DFT Study of the Torsional Potential in Ethylbenzene and Ethoxybenzene: The Smallest Prototypes of Alkyl− and Alkoxy−Aryl Mesogens

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The intramolecular torsional potential of ethylbenzene and ethoxybenzene has been calculated using the B3LYP density functional method with a triple-ζ polarized basis set. In its completely optimized geometry, ethylbenzene has the torsional angle at 90°, that is in correspondence of conformation with the plane containing $C-CH_2-CH_3$ perpendicular to the phenyl ring, while, in agreement with recent literature data, a very little pronounced energy maximum at ≃20° and a shallow local minimum at 0° have been found. The ethoxybenzene molecule has its minimum geometry where both the ring and the ethyl group lie in the same plane, being in trans position with respect to the $O-CH_2$ bond. The resulting data have then been fitted onto analytical functions, to be employed both in LXNMR spectroscopy and in computer simulations of realistic models of liquid crystals containing the alkyl−aryl and alkoxy−aryl linkages.

1. Introduction

In the field of liquid crystals, it is customary to divide the complex mesogenic molecules in two relevant kinds of building blocks: the so-called rigid cores and the flexible tails.[1]

The former are formed by a series of phenyl rings connected with each other directly or through linking units of different nature. At least in calamitic molecules, this kind of building block is not completely unflexible; for example, the dihedral angle in the biphenyl core of 4-cyano-4′-pentylbiphenyl (5CB) molecule, varies from 0° in the solid phase[2] to ≃ 35° in the nematic phase.[3] In the condensed phase, in fact, due to relatively small torsional barriers,[4,5] intermolecular interactions can force the core in a less favorable conformation. Although not devoid of flexibility, nevertheless these cores can still be intended as rigid, in the sense of being capable of conferring such a stiffness that allows the molecule to assume the necessary anisotropic shape.

Flexible aliphatic chains, though not a necessary feature, are extremely common and of importance in decreasing the temperature at which, under normal pressure conditions, a mesophase can occur.[1] Moreover, the delicate interplay between intra- and intermolecular forces that drives the phase transitions is strongly affected by the chain conformation, which seems to change from the all-trans configuration to gauche states by increasing the temperature.[6−8]

Clearly, the region at which core and tail encounter one another can play an important role in the molecular structure−properties relationships. Very commonly an alkyl−aryl or an alkoxy−aryl linkage is found in liquid-crystal-forming molecules; a good description of this joint region may be crucial in reproducing the correct mesomorphic behavior of the material. This is not surprising if one considers that the alkyl−aryl or alkoxy−aryl joint drives the core−tail relative orientation, defining in such a way the overall shape of the molecule.

The experimental technique of choice for investigating the conformational equilibria of flexible molecules in fluid phases is Liquid Crystal NMR (LXNMR) spectroscopy;[9] the suitable molecule of interest is dissolved in a nematic solvent, and its ^1H NMR spectrum is registered. The latter is then analyzed to furnish a set of partially averaged nuclear dipolar coupling data to be treated with existing theories. One of them,[10] based on the Maximum Entropy (ME) principle[11] has its strength in giving completely a posteriori, least biased, information on the nature of internal rotational motion under examination. Recently, a ME study[12] of the rotation of the ethyl moiety around the phenyl ring in the ethylbenzene molecule has shown, for instance, that, apart from the well-established absolute energy minimum corresponding to the conformation in which the ethyl group lies perpendicular to the ring,[13−15] a shallow relative energy minimum also exists when the ethyl group is in the plane of the hexagon, in agreement with quantum chemical outcomes.[14] However, an intrinsic problem in the ME method is the dependence of its results on the orientational order of the solute molecule. Although the ME method can give sound qualitative results even at low orientational order, as the latter decreases the nuclear dipolar couplings tend to zero and every piece of information carried by them on the conformational distribution of the solute gradually loses its quantitative significance. In ref 12, an attempt to overcome this problem was proposed by combining the information coming from the experimental data with that coming from ab initio calculations. The latter have to be considered as an additional source of information entering the ME scheme. Once the orientational order drawback of the ME method is solved, a more effective investigation of the more subtle solvent effects can also be undertaken. Clearly, the just-mentioned method relies on the accuracy of the employed torsional potential.

