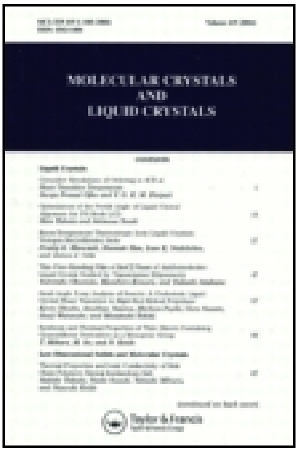

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The Influence of Some Wing Groups on the Mesogeneity

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The Influence of Some Wing Groups on the Mesogeneity

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We compare the mesogenic properties of two-ring compounds, substituted at one end with n-alkyl groups and at the other end with alkyl, alkyloxy, ω-fluorinated alkyloxy, methylenoxy-alkyl and acyloxy groups. The different groups have different effect on the mesogeneity, and their effect is different when they are attached at benzene resp. cyclohexane rings. In order to find out rational reasons for this behaviour we performed quantum chemical calculations on the density functional theory and ab initio *level. Contrary to existing opinions, in cyclohexane derivatives the calculated axial conformers were proven to have so low stability that in the thermal equilibrium they do not play a role. In alkyloxy compounds* gauche *conformers were found to be more stable than the most elongated all-*trans *conformers.*

Keywords Alkyloxy *gauche* effect; chemical structure; conformation; mesogenic properties; quantum chemical calculation

1. Introduction

The connection between chemical structure of a compound and its mesogenic properties is an old, often discussed, but never completely solved problem. Already Vorländer as early as 1907 [1] detected that in order to exhibit mesogenic properties the most elongated molecular shape is most advantageous. His findings have been supported by a huge number of syntheses of calamitic liquid crystals [2]. The experimental data have been explained by molecular statistical theories [3,4]. In the simplest case rod-like particles when condensed to a critical density orient themselves with their long axes parallel one to another, forming a nematic liquid crystalline phase. In order to obtain the critical density attractive forces between the molecules are necessary. In the so-called van der Waals theories these attractive forces (dipolar and dispersion forces) are added to the intermolecular potential. The main factor for the mesogeneity, however, is the length-to-breadth ratio of the molecules. In most of

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This paper has not been published before and it has not been sent simultaneously for publication elsewhere.

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the theories the molecules are treated as stiff particles; as an improvement in some theories molecular flexibility is introduced. In reality, however, the majority of the molecules forming liquid crystals are not exactly rod-like and they can exist in different conformations, which may have quite different molecular shape. Therefore in order to find the connection between molecular shape and liquid crystalline properties it is not enough to consider one molecular conformation (say the most stable conformer), because there may be additional conformers of differing shape, which exist in amounts according to their relative stability in a Boltzmann equilibrium. The aim of this study is to gain insight in the Boltzmann equilibrium by quantum chemical calculation of the most important conformers of the different compounds.

2. Chemical Compounds

Most of the calamitic compounds may be described by the general formula

$$R^1\text{-Core-}R^2$$

in which $R^1$and R^2 are flexible wing groups, attached endstanding to the stiff core.

The effect of different wing groups on the mesogenic properties is better visible when the core is relatively small. We choose two-ring compounds containing benzene and cyclohexane rings (Tables 1–5).

Table 1. Phenyl cyclohexane derivatives with five-membered wing group

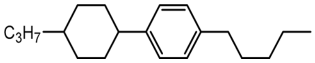
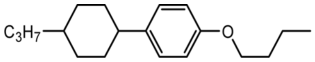
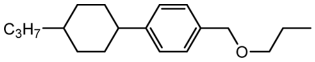
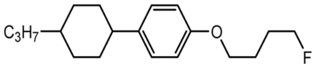
No.	Structure	Transition temp. (°C)	Ref.
1-1		Cr. −5 [N −32] I	[7]
1-2		Cr. 35.5 (N 33) I	[8]
1-3		Cr. −4 [N −47] I Cr. −4N −3 I	[9] [10]
1-4		Cr. 31.8 (N 30.2) I	[11]

Table 2. Phenyl cyclohexane derivatives with four-membered wing groups

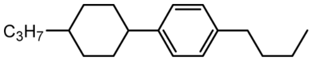
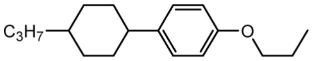
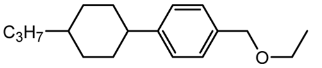
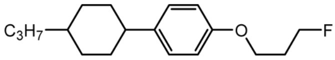
No.	Structure	Transition temp. (°C)	Ref.
2-1		Cr. < 0 I	[12]
2-2		Cr. 53.2 (N 15.2) I	[13]
2-3		Cr. 8.5 I	[10]
2-4		Cr. 38.5 [N −2.8] I	[14]

