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On the Interaction Energy Between Some Nematogenic Molecules

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On the Interaction Energy Between Some Nematogenic Molecules

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Calculation of the interaction energies between nematogenic MBBA and PAA molecules have been performed in the framework of the Rayleigh-Schrödinger perturbation theory, supplemented with the empirical repulsive term. The predominant role of dispersion interaction as well as negligibly small induction energy have been found. The electrostatic contribution to the interaction energy has been discussed. Some remarks relating to the possible mode of molecular motion have also been made.

1 INTRODUCTION

Intermolecular forces are essential for understanding the structure of nematic liquid crystals (NLC) and the transition from the nematic to isotropic phase. They constitute a basis for deriving microscopic models and the theory of the nematic liquid-crystalline state.

There are two complementary groups of these theories.[1,2] The first includes theories based on the assumption that the orientational ordering of the NLC molecules is primarily the result of anisotropy of the intermolecular attractive forces of relatively long range and in particular of dispersion force.[3,4]

The second group of theories, initiated by Onsager,[5] ascribes the greatest importance as regards the properties of NLC to short range anisotropic intermolecular repulsive forces.[6,7] The attractive forces are made responsible

solely for the high density of NLC, and their anisotropy is regarded to be a factor of secondary significance.[8]

At present there is a range of results both theoretical and experimental[2,8] which reveal distinctly the imperfection of both extreme approaches. Theories have therefore also been developed which take account of the anisotropy of both attracting and repulsive interactions.[2,9-13]

Such a state of art justifies undertaking theoretical calculations of the energy of interaction between two nematogenic molecules. Such studies can provide information about the relative role of various types of interactions and allow to estimate the order of magnitude and anisotropy of the contributions to the energy due to these interactions. The interaction potential curves obtained in this way would permit an improved and more quantitative approach to the construction of the nematic state models. As far as we know only few results of such studies for liquid crystals have been published so far[14-16] and these are of preliminary character.

In the present work we have performed calculations of the interaction energy between molecules of selected NLC's, i.e. MBBA (*N*-(*p*-methoxybenzylidene)-*p*-butylaniline) and PAA (*p*-azoxyanisole) as well as between BA (benzylidene aniline) molecules which constitute the skeleton of certain NLC's. In terms of the perturbation theory we distinguish the electrostatic, induction and dispersion portions of the interaction energy as well as the valence repulsive energy. The first three contributions have been calculated by methods similar to those used by Rein *et al.*[17] The valence repulsive energy which does not occur in the polarization perturbation theory,[18] was estimated making use of the repulsive part of the Lennard-Jones (12-6) or Buckingham (exp-6) potential.[19] The computational method used in the present work involves a range of simplifying assumptions. Therefore the results obtained should be regarded as semiquantitative estimates, comparative rather than absolute.

2 METHOD

Calculations of the interaction energies were performed by the classical Rayleigh-Schrödinger perturbation theory (so-called polarisation approximation).[18] This method does not take into account the exchange phenomena. Thus, the energy of interaction is approximated by

$$E_{\text{int}} = E_{\text{es}} + E_{\text{ind}} + E_{\text{dis}} + E_{\text{rep}} \tag{1}$$

The electrostatic energy E_{es} was found using the atomic multipole expansion

of the potential via the second London scheme.[20] The expansion was truncated after the dipole term. Thus we get the following expression

$$E_{es} = \sum_{r=1}^{N_A} \sum_{s=1}^{N_B} \sum_{i=0}^{1} \sum_{j=0}^{1} E_{ij}^{rs} \tag{2}$$

where N_A, N_B are the numbers of atoms in molecules A and B, respectively. The indices i, j have the following meaning: $i, j = 0$ denotes monopole (net charge) terms, $i, j = 1$ denotes atomic dipole terms of atoms r/s of molecules A/B, respectively. For example, E_{01}^{rs} denotes the energy of electrostatic interaction between the net charge q of atom r of molecule A and the atomic dipole moment μ_k of atom s of molecule B.

