# Nematogenic Behaviour of EPPV in a Dielectric Medium. A Theoretical Study

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Z. Naturforsch. **56a,** 371–375 (2001); received December 4, 2000

4-(4′-ethoxyphenylazo) phenyl valerate (**EPPV**) is a nematic liquid crystal, which shows a nematic mesophase at 352 K and becomes an isotropic melt at 401 K. A theoretical study of the molecular ordering has been carried out on the basis of intermolecular interaction energy calculations. The **CNDO/2** method has been employed to compute the net atomic charge and atomic dipole components at each atomic centre of the molecule. Modified Rayleigh-Schrödinger perturbation treatment has been employed to calculate the interaction energy between a molecular pair. The probability of the occurrence of a particular configuration in a dielectric medium has been calculated using the Maxwell-Boltzmann formula. The flexibility of various configurations has been studied in terms of the variation of the probability due to a small departure from the most probable configurations. On the basis of stacking, in-plane and terminal interactions, all possible geometrical arrangements between a molecular pair have been considered, and the most favourable configuration of pairing has been obtained. An attempt has been made to explain the nematogenic behaviour of liquid crystals based on the parameters introduced in this paper.

*Key words:* CNDO/2 Method; Interaction Energy; Statistical Distribution.

## Introduction

Several workers [1–3] have emphasized semiempirical calculations to explain liquid crystallinity. Perrin and Berges have employed **PCILO** (*Perturbational Configuration Interaction of Localized Orbital*), **INDO** (*Intermediate Neglect of Differential Overlap*) etc. methods to analyse (i) the internal rotations, (ii) the possibility of motion in the aromatic core as well as in the terminal chains, and (iii) the influence of the conjugation between the oxygen lone pairs and the benzene ring on the internal rotations in several mesomorphic compounds [4–7].

Further, it has been argued that a detailed analysis of the pair interactions between molecules of crystal lattices is expected to offer a better understanding of the mesomorphism [5]. Tokita et al. [8] used Rayleigh-Schrödinger perturbation theory with Lennard-Jones potential functions to calculate intermolecular interactions between a couple of pure neamatogenes. The angular dependence of the dispersion energy obtained by them partially agrees with the Maier-Saupe theory and qualitative by agrees with those of others [9–11]. However, it has been observed that ‘6-exp’ type potential functions are more effective in explaining the molecular packing than the Lennard-Jones potential [12].

Sanyal and coworkers, using second order perturbation theory, evaluated intermolecular interactions between pairs of some mesogenes [13–16]. These authors have attempted to explain the relative preference of different configurations on the basis of interaction energy values. These values, however, do not reflect the actual relative preference, which can only be obtained through the probabilities corresponding to each configuration. It, therefore, seems to be important to investigate the relative freedom of the molecule to depart from the minimum energy configuration in terms of the variation of orientation and the translation along the long molecular axis.

In the present communication, probability calculations for a pair of **EPPV** molecules in a dielectric medium (i.e. the non-interacting and non-mesogenic solvent benzene) have been examined at an intermediate distance of 6 Å for stacking and 8 Å in case of planar interactions. Similarly, a distance 22 Å has been kept for terminal interactions. The choice of the distance has been made to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the range of short and medium range interactions. The average dielectric constant of benzene has been taken as 2.25 for the entire temperature range [17].

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The thermodynamic data shows that **EPPV** forms a nematic mesophase at 352 K and becomes an isotropic melt at 401 K [18].

## Method of Calculation

The molecular geometry of the **EPPV** molecule has been constructed on the basis of the published crystallographic data with the standard values of bond lengths and bond angles [18]. In second order perturbation theory as modified for intermediate range interactions [19], the total interaction energy ($E_{\text{total}}$) between a pair of molecules is given by

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

where $E_{\text{el}}$, $E_{\text{pol}}$, $E_{\text{disp}}$ and $E_{\text{rep}}$ represent electrostatic, polarization, dispersion and repulsion energy components, respectively. According to the multicentered-multipole expansion method [20], the electrostatic energy may be expressed as the sum of interaction terms between atomic multipoles of successively higher orders:

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

where $E_{\text{QQ}}$, $E_{\text{QMI}}$ and $E_{\text{MIMI}}$ etc. are monopole-monopole, monopole-dipole, dipole-dipole, etc. interaction terms caused by higher order multipoles. As for most molecular systems [21], the evaluation of the electrostatic energy up to the dipole-dipole term has been found adequate.

The interaction energy obtained from these computations was used to calculate the probability of each possible configuration in a molecular pair employing the Maxwell-Boltzmann formula [22]

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

where $P_i$ is the probability of occurrence of a particular configuration $i$ and $\varepsilon_i$ is the energy of the configuration $i$ relative to the minimum energy configuration.

The net atomic charge and corresponding atomic dipole component at each of the atomic centres of the molecules have been computed by the **CNDO/2** method [23].