Table 3. Alkyloxy chain length dependence of transition temperatures

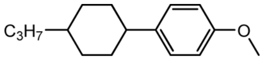
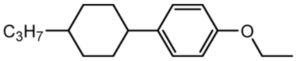
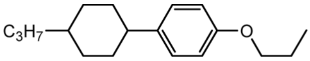
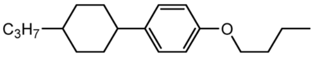
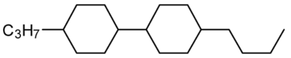
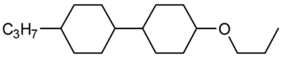
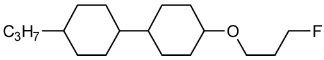
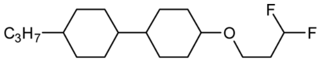
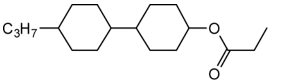
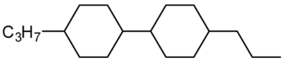
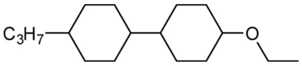
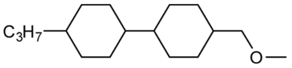
No.	Structure	Transition temp. (°C)	Ref.
3-1		Cr. 32 (N11) I	[15]
3-2		Cr. 41 (N 37) I	[17]
2-2		Cr. 53.2 (N 15.2) I	[13]
1-2		Cr. 35.5 (N 33) I	[8]

Table 4. Cyclohexane derivatives

No.	Structure	Transition temp. (°C)	Ref.
4-1		Cr. −8.3 SmB 93 I	[18]
4-2		Cr. 13.5 SmB 62.1 I	[19]
4-3		Cr. 22.7 SmB 61.5 I	[16]
4-4		Cr. 24.3 SmB 50.1 I	[16]
4-5		Cr. 68.5N 78.3 I	

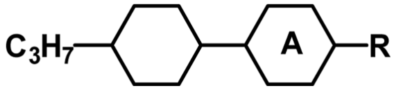
At a glance compounds 1–1 and 1–2 should have quite similar molecular shape. The large difference in the clearing temperatures points at differences, which are to be explained. Also the very different clearing temperatures of compounds 1–2 and 1–3 cannot be explained by a simple static molecular model. These examples and the cases shown in the following tables prove the necessity of a more detailed investigation using quantum chemical tools.

Table 5. Positional change of oxygen in cyclohexane derivatives

No.	Structure	Transition temp. (°C)	Ref.
5-1		Cr. 64.8 SmB 82.1 I	[18]
5-2		Cr. 48.4N 49.5 I	[15]
5-3		Cr. 44.8 SmX 51N 52 I	[20]

3. The Calculations

The calculations have been performed with the density functional theory DFT B88-LYP/6-31G* [5] and the *ab initio* method MP2/6-311++G(d,p) [6]. We choose materials of the following general formula as model compounds.



Ring A can be benzene or cyclohexane. In the calculations the main part of the molecules was unchanged in their most stable conformation; the cyclohexane ring in the chair conformation is *equatorial/equatorial* substituted, the propyl group is all-*trans*. The changes of conformation concern only the substituents R.

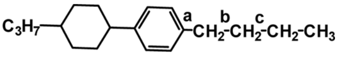
4. Benzene Derivatives

The calculations are concentrated on the orientation of the butyl group relative to the benzene ring, and the conformations within the butyl group. The results are presented in Table 6.

Figure 1 shows the conformer 6-1. The alkyl chain is directed nearly perpendicular to the benzene ring plane, which makes the molecule relatively bulky. The two rings are twisted by an angle of about 90°. The conformation of 6-2 is formed from 6–1 by the dihedral angle a with opposite sense and practically has the same energy. The small dipole moment proves that the polar intermolecular interaction is very small. The packing fraction of such molecules is moderate [31]. These facts show that the alkyl chain is providing only moderate mesogeneity, even in the all-*trans* conformation. As 6-3 shows, conformers with *gauche* conformations possess higher energy than the all-*trans* conformer, and accordingly exist in the thermal equilibrium with lower existence probability. These conformers possess also certain bulkiness and do not support the mesogeneity.

Calculating the different conformations by turns around the bond a we found 4 minima.

Table 6.



No.	Dihedral a[a]	Dihedral b[b]	Dihedral c[c]	Energy a.u.	ΔE[d] kJ/mole	μ D
6-1	−82.5	*t*	*t*	−741.72309	0	0.12
6-2	81.9	*t*	*t*	−741.72301	+0.21	0.17
6-3	−104.4	+*g*	*t*	−741.72229	+2.10	0.18

[a] dihedral angle a (C9-C10-C29-C37); see Figure 1.
[b] dihedral angle b (C10-C29-C37-C38).
[c] dihedral angle c (C29-C37-C38-C39).
[d] ΔE = E (actual conformer) – E (all *trans* conformer).

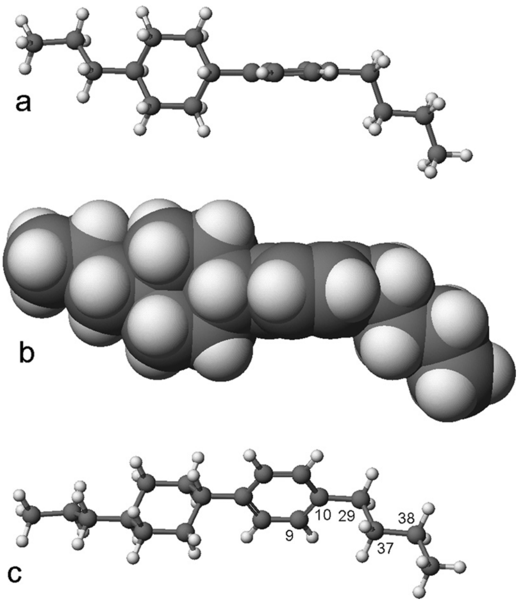


Figure 1. Compound 2-1, conformer 6-1: (a), (c) ball and stick model; (b) space filling model. In (c) the numbers of the relevant atoms are given.

