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Theoretical Study of Ordering in Liquid Crystals with the Help of Intermolecular Interaction Energy Calculations Part I–Anisaldehyde Azine

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The ordering of mesogenic compounds in the liquid phase has been investigated using intermolecular interaction energy calculations taking Anisaldehyde azine ($CH_3 - O - C_6H_4 - CH = N - N = CH - C_6H_4 - O - CH_3$) as a specific example. The molecular structure has been taken from literature. Computations of atomic net charges and dipole moments have been carried out using CNDO/2 method. The multicentered-multipole expansion method has been employed to evaluate the various interaction energy terms viz. electrostatic, polarisation, dispersion, and repulsion. Distance as well as orientation has been changed with a view toward locating the minimum energy configuration. The large interaction energy value obtained through these calculations has been used to explain the liquid crystalline behaviour of this substance. The minimum energy configuration also supports the theoretical findings about the existence of the nematic phase and a high transition temperature.

INTRODUCTION

Theoretical studies on conformational properties of liquid crystals have attracted a number of workers.[1–6] It has been realized that a systematic study of the intermolecular interactions between such molecules[1] will be useful in order to explain their inherent tendency to retain order even in the liquid state.

A nematic liquid crystal, Anisaldehyde azine [$CH_3 - O - C_6H_4 - CH = N - N = CH - C_6H_4 - O - CH_3$], has been chosen which is a liquid crystal with a transition temperature of 169°C for the solid-nematic and 181°C for the Nematic-Isotropic liquid phase. Crystallographic studies[7] show the existence of a small angle between the long axis of two adjacent molecules which suggest a cholesteric trend although the rod like structure and other physiochemical properties of this molecule puts this in the nematic class. A systematic study of the intermolecular interaction between two Anisaldehyde azine molecules has, therefore, been undertaken.

METHOD OF CALCULATION

Second order perturbation treatment as modified by Caillet and Claverie[8-10] for intermediate range interactions has been employed for the evaluation of intermolecular interaction energies between the molecules of Anisaldehyde azine. The total interaction energy, E_{tot} may be expressed as the sum of various terms contributing to the total energy.

$$E_{tot} = E_{el} + E_{pol} + E_{disp} + E_{rep} \tag{1}$$

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

ELECTROSTATIC ENERGY

According to the Multicentered-Multipole expansion method as developed by Rein and coworkers,[11] the electrostatic energy may be expressed as the sum of interaction terms between atomic multipoles of successively higher orders

$$E_{el} = E_{QQ} + E_{QMI} + E_{MIMI} + E_{Qq} + E_{Mq} \tag{2}$$

where E_{QQ}, E_{QMI}, E_{MIMI}, E_{Qq}, E_{Mq} etc. are the monopole-monopole, monopole-dipole, dipole-dipole, monopole-quadrupole, and dipole-quadrupole terms respectively. In general for most molecular systems up to the first three terms have been found to be adequate.[12,13] The expressions for these terms are given below. The monopole-monopole

interaction term E_{QQ} is given by

$$E_{QQ} = C\sum_{i,j} \frac{q_i \cdot q_j}{r_{ij}} \tag{3}$$

where q_i, q_j are the monopole on each atomic centre of the interacting molecules i and j, r_{ij} is the interatomic distance and C is a conversion factor (≈ 332) which expresses the energy in kilo calories per mole of the dimer.

The monopole-dipole interaction term is

$$E_{QMI} = C\sum_{i,j} q_i \boldsymbol{\mu}_j \frac{\mathbf{r}}{r^3} \tag{4}$$

while the dipole-dipole interaction term is given by

$$E_{MIMI} = C\sum_{i,j} \frac{1}{r^3}\left[\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j - 3\left(\boldsymbol{\mu}_i \cdot \frac{\mathbf{r}}{r}\right)\left(\boldsymbol{\mu}_j \cdot \frac{\mathbf{r}}{r}\right)\right] \tag{5}$$

where $\boldsymbol{\mu}_i$, $\boldsymbol{\mu}_j$ represent the atomic dipoles, the subscript of r has been removed without any change in its meaning and other notations have the same meanings as in equation 3. The atomic net charges and dipole moments may be evaluated by using usual quantum mechanical [all valence electron] methods. In these computations CNDO/2[14] method has been used.

POLARISATION ENERGY

The polarisation energy of a molecule (s) is obtained as a sum of polarisation energies for the various bonds

$$E_{\text{pol}}^{(s)} = C(-\tfrac{1}{2})\sum_{u}^{(s)} \mathscr{E}_u^{(s)} \overline{\overline{A}}_u^{(s)} \mathscr{E}_u^{(s)} \tag{6}$$

where $\overline{\overline{A}}_u$ is the polarisability tensor of the bond u and $\mathscr{E}_u^{(s)}$ is the electric field created at this bond by all surrounding molecules. If the molecular charge distributions are represented by the atomic charges, it is found that

$$\mathscr{E}_u^{(s)} = \sum_{t \neq s} \sum_{\lambda}^{(t)} q_\lambda^{(t)} \frac{\mathbf{R}_{\lambda u}}{R_{\lambda u}^3} \tag{7}$$

where $\mathbf{R}_{\lambda u}$ is the vector joining the atom λ in molecule (t) to the 'centre of polarizable' charge on the bond u of molecule (s).