The successive terms have been calculated from the formulae:

$$E_{00}^{rs} = \frac{qq'}{R} \tag{3}$$

$$E_{01}^{rs} = \frac{q\mu_k R_k}{R^3} \tag{4}$$

$$E_{11}^{rs} = \frac{\mu_k \mu_k'}{R^3} - 3\frac{\mu_k R_k \mu_l R_l}{R^5} \tag{5}$$

where the primed quantities refer to the s centre and the unprimed ones to the r centres. R_k denotes the vector pointing from r to s. The tensor summation convention is applied here, and $R_k P_k = R_1 P_1 + R_2 P_2 + R_3 P_3$, $R = (R_k R_k)^{1/2} = |\mathbf{R}|$.

Multipole moments M^s of the s atom can be calculated in terms of the CNDO/2 method[21] as follows:

$$M^s = -|e| \sum_{\lambda \in s} P_{\lambda\lambda} \int \chi_\lambda(r) \hat{M} \chi_\lambda(r) \mathrm{d}v$$

$$- 2|e| \sum_{\substack{\lambda \in s \\ \lambda < \sigma}} \sum_{\sigma \in s} P_{\lambda\sigma} \int \chi_\lambda(r) \hat{M} \chi_\sigma(r) \mathrm{d}v \tag{6}$$

where χ_λ is the atomic orbital centered on the s atom and $\hat{M}$ is the operator of the respective multipole moment (for monopole $\hat{M} = 1$ and for dipole $\hat{M} = r_k$). $P_{\lambda\sigma}$ is the element of the density matrix P in the atomic χ-orbitals basis. The summations are carried out over the atomic orbitals included in all occupied molecular orbitals.

Induction E_{ind} and dispersion E_{dis} energies were calculated from the formulae of Rein *et al.*,[17] using the experimental values for bond polarizabilities and ionization potentials:[22]

$$E_{ind} = \frac{1}{2}\sum_{m=1}^{bA}[{}^{m}\alpha^{T}E_{l}^{m}E_{l}^{m} + \mathrm{d}^{m}(E_{l}^{mm}\gamma_{l})^{2}] - \frac{1}{2}\sum_{n=1}^{bB}[{}^{n}\alpha^{T}E_{l}^{n}E_{l}^{n} + \mathrm{d}^{n}(E_{l}^{nn}\gamma_{l})^{2}] \tag{7}$$

$$E_{dis} = \frac{1}{4}\frac{{}^{A}I\,{}^{B}I}{{}^{A}I + {}^{B}I}\sum_{i=1}^{b_A}\sum_{j=1}^{b_B}\frac{1}{R_{ij}^{6}}\{6\,{}^{i}\alpha^{T}\,{}^{j}\alpha^{T} + {}^{i}\alpha^{T}\mathrm{d}^{j}[3({}^{j}\gamma_{k}r_{k})^{2} + 1] + {}^{j}\alpha^{T}\mathrm{d}^{i}[3({}^{i}\gamma_{k}r_{k})^{2} + 1] + \mathrm{d}^{i}\mathrm{d}^{j}[3\,{}^{i}\gamma_{k}r_{k}\,{}^{j}\gamma_{l}r_{l} - {}^{i}\gamma_{k}\,{}^{j}\gamma_{k}]\} \tag{8}$$

where ${}^{i}\gamma_{k}$ and r_{k} are the unit vectors in the direction of the i-bound and R_{ij} (the vector joining the midpoints of the i/j bonds), respectively, α^{L}, α^{T} denote longitudinal and transversal bond polarizabilities, respectively, $\mathrm{d} = \alpha^{L} - \alpha^{T}$: b_A, b_B are the numbers of bonds and ${}^{A}I$, ${}^{B}I$ are the ionization potentials of molecules A and B, respectively. E_{l}^{m}, E_{l}^{n} are the vectors of the electric fields at the centre of the m/n bond of the respective molecule due to the charge distribution of the other molecule.

In our approach E_{l}^{m} in Eq. (7) has the form:

$$E_{l}^{m} = \sum_{s=1}^{N_B}\left[\frac{q^{s}R_{l}}{R^{3}} - \frac{\mu_{l}^{s}}{R^{3}} - 3\frac{\mu_{k}R_{k}R_{l}}{R^{5}}\right] \tag{9}$$

where R_l is the vector joining the s-th atom of molecule B and the m-th bond of molecule A.