The dihedral angles of conformers 7-1 and 7-2 are different by 179^0, and they have nearly the same energy. The conformers have quite different shape (Fig. 2), 7-1 is slightly bent and 7-2 is more stretched. They are dominating in the thermal equilibrium. Due to their much higher energies conformers 7-3 and 7-4 are nearly neglectable. The situation is in good agreement with the results of *ab initio* calculations on the HF level in a banana shaped compound with phenyl-alkyloxy groups, where two low level and two high level minima were found [21]. The energy of the maximum is only slightly higher than that of the high minimum.

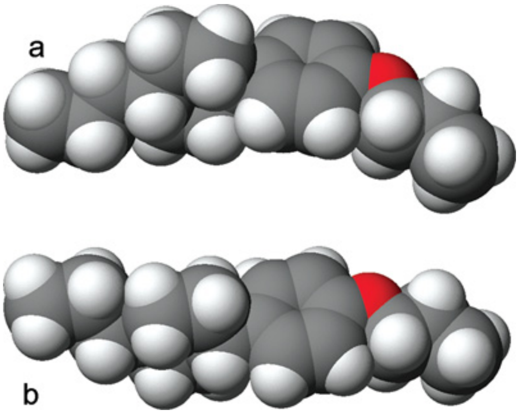
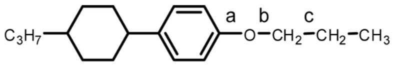


Figure 2. Compound 2-2: (a) conformer 7-1; (b) conformer 7-2. (Figure appears in color online.)

Table 7. The dihedral angle a, b, c and energy calculated



No.	Dihedral a[a]	Dihedral b[b]	Dihedral c[c]	Energy a. u.	ΔE[d] kJ/mole	μ D
7-1	17.8	*t*	*t*	−777.63933	0	1.34
7-2	−161.2	*t*	*t*	−777.63930	+0.07	1.18
7-3	−74.6	*t*	*t*	−777.63524	+10.738	1.15
7-4	74.6	*t*	*t*	−777.63539	+10.344	1.22
7-5	28.7	67.0	*t*	−777.63658	+7.220	1.46
7-6	8.1	*t*	64.8	−777.64050	−3.072	1.22

[a] dihedral angle a (C9-C10-O29-C37).
[b] dihedral angle b (C10-O29-C37-C38).
[c] dihedral angle b (O29-C37-C38-C39).
[d] ΔE = E (actual conformer) – E (all *trans* conformer).

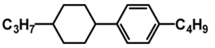
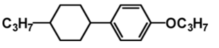
The dihedral b has two minima (*t, g*), with the *gauche* minimum (conformer 7–5 in Table 7) having much higher energy than the *trans* conformer 7-1. This is, its existence probability in the thermal equilibrium is quite low.

There may be the discussion that in phenyl-alkyloxy compounds the aromatic part is elongated by conjugation of the lone-pair electrons of O atom with the aromatic ring, and thus the polarizability is substantially increased. In order to check this idea we calculated the polarizabilities of the all-*trans* conformers of a pheny-butyl and a phenyl-propyloxy compound (Table 7a). The average polarizability is nearly equal, and the polarizability in long direction (a_z) is increased by about 5%. This small increase will support the intermolecular attraction, but is too small in order to explain the large increase of the clearing temperature.

It must be emphasized that there are two conformers in which dihedrals c are ±*gauche*, that have lower energy than the all-*trans* conformer 7-1. The +*gauche* conformer 7-6 is shown in Figure 3. The shape is somewhat more bulky than the all-*trans* conformer. The alkyloxy chain is forming an open five-membered ring, in which O29 and H54 have special interaction. The distance d(O29...H54) = 2.656 Å, Å, this is much less than the sum of the van der Waals radii of the two atoms (d = 2.72 Å [30]).

In the literature usually it is assumed that in alkyloxy groups the most stable conformation is all-*trans* [23,24]. In the solid state alkyloxy groups often show the all-*trans* conformation [25], but structures with *gauche* conformations are less seldom than expected [26]. For comparisons of the calculated molecular length with physical properties often the all-*trans* conformation is used [27].

Table 7a. Polarizabilities calculated with CAChe/PM5

Compound	Conf.	a_x	a_y	a_z	a_{is}
	6-1	237.7	203.1	390.3	289.0
	7-1	188.5	272.1	410.4	290.3

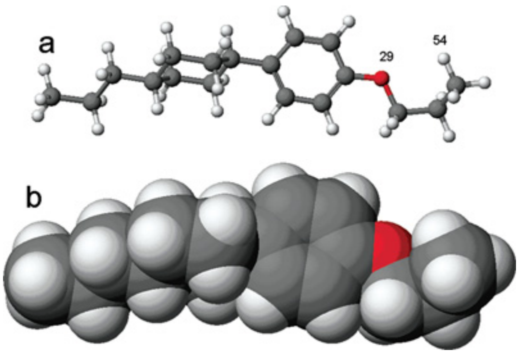


Figure 3. Conformer 7-6: (a) ball and stick model; (b) space filling model. (Figure appears in color online.)

During performing quantum chemical calculations with different methods we found, that in alkyloxy moieties generally not the all-*trans* conformation is most stable, but a conformer containing a *gauche* conformation. The formation of open five-membered rings has been observed earlier in poly-methylenoxy compounds and interpreted as special interaction between O and H atoms [22].

