Molecular Ordering in Non-Liquid Crystalline versus Liquid Crystalline Materials with Special Reference to DADMBP – A Computational Analysis

Durga Prasad Ojha

Centre for Liquid Crystal Research and Education (CLCRE), Faculty of Physical Sciences,
Nagarjuna University, Nagarjuna Nagar (A.P.) – 522 510, India

Reprint request to Dr. D. P. O.; Fax: +91-0863-235900

Z. Naturforsch. **57a,** 194–198 (2002); received February 8, 2002

A computational analysis of the molecular ordering of the non-liquid crystalline biphenyl derivative 4,4′-diamino-3,3′-dimethylbiphenyl (**DADMBP**) has been performed. The **CNDO/2** method has been employed to compute the net atomic charge and atomic dipole components at each atomic centre. The modified Rayleigh-Schrödinger perturbation theory along with the multicentered-multipole expansion method has been employed to evaluate the long-range interactions, while a "*6-exp*" potential function has been assumed for short-range interactions. On the basis of stacking, in-plane and terminal interaction energy calculations, all possible arrangements of a molecular pair have been considered. It is found that, if a suitable functional group is attached to **DADMBP**, so that the length to breadth ratio is increased, the molecule will show a change in the long-range order, the phase transition temperature and other liquid crystalline properties. The results are compared with those for the liquid crystalline compounds 4-(4′-ethoxyphenylazo)phenyl valerate (**EPPV**) and 4,4′-di-*n*-propoxy-azoxybenzene (**DPAB**).

Key words: DADMBP; CNDO/2 Method; Quantum Chemistry; Computer Simulation.

Introduction

Liquid crystals have industrial, technological and biomedical applications [1, 2]. The interactions of mesogenic compounds have been studied by several semiempirical calculations [3–5]. Tokita et al. [6] used the Lennard-Jones potential to calculate the intermolecular interactions between a couple of pure nematogens. The angular dependence of the dispersion energy obtained by them partially agreed with Maier and Saupe and others. However, it has been observed that, instead of the Lennard-Jones potential, the Buckingham '6-exp' type potential function is more suitable to deal with molecular packing [7].

Computer simulations are increasingly influential in placing empirical structure-property relationships on firm theoretical foundations [8–11]. The anisotropy in the molecular interaction is responsible for the existence of liquid crystalline phases [12, 13]. It is generally agreed that the prime requirement for the formation of thermotropic liquid crystals is an anisotropy in the molecular interaction [14].

In view of the importance of statistical calculations to identify the characteristic features of liquid crystalline compounds in terms of the pair energies and configurational probabilities [15–17] it seems appropriate to extend similar studies to non-liquid crystalline compounds. For the present investigation **DADMBP** has been chosen. It itself does not form liquid crystals, but it does with suitable substituents. Biphenyls [18], a special class of molecules, form liquid crystalline phases.

In the following an attempt has been made to explain the results of the configurational probability distribution between a pair of **DADMBP** molecules based on interaction energy calculations during stacking, in-plane and terminal interactions. The results are compared with those obtained for two liquid crystalline materials: 4-(4′-ethoxyphenylazo)phenyl valerate [15] and 4,4′-di-*n*-propoxy-azoxybenzene [16].

Simplified Formula and Computational Details

In order to achieve the interaction picture of a pair of non-mesogenic molecules, the following computations have been carried out:

(A) *Computation of Interaction Energy at Various Configurations:* For the calculation a modified second order perturbation method [19] has been used. The total interaction energy E_{total} between a pair of **DADMBP** molecules has been computed as a sum of various contributions:

$$E_{\text{total}} = E_{\text{el}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{rep}},$$

where E_{el}, E_{pol}, E_{disp}, and E_{rep} represent the electrostatic, polarization, dispersion and repulsion terms.

According to the multicentered-multipole expansion method developed by Rein [20], the electrostatic energy may be expressed as the sum of interaction terms between atomic multipoles of successively higher orders:

$$E_{\text{el}} = E_{\text{QQ}} + E_{\text{QMI}} + E_{\text{MIMI}} + E_{\text{Qq}}, E_{\text{Mq}},$$

where E_{QQ}, E_{QMI}, E_{MIMI}, E_{Qq}, E_{Mq} are the monopole-monopole, monopole-dipole, dipole-dipole, monopole-quadrupole, and dipole-quadrupole terms, respectively. For most molecular systems the first three terms have been found to be sufficient [21]. In the present computations, the **CNDO/2** method has been used [22].