## Energy Minimization

Energy minimization has been carried out for stacking, in-plane and terminal interactions. One of the interacting molecules is kept fixed while both lateral and angular variations are introduced for the other molecule. Accuracy upto 0.1 Å in translation and 1° in rotation has been achieved. For rotation, the origin has been chosen on an atom close to the centre of mass of the molecule, the $X$-axis along a bond parallel to the long molecular axis, the $Y$-axis in the plane of the molecule and the $Z$-axis perpendicular to the molecular plane. The necessary formulae may be found in [24–28].

As mentioned earlier, though the aim of the present investigation is to calculate the probability distribution of different configurations in a dielectric medium, the terms like stacking, in-plane and terminal interactions will be used to maintain continuity with my previous works.

## Results and Discussion

The molecular geometry is shown in Figure 1.

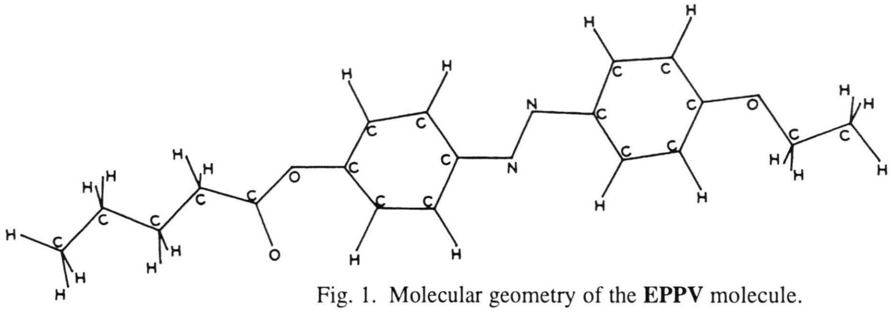

Fig. 1. Molecular geometry of the **EPPV** molecule.

## Stacking Interactions

The second molecule has been placed at a separation of 6 Å along the $Z$-axis with respect to the fixed molecule. The variation of various energy components on translation along the long molecular axis has been studied, and it has been observed that all the components increase with increasing overlapping, although the in-

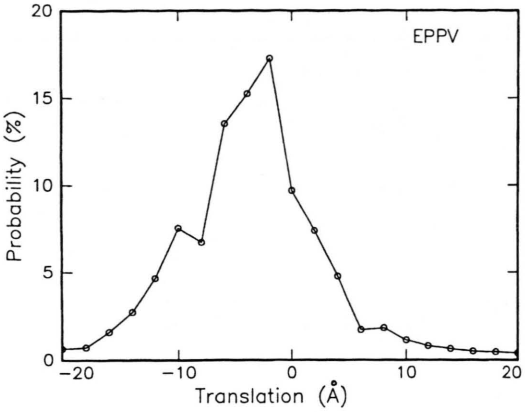

Fig. 2. Variation of the probability on translation along the long molecular axis during stacking interactions in benzene at 401 K.

crease is small for the electrostatic and polarization terms. The probability (Fig. 2) is almost constant for ±2 Å near the equilibrium position, which shows that sliding of one molecule over the other is energetically allowed for a small range which may be correlated with the fluidity of the compound maintaining its alignment in the mesophase.

## In-plane Interactions

The interacting molecule has been kept at a separation of 8 Å along the $Y$-axis with respect to the fixed one. The variation of various interaction energy components on translation along the $X$-axis has been studied. Humps appear because of the violation of van der Waals contact for the C(H)–C(H) distance. A slight increase in the separation will obviously remove such regions. The translational freedom is much more pronounced than for the stacking interactions. The variation of the probability with respect to translation along the long molecular axis (Fig. 3) shows sharp maxima corresponding to the minimum energy point with more than 12% probability at the nematic-isotropic transition temperature.

## Terminal Interactions

The length of the molecule is approximately 20 Å. To investigate the terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the $X$-axis by 22 Å with respect to the fixed one. Figure 4 shows the effect of rotation about the $X$-axis. The terminal interactions are much weaker than the stacking or in-plane interactions.

The most prominent energy minima (maximum of probability) of the above mentioned interactions are further refined with an accuracy of 0.1 Å in translation and 1° in rotation. It has been observed that, due to the planarity of the molecule, the refinement corresponding to the stacking energy is much larger than the in-plane and terminal interaction energies.

The probability distribution of different modes of interactions (i.e. stacking, in-plane and terminal interactions) is shown in Table 1. It may be observed that

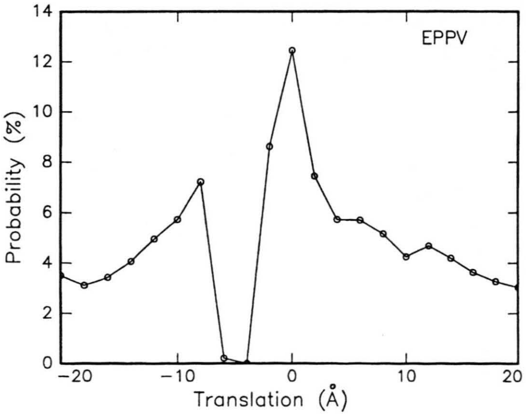

Fig. 3. Variation of the probability on translation along the long molecular axis during in-plane interactions in benzene at 401 K.