In order to obtain more insight in the nature of the interaction between O and H we calculated derivatives of methyl-propylethers, with substituents X of different polarity in C5.

$$\overset{1}{CH_3}\text{--}\overset{2}{O}\text{--}\overset{3}{CH_2}\text{--}\overset{4}{CH_2}\text{--}\overset{5}{CH_2}X$$

The results are collected in Table 8. The partial charges in O2 are not very different in the compounds, but the polarity of H10 is increasing with enhanced polarity

Table 8. Calculated properties (*ab initio*) of subst. methyl-n-propyl-ethers **2** **CF_3–O–CH_2–CH_2X**

X	E (RHF)	E (MP2)	ΔE (RHF) (kJ/mole)	ΔE (MP2) (kJ/mole)	σ (O2)	σ (H10)	Δσ	d (O2...H10) (Ã)
H a*t*	−232.204606	−233.028619	–	–	−0.1418	0.1403	0.2821	–
H *g*	−232.204494	−233.029185	+0.29	−1.49	−0.1327	0.1651	0.2978	2.622
CH_3 a*t*	−271.248538	−272.225505	–	–	−0.1322	0.1292	0.2614	–
CH_3 *g*	−271.248498	−272.226215	+0.11	−1.86	−0.1187	0.1579	0.2766	2.598
F a*t*	−331.084802	−332.108243	–	–	−0.1384	0.1643	0.3027	–
F *g*	−331.086596	−332.110632	−4.71	−6.27	−0.1388	0.1873	0.3261	2.612
Cl a*t*	−691.133691	−692.088587	–	–	−0.1359	0.1879	0.3238	–
Cl *g*	−691.135523	−692.090864	−4.81	−5.98	−0.1306	0.2121	0.3427	2.589
Br a*t*	−244.767797	−245.702079	–	–	−0.1364	0.1985	0.3349	–
Br *g*	−244.769609	−245.704371	−4.76	−6.02	−0.1368	0.2206	0.3574	2.587

ΔE = E (actual conformer) – E (all-*trans* conformer).

σ (O2) and σ(H10) charges on the respective atoms calculated with the procedure of Mulliken.

Δσ = differences of the charges σ(O2) and σ(H10). H10 is the hydrogen nearest to O in the open five-membered ring.

of the substituents X. Thus also the difference $\Delta\sigma$ of the polarities of O2 and H10 is increasing, and roughly speaking in the same sense ΔE is growing. In Table 8 the results of the *ab initio* calculation on the HF and MP2 level are shown. It should be noted that the HF method underestimates the interaction energies between O2 and H10 because only the electrostatic interaction is included as the effective term within this approximation. At the MP2 level of theory, the correlation term is additionally included as the dispersion energy between O2 and H10. We see that the electrostatic interaction between O2 and H10 is increasing with growing $\Delta\sigma$, but the dispersion interaction shows a somewhat irregular trend. With low polar substituents X the dispersion interaction is dominating, with higher polar X the electrostatic interaction is prevailing. This is because the electrostatic interaction is due to the polarities of the charges on atoms, and the dispersion interaction is mainly due to the van der Waals interaction. This is also confirmed by the fact that the differences between MP2 and HF energies are similar (about 1.5 kJ/mole) among all molecules.

The distances d (O2-H10) in all cases are lower than the sum of the van der Waals radii of O and H (2.72 Å), and except the case X=CH_3, decreases with increasing polarity of X.

The *gauche* effect seems comparable to the case of the anomeric effect in oxanes and dioxanes [28], which has been discussed by Takahashi et al. [29] as being due partly to the formation of a weak hydrogen bond. Weak hydrogen bonds according to Desiraju and Steiner [30] contain electrostatic and dispersion interaction energies.

In the literature the anomeric effect is discussed somewhat controversial. On the one hand, there may be an interaction (hyperconjugation) between the lone electron pair of the heteroatom and the σ^* orbital of the C–H bond [28]. On the other hand, there may be a polar interaction between the heteroatom and the activated or non-activated hydrogen. Takahashi *et al.* [29] point at the role of weak hydrogen bonds in stabilizing the anomeric systems. According to their explanation, the weak hydrogen bond is formed in open five-membered rings with the interatomic distance of the atoms forming this bond shorter than the sum of their van der Waals radii. Both their criteria are valid in our calculated examples.

Quite recently by high level quantum chemical calculations Mo [33] has shown that hyperconjugative interactions are not responsible for the anomeric effect.

We would prefer to describe the effect as the formation of a weak hydrogen bond, stabilized partly by dispersion interaction (non polar part of ΔE_{MP2}), partly by polar interaction (ΔE_{RHF}). With less activated hydrogens the non polar interaction is dominating, with higher activated hydrogens the polar interaction is dominating.

This compound does not have a well elongated conformer. As Figure 4 shows the two rings are oriented nearly perpendicular one to another, and the fluoropropyloxy group is nearly perpendicular to the benzene ring plane. The other conformers are not less bulky. It is remarkable that conformer 9-3 which contains an open five-membered ring in which O and H can form a hydrogen bond is much more stable than conformer 9-1. Conformer 9-4 (Fig. 5) is quite bulky, and most stable. This high stability is due to the formation of an open five-membered ring with a weak hydrogen bond (Fig. 5c; distance O29 ... H53 = 2.664 Å; sum of the van der Waals radii = 2.70 [32]).) and an open five-membered ring with another bond between F55 and H50 (Fig. 5d; distance F55 ... H50 = 2.618 Å, sum of the van der Waals radii = 2.70 [32]). Contrary to the usual situation in which conformers with larger dipole moments are less stable, conformer 9–4 is most stable and has the largest dipole moment. In the Boltzmann equilibrium it is the dominating conformer.