DISPERSION AND SHORT RANGE REPULSION ENERGIES

These two terms are considered together because several semiempirical expressions viz. Lennard Jones or Buckingham type approach actually proceeds in this way. Kitaigorodski[15] introduced a Buckingham formula, whose parameter were later modified by Kitaigorodski and Mirskaya[16] for hydrocarbon molecules and several other molecules finally gave the expression

$$E_{\text{disp}} + E_{\text{rep}} = \sum_{\lambda}^{(1)} \sum_{\nu}^{(2)} E(\lambda, \nu)$$

$$E(\lambda, \nu) = K_\lambda K_\nu \left(- \frac{A}{Z^6} + Be^{-\gamma Z} \right) \tag{8}$$

where $Z = R_{\lambda\nu}/R^0_{\lambda\nu}$; $R^0_{\lambda\nu} = [(2R^{\text{W}}_\lambda)(2R^{\text{W}}_\nu)]^{1/2}$ where R^{W}_λ and R^{W}_ν are the Vander Waals radii of atoms λ and ν respectively. The parameters A, B and γ do not depend on the atomic species. But $R^0_{\lambda\nu}$ and the factor K_λ, K_ν allow the energy minima to have different values according to the atomic species involved. The recent values of these parameters may be found in literature.[9,10]

ENERGY MINIMIZATION

In the present work, computations have been carried out between a molecule pair of Anisaldehyde azine. One of these molecules has been treated as fixed in position while the distance of the other has been varied with respect to the fixed molecule and a minimum energy point has been obtained. The molecule is then rotated about the axis perpendicular to the molecular long axis at an interval of 10° and the corresponding energies are calculated. The minimum energy so obtained is then taken as a starting point and the entire process is again repeated at smaller intervals. The final configuration obtained is refined through very small variations in distance as well as in angle. The whole process of optimisation is carried out with the help of computer program on a CDC 'Cyber' computer.

RESULTS AND DISCUSSION

The molecular structure and reference numbers of various atomic positions of Anisaldehyde azine are shown in fig. 1. Table I lists the various atomic coordinates along with the atomic net charges and atomic dipole moments calculated using CNDO/2 method. The

TABLE I

Coordinates atomic charges and atomic dipole components for anisaldehyde azine

Atoms	X	Y	Z	Charge	DIPx	DIPy	DIPz
N1	0.000	0.000	0.000	− 1.106	1.142	− 1.449	− 0.109
C2	1.306	0.000	0.000	0.099	− 0.151	0.070	− 0.134
C3	2.072	1.264	0.000	− 0.014	0.046	0.025	0.021
C4	1.470	2.536	− 0.085	0.033	0.150	0.003	0.066
C5	2.259	3.669	0.010	− 0.052	0.095	− 0.122	− 0.111
C6	3.629	3.577	0.009	0.190	0.127	0.148	0.053
C7	4.269	2.333	0.081	−0.043	− 0.173	0.029	0.012
C8	3.507	1.184	0.114	0.022	− 0.026	0.129	− 0.048
O9	4.490	4.662	0.036	− 0.219	− 1.325	0.174	− 0.176
C10	3.923	5.999	− 0.135	0.120	0.084	− 0.284	0.032
N11	− 0.518	− 1.311	− 0.071	− 0.079	− 1.167	1.415	0.031
C12	− 1.784	− 1.302	− 0.113	0.083	0.172	− 0.090	− 0.076
C13	− 2.557	− 2.587	− 0.292	0.021	− 0.255	− 0.042	0.025
C14	− 1.897	− 3.912	− 0.407	− 0.015	− 0.155	0.045	0.031
C15	− 2.644	− 5.082	− 0.509	− 0.026	0.015	0.157	0.006
C16	− 4.032	− 4.972	− 0.513	0.195	− 0.017	− 0.255	− 0.047
C17	− 4.680	− 3.755	− 0.408	− 0.351	2.731	0.369	0.044
C18	− 3.882	− 2.620	− 0.296	− 0.126	− 0.207	− 0.277	− 0.105
O19	− 4.854	− 6.085	− 0.667	− 0.221	1.335	− 0.182	− 0.040
C20	− 4.246	− 8.365	− 0.785	0.133	− 0.091	0.277	0.027
H21	1.841	− 0.919	− 0.240	− 0.013	0.000	0.000	0.000
H22	0.386	2.628	− 0.150	0.001	0.000	0.000	0.000
H23	1.793	4.653	− 0.036	0.004	0.000	0.000	0.000
H24	5.356	2.279	0.139	0.013	0.000	0.000	0.000
H25	3.993	0.209	0.154	− 0.002	0.000	0.000	0.000
H26	− 2.319	− 0.352	− 0.129	− 0.013	0.000	0.000	0.000
H27	− 0.810	− 3.975	− 0.359	0.001	0.000	0.000	0.000
H28	− 2.158	− 6.054	− 0.587	0.007	0.000	0.000	0.000
H29	− 5.850	− 3.600	− 0.354	0.001	0.000	0.000	0.000
H30	− 4.365	− 1.647	− 0.212	− 0.007	0.000	0.000	0.000
H31	3.203	6.192	0.660	− 0.007	0.000	0.000	0.000
H32	4.721	6.740	−0.091	0.003	0.000	0.000	0.000
H33	3.423	6.060	−1.101	− 0.007	0.000	0.000	0.000
H34	− 3.660	− 7.573	0.110	− 0.019	0.000	0.000	0.000
H35	− 5.019	− 8.125	− 0.889	− 0.008	0.000	0.000	0.000
H36	− 3.593	− 7.378	− 1.658	− 0.019	0.000	0.000	0.000