As it was already mentioned, exchange effects are not accounted for in the polarization perturbation method. So in order to estimate roughly the position and depth of the interaction energy minimum we added formally the repulsive energy E_{rep} taking the repulsive term of the Lennard-Jones potential:

$$E_{rep} = \sum_{r=1}^{N_A}\sum_{s=1}^{N_B}\frac{\mathrm{d}_{rs}}{R_{rs}^{12}} \tag{10}$$

or of the Buckingham potential:

$$E_{rep} = \sum\sum b_{rs}\exp(-c_{rs}R_{rs}) \tag{11}$$

We hope, that E_{rep} in this form should give better results than the use of Van der Waals contacts.[23]

We calculated E_{rep} according to Eq. (10) using two different sets of d_{rs} parameters (denoted as S_1 and S_2, respectively) which have been determined by Scheraga.[24] The set of parameters b_{rs} and c_{rs} in Eq. (11) (denoted as K) has been determined by Kitaigorodsky.[25]

The calculations of E_{es} and E_{ind} have been performed using not only the charge distributions determined by means of the CNDO/2 method but also the net charges on the atoms obtained by the Hückel and Del Re method.[26]

3 RESULTS AND DISCUSSION

3.1 Testing calculations

Some calculations have been performed to test the method described.

The dependence has been tested of the interaction energy of the system $(BA)_2$ on the choice of parameters in term E_{rep} and on the method used to determine the charge distribution of electrons in the interacting molecules. The geometry of BA molecule was assumed to be such as determined experimentally.[27] The origin of the local coordinate system was chosen at the midpoint of the C=N bond, as is shown in Figure 1. The atoms C7, N8, C9, C12, H23, C6, C3 and H17 (see Figure 1) lie in the XY plane. The aniline ring is twisted around the N8–C9 axis by an angle of 55° and the benzylidene ring is twisted around the C6–C7 axis by an angle of 10° in the opposite direction. This lack of coplanarity of the BA molecule is confirmed also in a theoretical way.[28]

The calculation have been performed for the $(BA)_2$ system configurations obtained by the parallel translations of the second molecule with respect to the first one along the z-axis (see Figure 1) and by the subsequent rotations by the angle ϕ of this second molecule around the same z-axis.

The dependence of E_{int} on the E_{rep} parameters is visualised in Figure 2 where it is seen that the three approaches gives similar estimations of the minimum of the E_{int} curve: $R_m = (5.3 \pm 0.2)$ Å and $E_{min} = (-1.0 \pm 0.2)$

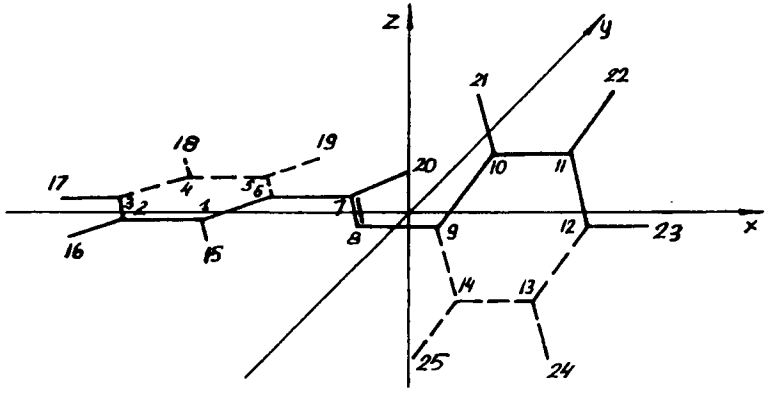


FIGURE 1 The coordinate system and numbering of atoms in the BA molecule.