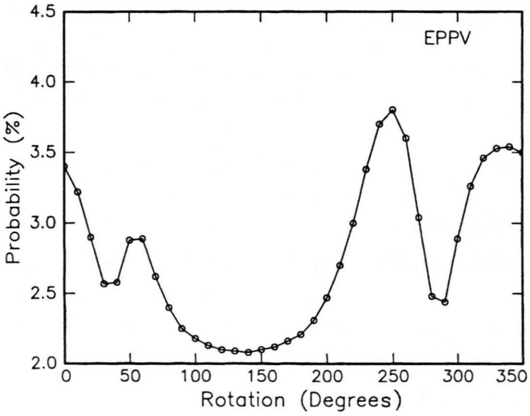

Fig. 4. Variation of the probability on rotation about the $X$-axis during terminal interactions in benzene at 401 K.

Table 1. Relative probabilities of different minimum energy configurations obtained during stacking, in-plane and terminal interactions in vacuum (A) and in benzene (B). Average dielectric constant of benzene = 2.25.

| Configuration | Energy in vacuum kcal/mole | Energy in benzene kcal/mole | Probability (%) at Temperature | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 300 K | | 401 K | | 450 K | |
| | | | A | B | A | B | A | B |
| $X(180^\circ)$ $Y(0^\circ)^+$ | –2.799 | –1.244 | 0.1 | 3.3 | 0.5 | 5.9 | 0.9 | 6.9 |
| $Y(0^\circ)^+$ | –5.166 | –2.296 | 5.3 | 19.3 | 10.2 | 21.9 | 12.4 | 22.5 |
| $Y(0^\circ)^+$ | –6.881 | –3.058 | 94.3 | 69.1 | 87.9 | 57.1 | 84.5 | 52.6 |
| $Y(0^\circ)^*$ | –2.601 | –1.156 | 0.1 | 2.8 | 0.4 | 5.2 | 0.7 | 6.3 |
| $Y(0^\circ)^*$ | –3.184 | –1.415 | 0.2 | 4.4 | 0.9 | 7.3 | 1.4 | 8.4 |
| $Y(0^\circ)^{**}$ | –1.323 | –0.588 | 0.0 | 1.1 | 0.1 | 2.6 | 0.2 | 3.3 |

$^+$ Stacking Interactions; * In-plane Interactions; ** Terminal Interactions.

Table 2. Comparative picture of translational and rotational rigidities along the long molecular axis ($X$-axis) during stacking, in-plane and terminal interactions between a pair of **EPPV** molecules in benzene.

| Temperature (K) | Translational Rigidities | | Rotational Rigidities |
|---|---|---|---|
| | Stacking Interactions | In-plane Interactions | Terminal Interactions |
| 300 | 0.76 | 0.89 | 0.53 |
| 401* | 0.69 | 0.77 | 0.52 |
| 450 | 0.67 | 0.74 | 0.51 |

* Nematic – Isotropic Transition Temperature.

configuration $Y(0^\circ)$ has the maximal relative probability (≃ 94%) at room temperature with an energy −6.881 kcal/mole in vacuum. Further, it is clear that in the dielectric medium the probabilities are redistributed and there is a considerable rise in the probabilities of interactions, although the order of preference remains the same.

## Correlation of the Results with the Nematic Character

To understand the molecular behaviour in terms of their relative order the following parameters have been calculated:

### *(a) Translational Rigidity*

This has been defined as the ratio of the probabilities of being at the most probable point to that having ± 2 Å displacement along the long molecular axis. Table 2 compares the translational rigidities along the long molecular axis for stacking and in-plane interactions. It may be noted that in the case of stacking the rigidity decreases slowly with the increase in temperature, while the rapid decrease of the same in case of in-plane interactions indicates that the values obtained at lower temperature is abnormally high due to a possible contact, as seen in Figure 3.

It may, therefore, be concluded that the molecule is more free for translation during in-plane interactions. However, the comparable values in both cases show that the molecule does not much prefer forming stacked layers, hence justifying the nematic character.

### *(b) Rotational Rigidity*

This has been defined as the ratio of the probabilities being at the most probable point to that having ± 10° rotation along the long molecular axis. Table 2 gives the rotational rigidities at different temperatures during terminal interactions. The table clearly shows that during terminal interactions, the molecule can rotate freely about its long molecular axis. These observations comply with the nematic character of the molecule.

These two parameters may be helpful to understand the mesogenic character of the molecule. A comparative study on other systems may lead to more general conclusions.

### *Acknowledgement*

The financial support rendered by the Department of Science & Technology, New Delhi, India is gratefully acknowledged.

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