Keeping one of the **DADMBP** molecules fixed in a position while the second molecule is rotated at intervals of 10°, a minimum energy point is obtained. The molecule is then translated along its long axis at steps of 2 Å, and the corresponding energies are calculated. The minimum energy so obtained is then taken as starting point and the entire process is repeated at smaller intervals. The association energy is minimized with respect to translation and rotation about all axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to the other has been achieved.

In the used orthogonal co-ordinate system the X-axis lies along the long molecular axis, the Y-axis lies perpendicular to the plane of molecule and Z-axis lies perpendicular to the X- and Y-axis. The origin has been chosen almost at the mid point of the molecule.

(B) *Computation of the Intrinsic Probability of Each Configuration:* The total interaction energy obtained through these computations was used as an input to calculate the intrinsic probability of each configuration with the help of the Maxwell-Boltzmann formula [23]

$$P_i = \exp(-\beta\varepsilon_i)/\textstyle\sum_i \exp(-\beta\varepsilon_i); \; \beta = 1/kT,$$

where P_i is the probability of the occurrence of a particular configuration, and ε_i is the energy of a configuration i relative to the minimum energy configuration.

The molecular geometry of **DADMBP** has been constructed on the basis of the published crytallographic data with standard values of bond lengths and bond angles [24].

Results and Discussion

The molecular geometry is shown in Figure 1. The net charge and dipole moment components corresponding to each atomic center are listed in Table 1, while the

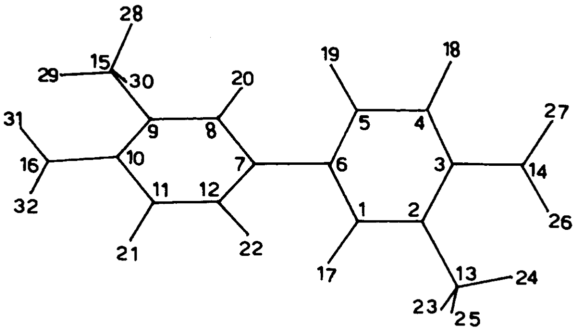

Fig. 1. The geometry of the 4,4′diamino-3,3′dimethlbiphenyl (DADMBP) molecule with its 32 atomic index numbers. (Scale: 1 cm = 1 Å with X-axis along 1–2 bond.)

Table 1. Calculated molecular charge distribution of 4,4′-diamino-3,3′-dimethylbiphenyl (**DADMBP**) using the **CNDO/2** method.

Sl. No.	Atom	Charge	Atomic dipole components		
			μ_X	μ_Y	μ_Z
1	C	–0.013	0.084	0.121	0.022
2	C	–0.009	–0.016	0.029	–0.009
3	C	0.137	0.147	–0.017	0.025
4	C	–0.053	–0.069	–0.165	–0.019
5	C	0.012	0.040	–0.105	0.002
6	C	0.013	0.039	–0.014	–0.052
7	C	0.001	–0.080	0.044	–0.029
8	C	–0.005	–0.094	–0.085	–0.046
9	C	–0.011	–0.019	–0.002	–0.061
10	C	0.139	–0.166	–0.032	0.011
11	C	–0.065	0.076	0.138	–0.094
12	C	0.019	–0.026	0.059	0.049
13	C	–0.012	–0.063	0.121	0.002
14	N	–0.258	–0.073	0.008	–0.003
15	C	–0.012	0.069	–0.092	–0.071
16	N	–0.249	0.089	–0.004	0.004
17	H	–0.004	0.000	0.000	0.000
18	H	0.006	0.000	0.000	0.000
19	H	–0.016	0.000	0.000	0.000
20	H	–0.009	0.000	0.000	0.000
21	H	0.007	0.000	0.000	0.000
22	H	–0.022	0.000	0.000	0.000
23	H	0.006	0.000	0.000	0.000
24	H	–0.005	0.000	0.000	0.000
25	H	0.005	0.000	0.000	0.000
26	H	0.098	0.000	0.000	0.000
27	H	0.096	0.000	0.000	0.000
28	H	0.005	0.000	0.000	0.000
29	H	–0.005	0.000	0.000	0.000
30	H	0.004	0.000	0.000	0.000
31	H	0.098	0.000	0.000	0.000
32	H	0.100	0.000	0.000	0.000

Table 2. Data of **DADMBP**. Total energy[a] = – 135.05 a.u., binding energy[b] = – 16.37 a.u., total dipole moment = 0.17 debyes.

