound 11Et (□, ■) as a function of the reciprocal temperature $1/T$ (cooling trace).

shifts are solely explained in terms of the different phase transition temperatures of the isomers. Consequently, reorientations around the long molecular axis are more sensitive to the shift of the methylene unit than the reorientations around the short molecular axis. In accordance to theory, it can be concluded from Fig. 10 that the shift of the methylene unit has almost no effect on the mechanisms of reorientations of entire molecules around the short as well as the long molecular axis, to a first approximation, and, in turn, this result confirms the assignment of dielectric dispersions presented.

No data within the Sm-*B* and the Sm-*E* phase of isomer 11Et is included in Fig. 10, but, for the complete temperature range of mesophases, the dependence of the dielectric dispersions located in the high-frequency regime are depicted in Fig. 11. This diagram closely resembles that of the homologs 8Me and 7Me depicted in Figs. 5 and 6, respectively. Reorientations of entire molecules around their long axis are observed in the isotropic and the Sm-*A* phase of the isomer 11Et, but, in contrast to the behavior of the homologs 8Me and 7Me, a dielectric dispersion related to intramolecular reorientations appears already in the Sm-*B* phase as it is concluded from the discontinuous dielectric behavior observed at the Sm-*A* to Sm-*B* phase transition. Both, the relaxation frequency and dielectric increment related to intramolecular reorientations are larger than the respective values characterizing reorientations of entire molecules around the long axis at higher temperatures. Consequently, the average lateral dipole moment of the 11Et molecule, which incorporates all contributions of polar sites of the molecule, is smaller than the dipole moment related to the intramolecular reorientation of at least one dipolar site. This observation is easily understood in terms of a minimization of the lateral dipole moment due to an almost antiparallel correlation of intramolecular dipole moments.

The relaxation frequency related to intramolecular reorientations decreases with decreasing temperature, and a discontinuity is observed in the vicinity of the Sm-*B* to Sm-*E* phase transition. It is worth pointing out that this dielectric dispersion does not cease in the high-temperature crystalline state (Cryst$_2$) of compound 11Et but it slows down at the crystallization of the Sm-*E* phase. Nevertheless, these intramolecular reorientations are locked out in the low-temperature crystalline state of compound 11Et as concluded from the decrease of the dielectric increment below 77 °C. Therefore, the high temperature crystalline phase of compound 11Et belongs to a disordered crystalline phase.

Unfortunately, intramolecular reorientations in both isomeric compounds, 12Me and 11Et, of approximately equivalent molecular length cannot be compared directly. Intramolecular reorientations were not observed below 1 GHz in the Sm-*E* phase of isomer 12Me (cf. Fig. 9). The relaxation frequencies f_3 assigned to intramolecular reorientations observed within the Sm-*E* phase of homologs 7Me, 8Me exhibiting a carboxymethyl unit and the isomer 11Et carrying a carboxyethyl unit are compared in Fig. 12. The relaxation frequency f_3 is independent of the molecular length within the homologous series but the isomer 11Et exhibits a significantly larger relaxation frequency. This finding supports the assignment of this dielectric dispersion observed in the high-frequency regime of the dielectric spectrum to an intramolecular reorientation of polar sites, probably the carboxymethyl site within the homologs 7Me and 8Me or the carboxyethyl unit in compound 11Et.

IV. SUMMARY

Reorientations of entire molecules around their short and their long molecular axes as well as intramolecular reorientations of dipolar sites have been studied in the isotropic, the Sm-*A*, Sm-*B*, and Sm-*E* phases of a homologous series of nonchiral stilbenes and two isomeric compounds of equal molecular length. Reorientations of entire molecules are present in the Sm-*A*, Sm-*B*, and Sm-*E* phases and their relaxation frequency f_1 increases remarkably with increasing molecular length. The nematic order parameter S is not an appropriate quantity to describe the temperature and molecular length dependence of f_1 exclusively, and the free volume has to be taken into consideration. Evidence is presented for an interdependence of reorientations of entire molecules around their long and short axes. In general, reorientations of entire molecules around their long axis with a relaxation frequency f_2 are active in the Sm-*A* and Sm-*B* phases of the homologs, but these are, at least partially, locked out within the Sm-*E* phase of the shorter homologs 7Me and 8Me. The relaxation frequency f_2 increases with increasing molecular length. Two isomeric compounds 12Me and 11Et possessing an equal molecular length exhibit a very similar temperature dependence of the reorientations of entire molecules around their short and long axes, respectively.

Within the Sm-*E* phase of the shorter homologs, 7Me and 8Me, an additional dielectric dispersion within the high-frequency regime is detected which is independent of the molecular length but dependent on the molecular constitution. This mode has been addressed to intramolecular reorientations.

ACKNOWLEDGMENTS

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