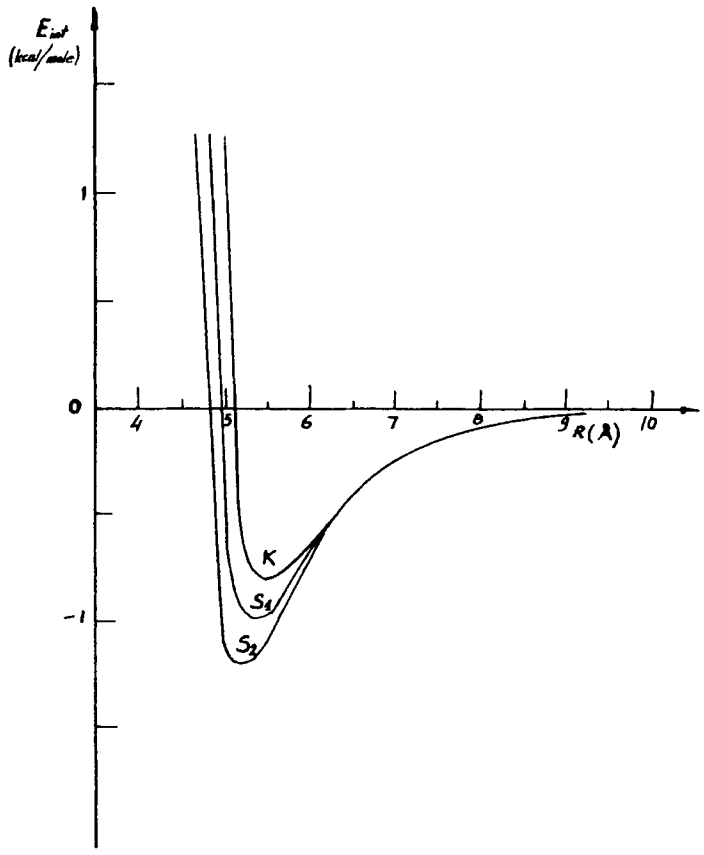


FIGURE 2 The interaction energy of the $(BA)_2$ system calculated using three different estimations of E_{rep} (see text). Net charges and atomic dipoles are taken from CNDO/2 calculations.

kcal/mole. In the further calculations the Lennard–Jones estimation of E_{rep} with the S_1 set of parameters will be used.

The results of calculating E_{int} using the Hückel plus Del Re and the CNDO/2 methods for the estimation of E_{el} and E_{ind} are compared in Table I. One can see that the results for E_{es} and E_{ind} obtained by the first method, in spite of its simplicity, are comparable with those of the CNDO/2 method.

Moreover the important conclusions can be drawn as to the ϕ angle dependence of E_{int} for the distances considered: (i) the dispersion interaction gives the major contribution to E_{int}; (ii) E_{ind} is negligibly small as compared with E_{dis} and E_{es}; (iii) the parallel ($\phi = 0°$) and antiparallel ($\phi = 180°$) configurations are approximately equivalent; (iv) E_{int} is strongly anisotropic with respect to the ϕ angle dependence.

TABLE I

The interaction energy of $(BA)_2$ system for the Hückel and Del Re and CNDO/2 electron charge distributions.[a]

		Hückel and Del Re		CNDO/2				Hückel and Del Re	CNDO/2
R	ϕ	E_{es}	E_{ind}	E_{es}	E_{ind}	E_{dis}	E_{rep}	E_{int}	E_{int}
	0°	0.4	−0.04	0.3	−0.02	−1.5	0.2	−1.0	−1.1
	90°	0.2	−0.04	−0.01	−0.02	−0.9	0.03	−0.7	−0.9
6.0									
	180°	−0.3	−0.04	−0.2	−0.02	−1.4	0.1	−1.7	−1.6
	270°	0.1	−0.04	0.1	−0.02	−0.9	0.3	−0.7	−0.6
	0°	0.2	0.0	0.1	0.0	−0.1	0.0	0.01	−0.04
	90°	0.04	0.0	0.0	0.0	−0.1	0.0	−0.1	−0.1
9.0									
	180°	−0.1	0.0	−0.1	0.0	−0.1	0.0	−0.2	−0.2
	270°	0.02	0.0	−0.02	0.0	−0.1	0.0	−0.1	−0.1

[a] In all the tables the distances are given in Angstroms and energies in kcal/mole.

It seems worthwhile to point to the consistency of $R_{min} = (5.3 \pm 0.2)$ Å with $R_{min}^{exp} \approx 6.0$ Å estimated from crystallographic data regarding structure of the BA elementary cell.[29]

We have also compared E_{ind} and E_{dis} calculated using the isotropic and anisotropic bond polarisabilities. The results are summarized in Table II. It is seen that the bond polarisability anisotropy does not change the character of the results, lowering only by about 12% the value of E_{dis}. A similar situation was observed for other geometries.