Dipole moment components	μ_X	μ_Y	μ_Z
Electron densities[+]	–0.09	–0.00	0.02
sp*	–0.06	0.00	–0.08
pd**	0.00	0.00	0.00
Total[++]	–0.16	0.00	–0.06

[a] The total energy corresponds to the sum of the atomic as well as electronic energies of all the constituents of the molecule in the equilibrium geometry.

[b] The binding energy of a molecule is the difference between the total energy and the sum of the atomic energies of the constituent atoms.

[+] Contribution to dipole moment components due to electron densities.

sp* hybridization moment

pd** hybridization moment

[++] Sum of the electron density- and hybridization-contribution to the dipole moment components.

Table 3. A comparative picture of the calculated total energy, binding enery and total dipole moment of non-liquid crystalline **DADMBP**, with the liquid crystalline compounds **EPPV** and **DPAB** using the **CNDO/2** method.

Molecule	Total energy (a.u.)	Binding energy (a.u.)	Dipole moment components (debyes)			
			μ_X	μ_Y	μ_Z	μ
DADMBP	–135.05	–16.37	–0.09	–0.00	0.02	0.17
DPAB	–223.57	–22.15	–1.01	0.57	0.89	1.46
EPV	–230.56	–22.96	–0.39	–0.29	–0.47	0.86

total energy, the binding energy and the total dipole moment, along with its components, are given in Table 2. Table 3 presents comparative pictures of the total energies, binding energies and total dipole moments of non-liquid crystalline **DADMBP**, with the liquid crystalline compounds **EPPV** and **DPAB**. As evident from Table 3, the total energy and binding energy of these molecules exhibit the order:

$$\textbf{EPPV} > \textbf{DPAB} > \textbf{DADMBP}\,,$$

while the dipole moments exhibit the order

$$\textbf{DPAB} > \textbf{EPPV} > \textbf{DADMBP}\,.$$

Stacking Interactions

A study of the variation of the total stacking energy as a function of interplanar separation between two **DADMBP** molecules corresponding to four distinct sets of rotation, viz. $X(0°)\ Y(0°)$, $X(180°)\ Y(0°)$, $X(0°)\ Y(180°)$, $X(180°)$, $Y(180°)$, has been carried out, and it has been observed that the optimum interplanar separation of a pair of stacked **DADMBP** molecules depends exclusively on the rotations of one of the molecules about the X-axis and Y-axis with respect to the other. The complex corresponding to $X(0°)\ Y(0°)$ is more stable than the others. A deep and sharp minimum (maximum of probability) is observed for the rotational set $X(0°)\ Y(0°)$, where the two **DADMBP** molecules are exactly one above the other with their planes separated by 3.4 Å. The variation of the probability with respect to rotation about the Z-axis is shown in Figure 2. Although, a sharp peak is noticed at the equilibrium position for rotation in the range of ± 10°, the probability of having oriented stacked dimers is half of the maximum values. The variation of the probability on translation

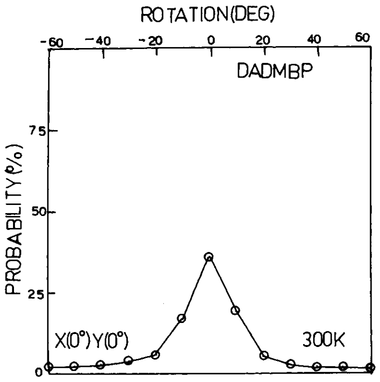

Fig. 2. The probability of rotation about the Z-axis during stacking interactions corresponding to the configuration $X(0°)\ Y(0°)$ at room temperature.

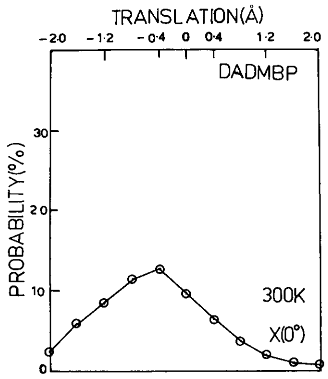

Fig. 3. The probability of translation along the Y-axis during stacking interactions at room temperature.

along the long molecular axis (*X*-axis) has also been studied, with the expected result.