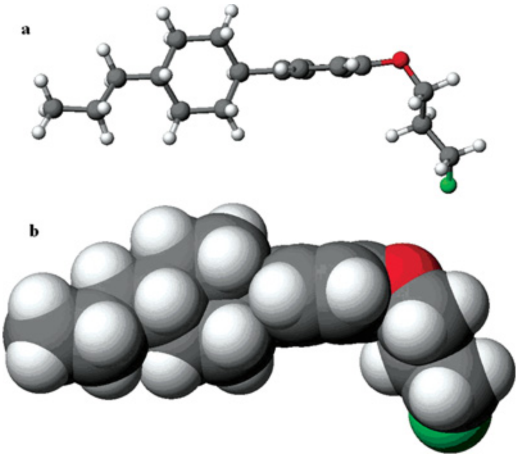


Figure 4. Conformer 9-1: (a) ball and stick model; (b) space filling model. (Figure appears in color online.)

Dihedral a has 4 minima when the rest of the substituent is all-*trans* (Table 10, first 4 cases).The maxima, this is the activation energy of the rotation around a, is only about 2 kcal/mole. This should be the reason that the dihedrals a and b are strongly coupled and not independent one from another. When dihedral b is *gauche* (Table 10 cases 10-5 to 10-8), much more stable conformers are formed. Because in these conformers the substituent is nearly perpendicular to the ring plane, the molecular shape is bent and quite bulky. Also the conformers 10-1 to 10-4 are quite

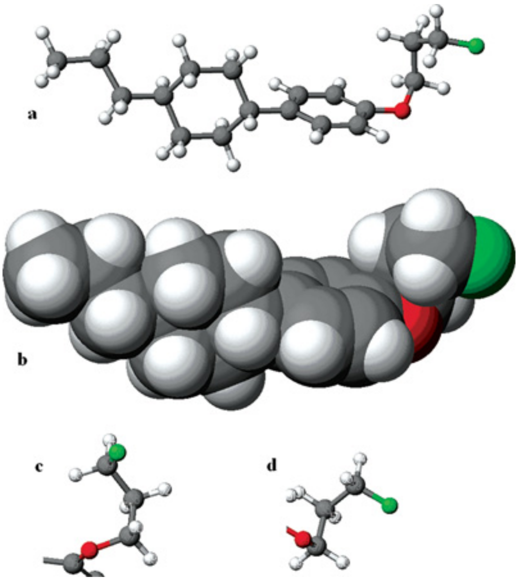
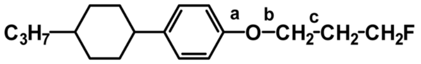


Figure 5. Conformer 9-4: (a) ball and stick model; (b) space filling model. Partial sights of the conformer: (c) open five-membered ring with hydrogen bond O. . .H; (d) open five-membered ring with hydrogen bond F . . . H. (Figure appears in color online.)

Table 9. The dihedral angle a, b, c and energy calculated



No.	Dihedral a	Dihedral b	Dihedral c	Energy a.u.	ΔE[a] kJ/mole	μ D
9-1	70.5	70.1	t	−876.85749	−0.68	1.49
9-2	−110.4	68.7	t	−876.85723	0	1.28
9-3	68.4	75.6	58.4	−876.85956	−6.12	1.85
9-4	31.9	62.7	58.2	−876.86212	−12.84	2.34

[a] ΔE = E(actual conformer) – E (conformer 9.2).

bulky. The very low clearing temperature of this compound (Table 1) is easily explainable by the effective bulky molecular shape of this compound.

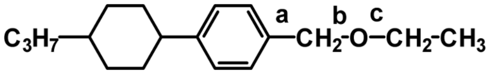
We have also calculated the next higher homologue of this series, this is $R = -CH_2-O-(CH_2)_2-CH_3$. This compound exhibits a behaviour similar to the lower homologue, except the fact the there are *gauche* conformers containing a weak hydrogen bond, which have slightly lower energy than the *trans* conformers.

5. Derivatives of Cyclohexane

$R = C_4H_9$

The butyl derivative of propylcyclohexyl-cyclohexane in the all-*trans* conformation in equatorial position has a most elongated molecular shape (Fig. 6a, b), the butyl group is in plane with the ring. On the other hand, the corresponding axial conformer is extremely bulky (Fig. 6c), but its energy is much higher than that of the equatorial conformer and thus in the thermal equilibrium the axial conformers practically

Table 10. The dihedral angle a, b, c and energy calculated



No.	Dihedral a	Dihedral b	Dihedral c	E a.u.	ΔE[a] kJ/mole
10-1	118.6	177.7	−178.7	−777.63274	+2.23
10-2	−119.2	178.8	179.3	−777.63245	+2.99
10-3	58.5	−179.1	179.7	−777.63266	+2.44
10-4	−58.9	178.1	−178.8	−777.63270	+2.34
10-5	45.0	65.0	175.6	−777.63359	0
10-6	−45.5	−63.8	−175.7	−777.63300	+1.55
10-7	133.6	−64.4	−176.5	−777.63312	+1.23
10-8	−140.0	65.5	176.8	−777.63354	+0.13

[a] ΔE = E (actual conformer) – E (conformer 10–5).