3.2 Calculations for MBBA and PAA molecules

The above described and tested method of E_{int} calculation was immediately applied to the molecules composing the NLC, i.e. the MBBA and PAA molecules.

The geometry of the central part of the MBBA molecule was taken from the BA molecule, except for the $-OCH_3$ group, whose atoms O1 and C20 lie in the XY plane (see Figure 3), and the C_4H_9 group, whose atoms C16, C17, C18 and C19 also lie in the XY plane. The spatial distribution of hydrogen atoms is determined by tetrahedral hybridisation of carbon atoms.

The geometry of the PAA molecule was taken from the experimentally determined structure.[30]

For calculation of the electron net charges and of atomic dipoles in terms of the CNDO/2 method the diagonal elements of the P matrix as well as those like $P_{2s,2px}$, $P_{2s,2py}$, $P_{2s,2pz}$ are needed for each atom except hydrogen (see

TABLE II

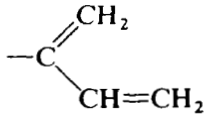
Induction and dispersion energy of $(BA)_2$ with isotropic and anistropic bond polarizabilities for the translation $R = 6$ Å.

	isotropic		anisotropic	
ϕ	E_{ind}	E_{dis}	E_{ind}	E_{dis}
0°	−0.04	−1.5	−0.04	−1.3
90°	−0.04	−0.9	−0.05	−0.8
180°	−0.04	−1.4	−0.04	−1.2
270°	−0.04	−0.9	−0.04	−0.8

Eq. 6). Since the MBBA and PAA molecules were too big for the CNDO/2 program we used, this molecule was divided into two molecular fragments M1 and M2. For example the M1 fragment of MBBA consisted of

$$CH_3O—C_6H_4—CH=N—R_1$$

and the M2 fragment of $C_4H_9—C_6H_4—N=CH—R_2$. The R_1 group was



and R_2 group was $—CH=CH_2$, simulating the benzine rings. The above mentioned matrix elements were obtained in the following way:

$$P_{\mu\nu} = \begin{cases} P_{\mu\nu}^{(1)} \text{ for atoms belonging only to M1} \\ \frac{1}{2}(P_{\mu\nu}^{(1)} + P_{\mu\nu}^{(2)}) \text{ for atoms belonging to M1 and M2} \\ P_{\mu\nu}^{(2)} \text{ for atoms belonging only to M2.} \end{cases}$$

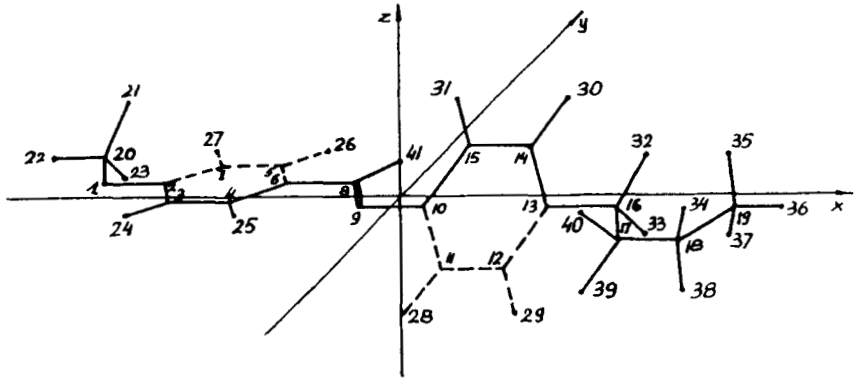


FIGURE 3 The coordinate system and numbering of atoms in the MBBA molecule.