Having refined the interacting configuration with respect to translation along the *Z*-axis and rotation about the *Z*-axis at the equilibrium, the energy was brought down. The translational motion in a stacked molecular pair along the *Y*-axis (Figure 3) was also investigated. It is seen that the molecules in a stacked pair can slide along *Y*-axis without much loss of probability.

In-plane Interactions

The variation of the interaction energy components with respect to translation (sliding) along the long molecular axis corresponding to a particular rotation of 0° about the *Y*-axis has been stacked, and the interaction energy is calculated for translations in the range of ± 26 Å at an interval of 2 Å. It has been observed that the long-range forces are smaller than the short-range forces during in-plane interactions. The dispersion energy component is mainly responsible for the attraction between pairs of **DADMBP** molecules. Figure 4 shows the variation of the probability with respect to the translation along the *X*-axis, while a similar analysis is presented in Figure 5 for translation along the *Y*-axis. It is seen that molecule can somewhat more along the *X*-axis and *Y*-axis. This shows that **DADMBP** molecules exhibit much translational as well as orientational freedom, which is less the case in liquid crystals.

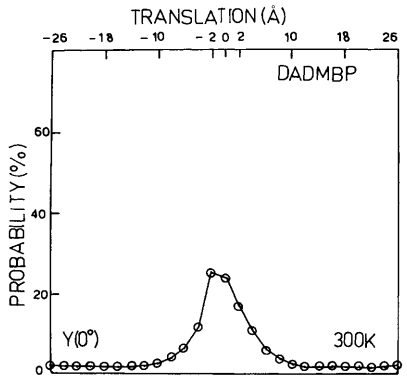

Fig. 4. The probability of translation along the *X*-axis during in-plane interactions at room temperature.

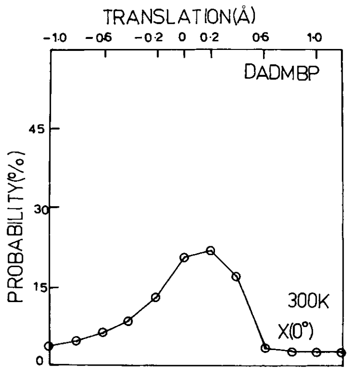

Fig. 5. The probability of translation along the *Y*-axis during in-plane interactions at room temperature.

Terminal Interactions

The variation of the intermolecular interaction energy on rotation about the *X*-axis has also been studied. Similar to the case discussed in the foregoing paragraph (in-plane interactions), the gross nature of various components remains unchanged. Terminal interactions are much weaker than stacking or in-plane interactions but become important if the molecules possess polar groups at the end or if there is the possibility of hydrogen bonding.

The energy corresponding to the optimum angle obtained initially has been further refined with an accuracy of 1° in rotation and 0.1 Å in translation. Details of the stacking, in-plane, and terminal interaction energy are listed in Table 4 with all the contributing terms to enable comparison.

Further, it has been observed that the large interaction energy and minimum energy configuration with the long molecular axes almost parallel to one another suggest a strong tendency to maintain order. Therefore, stacking interactions, which contribute much due to the in-plane and terminal dispersion forces, require much thermal activation and hence account for the high melting point of the system. At the melting point, thermal agitation will overcome the bindings of the **DADMBP** molecules in the crystal, and the system will pass direct-

Table 4. Dimer energy obtained during stacking, in-plane and terminal interactions between a pair of **DADMBP** molecules after refinement. Energy is expressed in kcal/mole.

Energy terms	Stacking energy	In-plane energy	Terminal energy
E_{QQ}	–0.07	0.56	–0.15
E_{QMI}	–2.14	–1.02	–0.23
E_{MIMI}	–1.39	–1.35	–0.33
E_{el}	–4.14	–1.81	–0.80
E_{pol}	–1.93	–0.97	–0.26
E_{disp}	–10.11	–7.19	–5.61
E_{rep}	3.38	1.89	0.98
E_{total}	–12.79	–8.08	–5.69

Table 5. A comparative picture of translational* and orientational rigidities** corresponding to the most probable configuration during stacking and in-plane interactions at room temperature (300 K).