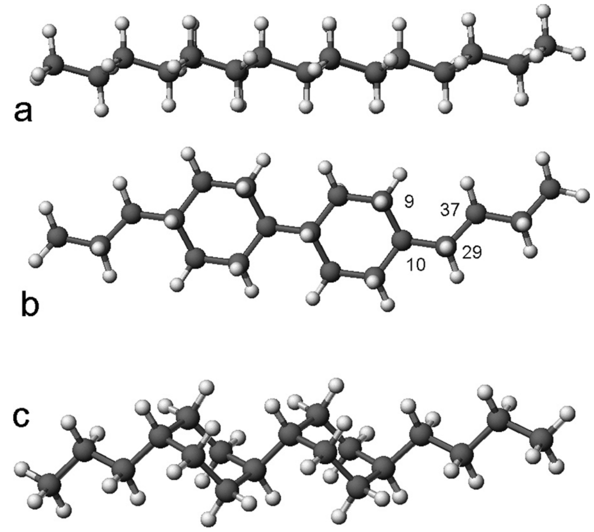


Figure 6. Compound 4-1, R = C_4H_9: (a), (b) *equatorial* conformer 11-1 in different projections; (c) axial conformer 11-2.

do not play a role. Because the molecule has a neglectable small dipole moment, polar interactions are not significant. The high clearing temperature obviously is due to the well elongated molecular shape.

$R = -OC_3H_7$

At a glance the equatorial all-*trans* conformation of this compound should have a similar shape as the butyl compound. The *axial* position is much less stable than the *equatorial*, the corresponding conformers do not play a role in the thermal equilibrium. But there are two conformers $c = \pm g$, which are more bulky than the all-*trans* conformers and they are slightly more stable (conformer 11-4; see Fig. 7). These conformers point at the existence of weak hydrogen bonds between O29 and H54, which are arranged in an open five-membered ring. These more bulky conformers, existing in substantial amounts in the thermal equilibrium, should be responsible for the much lower clearing temperature in comparison to the butyl compound.

$R = -CH_2-O-C_2H_5$

The most stable conformer 11-7 is slightly bent in the substituent (Fig. 8), which is nearly in the plane of the cyclohexane ring. There are several conformers with only slightly higher energy (11-8, 11-9), but more bulkiness (Fig. 8). The bulky conformer 11-10 has very high energy and practically does not exist in the Boltzmann equilibrium. In summary we can say, that the actual compound is effectively less extended than the analogous butyl compound, and therefore should have a substantially lower clearing temperature.

$R = -O(CH_2)_2-CH_2F$

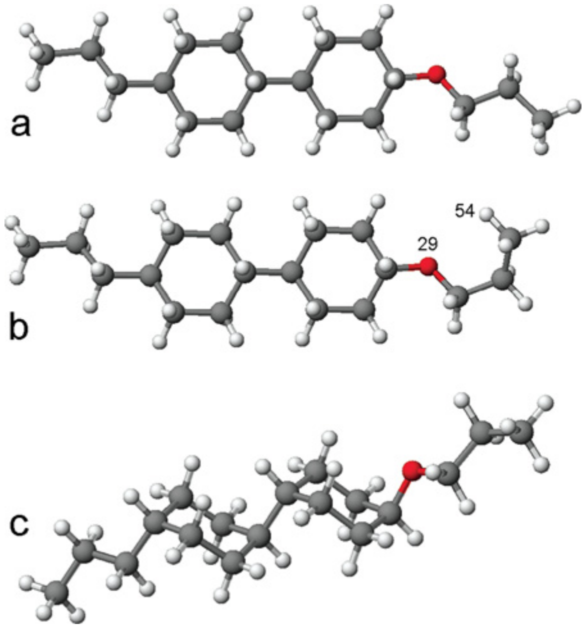


Figure 7. Compound 4-2, R=OC_3H_7: (a) *equatorial* all-*trans* (conformer 11-3); (b) *equatorial* + *gauche* (conformer 11-4); (c) *axial* all-*trans* (conformer 11-5). (Figure appears in color online.)

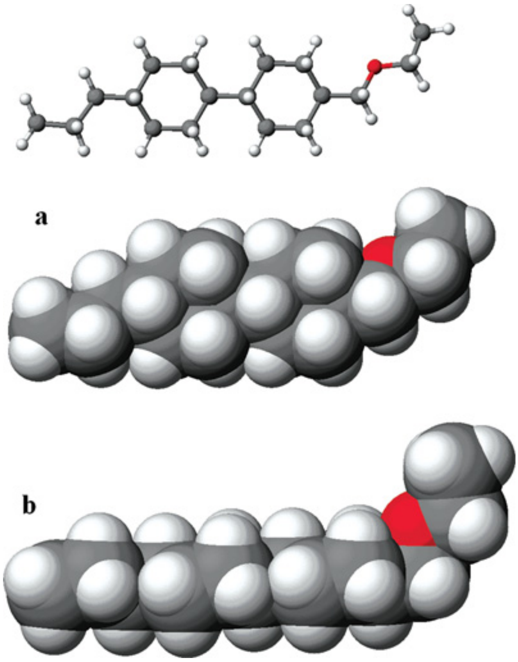
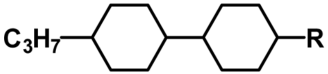


Figure 8. Compound R = $-CH_2-O-C_2H_5$: (a) conformer 11-7; (b) conformer 11-8. (Figure appears in color online.)