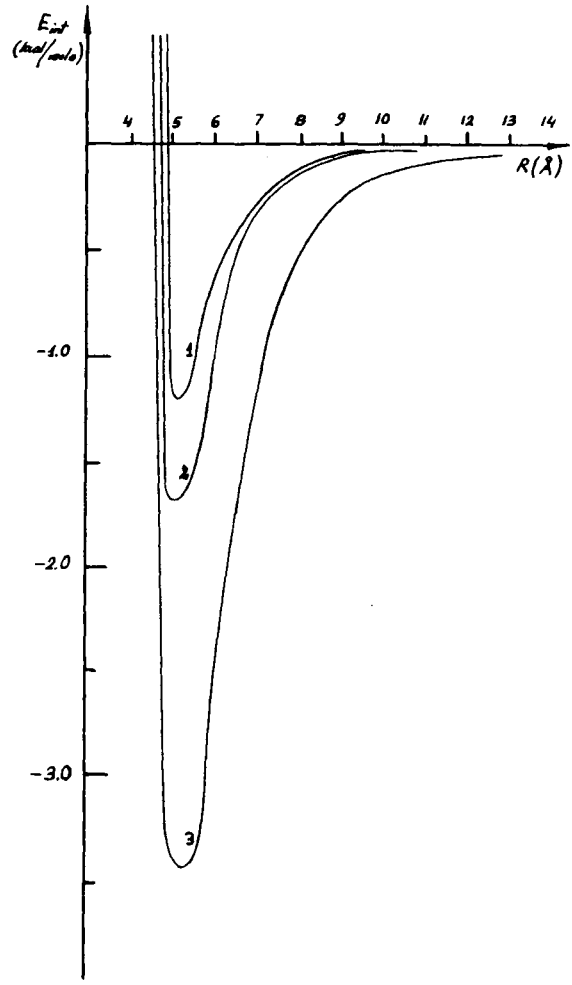


FIGURE 4 The interaction energy of $(BA)_2$, $(MBBA)_2$ and $(PAA)_2$ systems (curves 1, 2 and 3, respectively).

Comparison of net charges and of atomic dipoles at those atoms, which are common for the M1, M2 fragments and the BA molecule, has shown that the mean of the relative differences of the results is about 0.12. This means, that the above approximation of $P_{\mu\nu}$ elements is quite satisfying.

Basing on the results obtained the dependences of E_{int} on intermolecular distances have been calculated for the $(MBBA)_2$ and $(PAA)_2$ systems. They are shown in Figure 4, where by way of comparison a similar dependence for $(BA)_2$ is also presented. It is seen, that the minima for all these systems lie

TABLE III

Partitioning of E_{int} at $R = 6$ Å in the most stable configurations of some nematogenic molecules.

Molecular system	ϕ	E_{es}			E_{ind}		E_{rep}	E_{rep}	E_{int}	ω[c]
		E_{00}	E_{11}	E_{01}	$E_{0,\alpha}$[a]	$E_{1,\alpha}$[b]				
BA—BA	180°	−0.01	−0.1	−0.1	0.0	−0.02	−1.4	0.1	−1.6	89
PAA—PAA	0°	0.4	−0.5	−0.5	−0.1	−0.1	−2.2	0.3	−2.6	83
MBBA—MBBA	180°	−0.02	−0.2	−0.1	0.0	−0.03	−1.8	0.1	−2.0	90

[a] $E_{0,\alpha}$ = term arising from the interaction of net charges on A and induced dipoles on B molecule, similarly

[b] $E_{1,\alpha}$ = term arising from the interaction of atomic dipoles on A and induced dipoles on B molecule.

[c] $\omega = E_{dis}/E_{int} \times 100\%$.

approximately in the same region of $R_{min} = (5 - 6)$ Å, where R is the distance of the parallel translation of the second molecule of the systems with respect to the first one along the z-axis of the local co-ordinate systems (see Figures 1 and 3). The depth of the minima is of the order (1 − 3) kcal/mole. As it was mentioned earlier the value obtained for R_{min} compares well with the mean intermolecular distance in the BA solid crystal.

In our opinion particularly interesting is the partitioning of E_{int} into interactions of different types. This is demonstrated in Table III for the bimolecular systems under consideration. The values refer to the intermolecular distance $R = 6$ Å and the most stable configurations of the molecules in the system. It is clearly seen, that for all the systems considered the dispersion interactions play a predominant role. As it is shown in the last column of Table III, E_{dis} accounts for more than 80% of the total E_{int}. The contribution of E_{ind} is negligibly small for the distance $R = 6$ Å. The electrostatic interaction seems to be of secondary importance: E_{es} accounts for 15 − 30% of E_{dis}.