Our goal in this paper is to provide, by a quantum-mechanical study, such kind of potential for ethylbenzene and, due to the almost ubiquitous nature of the alkoxy−aryl linkage as outlined above, also for ethoxybenzene. Even the latter, a two rotors system, was studied by the ME and ab initio quantum chemical methods[16] and also in this case the two approaches were found in accord.

Apart from the use in the ME method, such analytical expressions find a straightforward application in realistic models

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TABLE 1: Computed Torsional Barriers for Ethylbenzene[a]

ϕ	ΔE	ΔE^{b}
0	4.452	5.443
max	4.523 (20)	5.502 (17.8)
90	0.000	0.000

[a] All energies are in kJ/mol and all angles are in degrees; max means the energy of the maximum, whose dihedral angle is indicated in parentheses. [b] Ref 14. The results of ref 14 were obtained at the HF/DZP level.

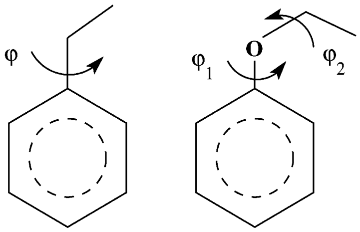

Figure 1. Definition of the dihedral angles for the two molecules. The above conformations are defined as $\phi = 0°$ and $\phi_1 = \phi_2 = 0°$ for ethylbenzene and ethoxybenzene, respectively.

for liquid crystal computer simulations.[17] This constitutes the second, equally important reason which has prompted us to perform the calculations described below, in Section 2, and whose results are presented and discussed in Section 3. Section 4 eventually concludes this paper.

2. Computational Details

All the calculations have been executed by the Gaussian 98 package,[18] making use of the B3LYP density functional method[19] with the 6-311G(2d,p) basis set. DFT calculations were preferred to the MP2 method in consideration of the greater basis set sensitiveness of the post-SCF technique. Indeed, in recent torsional barriers calculations[4,20] performed with both methods on similar molecules, a better agreement with experimental measures was obtained by the use of the B3LYP method. For both molecules, the minimum energy conformation was obtained by a complete geometry optimization. For ethylbenzene (Table 1), all calculations were performed without any symmetry restriction but the dihedral ϕ (see Figure 1), which was increased by 15° in a stepwise manner from an initial value of 0 to a final value of 90°. Moreover, in the region [10°; 30°] a step of 5° was employed. In the ethoxybenzene molecule, a similar procedure was adopted, optimizing all internal coordinates except ϕ_1 and ϕ_2 (see Figure 1), which were again varied by steps of 15°, each in the range [0°; 180°]. The whole range [0°; 360°] × [0°; 360°] was then recovered exploiting the molecular symmetry.

The DFT data have been finally fitted, through a minimization routine,[21] onto a cosine series, to provide analytical expression for the torsional potentials. The symmetry of ethylbenzene imposes that $V(\phi) = V(\phi + \pi)$, so such expression reduces to

$$V(\phi) = \sum_{n=0}^{K} c_n \cos(2n\phi) \tag{1}$$

In view of the symmetry of ethoxybenzene ($V(\phi_1, \phi_2) = V(-\phi_1, -\phi_2)$), a fitting function can be written as

$$V(\phi_1, \phi_2) = \left(\sum_{n_1=0}^{K_1} c_{n_1} \cos(n_1\phi_1) + \sum_{n_2=0}^{K_2} c_{n_2} \cos(n_2\phi_2)\right)(1 + g(\phi_1, \phi_2)) \tag{2}$$

where

$$g(\phi_1, \phi_2) = \sum_{n_1=1}^{K_{g_1}} \sum_{n_2=1}^{K_{g_2}} [c_{n_1,n_2} \cos(n_1\phi_1) \cos(n_2\phi_2) + s_{n_1,n_2} \sin(n_1\phi_1) \sin(n_2\phi_2)] \tag{3}$$

It is worth noticing that, in the last expression, the function $g(\phi_1, \phi_2)$ is strictly related to the correlation between the two dihedral angles. In the absence of coupling, in fact, this function is equal to zero. This method to treat the correlation between the angles is not of course the unique one. Another possibility, not tried here, is to consider even for ethoxybenzene a form of the torsional potential analogous to that employed for ethylbenzene but with coefficients c_n now functions of the angle ϕ_2. For every ϕ_2 considered, a fit supplies the coefficients $c_n(\phi_2)$, while the coefficients for intermediate values of ϕ_2 can be obtained by interpolation. The chosen fitting formula, however, permits a more straightforward modification of those parts, in existing computer simulation codes, devised for the computation of torsional potentials.

