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Liquid crystalline polyethers based on conformational isomerism

17. Some considerations on the "rigidity" of "rod-like" mesogens*

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SUMMARY

A critical discussion of the *rigid rod-like* and *flexible rod-like groups* used most frequently in the design of rod-like mesogenic units is presented. Based on the literature data on the potential energy difference and the rotational energy barrier of their extended and kinked configurational isomers and respectively conformers, we suggest a classification in *rigid rod-like groups* (the rod-like shape of the molecule is rigid although there is free rotation about some of its C-C bonds, like for example oligo-*p*-phenylenes, diphenyl-acetylenes , etc., and configurational isomers which require a high rotational energy barrier or activation energy like for example, stilbene), *semirigid* or *semiflexible rod-like groups* (conformationally flexible but of medium rotational energy barrier like for example aromatic esters and amides) and *flexible rod-like groups* (conformationally flexible groups which require a low rotational energy barrier, i.e., within the same range of values with that of n-butane, like for example: 1,2-diphenylethane and phenyl benzyl ether derivatives).Therefore, *rigid, semirigid* or *semiflexible,* and *flexible* refer to the ability of the rod-like molecule to change its rod-like shape.

INTRODUCTION

The traditional pathway used to synthesise low molar mass liquid crystals[1,2] and both, main chain [3-7] and side-chain[8] liquid crystalline polymers is based on the use of *rigid rod-like mesogenic units.* Recently, we have advanced the concept of *flexible rod-like mesogens* or *rod-like mesogens based on conformational isomerism* and used it in the synthesis of both side chain[8,9] and main chain[10] liquid crystalline polymers. Low molar mass liquid crystals based on flexible mesogens were discussed in some of our previous publications.[8,9,10a-f] We have also advanced a simple thermodynamic scheme which correlates the thermodynamic stability of a certain phase with the rigidity of the molecule or macromolecule.[11] The goal of this paper is to provide a critical discussion of the concept of rod-like groups which are frequently used to generate rod-like mesogenic units. Depending on their conformational or configurational rigidity we will suggest their classification as *rigid rod-like, semirigid* or *semiflexible rod-like* and *flexible rod-like* groups.

DISCUSSION

Rigid Rod-Like Groups

Rigid rod-like mesogenic units as diphenylacetylene **1**, oligo-*p*-phenylene **2**, and benzoxazole **3** derivatives are based on linearly substituted aromatic or heterocyclic rings. They exhibit free rotation about certain C-C bonds as in the case of **1-3**, but this rotation does not perturb the elongated or extended shape, and the molecule retains its *rigid rod-like character*. Therefore, in *rigid rod-like mesogenic units, rigid* refers to the rigidity of the linear shape.

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[*] Part 16: G. Ungar, J. L. Feijo, V. Percec and R. Yourd, Macromolecules, in press

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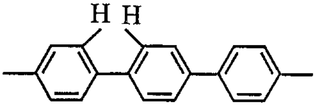

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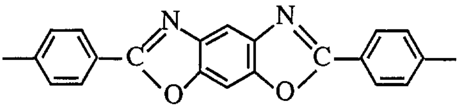

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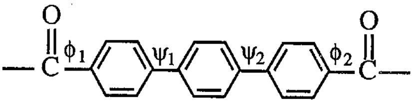
In oligo-*p*-phenylene **2** the steric interaction of the ortho hydrogens impede this internal rotation and the conjugation effect reinforces the rigidity due to the double bond character of the C-C bond between the phenylene rings. A ^{13}C-NMR study[12] of **4** showed an energy barrier of 5 kcal/mol for the internal rotation of the outer rings. The PCLIO (Perturbative Configurational Interaction using Localized Orbitals, a method using semiempirical quantum mechanics), conformational calculations provided for this rotation a value of about 4.8 kcal/mol.[13]



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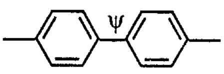

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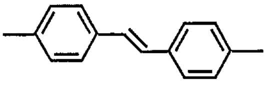

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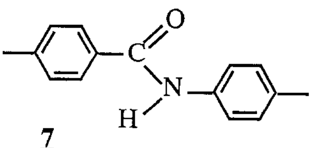
The mimimum energy is at $\phi_1=\phi_2=0$ or $\phi_1=0$, $\phi_2=180°$. In the case of **5**, the energy barrier is of 1.9 kcal/mole and the minimum energy is at $\phi=40°$. This value is in close agreement with the experimental value obtained in vapor state (i.e. $\phi=42°$).[13] If the aromatic rings are connected via a double bond as in the case of stilbene **6** the molecule exhibits cis and trans configurational isomers. The structure of the trans isomer is energetically more favorable. The trans isomer can be isomerized into the cis one, but the activation energy for this transformation is very high and, therefore, makes this molecule almost rigid. Kalinowski and Kessler[14] have reported an activation energy of 42.8 kcal/mol for the thermal uncatalized isomerization of stilbene.

