Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Quantum chemical studies on the conformational behaviour of substituted banana-shaped mesogens with a central 1,3-phenylene unit

S. Ananda Rama Krishnan[a]; W. Weissflog[a]; R. Friedemann[a]
[a] Department of Chemistry, Martin Luther University, Halle-Wittenberg, Kurt-Mothes-Str. 2, D-06120 Halle (Saale), Germany

To cite this Article Krishnan, S. Ananda Rama , Weissflog, W. and Friedemann, R.(2005) 'Quantum chemical studies on the conformational behaviour of substituted banana-shaped mesogens with a central 1,3-phenylene unit', Liquid Crystals, 32: 7, 847 — 856

To link to this Article: DOI: 10.1080/02678290500231604

URL: http://dx.doi.org/10.1080/02678290500231604

Liquid Crystals, Vol. 32, No. 7, July 2005, 847–856

Quantum chemical studies on the conformational behaviour of substituted banana-shaped mesogens with a central 1,3-phenylene unit

S. ANANDA RAMA KRISHNAN, W. WEISSFLOG and R. FRIEDEMANN*

Department of Chemistry, Martin Luther University, Halle-Wittenberg, Kurt-Mothes-Str. 2, D-06120 Halle (Saale), Germany

(*Received 24 January 2005; accepted 6 April 2005*)

Ab initio and DFT calculations on the HF/STO-3G and B3LYP/6-31G(d) level were performed on the conformational behaviour of isolated banana-shaped molecules of 1,3-phenylene bis[4-(4-*n*-hexyloxyphenyliminomethyl)benzoate] systems (P-6-O-PIMB). The influence of small substituents in both the central phenyl ring and the external phenyl rings on the shape, polarity and flexibility of these molecules was investigated by one- and two-fold relaxed potential energy scans in a systematic way. The effect of substituents on the global polarity of banana-shaped mesogens was analysed by the magnitude and direction of the dipole moment and its components in relation to the long axis of the molecules. Moreover, a simple model for the calculation of the bending angle was tested for banana-shaped molecules with a central 1,3-phenylene unit. The findings for the isolated banana-shaped molecules are correlated with solid state X-ray and liquid crystalline state NMR results. Banana-shaped molecules with both hexyloxy (P-6-O-PIMB) and hexyl (P-6-PIMB) terminal chains are included to study the effect of substituents in the external phenyl rings on the flexibility of these chains. An attempt will be made to correlate the results with experimental findings on banana-shaped mesogens.

1. Introduction

Bent-core or banana-shaped mesogens represent a new sub-field in liquid crystal research and supramolecular chemistry. A main reason for the significant interest in such banana-shaped mesogens is their ability to generate supramolecular chirality from achiral molecules [1, 2]. Thus bent-core mesogens open the way to new materials with ferroelectric and antiferroelectric properties for electro-optical applications [3, 4]. Several classes of banana-shaped molecules have been synthesized in the last five years, most of them containing a central 1,3-phenylene unit [5–12]. The new mesophases of these compounds were characterized by means of X-ray diffraction [2, 3, 11] and nuclear magnetic resonance (NMR) spectroscopy [13–18], as well as dielectric and electro-optical experiments [19, 20]. It was shown that the introduction of small substituents both onto the central 1,3-phenylene unit and the legs of these molecules leads to significant changes in their phase behaviour [3, 7]. Obviously, such substitutions influence the shape, polarity and flexibility of the molecules and cause a different aggregation of the bent-core mesogens. In order to study the effect of substitution on the properties of bent-core molecules in a systematic way we have performed Hartree–Fock (HF) and density functional theory (DFT) calculations on the 1,3-phenylene bis[4-(4-*n*-hexyloxyphenyliminomethyl)-benzoate] systems (P-6-O-PIMB) shown in figure 1 and table 1.

Up to now theoretical calculations on the molecular structure of bent-core molecules on the *ab initio* level were performed in a limited way. Imase *et al.* [21] have carried out DFT calculations on three-ring model systems of banana-shaped molecules. Recently, quantum chemical calculations have taken into account the central core of five-ring banana-shaped mesogens without terminal alkoxy chains [22]. Other authors have used semi-empirical methods on the AM1 level for conformational studies on banana-shaped monomers [23]. Therefore, we have calculated relaxed potential energy surface (PES) scans for substituted bent-core systems with a central 1,3-phenylene unit including one torsion angle (relaxed rotational barriers), as well as two-fold representations (Ramachandran-like

---

*Corresponding author.
Email: rudolf.friedemann@chemie.uni-halle.de

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500231604

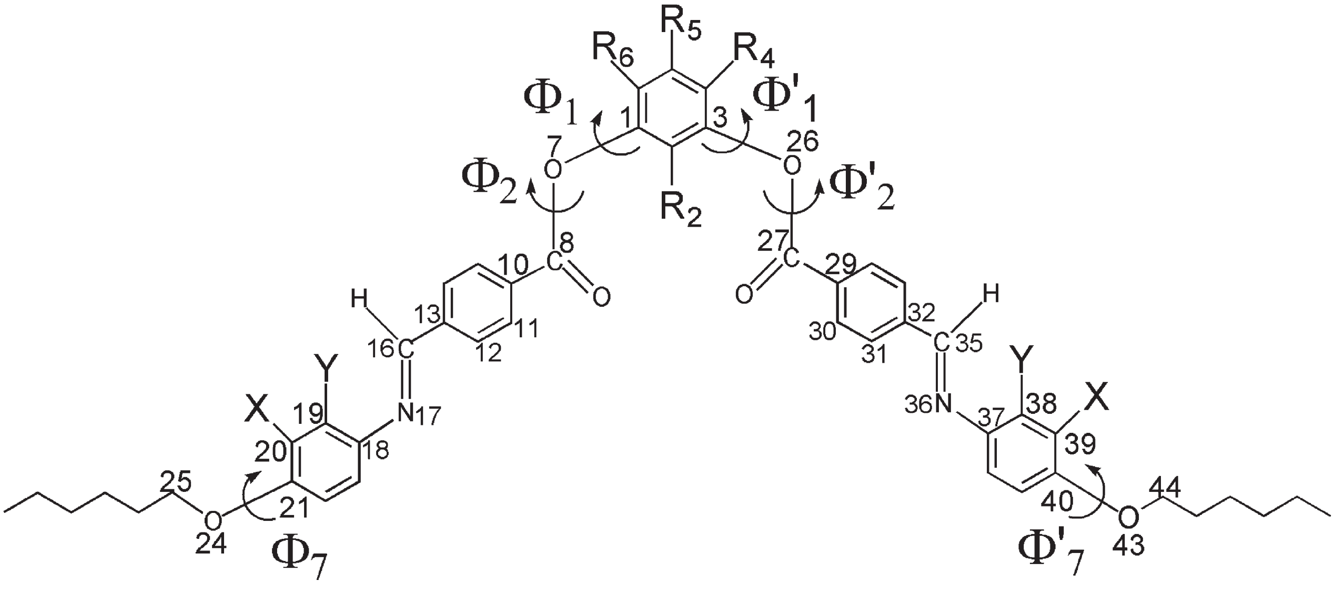

Figure 1. Definition of significant torsion angles and numbering of the systems.

plots) for a systematic conformational analysis with more sophisticated methods. The applicability of the HF method for calculations on the molecular structure of bent-core systems was checked by comparing DFT studies.