3. Results and Discussion

Ethylbenzene. The torsional potential for the ethylbenzene molecule is shown in the lower panel of Figure 2. The minimum geometry is achieved when the $C-CH_2-CH_3$ plane lies perpendicular to the benzene ring. In agreement with experimental data,[12] the energy maximum is localized at ≃20° and the conformation corresponding to 0° is a local shallow minimum. This agrees also with previous calculations,[14] as reported in Table 1. Comparing the two methods, the difference between the barrier heights at 0° is an indication that the correlation energy is more effective in the planar conformation.

The gross features of the torsional energy curve are essentially defined by repulsive interactions between the methyl and the phenyl groups, which increase as the CH_3 comes closer to the ring plane. By plotting the $C-CH_2-CH_3$ angle as a function of the ϕ dihedral (see Figure 2), it can be seen how this angle is forced to increase in going from a perpendicular to a planar conformation, the shape of the curve being almost equal to the torsional potential one, except for the location of the maximum. In fact, this last feature cannot be ascribed only to the repulsion between the carbons.

One reason for the location of the maximum, can be found by looking at the conformation of the methyl group with respect to the chain. As shown in the upper panel of Figure 2, when the chain is coplanar to the ring (i.e., $\phi = 0°$) the methyl group lies in the staggered conformation with respect to the CH_2, which minimizes the repulsion with both the hydrogens of the ring and those of the methylene group. However, when the torsional angle ϕ is fixed to values around 20°, the staggered conformation is no longer favored with respect to the ring, and a deviation of almost 5° can be seen when $\phi = 25°$. This last methyl conformation, though, results in an increase in energy with respect to the hydrogens of the neighboring methylene group, thus yielding the reported shape of the torsional potential.

On the other hand, apart from the main repulsive effects, the location of the minimum is due also to a small hyper-conjugation effect, which is confirmed by the shortening of the CH_2-C bond in going from $\phi = 0°$ to $\phi = 90°$, as reported in Figure 2c.

The calculated data were than fitted by the means of eq 1. In Figure 3, both the calculated points and the fitted curve are reported. Even with $K = 3$, a good fit is achieved, being its root-mean-square deviation, RMS = 0.113 kJ/mol. The im-

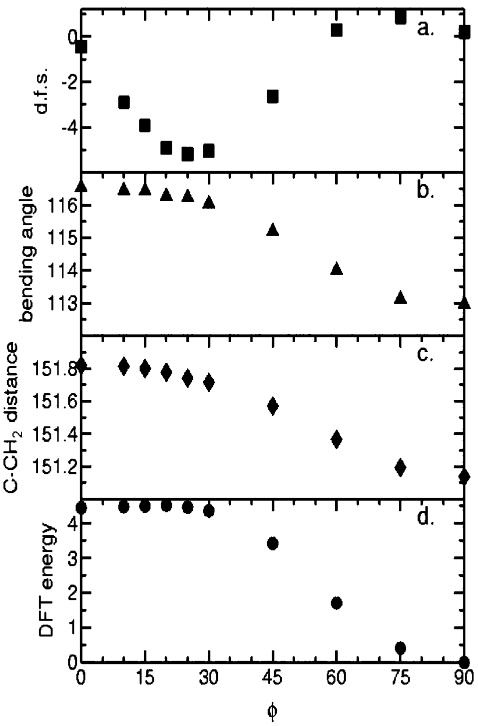

Figure 2. Ethylbenzene. (a) Conformation of the methyl group with respect to the CH_2, as a function of the torsional angle ϕ. Distortion from staggered conformation (dfs) is reported in degrees. (b) Value of the bending angle $C-CH_2-CH_3$ as a function of the torsional angle ϕ. (c) $C-CH_2$ bond length in pm. (d) DFT computed energies in kJ/mol.