Semirigid Rod-Like Groups

The second group of mesogenic units have both conformational and configurational character and refer to *semiflexible molecules* such as amides **7** and esters **8**. However, due to electronic reasons, the rotation about the C-O or C-N bond of **7** and **8** is retarted and can be even prohibited. In esters like **8**, there is rotation about three bonds: R, S and T.



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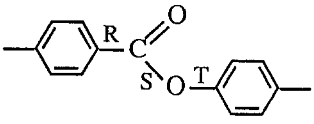

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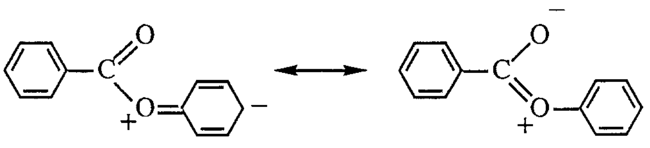
The most important rotation is about the S-bond, since it determines the kinked (cis) or extended (trans) conformation of the molecule. Theoretical calculations[15] suggest that the trans conformation represents the most stable structure. The arguments for this statement are as follows. In the trans-form of esters and acids there is a better O_n-C_σ*"hyperconjugation" which decreases the free energy of this conformer.[15] The steric effect in the cis form makes it more unstable than the trans form . The potential energy of the cis form is higher than that of the trans form with 7.9 kcal/mol. In the energy profile there is a hump at 90° which is due to the O_p-C_π* overlap which creates a double bond character on the O-C bond. This barrier is smaller for aromatic esters than for aliphatic esters. This is because the delocalization of p-electrons of the oxygen on the aromatic ring attached to the oxygen gives the structure 9 which competes with the contributor 10. This conclusion is supported by the difference between the C-O bond length of aliphatic and aromatic esters. The C-O bond length is 1.33 Å in alkyl benzoate and 1.36 Å in alkyl benzoate[15]. This last value is the closest to the typical ether C-O bond length of 1.42-1.43 Å. This double bond character creates a configurational character for the cis and trans conformers of esters and amids and subsequently, these compounds behave close to the class of rigid mesogens. Therefore, they should be classified as *semirigid or semiflexible rod-like mesogens.*

The structure and conformational behavior of amids 7 is very close to that of esters 8. The different resonance structures 11, 12 and 13 of a typical amide molecule[16] are similar to those of esters. Due to its double bond character, the contribution of 12 hinders the rotation about the C-N bond.



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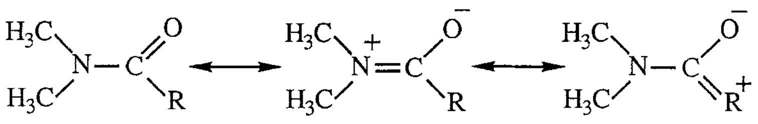
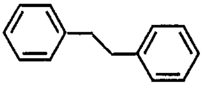


11 12 13

Pauling[16] predicted a rotational energy barrier of 21 kcal/mol which corresponds to about 40% double bond character for the C-N bond of amides. This double bond character decreases due to the participation of 13, especially when R =aryl. This double bond character contribution was demonstrated by NMR studies performed on $(CH_3)_2$ N-C(O)-R. When R is CH_3- the rotational energy barrier is 18.9 kcal/mol[17] and decreases to 14.4 kcal/mol[18] for R=phenyl. On the basis of an NMR study, Tadokoro et al[19] reported a rotational energy barrier of about 20 kcal/mol for the rotation about the C-N bond of phenyl benzamide.

Flexible Rod-Like Groups

The third class of rod-like molecules are *flexible*. 1,2-Disubstituted ethane 14 and methyleneoxy or benzylethers 15 derivatives belong to the class of *flexible mesogenic units*. Before discussing the fully *flexible rod-like mesogens* or the mesogens based on *conformational isomerism*, let us briefly recapitulate the conformational behavior of n-butane molecule 16. n-Butane exhibits a number of different conformers. Out of them, the most stable are the gauche 17 and 18 and the anti 19. The electron diffraction study[20,21] of n-butane in gas phase (at 287 °K)[20] provided an energy difference of 0.6 kcal/mol between the gauche and the anti conformers.



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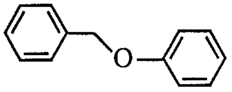

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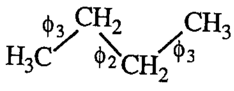

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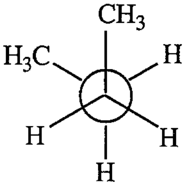

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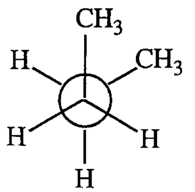

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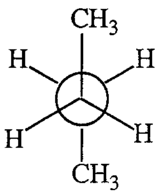

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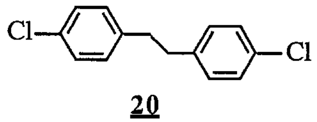
The same parameter was determined by Raman spectroscopy[22] (0.77 kcal/mol) and ^{1}H-NMR spectroscopy[23] (0.68 kcal/mol). The most recent Raman study[24] performed on n-butane in gas phase shows a potential energy difference of 0.966±0.054 kcal/mol between its gauche and anti conformers. Theoretical SCF-MO (Self Consistent Field-Molecular Orbitals) based calculations[25] led to a rotational energy barrier at ϕ_2=60° (when CH_3- group is eclisped with a hydrogen atom) of 3.7 kcal/mol and to a potential energy difference of 1.19 kcal/mol. Flory et al[26] have calculated a rotational energy barrier of 2.8 kcal/mol and a potential energy difference of 0.53 kcal/mol. Consequently, the theoretical and experimental results of n-butan agree.