The effect of substituents on the polarity of banana-shaped mesogens was investigated by analysis of the magnitude and direction of the dipole moment and its components in relation to the long axis of the molecules. Energy-weighted simple mean values were calculated to regard the effect of preferred conformers on the dipole moment in an easy way. For banana-shaped molecules the bending angle α is a relevant parameter which can be measured by NMR experiments [3]. A simple model for the calculation of the bending angle was introduced for molecules of the 1,3-phenylene type. The influence of small substituents both at the central unit and the legs on the bending angle was studied. The findings on the isolated banana-shaped molecules are related to the results of liquid crystalline state NMR and solid state X-ray experiments. Moreover, hexyloxy and hexyl groups were considered in order to study the flexibility of different terminal chains, especially under the influence of adjacent substituents in the bent-core systems.

2. Details of the computation

The program package Gaussian 98 [24] was used for the *ab initio* HF/STO-3G calculations and the DFT studies

Table 1. Acronyms of the systems.

System	R_2	R_4	R_5	R_6	X	Y	T/°C [b][7]
P-6-O-PIMB P-6-PIMB[a]	H	H	H	H	H	H	B_2 174 I
DCl-P-6-O-PIMB	H	Cl	H	Cl	H	H	N 148 I
DCl-P-6-O-PIMB-*X*-F DCl-P-6-PIMB-*X*-F[a]	H	Cl	H	Cl	F	H	SmA 129 I
DCl-P-6-O-PIMB-*Y*-F	H	Cl	H	Cl	H	F	N 128 I
DCl-P-6-O-PIMB-*X*-Cl	H	Cl	H	Cl	Cl	H	N 109 I
F-P-6-O-PIMB	H	H	F	H	H	H	B_2 180 I
F-P-6-O-PIMB-*X*-F	H	H	F	H	F	H	B_2 164 I
F-P-6-O-PIMB-*Y*-F	H	H	F	H	H	F	Cr 144 I
NO_2-P-6-O-PIMB	NO_2	H	H	H	H	H	B_7 177 I
NO_2-P-6-O-PIMB-*Y*-CH_3	NO_2	H	H	H	H	CH_3	Cr 137 I
NO_2-P-6-O-PIMB-*Y*-CF_3	NO_2	H	H	H	H	CF_3	Cr 140 I

[a] Systems with hexyl terminal chains.
[b] Clearing temperature for systems with octyloxy terminal chains.

on the B3LYP/6-31G(d) level. The applicability of the HF method with a small basis set on the bent-core molecules was shown by comparing studies with DFT calculations. The HF and DFT calculations on the bent-core systems indicate a remarkable qualitative agreement on the stability and the conformational behaviour of such molecules. This was also confirmed by our theoretical studies on larger biochemical and mesogenic systems [25, 26]. Therefore, most of the calculations were carried out with the *ab initio* HF method to limit the computational effort.

For a systematic study on the conformational behaviour of the bent-core molecules, the relaxed rotational barriers and two-fold PES scans (Ramachandran-like plots) were calculated for significant torsion angles (see figure 1) of the legs. The energetically preferred structures were obtained by a full optimization from different starting structures including twisted and planar ones. The one- and two-fold PES scans were generated by fixing of the corresponding torsion angles and a complete optimization of the other parameters in a stepwise manner. Planar structures result from a partial optimization with fixed values for the relevant torsion angles. The dipole moment and its components were considered to give some indication of the magnitude and the direction of global polar effects. Conformations with a relative energy of less than $10\,\mathrm{kJ\,mol^{-1}}$ were taken into account to obtain energy-weighted simple mean values of the dipole moment and its components in a very easy way. In figure 2 the orientation of the coordinate system is shown in relation to the central ring to define the direction of the dipole moment and its components. The sense of direction of the dipole moment corresponds from the negative to the positive centre of charge as generally considered.

For a further qualitative comparison of the effect of substitution in the 1,3-phenylene systems, we have defined a simple procedure for the calculation of a global pattern of charges along the legs of the molecules. The atomic net charges of the molecules were calculated from the fit to reproduce the electrostatic potential within the HF and DFT methods (ESP charges). For the phenyl rings and the connecting groups, ESP group charges are obtained by summarizing the charges of the corresponding atoms. For the phenyl rings only the carbon atoms are taken into account. The ESP group charges are localized at the centres of the rings as well as at the centres of the C–O and the C=N bonds of the connecting groups. In this way the ESP group charges and their positions are comparable in the most stable conformers of the five-ring mesogens of the 1,3-phenylene type.

A simple model was introduced to define the bending angle α for the five-ring systems with a central 1,3-phenylene unit; the procedure is illustrated in figure 3. The centres of the five aromatic rings are calculated for the corresponding conformers. From the central points of the rings BAB′ and CAC′ the angles α_1 and α_2 are obtained, respectively. The bending angle α is indicated as the mean value of α_1 and α_2. This model allows a simple quantification of the bent property of conformations for such banana-shaped mesogens.

3. Results and discussion

3.1. *Planar and twisted conformations*

The results of the conformational studies on the systems P-6-O-PIMB and the 4,6-dichloro-substituted compound (DCl-P-6-O-PIMB) are summarized in table 2. Both the HF and the DFT methods indicate that the twisted conformers are energetically preferred in comparison to the planar ones by about $20\,\mathrm{kJ\,mol^{-1}}$ (HF) and $10\,\mathrm{kJ\,mol^{-1}}$ (DFT). From X-ray investigation of DCl-P-6-O-PIMB in the solid state, a twisted structure

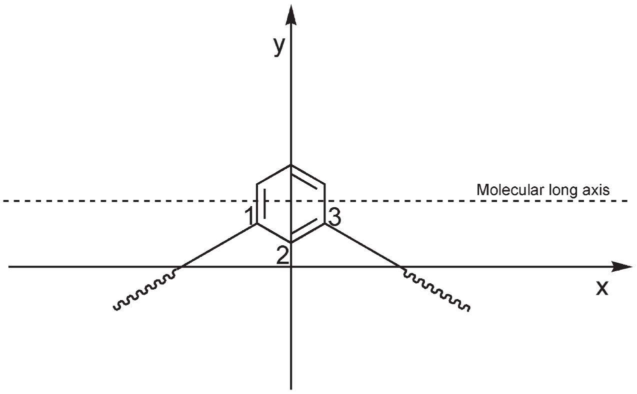

Figure 2. Coordinate system for explanation of the components of the dipole moment in 1,3-phenylene type molecules.