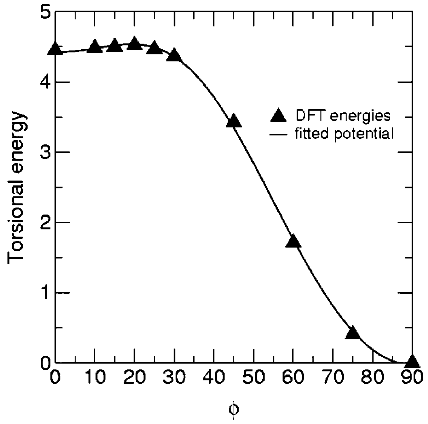

Figure 3. Torsional potential for ethylbenzene: DFT data (triangles) and fitted curve (solid line). All energies are in kJ/mol.

TABLE 2: The Coefficients c_n for the Torsional Potential Curve of Ethylbenzene

n	c_n (kJ/mol)
0	2.7706
1	2.3556
2	−0.5799
3	−0.1293

provement is very little with larger K, and having in mind to use such torsional potential in computer simulations, we think that the truncation of the cosine series at $K = 3$ is a good compromise between accuracy of the data and speed of the future calculations. The coefficients obtained are given in Table 2. The torsional potential of ethylbenzene has been very recently studied also in ref 21, at MP2/cc-pVTZ and B3LYP/cc-pVTZ. The fact that the results in ref 21 do not show any little pronounced energy maximum around 20° is probably due to their wide grid of points in that region.

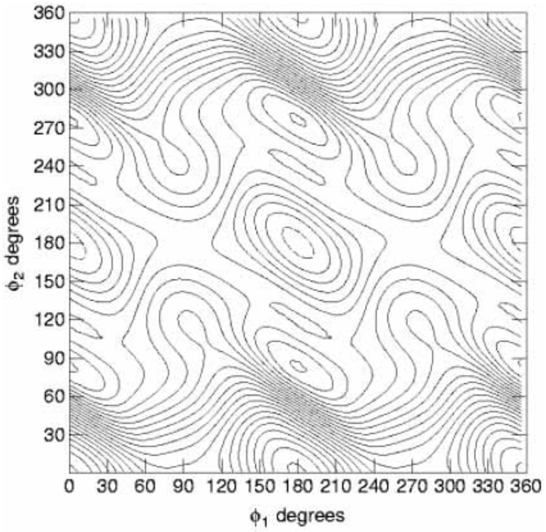

Figure 4. Torsional potential for ethoxybenzene. All energy values are in kJ/mol; curves are drawn every 2.0 kJ/mol. A dashed line is used for the lowest energy curve.

TABLE 3: Energy Barrier Values in Ethoxybenzene for Most Significant Conformations[a]

ϕ_1	ϕ_2	ΔE	ΔE^b
0	0	47.45	49.12
0	180	0.00	0.00
90	0	31.34	25.10
90	180	11.46	9.41

[a] All energies are in kJ/mol. [b] Ref 16. Literature data were reported according to the definition of dihedrals given in this paper.

Ethoxybenzene. The two-dimensional plot (see Figure 4) obtained from the calculation of the ethoxybenzene torsional potential, shows an absolute minimum at $\phi_1 = 0°$ and $\phi_2 = 180°$, i.e., when the ethoxy chain lies in the same plane as the ring, with the ring itself and the ethyl group in trans position with respect to the $O-CH_2$ bond. On the contrary, the maximum energy conformation is reached when $\phi_1 = \phi_2 = 0°$, with a barrier height of 47.4 kJ/mol.

This plot agrees well with the one reported in previous work[16] performed at an MP2/PS-31G* level (note that in ref 16 the ϕ_2 angle was defined in an opposite manner, being 0° in the fully optimized geometry). DFT and literature results for the more significant conformations are reported in Table 3. The small differences in barrier heights, more evident in the (90°, 0°) conformation, can be ascribed both to the smaller basis set adopted in the literature work[16] and to the different method employed, which we expect to be less accurate with respect to the present calculation. Indeed, there is general agreement[4,20] in assuming MP2 method more basis set demanding.