Molecule	Translational rigidities along *X*-axis		Rational rigidities about *Z*-axis
	Stacking interactions	In-plane interactions	Stacking interactions
EPPV	1.02	1.75	0.98
DPAB	2.94	1.24	0.76
DADMBP	0.84	0.59	0.52

* This has been defined as the ratio of the probabilities being at the most probable point to having ± 2 Å displacement along the long molecular axis.

** This has been defined as the ratio of the probabilities being at the most probable point to having ± 10° rotation about the *Z*-axis.

ly to an isotropic melt. However, the inherent tendency of the molecules to retain order even after melting does not escape notice. Hence, if a suitable functional group is attached to the molecule so that the length to breadth ratio is increased with dispersion energy, the molecules will show a change in the long-range order, transition temperature and other related liquid crystalline properties.

A comparative picture of transitional and orientational rigidities is shown in Table 5 for two liquid crystalline (**EPPV** & **DPAB**) and one non-liquid crystalline (**DADMBP**) compound, as can be seen in Table 5, in case of **DADMBP**, the transitional rigidity is very small during *X*-sliding as compared to the liquid crystals, which indicates that the **DADMBP** molecules are quite free to translate along the long molecular axis. Almost a similar situation is noticed for orientational freedom and translations along the *Y*-axis (see Figure 5). This strongly suggests that the **DADMBP** molecules exhibit much translational and orientational freedom, which is less probable in case of liquid crystals.

Conclusion

A probability calculation of the present kind can be useful in distinguishing the non-liquid crystalline from the liquid crystalline behaviour of compounds.

Acknowledgement

Financial support rendered by the Department of Science & Technology (Grant No. SP/S2/M-45/94), New Delhi, India is gratefully acknowledged.

[1] B. Bahadur, ‘Liquid Crystal Applications and Uses’, World Scientific Pub., Vol. 1 1990.
[2] P. G. de Gennes and J. Prost, The Physics of Liquid Crystals, Clarendon Press, Oxford 1993.
[3] F. Laupretre and L. Monnerie, Eur. Poly. J. **14,** 573 (1978).
[4] D. Sy and M. Patak, J. Physique Lett. **40,** 137 (1979).
[5] M. Cotrait, P. Marsau, M. Pesquer, and V. Volpilhac, J. Physique **43,** 355 (1982).
[6] K. Tokita, K. Fujimura, S. Kondo, and M. Takeda, Mol. Cryst. Liq. Cryst. Lett. **64,** 171 (1981).
[7] G. S. Pawlay, Phys. Stat. Sol. **20,** 347 (1987).
[8] M. P. Allen and M. A. Warren, Phys. Rev. Lett. **78,** 1291 (1997).
[9] G. R. Luckhurst and S. Romano, Liquid Crystals **26,** 871 (1999).
[10] M. R. Wilson, Liquid Crystals **21,** 437 (1996).
[11] S. Sarman, Molecular Physics **98,** 27 (2000).
[12] P. Sarkar, S. Paul, and P. Mandal, Mol. Cryst. Liq. Cryst. **365,** 535 (2001).
[13] D. P. Ojha, D. Kumar, and V. G. K. M. Pisipati, Z. Naturforsch. **56a,** 730 (2001).
[14] M. A. Bates and G. R. Luckhurst, Liquid Crystals **24,** 229 (1998).
[15] M. Roychoudhury and D. P. Ojha, Mol. Cryst. Liq. Cryst. **213,** 73 (1992).
[16] D. P. Ojha, Phase Transitions **72,** 211 (2000).
[17] D. P. Ojha, D. Kumar, and V. G. K. M. Pisipati, Cryst. Res. Technol. **37,** 83 (2002).
[18] H. H. Sutherland and Z. Ali-Abid, Acta Cryst. **C42,** 432 (1986).
[19] P. Claverie, in Intermolecular Interactions: From Diatomic to Biopolymers, (B. Pullman ed.), John Wiley, New York 1978, p. 69.
[20] R. Rein, in Intermolecular Interactions: From Diatomic to Biopolymers, (B. Pullman ed.), John Wiley, New York 1978, p. 307.
[21] R. Rein, Adv. Quant. Chem. **7,** 335 (1973).
[22] J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory, Mc-Graw Hill, New York 1970.
[23] D. P. Ojha, Z. Naturforsch. **56a,** 319 (2001).
[24] S. A. Chawdhury, A. Hargreaves, and R. A. L. Sullivan, Acta Cryst. **B 24,** 1222 (1968).