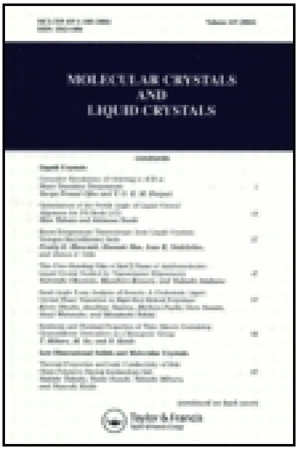

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Conformational Studies on Mesogenic Monomers and Dimers

Rudolf Friedemann [a], Sylvia Uslar [a] & Wolfgang Uslar [a]
[a] Department of Chemistry, Martin Luther University, Halle/S, G. D. R.

Version of record first published: 22 Sep 2006.

To cite this article: Rudolf Friedemann, Sylvia Uslar & Wolfgang Uslar (1990): Conformational Studies on Mesogenic Monomers and Dimers, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 192:1, 155-160

To link to this article: http://dx.doi.org/10.1080/00268949008035623

Mol. Cryst. Liq. Cryst. 1990, Vol. 192, pp. 155–160
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

CONFORMATIONAL STUDIES ON MESOGENIC MONOMERS AND DIMERS

RUDOLF FRIEDEMANN, SYLVIA USLAR AND WOLFGANG USLAR
Department of Chemistry, Martin Luther University,
Halle/S., G.D.R.

Abstract The conformational properties of the isolated alkyl substituted cyano-biphenyls, cyano-phenyl-cyclohexanes and cyano-phenyl-1,3-dioxanes are studied by molecular mechanics and by a point charge model. Especially the relative orientation of the rings and the flexibility of the alkyl groups are investigated. Structures with kinks in the alkyl chains and the length-broad relation(L/B) of the energetically preferred conformers are calculated. In the disubstituted cyclohexanes and 1,3-dioxanes the e,e conformers are more stable than the a,a ones. Moreover, the molecular mechanics calculations are extended to the dimers of benzene, biphenyl, cyano-biphenyl and 4-n-hexyl-4'-cyano-biphenyl in order to investigate the preferred structures.

INTRODUCTION

Information on the conformational and structural behaviour of isolated molecules and molecular dimers may be helpful in the first step for deeper understanding of the relationship between structure and properties in crystalline and liquid crystalline states. Therefore we have performed calculations on mesogenic monomers and dimers within the model of local electron pairs (LEP)[1] and the molecular mechanics method(MMP2)[2] from Allinger. In this work we report the results of our theoretical studies on 4-n-alkyl-4'-cyano-biphenyls (n-CB; n=3-6,8), 4-n-alkyl-1-(4'-cyano-phenyl)-cyclohexanes (n-CPC; n=3-6,8), 2-(4'-cyano-phenyl)-5-n-octyl-1,3-dioxane (8-CP2,5D) and 5-(4'-cyano-phenyl)-2-n-octyl-1,3-dioxane(8-CP5,2D) as well as on the dimers of benzene, biphenyl, CB and 6-CB. The purpose of the conformational studies is to investigate the energetical and structural properties of the isolated mesogenic compounds. A principal point of interest is the investigation of the arrangements of the rings and the orientation and flexibility of the alkyl chains. On the disubstituted cyclohexane and dioxane derivatives the stability of the e,e and a,a conformers is discussed. Moreover, the effects of kinks in the alkyl chains on the energetical properties and on the length-broad relation of the mesogenic compounds are investigated. The structural studies on the dimers are performed in order to calculate the preferred arrangements of the molecules and the influence of the intermolecular interactions on intramolecular changes. Furthermore the applicability of the used MMP2 version for treating intermolecular interactions is tested. Until now calculations on such systems are carried out on a limited scale[3,4,5].