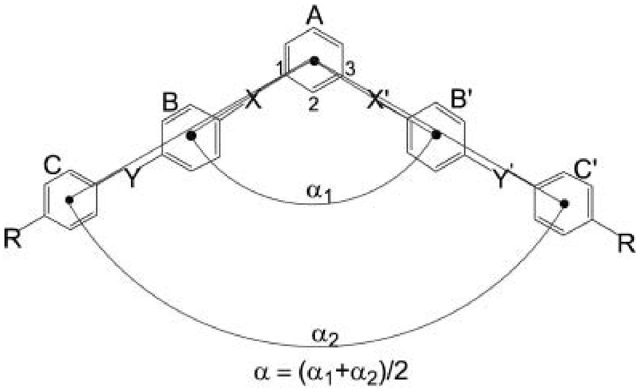

Figure 3. Simple model for the calculation of the bending angle α.

Table 2. Comparison of HF and DFT results on the conformers of P-6-O-PIMB and DCl-P-6-O-PIMB.

		HF					DFT				
System	Conformer	E_r/kJ mol^{-1}	μ/D	α/°	Φ_1/°	Φ'_1/°	E_r/kJ mol^{-1}	μ/D	α/°	Φ_1/°	Φ'_1/°
P-6-O-PIMB	twisted	0 (−2299.1504)[a]	3.67	129	239	239	0 (−2342.6816)[a]	4.76	121	249	252
	planar	21	4.09	118	180	180	7	6.80	114	180	180
DCl-P-6-O-PIMB	twisted	0 (−3207.1500)[a]	5.98	126	59	59	0 (−3261.8643)[a]	4.15	115	50	54
	planar	19	3.50	123	0	0	11	2.26	125	0	0
	X-ray	2604	0.40	140	73	94	2187	0.79	140	73	94
	X-ray-like[b]	12	0.90	135	73	94	17	1.18	134	73	94

[a] Total energy (Hartree) of the most stable conformers in parentheses.

[b] All torsion angles are fixed as in X-ray, but bond length and bond angles are optimized.

was also found [27]. In both methods the relative energy of the X-ray conformer is very high. The partially optimized conformers of DCl-P-6-O-PIMB with fixed torsion angles, as in the X-ray structure but optimized bond lengths and angles (X-ray-like conformers), are relatively stable twisted forms 12 kJ mol^{-1} (HF) and 17 kJ mol^{-1} (DFT). Obviously, the high relative energy of the X-ray conformer results mainly from deviations in the bond length, especially of the C–H bonds.

Moreover, the calculations on the isolated molecules indicate the conformational flexibility of the bent-core mesogens. The values of the dipole moment and the bending angle depend significantly on the conformers and the substituents at the central ring. It is remarkable that the X-ray and X-ray-like conformers show very small dipole moments and relatively large bending angles related to the most stable one which is obviously caused by packing effects. This is illustrated by a superposition of the preferred HF and DFT conformers as well as the X-ray structure in figure 4. For P-6-OPIMB we have calculated the relaxed rotational barriers related to the torsion angles Φ_1 and Φ_2 within the HF and DFT methods. Both methods indicate similar results for the barriers of Φ_1, 8 kJ mol^{-1}(HF) and 6 kJ mol^{-1}(DFT), as well as of Φ_2 40 kJ mol^{-1}(HF) and 40 kJ mol^{-1}(DFT). Moreover, the trends of the HF and DFT curves are comparable. These results support our procedure of performing systematic calculations on the banana-shaped molecules on the HF level with a reasonable computational effort.

3.2. *Effect of substituents in the central phenyl ring*

The influence of a substitution in the 1,3-phenylene unit on the flexibility of the isolated bent-core molecules was investigated by a systematic analysis of the relaxed rotational barriers in relation to the significant torsion angles Φ_1 and Φ_2 (see figure 1). First, the relaxed rotational barrier of the leg with respect to the torsion angle Φ_1=C2–C1–O7–C8 was calculated.

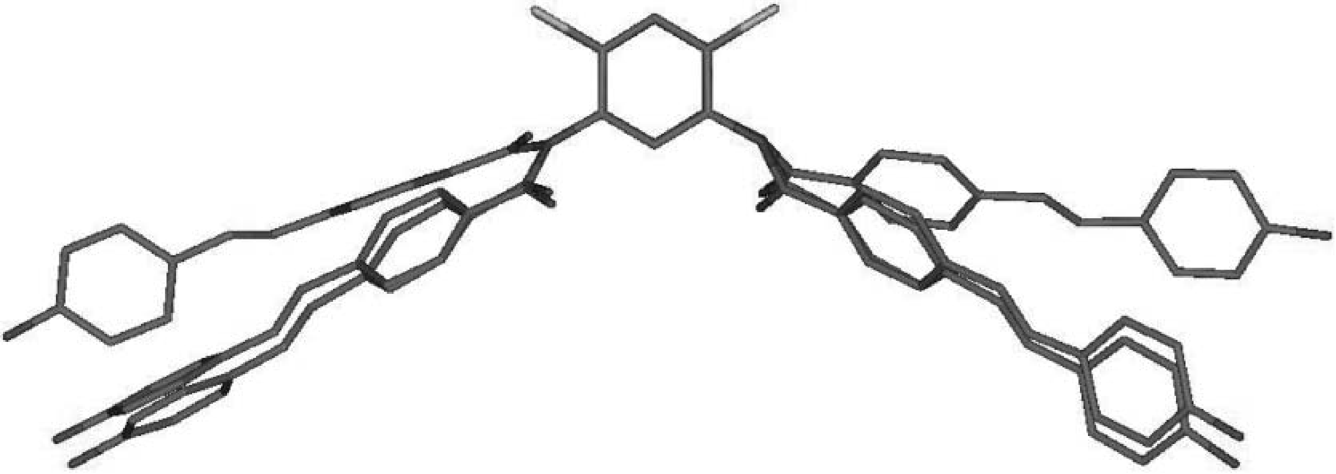

Figure 4. Superposition of DCl-P-6-O-PIMB conformers related to the 1,3-phenylene central unit (above: X-ray, middle: DFT, below: HF).