The relation $|E_{ind}| < |E_{es}| < |E_{dis}|$ given before is valid also for all the orientations and distances considered. This is illustrated by the curves in Figure 5 which present the distance dependences of E_{es}, E_{ind} and E_{dis} for the "antiparallel" configuration ($\phi = 180°$, see description of the $(BA)_2$ configuration) of the $(MBBA)_2$ system. The values have been found using the Hückel plus Del Re method of charge distribution calculation.

The domination of E_{dis} is rather unexpected, because the molecules considered have relatively large dipole moments. Using the CNDO/2 method we obtained $\mu = 1.6$ D, $\mu = 3.1$ D and $\mu = 2.6$ D for BA, MBBA† and PAA,

† The Hückel plus Del Re method gives for MBBA $\mu = 2.8$ D, the experimental value [31] being 2.2 D.

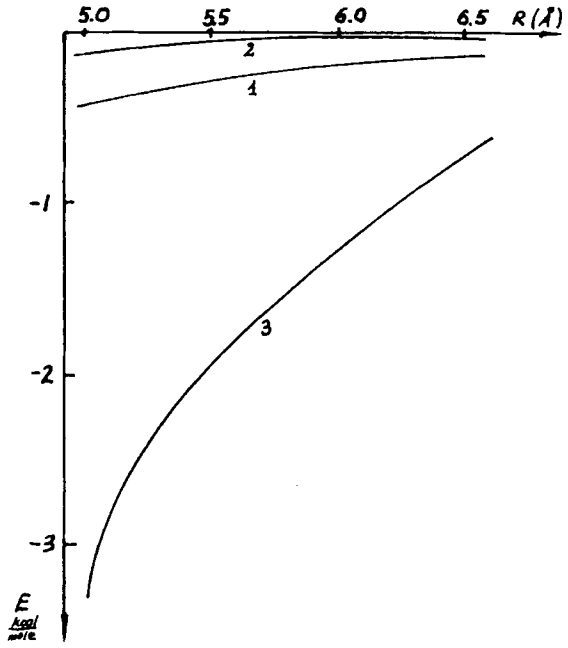


FIGURE 5 The distance dependences of E_{es}, E_{ind} and E_{dis} (curves 1, 2 and 3, respectively) for the antiparallel orientation of the $(MBBA)_2$ system.

respectively. We also calculated in the same way the quadrupole moment of PAA obtaining $Q = 1/3\ \mathrm{Tr}\ Q_{ij} = 15.22$ au $= 20.5 \times 10^{-24}$ esu $\cdot$ cm^2 $= 68.3 \times 10^{-40}$ Cm^2.

This result would suggest the dominant role of E_{es}. Our results indicate that for the internuclear distances close to the minimum of $E_{int}(R = 5\text{–}6$ Å) the average value of $|E_{es}|/|E_{dis}|$ is only 0.15–0.30.

The electrostatic energy E_{es} is a factor which reveals energetical differences between the "parallel" and "antiparallel" configurations, as well as between the "face to back" and "face to face" configurations of two molecules. This is demonstrated in Table IV, where the results related to the various configurations of the molecules in the $(MBBA)_2$ system are summarized. In this table ϕ is, as before, the angle of rotation of the translated molecule around the Oz axis, which indicates the direction of the translation, ψ—denotes the rotation angle of the translated molecule around its Ox axis (the "long" axis of this molecule). Thus $\phi = 0°$ for the "parallel" orientation, and $\phi = 180°$ for the "antiparallel" one. Similarly, when $\psi = 0°$, we have "face to back" orientation, and when $\psi = 180°$ the orientation is "face to face." It is seen that for the parallel and antiparallel orientations ($\phi = 0°$ and $\phi = 180°$, respectively; $\psi = 0°$) the E_{dis} values do not differ significantly one from the other. The

TABLE IV

Contributions to the interaction energy for the different molecular orientations in the $(MBBA)_2$ sy