In Figure 5 the variation of some significant quantities is reported as a function of the dihedral ϕ_1, having fixed the ϕ_2 angle to 0° and 180°. From the lower panel of this plot, where the torsional energy variation is reported, it is evident that the two rotors are strongly coupled, the shape of the potential curve being strongly dependent on the ϕ_2 value.

Indeed, when ϕ_2 is fixed at 180°, the torsional energy has its (absolute) minimum value at $\phi_1 = 0°$, and reaches its maximum (11.46 kJ/mol) for $\phi_1 = 90°$. On the contrary, if ϕ_2 is kept at 0°, the molecule is found in its most unfavorable conformation (47.4 kJ/mol) for planar geometry ($\phi_1 = 0°$) and relaxes to more stable geometry (31.34 kJ/mol) as ϕ_1 approaches 90°.

This behavior arises mainly from the different kind of interactions that contribute to realize the shape of the torsional

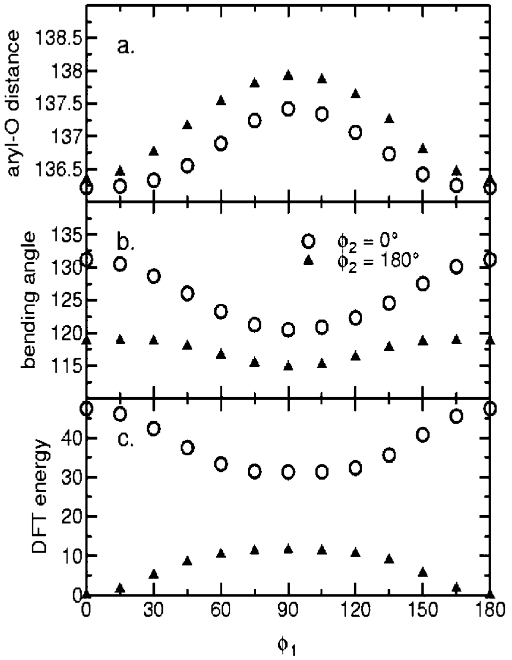

Figure 5. (a) Aryl−oxygen distance (C−O). (b) Bending angle C−O−CH$_2$. (c) DFT energies. All angles are given in degrees, distances in pm, and energies in kJ/mol.

potential. When ϕ_2 is fixed at 0°, the benzene ring and the ethyl chain are in cis position with respect to the O−CH$_2$ bond. In this conformation, the main forces are due to the repulsion between the methyl group and the ring, and the less unfavorable conformation is achieved when these forces are minimized (i.e., at $\phi_1 = 90°$). This trend is confirmed by plotting the value of the bending angle C−O−CH$_2$ (Figure 5b) which varies from a value of 131.2° to a value of 120.5° in going from $\phi_1 = 0$ to $\phi_1 = 90°$.

On the other hand, the variation of this angle when $\phi_2 = 180°$ is much less pronounced and it averages to smaller value ($\simeq$ 116°). In this case, since the repulsive forces are smaller, the conjugation effects between the oxygen atom and the ring must also be taken into account for a deeper understanding of the potential curve. In the upper panel of Figure 5 the aryl−oxygen bond length is reported as a function of the dihedral ϕ_1. It can be seen that when the ring lies in the same plane as the chain, the distance between the ring and the O atom is smaller (136.3 pm) with respect to the value at $\phi_1 = 90°$ (138.0 pm). In the planar conformation, thus, the position of the minimum arises from the conjugation effects due to the partial overlap between the nonbonded orbitals of the oxygen and the π-orbitals of the phenyl ring. This last feature holds also for $\phi_2 = 0°$, but in this case the magnitude of the repulsion is such as to overcome this feature.