The results for the unsubstituted as well as for the dichloro-, fluoro- and nitro-substituted molecules are illustrated in figure 5 (*a*).

The curves show a significant effect of the substitution on the flexibility of the legs related to the type and position of the substituents. For the molecules P-6-O-PIMB and F-P-6-O-PIMB, the barriers are generally lower than 10 kJ mol^{-1} over the whole range of Φ_1. In the molecules DCl-P-6-O-PIMB and NO_2-P-6-O-PIMB the rotational barriers are remarkably increased to 40 kJ mol^{-1}. This is caused by a strong repulsion between the substituents on the central phenyl ring and the adjacent carbonyl group, especially in conformations with $\Phi_1 = 180°$ (DCl-P-6-O-PIMB) and $\Phi_1 = 0°$ (NO_2-P-6-O-PIMB). In all cases the preferred conformers are found in Φ_1 ranges of 60°–120° and 240°–300°, which is in agreement with the X-ray structure of DCl-P-6-O-PIMB [27]. The strong effect of the chlorine substitution on the conformational flexibility of the legs can also be illustrated by Ramachandran-like plots with respect to the torsion angles Φ_1 and Φ_1' (figure 6). The introduction of two chlorine atoms in the 4- and 6-positions of the central unit decreases the conformational flexibility of the bent-core molecules. This follows from the significantly higher values of the relative energy for the global and local maxima in the two-fold relaxed PES scan of DCl-P-6-O-PIMB. In some way it could be a reason for the loss of B-phases in DCl-P-6-O-PIMB in comparison with P-6-O-PIMB [7].

The dependency of the dipole moment μ on conformers with constraints to the torsion angle Φ_1 is shown in figure 5 (*b*). Within a considered bent-core molecule the magnitude of the dipole moment varies by about 1–2 D with variation of the torsion angle Φ_1. The curves show the common trend in the dipole moment μ (NO_2-P-6-O-PIMB)$<\mu$ (P-6-O-PIMB)$<\mu$ (F-P-6-O-PIMB)$<\mu$ (DCl-P-6-O-PIMB). The sequence is also supported by the energy-weighted simple mean values of the dipole moment and its components (table 3), where conformations with a relative energy less than 10 kJ mol^{-1} are considered. The main contribution to the dipole moment comes from the μ_y component oriented perpendicular to the long axis of the molecule and parallel to the plane of the central ring (figure 2). The negative sign indicates the direction of μ_y from C5 to C2 in this type of bent-core molecules. The large differences in the dipole moments, especially in NO_2-P-6-O-PIMB and DCl-P-6-O-PIMB, can be seen as indications of their different phase behaviour and mesophase stability [3] caused by their diverse global polarity. The results show a relatively large effect on the values of the μ_y component of the dipole moment in

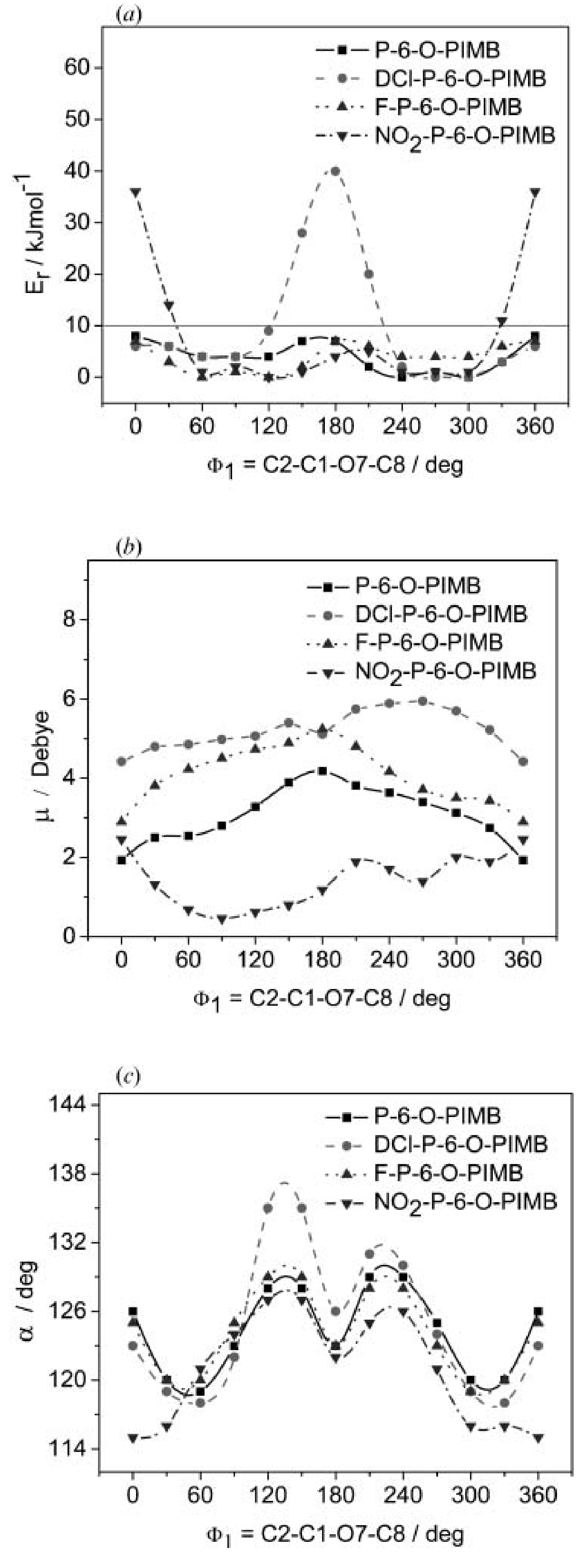

Figure 5. One-fold scans (HF) related to the torsion angle Φ_1: (*a*) relative energy E_r, (*b*) dipole moment μ, (*c*) bending angle α.

the bent-core molecules considered. Obviously, the μ_y component is more important in banana-shaped than in calamitic mesogens with respect to the formation of smectic layers.

The results of the ESP group charges (HF method) for the most stable conformers of the 1,3- phenylene systems with substitutions on the central ring are illustrated in figure 7. The ESP group charges show that the electron density is significantly decreased on the central ring in the sequence P-6-O-PIMB>NO_2-P-6-O-PIMB>F-P-6-O-PIMB>DCl-P-6-O-PIMB. A similar trend was found for the ESP group charges on the ester groups and the external rings. But the effect is weaker. Whereas the charges at the intermediate rings are nearly the same for the molecules considered, it is remarkable that the ESP group charges show alternating values on the rings along the legs in all cases. The ESP group charges obtained by the DFT method show an analogous tendency but the values are generally smaller. The findings are in agreement with the maximum values of the calculated electrostatic potential on the rings in similar molecules by Bedel *et al.* [28].