Table 11. Calculated properties



No.	R	S	Dihedral a	Dihedral b	Dihedral c	Dihedral F53C39CC resp. H53C39CC	E a.u.	ΔE kJ/mole	D (O…H) Å
11-1	C_4H_9	*eq*	−64.5	175.0	180.0	–	−745.29930	0	–
11-2		*ax*	68.4	179.6	−178.5	–	−745.28451	+38.83	–
11-3	OC_3H_7	*eq*	−65.8	−156.7	−176.5	–	−781.21456	0	–
11-4		*eq*	−64.8	−156.1	66.0		−781.21470	−0.37	2.659
11-5		*ax*	63.8	156.2	177.8	–	−781.20301	+30.33	–
11-6		*ax*	64.0	161.0	60.7	–	−781.21387	+29.90–0.43[c]	2.682
11-7	CH_2-O-C_2H_5	*eq*	−63.1	178. 1	179.9		−781.21313	0	
11-8		*eq*	61.4	179.8	−179.6		−781.21294	+0.50	
11-9		*eq*	−173.0	−178.4	−179.6		−781.21298	+0.39	
11-10		*eq*	−97.3	72.6	−100.3		−781.20265	+27.52	
11-11	$OC_2H_4CH_2F$	*eq*	−65.4	−151.8	−175.7	−179.2[a]	−880.43762	0	–
11-12		*eq*	−81.0	−77.9	−167.4	−60.2[a]	−880.43863	−2.65	–
11-13		*eq*	−67.6	−166.4	−62.7	−65.2[a]	−880.44171	−10.38	2.577
11-14		*eq*	−64.9	−158.3	−54.1	−175.9[a]	−880.44010	−6.51	2.578
11-15		*ax*	56.2	61.5	165.9	179.0[a]	−880.42343	+37.26	–
11-16	$OCH_2CH_2CF_2H$	*eq*	−82.0	−82.8	−175.9	178.3[b]	−979.68281	0	–
11-17		*eq*	−112.0	73.4	173.6	−178.2[b]	−979.68127	+4.04	
11-18		*eq*	−80.1	−110.7	62.2	−64.8[b]	−979.68368	−2.28	2.797
11-19		*eq*	−84.6	−80.7	−58.1	57.0[b]	−979.68366	−2.23	2.699

(*Continued*)

Table 11. Continued

No.	R	S	Dihedral a	Dihedral b	Dihedral c	Dihedral F53C39CC resp. H53C39CC	E a.u.	ΔE kJ/mole	D (O…H) Å
11-20		*ax*	54.0	62.9	172.9	61.1[b]	−979.66790	+39.15	–
11-21	OCO-C_2H_5	*eq*	−81.2	−178.8	−177.5		−855.27134	0	–
11-22		*eq*	−82.5	−175.8	66.4		−855.27009	+3.28	2.698
11-23		*ax*	81.1	−177.9	178.5		−855.26699	+11.42	–
11-24		*ax*	81.0	−177.4	57.3		−855.26558	+15.12 + 3.70[c]	2.641

S = position of both substituents in the right ring.
The chain forming atoms in R are numbered in the sequence 9-10-29-37-38-39.
a = dihedral angle of atoms 9-10-29-37.
b = dihedral angle of atoms 10-29-37-38.
c = dihedral angle of atoms 29-37-38-39.
ΔE = E (actual) – E (all-*trans*).
d(O…H) = distance of the O and H in the open five-membered ring of the *gauche* conformers.
[a] dihedral angle of atoms F53-C39-C38-C37.
[b] dihedral angle of atoms H53-C39-C38-C37.
[c] $\Delta E = E_{ax}$ (actual) – E_{ax} (all-*trans*).

This compound is more polar compared to $R = -OC_3H_7$. Higher polarity due to increased intermolecular attraction usually causes higher packing fraction and thus higher clearing temperatures, in molecules of comparable shape. We see this different polarity in the dipole moments of the compounds (Table 11 compound 4-2 conformer 11-3 $\mu = 0.93$ D ; compound 4-3, conformer 11-11 $\mu = 2.57$ D). But surprisingly both compounds have nearly the same clearing temperature. In this compound the *axial* position is energetically very unfavourable and thus will not occur in substantial amounts. Several conformations exist which are more stable than the all-*trans* conformer 11-11. The conformer 11-13 is characterized by the formation of an open five-membered ring in which O29 is in interaction with one hydrogen of the endstanding $-CH_2F$ group. In conformer 11-12 the fluorine atom is in interaction with an endstanding H atom, within an open five-membered ring. And in the exceptionally stable conformer 11-13, O as well as F are forming open five-membered rings and the special interactions with H atoms.

As visible in Figure 9, these conformers are relatively bulky. Since they exist in high amounts in the Boltzmann equilibrium, they develop a remarkably decreasing trend with respect to the mesogeneity of the compound.

$R = -O - (CH_2)_2 - CHF_2$

This compound has a remarkably lower clearing temperature than the former compounds. Similar to the former cases, the axial conformers are much less stable (conformer 11-20) than the equatorial and thus do not play a substantial role in the Boltzmann equilibrium. There is no all-*trans* conformation of the $-O(CH_2)_2CHF_2$ group. Especially dihedral b can exist in two minima (conformers 11-16, 11-17 in Table 11) which are quite bulky (Fig. 10). There are several *gauche* conformers in the *equatorial* position (conformers 11-18, 11-19, see Fig. 10) with higher stability than the conformer 11-16. They are also quite bulky. According to former experience in these conformers the open five-membered rings with O and F interacting with hydrogen are formed.