The DFT data were first fitted without taking correlation between the two rotors into account, i.e., by imposing $g(\phi_1, \phi_2) = 0$. As expected, no satisfactory set of parameters was achieved; even making use of many parameters the root-mean-square deviation was no lower than 5.0 kJ/mol and the maximum absolute error (MAE) was 10.5 kJ/mol. The correlation between dihedrals was then taken into account. A second fitting was performed, using 18 parameters, yielding a RMS of 0.8 kJ/mol with a MAE of 2.0 kJ/mol. Fitted curves together with DFT energies are reported in Figure 6, while parameter values are given in Table 4. Clearly a better agreement can be achieved by increasing the number of parameters, but the reported values seem a good compromise between accuracy and computational cost, if again the potential is to be used in computer simulations.

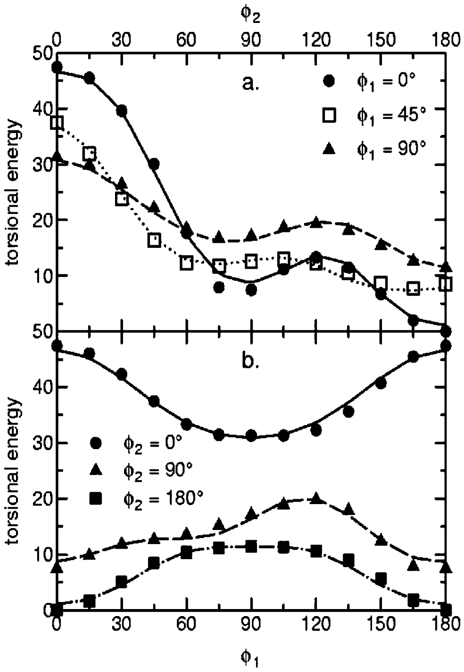

Figure 6. Calculated DFT energies (symbols) and fitted curves (lines) for some significant conformations. Angles are reported in degrees and energies in kJ/mol.

TABLE 4: Fitted Coefficients c_{n_1,n_2} and s_{n_1,n_2}, in kJ/mol, for Expressions (2) and (3); RMS and MAE of 0.8 and 2.0 kJ/mol Were Obtained, Respectively

n_1	n_2	c_{n_1,n_2}	s_{n_1,n_2}
0		18.740	
2		−2.628	
4		−0.109	
	1	12.355	
	2	4.418	
	3	3.640	
	4	−0.770	
2	1	1.222	
2	2		−0.448
2	3	0.397	−0.384
2	4	−0.460	0.565
4	3	0.586	−0.506
4	4	0.385	0.393

4. Conclusions

A B3LYP/6-311G(2d,p) calculation of the torsional potential of the ethylbenzene (1 rotor) and ethoxybenzene (2 coupled rotors) molecules has been performed. While in the former the minimum energy conformation is achieved when the ethyl chain lies in a plane perpendicular to the aromatic ring, in the latter the optimized geometry is reached when the chain and the ring are in the same plane, in trans position with respect to the O−CH$_2$ linkage. Moreover in ethylbenzene, the barrier height of slightly more than 4.5 kJ/mol does not exclude the possibility of a planar conformation at room temperature induced by the packing forces in condensed phase. In ethoxybenzene, on the contrary, the barrier of almost 48 kJ/mol ($\simeq 20k_BT$) seems to rule out the interconversion between the trans and the cis conformers.

Analytical forms of these torsional potentials were obtain by a least-squares fitting procedure, both to be employed in LXNMR and computer simulations of realistic models of liquid crystals. A certain degree of transferability[23] can to our advice be invoked to use the present analytical forms in such models. In 4 *n*-alkyl-4′-cyanobiphenyl (*n*CB) and *n*-alkoxy-4′cyanobiphenyl (*n*OCB) molecules, for instance, the substituents should not alter significantly the shape of the torsional potential. Indeed, a simulation of the 5CB molecule will be the object of a future work. Finally, it must be said that the inclusion of a correlation term, depending on two dihedrals, as in the case of ethoxybenzene, is not straightforward in common simulations, where the torsional intramolecular potential is usually expressed as a sum of uncoupled terms. This problem can be overcome by adding, to the commonly employed cosine series, some ad hoc intramolecular Lennard−Jones terms, which take into account the intramolecular interactions that lead to the coupling. The approach followed here, however, seems to us less arbitrary and perhaps more realistic.

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