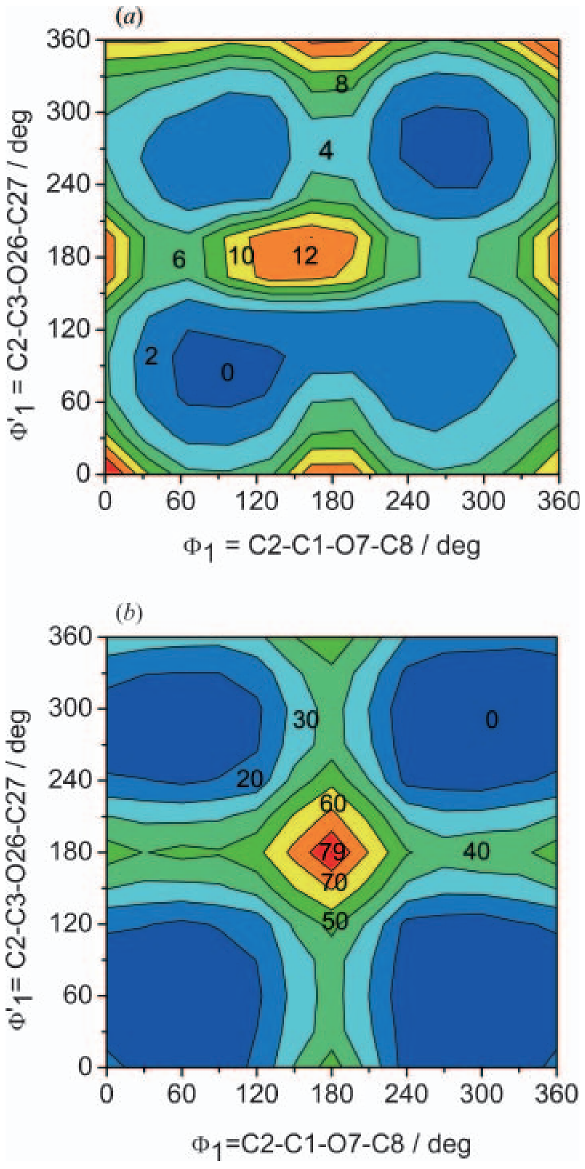

Figure 6. Two-fold potential energy surface scans (HF) related to the torsion angles Φ_1 and Φ'_1: (*a*) P-6-O-PIMB, (*b*) DCl-P-6-O-PIMB.

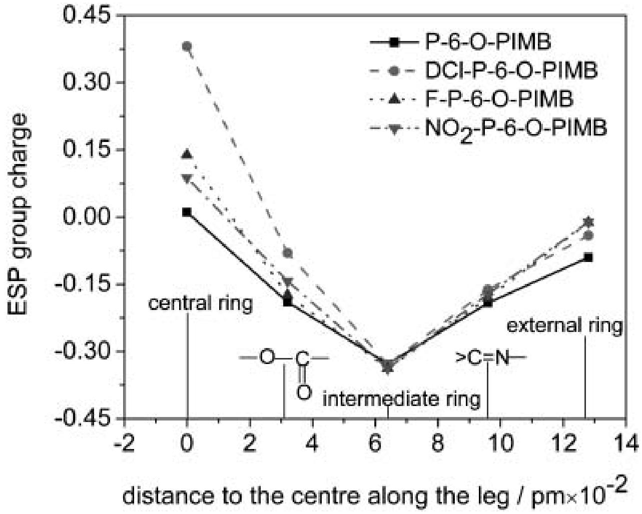

Figure 7. Electrostatic potential group charges along a leg of bent-core mesogens with substituents on the central phenyl ring (HF results).

Table 3. HF energy-weighted simple mean values of dipole moment and its components, for banana-shaped molecules with substituents on the central phenyl ring.

System	$\bar{\mu}_x$/D	$\bar{\mu}_y$/D	$\bar{\mu}_z$/D	$\bar{\mu}$/D	Φ_1/°	Φ'_1/°
P-6-O-PIMB	0.0 (0.0)[a]	−3.13 (−3.67)	0.0 (0.0)	3.13 (3.67)	239	239
DCl-P-6-O-PIMB	−0.07 (0.0)	−5.17 (−6.26)	−0.13 (0.0)	5.18 (5.98)	59	59
F-P-6-O-PIMB	−0.06 (0.0)	−4.10 (−4.75)	−0.09 (0.0)	4.12 (4.75)	125	125
NO_2-P-6-O-PIMB	−0.33 (0.0)	−0.07 (−0.68)	−0.35 (0.0)	0.54 (0.68)	132	132

[a] The μ values of the most stable conformers in parentheses.

Moreover, the conformers of the substituted banana-shaped molecules show remarkable changes of the bending angle α with respect to the torsion angle Φ_1, figure 5 (*c*). The highest values are found for DCl-P-6-O-PIMB and the lowest for NO_2-P-6-O-PIMB. This tendency is also indicated by the range of the minimum and maximum values of α with 115°–126° (NO_2-P-6-O-PIMB), 119°–128° (F-P-6-O-PIMB), 119°–129° (P-6-O-PIMB) and 119°–135° (DCl-P-6-O-PIMB), including conformers with a relative energy less than $10\,\mathrm{kJ\,mol^{-1}}$. The increased bending angle of DCl-P-6-O-PIMB is in agreement with liquid crystalline state NMR findings [3] and solid state X-ray data [27]. The calculated bending angles for P-6-O-PIMB and F-P-6-O-PIMB are comparable, which is supported by the NMR findings 122° and 116°–118°, respectively [3, 9].

The relaxed rotational barriers with respect to the torsion angle Φ_2=C1–O7–C8–C10 are illustrated in figure 8 for the bent-core molecules. In contrast to Φ_1, the conformational degree of freedom for Φ_2 is rather limited. It results in a relatively large rotational barrier of about $40\,\mathrm{kJ\,mol^{-1}}$ for $\Phi_2=0°$, which is independent of the substituents on the central unit. For this constraint the energetically preferred coplanar arrangement of the carbonyl group and the adjacent phenyl ring is sterically hindered by a repulsion of rings A and B, it resulting in a less stable conformer.

3.3. *Effect of substituents in the external phenyl rings*

In order to investigate the influence of substituents at different positions of the external phenyl rings on the conformational behaviour of the terminal chains, the relaxed rotational barriers were calculated with respect to the angle Φ_7 (figure 1). The results for the fluorine- and chlorine-substituted DCl-P-6-O-PIMB systems are presented in figure 9. A fluorine substitution in positions 19 and 38 (see figure 1) of the external phenyl rings (DCl-P-6-O-PIMB-*Y*-F) has a minor effect on the conformational behaviour of the terminal hexyloxy chains.