The X-ray study [27] of diphenyl ethane suggests that in solid state the phenyl groups are located exclusively in the anti position. IR and Raman spectroscopy studies[28] performed on 1,2-diphenyl ethane and 1,2-di(*p*-chlorophenyl)ethane **20** also demonstrated that both molecules exist in solid state as anti conformers. An optical anisotropy study[29] performed by diffusion Rayleigh depolarization on solutions of 1,2-diphenylethane in CCl_4 and cyclohexane, shows that the anti conformer is preferred also in solution. In solution and Nujol mulls[28] of para substituted 1,2-diphenylethane derivatives some extra bands were observed suggesting the existence of the gauche conformer. At 25°C the ratio of anti to gauche is 84:16, but in case of 1,2-diphenylethane **14** the absence of any extra band suggests the possibility that the concentration of gauche conformer is too low to be detected by IR spectroscopy. A ^{13}C-NMR spectroscopy study[30] of 1,2-di(2,6-dimethylphenyl)ethane in CCl_4 solution showed a dynamic equilbrium of 7/3 anti to gauche conformations.

Theoretical calculations performed on 1,2-diphenylethane gave contradictory results. Ivanov et al[31] concluded that the gauche conformer of **14** is more stable than the anti one with 0.57 kcal/mol. Jacobus[32] also indicated that the gauche conformer is more stable and he obtained a difference of 1.15 kcal/mol between the anti and the gauche conformers. On the basis of LCAO-MO (Linear Combination of Atomic Orbitals-Molecular Orbitals) treatment of the benzene rings, Ivanov et al [31] showed that there is no difference in the stretch, bend, tortion and stretch-bend interactions but there is difference of the nonbonded interactions between the atoms of benzene rings which prefers the gauche conformer. A theoretical



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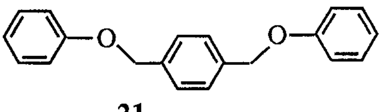

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study[33] by using the MM2/MMP2 (molecular mechanics based computer program) program provided data which are in agreement with the experimental results, suggesting that the anti-form is more stable than the gauche form. The energy difference between these conformers is of 0.95 kcal/mol and increases to 1.59 kcal/mol when point charge and electrostatic interactions are also considered. Jonsson et al[34] calculated the conformational energy barrier of α,α'-diphenyl-*p*-xylene **21**, as a model compound for the polymers based on benzylether mesogenic units. The potential energy barrier to move one of the outer rings to the position where it becomes linear is 3.87 kcal/mol.

From this discussion it is clear that in crystalline state only the anti conformer exists. However in solution both the anti and the gauche conformers exist in a dynamic equilibrium. To our knowledge, the rotational energy barrier of 1,2-diphenylethane is not available. Ivanov et al[31] calculated the potential energy at different values of torsional angle (Ph-C-C-Ph) i.e., when they are in the anti, gauche, and eclipse forms. In the eclipse form, the two rings are in the closest geometry (the steric and other nonbonded interactions are maximum). Depending on the method used, the calculated energy of the eclipse form is 3.61, 3.49 and 1.95 kcal/mol. This conformer has the maximum potential energy suggesting that the conformational energy barrier should be lower than the above mentioned values because during the gauche to anti or anti to gauche conformational change the benzene rings eclipse with the ethylenic hydrogen atoms, and this steric interaction is less than for two benzene rings.

Conclussion

In conclusion, based on the difference between the rotational energy barrier of different configurational isomers or conformers of rod-like groups we suggest their classification into three categories: *rigid, semirigid or semiflexible,* and *flexible. Rigid rod-like groups* are rigid units whose shape is rigid like for example **1**, **2**, and **3**, and configurational isomeric units which require a high rotational energy barrier or activation energy, like for example stilbene (ΔEa=42.8 kcal/mol). *Semirigid or semiflexible rod-like groups* are conformationally flexible, but due to some electronic reasons they behave like configurational isomers of medium rotational energy barrier. Classic examples are aromatic amids and esters (ΔEa=14.4 kcal/mol and 7.1 kcal/mol respectively). The rotational energy barrier of these molecules is less than half that of rigid molecules but is much higher than that of flexible molecules. *Flexible rod-like groups* are conformationally flexible groups whose rotational energy barrier is within the same range of values with that of butane (ΔEa=2.8-3.7 kcal/mol). Classic examples are phenylbenzylether (ΔEa=3.87 kcal/mol) and 1,2-diphenylethane (ΔEa=3.61 kcal/mol) based molecules.

ACKNOWLEDGEMENT

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