RESULTS AND DISCUSSIONS

Monomers

Within the MMP2 method an all-trans arrangement of the alkyl chain was obtained for the most stable conformers of n-CB. In contrast to this result the energetically preferred structures in the LEP model show a back folded orientation of the alkyl tail to the neighboured benzene ring, while conformations with an all-trans arrangement of the alkyl group correspond to local minima. This is illustrated for the favoured MMP2 and LEP structures of

6-CB in Figure 1. Similar results were also obtained for the n-CPC compounds. It results in extended arrangement of the alkyl chain in the preferred MMP2 structures and a folded one in the most stable LEP conformers.

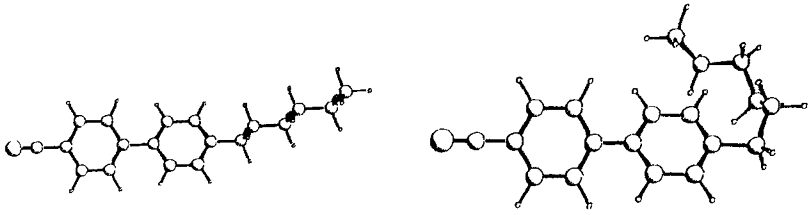

FIGURE 1 6-CB(1)/MMP2(left) and 6-CB(1)/LEP(right)

The calculated values of the dihedral angle between the phenyl rings in the n-CB series of 27^{o}(MMP2) and 32^{o} (LEP) are comparable with X-ray data[6]. In the n-CPC compounds both the MMP2 and LEP calculations show a nearly perpendicular orientation of the central plane of the cyclohexane ring with respect to the phenyl ring. This is in agreement with X-ray data of Paulus[7] on 8-CPC.

In order to get some information about the flexibility of the alkyl tail in the isolated n-CB and n-CPC molecules we have calculated the relaxed rotational MMP2 barriers about the alkyl-phenyl and alkyl-cyclohexyl bond in 8-CB and 8-CPC. The height of the barriers 6 kJ/mole(8-CB) and 10 kJ/mole (8-CPC) as well as the areas of free rotation of about 90^{o}(n-CB) and 40^{o} (n-CPC) are hints for a higher flexibility of the alkyl chain in 8-CB in comparison to 8-CPC. These findings correlate with NMR results[8].

Our MMP2 calculations on 8-CPC, 8-CP5,2D and 8-CP2,5D show that in the disubstituted chair-shaped cyclohexanes and 1,3-dioxanes the e,e conformers are preferred in comparison to the a,a ones. The following differences between the most stable a,a and e,e conformers in the disubstituted compounds are found 8-CPC (27 kJ/mole), 8-CP5,2D(17 kJ/mole) and 8-CP2,5D(11 kJ/mole).

Moreover, structures with kinks in the alkyl chains and the L/B relation of n-CB and n-CPC are investigated. Kinks are structures with the torsion angle sequence 60°, 180°, -60° in three adjacent C-C bonds of the alkyl chain. The L/B relation of the conformers was calculated based on the computation of the principal axis of the moment of inertia by a PC program. Both the LEP and MMP2 calculations on 8-CB and 8-CPC show that kink structures are quite energetically favoured conformers. The conformational energies as well as the L/B values are comparable with those of the most stable all-trans structures. Accordingly, kinks or kink-like arrangements should occur as possible structures in liquid crystalline state, too.

Dimers

The molecular mechanics calculations were extended to mesogenic dimers in order to test the MMP2 version for treating intermolecular interactions and to model surrounding effects in a very simple way. Especially the MMP2 calculations on the benzene dimer have shown that the addition of point charges is important. We have used net atomic charges of -0.15 on carbon and +0.15 on hydrogen[9]. In agreement with other molecular mechanics and ab initio calculations[9,10] we found that the T arrangement(edge-to-face) is more stable than the sandwich structure(face-to-face) by about 8 kJ/mole. The most stable dimer corresponds to a T shaped structure wagging one ring up(Figure 2).