The relaxed rotational barrier of DCl-P-6-O-PIMB-*Y*-F corresponds closely to that of DCl-P-6-O-PIMB (not shown in figure 9). Whereas a fluorine substitution in positions 20 and 39 (DCl-P-6-O-PIMB-*X*-F) increases the conformational flexibility of the hexyloxy groups, the larger chlorine atoms in these positions (DCl-P-6-O-PIMB-*X*-Cl) cause a remarkable increase of the relaxed rotational barrier for the side chains. This can be explained by the larger repulsion between the hexyloxy group and the adjacent chlorine atom, especially for the constraint $\Phi_7=0°$. Similar results were found in the systems F-P-6-O-PIMB-*X*-F and F-P-6-O-PIMB-*Y*-F. Clearly, substitutions in the central phenyl ring have less influence on the conformational behaviour of terminal chains. The substitution of methyl and trifluoromethyl groups in positions 19 and 38 of NO_2-P-6-O-PIMB has only a small effect on the relaxed rotational barrier of Φ_7 (figure 10). The curves for NO_2-P-6-O-PIMB-*Y*-CH_3 and NO_2-P-6-O-PIMB-*Y*-CF_3 are more structured in comparison with that for NO_2-P-6-O-PIMB, but the height of the barriers is comparable.

The energy-weighted simple mean values for the dipole moments and their components are summarized in table 4 for the bent-core molecules with substituents in the external phenyl rings. Generally, the polar effect of small substituents is less distinct than for corresponding substitution on the central phenyl ring. Significant

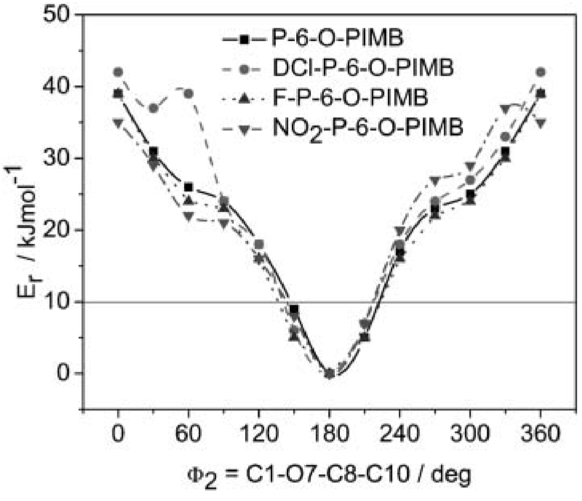

Figure 8. Relaxed rotational barriers (HF) related to the torsion angle Φ_2.

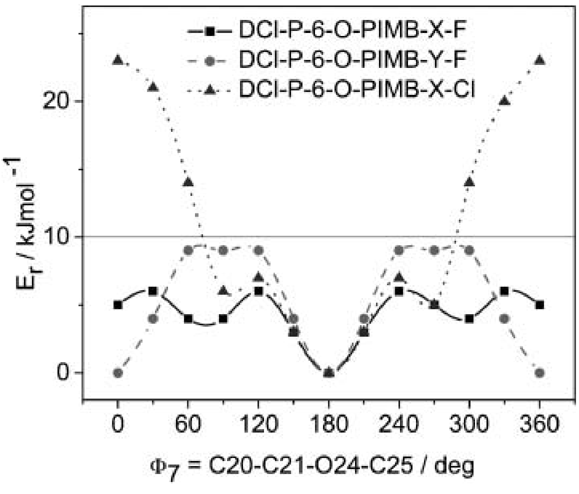

Figure 9. Relaxed rotational barriers (HF) related to the torsion angle Φ_7 for DCl-P-6-O-PIMB systems.

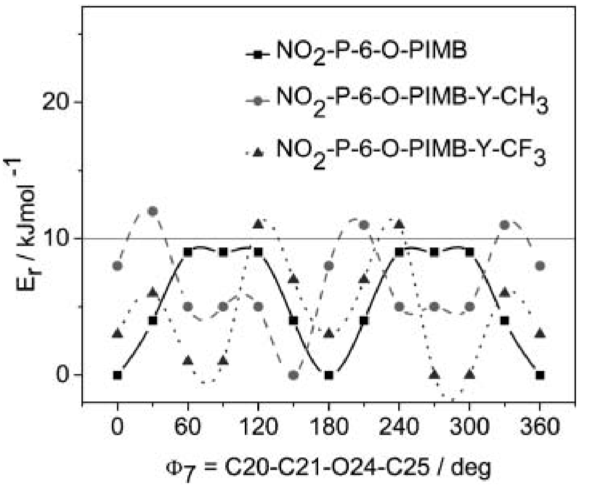

Figure 10. Relaxed rotational barriers (HF) related to the torsion angle Φ_7 for NO_2-P-6-O-PIMB systems.

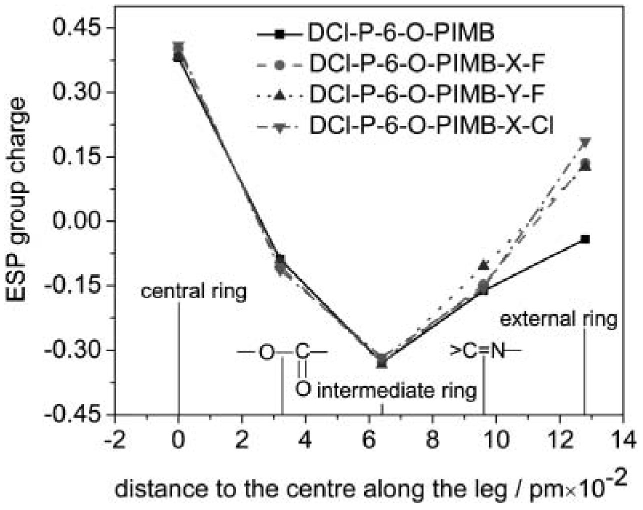

Figure 11. Electrostatic potential group charges along a leg of bent-core mesogens with substituents on the external phenyl rings (HF results).

changes in the largest component μ_y were found, especially in the chlorine (DCl-P-6-O-PIMB-*X*-Cl) and trifluoromethyl (NO_2-P-6-O-PIMB-*Y*-CF_3) substituted molecules.