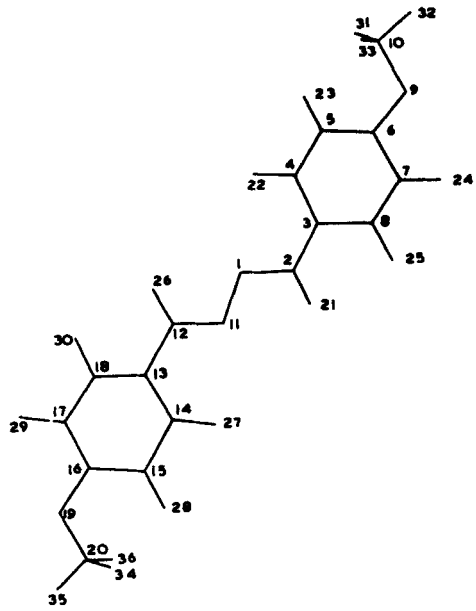

FIGURE 1 Structure of Anisaldehyde azine.

theoretically calculated dipole moment, its components and binding energy have been listed in table II. The minimum energy configuration of the two stacked Anisaldehyde azine molecule is shown in fig. 2. The total interaction energy of this configuration has been found to be -13.88 KCal/mole of dimer. The distribution of various energy components has given in table III. It may be observed that the large magnitude of the interaction energy itself suggests a high phase transition temperature for this compound. However, an exact correspondence between the value of the interaction energy and the transition temperature can be obtained after such data is available for a large number of similar systems. The perpendicular distance between two molecule is approximately 3.41 A°. As evident from fig. 2, at the minimum energy configuration, the long molecular axes of the two interacting molecule are not exactly parallel to each other (as generally expected for nematic liquid crystals). The angular displacement of one molecule with respect to the other is 12.7°. Thus the compound is not nematic in a strict sense. It has definitely a cholesteric trend although the molecular structure and other properties of this molecule puts it in nematic class. It may be noted here that

TABLE 2

Components	Dipole moments X	Y	Z
Densities	0.97	1.21	− 0.00
S.P	2.32	0.14	− 0.41
P.D	0.00	0.00	0.00
Total	3.29	1.35	− 0.41

Total dipole moment = 3.60 Debyes
Binding Energy = − 14.70 A.U

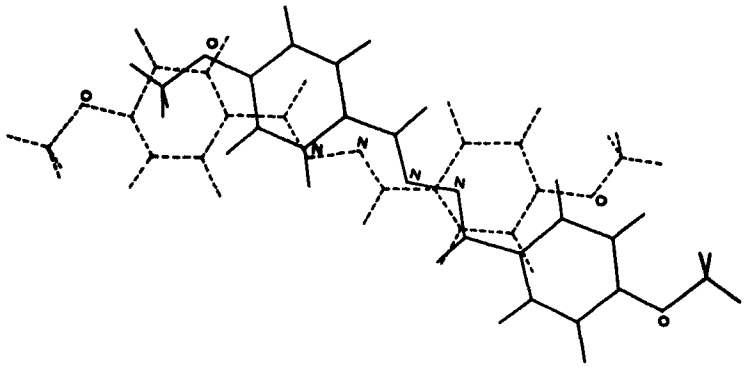

FIGURE 2 Two stacked Anisaldehyde azine Molecule.

TABLE 3

Interaction energy terms	Value (KCal/mole)
E_{QQ}	− 0.09
E_{QMI}	− 0.53
E_{MIMI}	− 0.71
$E_1(E_{QQ} + E_{QMI} + E_{MIMI})$	− 1.34
E_{pol}	− 1.23
E_{disp}	− 20.43
$E_2(E_{\text{pol}} + E_{\text{disp}})$	− 21.66
E_{rep}	9.12
$E_{\text{tot}}(E_1 + E_2 + E_{\text{rep}})$	− 13.88

crystallographic studies[7] have indicated the existence of such angular orientation with respect to each other in the solid phase, although the exact value of the angle has not been reported there.

CONCLUSION

The present theoretical investigation suggests that the persistent order found in most of the liquid crystal is due to the strong intermolecular interaction and that specific minimum energy configurations determine the alignment of the molecules with respect to one another even during transition state.

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