For our calculations on the dimer of biphenyl the net atomic charges were taken from Petterson[9], too. In the most stable structure the corresponding phenyl rings have a parallel arrangement (Figure 2).

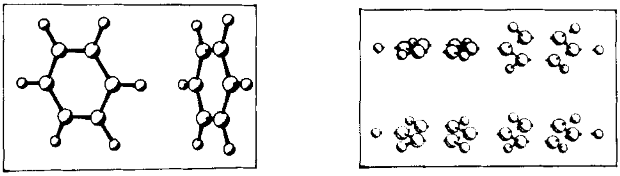

FIGURE 2 $(C_6H_6)_2$(left) and Biphenyl dimer(right)

The interplane distance is about 350 pm and the interring torsion angle arises to 41°. Similar results are also obtained without additional charges, but the interring torsion angle is reduced to 29°.

The used point charges in the calculation of the cyano-biphenyl dimer are obtained by an electronegativity equalization procedure[11] and scaling to the experimental dipole moment. The antiparallel arrangement(Figure 3) is more stable than the parallel one by 15 kJ/mole. The distance of the planes of the stacking phenyl rings is 360 pm and the interring torsion angle is about 30°. Without point charges it results nearly the same qualitative predictions.

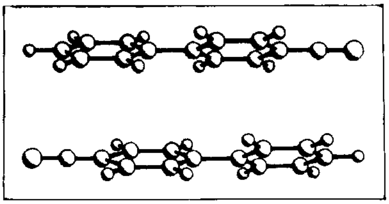

FIGURE 3 Most stable structure of the CB dimer

Within our MMP2 calculations on the 6-CB dimer we have obtained up to now the results without additional point charges only. In this case different to the molecular packing from X-ray findings[7] the parallel arrangement is more stable than the antiparallel one by about 22 kJ/mole(Figure 4). In both structures the corresponding interplane distances near 350 pm as well as the interring torsion angles of about 28° are comparable. The influence of additional point charges and further starting arrangements in the computations on the preferred structures of the 6-CB dimer will be investigated.

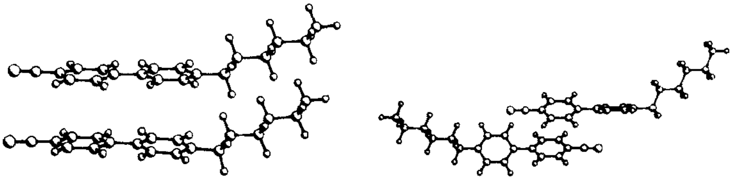

FIGURE 4 Preferred structures of the 6-CB dimer

REFERENCES

1. R. Friedemann and W. Gründler, Z. phys. Chem. (Leipzig), 265, 561 (1984)
2. N. L. Allinger and Y. H. Yuh, Q C P E, 13, 395 (1981)
3. J. R. Lalane, J. C. Rayez, B. Duguay, A. Proutiere and R. Viani, Chem. Physics, 101, 393 (1986)
4. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4899 (1977)
5. N. K. Sanyal, S. N. Tiwari and M. Roychoudhury, Mol. Cryst. Liq. Cryst., 140, 179 (1986)
6. W. Haase, H. Paulus and R. Pendzialek, Mol. Cryst. Liq. Cryst., 100, 211 (1983)
7. H. Paulus and W. Haase, Mol. Cryst. Liq. Cryst. (Lett.), 92, 237 (1983)
8. E. Kleinpeter, H. Köhler, A. Lunow, C. Tschierske and H. Zaschke, Tetrahedron, 44 1609 (1988)
9. I. Petterson and T. Liljefors, J. Comp. Chem., 8, 1139 (1987)
10. P. Carsky, H. L. Selzle and E. W. Schlag, Chem. Physics, 125, 165 (1988)
11. W. L. Jolly and W. B. Perry, J. Am. Chem. Soc., 95, 5442 (1973)