The ESP group charges of DCl-P-6-O-PIMB systems with different substituents in the external rings are shown in figure 11. The polar substituents cause a decrease of the electron density on the external rings, especially in the DCl-P-6-O-PIMB-*X*-Cl molecule. The ESP group charges on the azomethine fragments are changed only when the fluorine substituents are in positions (19 and 38) adjacent to the C=N group. Generally, the alternating behaviour of the ESP group charges on the rings along the legs is retained, with a low electron density on the central and external rings but a high electron density on the intermediate rings.

For comparison, calculations on the 1,3-phenylene bent-core molecules with hexyl groups as terminal chains were performed to study their conformational and electronic effects. The results are shown in figure 12 for the corresponding hexyloxy (P-6-O-PIMB and DCl-P-6-O-PIMB-*X*-F) and hexyl (P-6-PIMB and DCl-P-6-PIMB-*X*-F) systems. In the P-6-O-PIMB system the replacement of the terminal hexyloxy groups by hexyl (P-6-PIMB) leads to a shift of the positions of the minima and maxima, but the rotational barriers have comparable values, figure 12 (*a*). The DCl-P-6-O-PIMB-*X*-F and DCl-P-6-PIMB-*X*-F molecules, however, show a significant difference in the relaxed rotational barrier related to the C21–O24 and C21–C24 bonds, respectively, figure 12 (*b*). In the hexyl compound (DCl-P-6-PIMB-*X*-F) the barrier is increased by about 20 kJ mol^{-1} in comparison to the hexyloxy compound (DCl-P-6-O-PIMB-*X*-F). Obviously, the rotation of the hexyl chains are more hindered by the adjacent fluorine atoms in positions 20 and 39 than in the case of the hexyloxy chains. Moreover, replacement of the terminal hexyloxy chains by hexyl groups results in a lower value of the dipole moment: 6.26 D for DCl-P-6-O-PIMB-*X*-F and 4.87 D for DCl-P-6-PIMB-*X*-F.

Table 4. HF energy-weighted simple mean values of dipole moment and its components, for banana-shaped molecules with substituents on the external phenyl rings.

System	$\bar{\mu}_x$/D	$\bar{\mu}_y$/D	$\bar{\mu}_z$/D	$\bar{\mu}$/D
DCl-P-6-O-PIMB-*X*-F	−0.12 (0.0)[a]	−5.5 (−6.26)	−0.16 (0.0)	5.5 (6.26)
DCl-P-6-O-PIMB-*Y*-F	−0.02 (0.0)	−4.92 (−7.11)	−1.13 (0.0)	5.04 (7.11)
DCl-P-6-O-PIMB-*X*-Cl	−1.37 (−1.75)	−4.28 (−3.67)	−0.25 (+0.65)	4.51 (4.12)
F-P-6-O-PIMB-*X*-F	−0.11 (0.0)	−3.81 (−4.49)	−0.48 (−0.02)	3.85 (4.49)
F-P-6-O-PIMB-*Y*-F	−0.04 (0.0)	−4.94 (−5.39)	−0.21 (0.0)	4.94 (5.39)
NO_2-P-6-O-PIMB-*Y*-CH_3	−0.01 (0.0)	−0.84 (−1.05)	−1.34 (0.0)	1.58 (1.05)
NO_2-P-6-O-PIMB-*Y*-CF_3	−0.10 (−0.53)	−2.89 (−3.24)	−0.82 (+0.52)	3.01 (3.35)

[a] The μ values of the most stable conformers in parentheses.

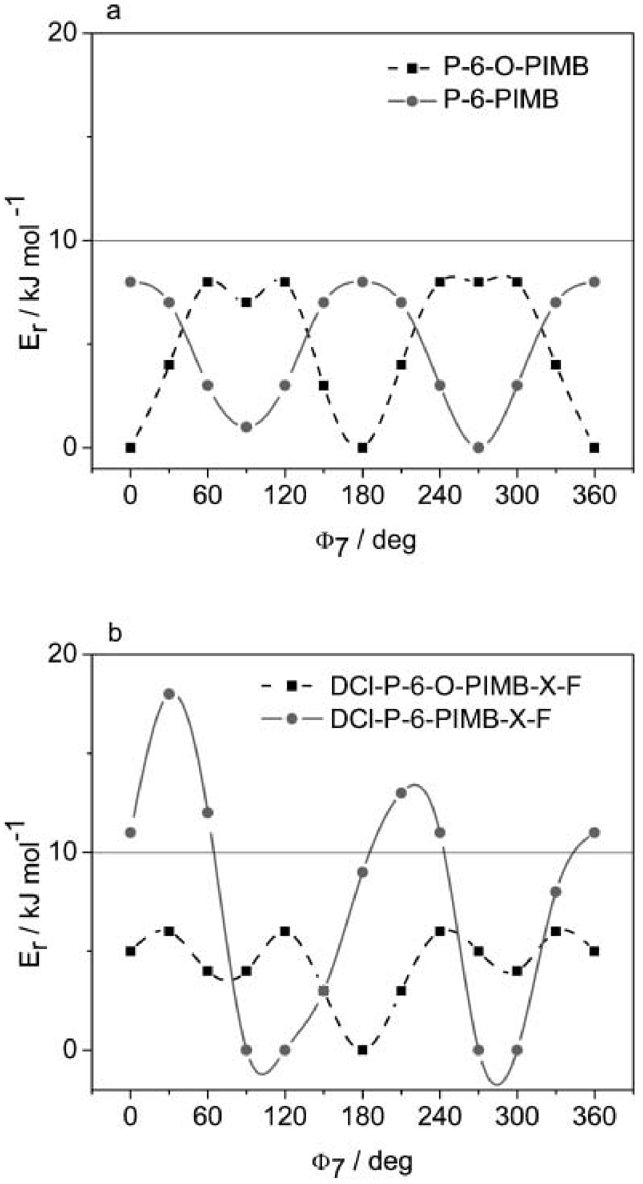

Figure 12. Relaxed rotational barriers (HF) related to the torsion angle Φ_7 for systems with terminal hexyloxy and hexyl chains: (*a*) unsubstituted, (*b*) substituted.

Therefore, different types of terminal chain can influence the phase behaviour, especially in laterally substituted bent-core mesogens.

4. Conclusions

Comparative conformational studies on the HF and DFT level were performed on substituted bent-core molecules of the 1,3-phenylene type. For P-6-O-PIMB and DCl-P-6-O-PIMB both methods show that twisted conformations are energetically preferred in comparison with planar arrangements, which is in agreement with X-ray investigations and NMR measurements. Moreover, dipole moments and bending angles exhibit the same trend for different conformers of both molecules within the HF and DFT methods. These findings support the procedure of performing HF calculations for one- and two-fold PES scans on the substituted banana-shaped systems, with only a reasonable computational effort. The unsubstituted compound P-6-O-PIMB shows a high conformational flexibility of the legs. Substituents at the 2-, 4- and 6-positions of the central phenyl ring decrease the range of conformational degree of freedom for these bent-core molecules. This was illustrated by relaxed rotational barriers and two-fold PES scans in relation to significant torsion angles. The introduction of fluorine (chlorine) substituents on the external phenyl rings decreases (increases) the relaxed rotational barriers of terminal chains, especially if they are attached in adjacent positions to the chains.