Since in the compound no conformers with optimally elongated molecules exist, the relatively low clearing temperatures are not surprising.

$R = -OCOCH_2CH_3$

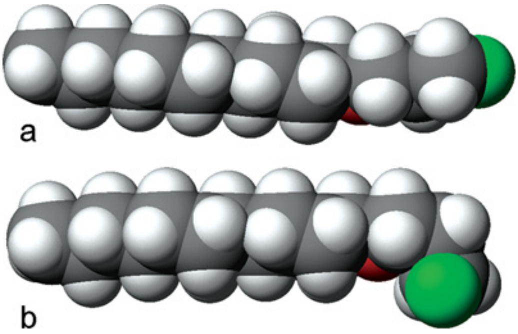


Figure 9. Compound 4-3, R = O-$(CH_2)_2CH_2F$: (a) conformer 11-11 (all-*trans*); (b) conformer 11-13 (-*gauche*). (Figure appears in color online.)

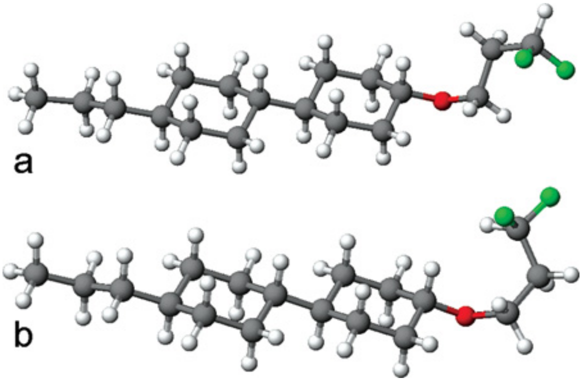


Figure 10. Compound 4-4, R = $-O(CH_2)_2CHF_2$: (a) conformer 11-16, *equatorial,* most elongated; (b) conformer 11-18, *equatorial, gauche*. (Figure appears in color online.)

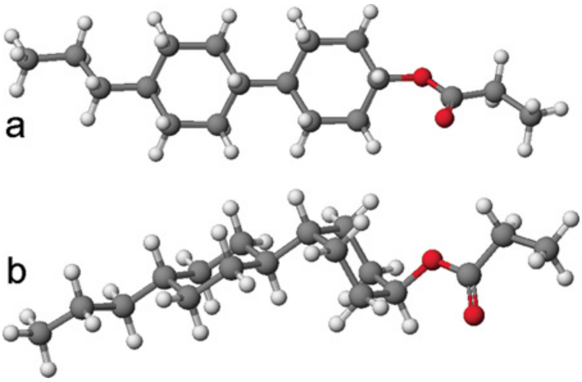


Figure 11. Compound 4-5, R = $-OCOCH_2CH_3$: (a) conformer 11-21, *equatorial* all-*trans*; (b): conformer 11-23, *axial* all-*trans*. (Figure appears in color online.)

In this compound the *equatorial* all-*trans* conformer is quite elongated (Fig. 11), and in contrast to the former molecules all the *gauche* conformers (which are more bulky) have lower stability. The *axial* conformers are less stable than the *equatorial*, but in lesser extent than in the former molecules. The reason may be a stabilization of the *axial* conformers due to special interaction between O29 and one of the *axial* H of the ring with distances distinctly smaller than the corresponding sum of the van der Waals radii, probably an anomeric effect. Since the molecules are not symmetric in relation to the long axis, this interaction is only with one of the two axial H atoms available in the ring. In the Boltzmann equilibrium, a large amount of the most stable and well elongated all-*trans* conformer exists and there is some polar interaction (for conformer 11-21 $\mu = 1.93$ D). Therefore, the clearing temperature is relatively high.

6. Conclusion

We have calculated several model compounds by quantum chemical methods. The model compounds consist of benzene and cyclohexane derivatives with different wing groups. We may expect that the features of our results are valid also in related compounds, this is heterocyclic compounds with related structures and higher homologs of the model compounds. The results may be summarized as follows:

- **Benzene derivatives**

Alkyl group
Nearly perpendicular to the ring plane and thus somewhat bulky, bulky conformers possess lower stability, low dipole moment, medium mesogeneity.
Alkyloxy group
Nearly in the plane of the ring and thus nicely elongated, more bulky *gauche* conformers possess higher stability, medium dipole moment, the energy barrier of rotation around the C-O single bond is nearly the same as in the alkyl group, high mesogeneity.
ω-Fluorinated alkyloxy groups
Similar to alkyloxy, bulky *gauche* conformers even more preferred, medium mesogeneity.
Alkyl group interrupted in β position by O
Most stable conformation is *gauche* and bulky, the elongated all-*trans* conformers possess much lower stability,
low mesogeneity.

- **Cyclohexane derivatives**

In all investigated cyclohexane derivatives the equatorial conformers are much more stable than the axial; the latter practically do not exist in the thermal equilibrium.
Alkyl group
In the most stable all-*trans* conformation in the ring plane and ideally elongated, smectic phases preferred, high mesogeneity.
Alkyloxy group
In the all-*trans* conformation similar to alkyl, several bulky *gauche* conformers more stable than the former, thus medium mesogeneity.
ω-Fluorinated alkyloxy groups
Similar to alkyloxy, but the *gauche* conformers even more preferred, medium mesogeneity.
Alkyl group interrupted in β position by O
The most stable conformer is slightly bent, several bent conformers with only slightly lower stability, medium mesogeneity.

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