Different effects in the conformational behaviour were obtained for systems with hexyloxy (P-6-O-PIMB) and hexyl (P-6-PIMB) terminal groups. Energy-weighted dipole moments and their components allow predictions on the magnitude and direction of global polar effects related to the type and position of the substitution. Moreover, from the calculation of ESP group charges, an alternating charge distribution on the phenyl rings along the legs was found in the bent-core systems considered.

A simple model for the calculation of the bending angle in systems with a 1,3-phenylene central unit was introduced. The range of the bending angle of energetically preferred conformers can be compared with the values from liquid crystalline NMR and solid state X-ray measurements. The results on isolated bent-core molecules can serve as reference data for further theoretical investigations on a force field level including dimers and larger clusters of such systems.

Acknowledgements

The authors are grateful to Deutsche Forschungsgemeinschaft for financial support of this work within the PhD graduate study programma Nr. 894/1 *Self-organisation by Coordinative and Non-covalent Interactions.*

References

[1] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe. *J. mater. Chem.*, **6**, 1231 (1996).
[2] D.R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Korblova, D.M. Walba. *Science*, **278**, 1924 (1997).

[3] G. Pelzl, S. Diele, W. Weissflog. *Adv. Mater.*, **11**, 707 (1999).

[4] C. Tschierske, G. Dantlgraber. *Pramana J. Phys.*, **61**, 455 (2003).

[5] R. Amaranatha Reddy, B.K. Sadashiva. *Liq. Cryst.*, **27**, 1613 (2000).

[6] J.P. Bedel, J.C. Rouillon, J.P. Marcerou, M. Laguerre, H.T. Nguyen, M.F. Achard. *Liq. Cryst.*, **27**, 1411 (2000).

[7] W. Weissflog, H. Nadasi, U. Dunemann, G. Pelzl, S. Diele, A. Eremin, H. Kresse. *J. mater. Chem.*, **11**, 2748 (2001).

[8] R. Amaranatha Reddy, B.K. Sadashiva. *Liq. Cryst.*, **30**, 1031 (2003).

[9] H. Nadasi, W. Weissflog, A. Eremin, G. Pelzl, S. Diele, B. Das, S. Grande. *J. mater. Chem.*, **12**, 1316 (2002).

[10] H.N. Shreenivasa Murthy, B.K. Sadashiva. *Liq. Cryst.*, **29**, 1223 (2002).

[11] D.A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Y. Takanishi, E. Korblova, D.R. Link, R.-F. Shao, W.G. Jang, J.E. Maclennan, O. Mondainn-Monval, C. Boyer, W. Weissflog, G. Pelzl, L.-C. Chien, J. Zasadzinski, J. Watanabe, D.M. Walba, H. Takezoe, N.A. Clark. *Science*, **301**, 1204 (2003).

[12] A. Eremin, H. Nadasi, G. Pelzl, S. Diele, H. Kresse, W. Weissflog, S. Grande. *Phys. Chem. chem. Phys.*, **6**, 1290 (2004).

[13] W. Weissflog, Ch. Lischka, S. Diele, G. Pelzl, I. Wirth, S. Grande, H. Kresse, H. Schmalfuss, H. Hartung, A. Stettler. *Mol. Cryst. liq. Cryst.*, **333**, 203 (1998).

[14] S. Diele, S. Grande, H. Kruth, Ch. Lischka, G. Pelzl, W. Weissflog, I. Wirth. *Ferroelectrics*, **212**, 169 (1998).

[15] G. Pelzl, S. Diele, S. Grande, A. Jakli, Ch. Lischka, H. Kresse, H. Schmalfuss, I. Wirth, W. Weissflog. *Liq. Cryst.*, **26**, 401 (1999).

[16] H. Dehne, M. Potter, S. Sokolowski, W. Weissflog, S. Diele, G. Pelzl, I. Wirth, H. Kresse, H. Schmalfuss, S. Grande. *Liq. Cryst.*, **28**, 1269 (2001).

[17] G. Pelzl, M.W. Schröder, U. Dunemann, S. Diele, W. Weissflog, C. Jones, D. Coleman, N.A. Clark, R. Stannarius, J. Li, B. Das, S. Grande. *J. mater. Chem.*, **14**, 2492 (2004).

[18] H. Kurosu, M. Kawasaki, M. Hirose, M. Yamada, S. Kang, J. Thisayukta, M. Sone, H. Takezoe, J. Watanabe. *J. phys. Chem. A*, **108**, 4674 (2004).

[19] A. Eremin, I. Wirth, S. Diele, G. Pelzl, H. Schmalfuss, H. Kresse, H. Nadasi, K. Fodor-Csorba, E. Gacs-Baitz, W. Weissflog. *Liq. Cryst.*, **29**, 775 (2002).

[20] G. Pelzl, S. Diele, A. Jakli, Ch. Lischka, I. Wirth, W. Weissflog. *Liq. Cryst.*, **26**, 135 (1999).

[21] T. Imase, S. Kawauchi, J. Watanabe. *J. mol. Struct.*, **560**, 275 (2001).

[22] Y.D. Ronald, K. Foder-Csorba, J. Xu, V. Domenici, G. Prampolini, C.A. Veracini. *J. phys. Chem. B*, **108**, 7694 (2004).

[23] K. Fodor-Csorba, A. Vajda, G. Galli, A. Jakli, D. Demus, S. Holly, E. Gacs-Baitz. *Macromol. Chem. Phys.*, **203**, 1556 (2002).

[24] M.J. Frisch, G.W. Trucks, H.B. Schegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Peterson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Sefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Chahacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople. *Gaussian 98*, Gaussian Inc., Pittsburgh, PA (1998).

[25] R. Friedemann, S. Naumann, J. Brickmann. *Phys. Chem. chem. Phys.*, **3**, 4195 (2001).

[26] R. Friedemann, S. Naumann. *J. mol. Struct (Theochem)*, **630**, 275 (2003).

[27] H. Hartung, A. Stettler, W. Weissflog. *J. mol. Struct.*, **526**, 31 (2000).

[28] J.P. Bedel, J.C. Rouillon, J.P. Marcerou, M. Laguerre, H.T. Nguyen, M.F. Achard. *J. mater. Chem.*, **12**, 2214 (2002).