		$\phi = 0°$						$\psi = 180°$			
R	Ψ	E_{es}	E_{ind}	E_{dis}	E_{rep}	E_{pert}	E_{int}	E_{es}	E_{ind}	E_{dis}	E_{re}
5.0	0°	0.9	−0.1	−3.2	0.7	−2.3	1.7	−0.4	−0.1	−3.3	0.
	90°	0.6	−0.2	−10.3	158.2	−9.9	148.0	0.03	−0.2	−7.6	14.
	180°	−0.6	−0.1	−3.8	2.1	−4.5	−2.4	0.5	−0.1	−3.3	0.
	270°	−0.1	−0.3	−11.2	27.0	−11.6	16.3	−0.8	−0.4	−9.4	76.
5.5	0°	0.7	−0.04	−1.9	0.2	−1.3	−1.1	−0.3	−0.05	−1.9	0.
	90°	0.4	−0.1	−5.0	12.7	−4.7	8.0	0.01	−0.1	−4.1	2.
	180°	−0.4	−0.1	−2.2	0.5	−2.7	−2.3	0.4	−0.1	−2.0	0.
	270°	−0.1	−0.2	−5.5	3.7	−5.7	−2.0	−0.6	−0.2	−4.6	9.
6.0	0°	0.5	−0.03	−1.2	0.1	−0.7	−0.7	−0.2	−0.03	−1.2	0.
	90°	0.3	−0.1	−2.7	1.8	−2.5	−0.7	−0.0	−0.1	−2.3	0.
	180°	−0.3	−0.04	−1.4	0.1	−1.7	−1.6	0.3	−0.03	−1.3	0.
	270°	−0.1	−0.1	−3.0	0.7	−3.1	−2.4	−0.4	−0.1	−2.5	1.

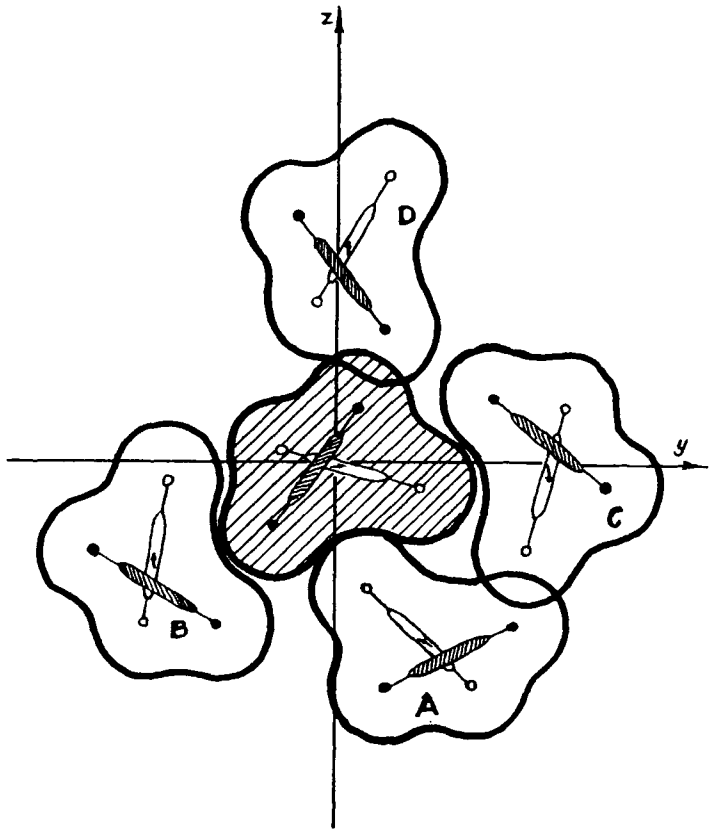


FIGURE 6 The YZ projection of the two interacting BA molecules. Forms A, B, C and D are the various sites of the second interacting molecule.

opposite situation appears for E_{es}, which changes the sign when the orientation is changed. This causes that differences occur between the values of $E_{pert} = E_{es} + E_{ind} + E_{dis}$ (the interaction energy without the repulsive term) but the antiparallel orientation is stabilized. A similar situation is observed for $\phi = 0°$, and the change of the angle from $\psi = 0°$ to $\psi = 180°$, when E_{es} favours energetically the $\psi = 180°$ (face to face) orientation.

Analogous behaviour of the E_{dis} and ϕ/ψ dependences of E_{es} has been observed for the $(BA)_2$ system. The situation is not so clear for $(PAA)_2$ where for the intermolecular distance of $R = 6$ Å the values of E_{dis} for parallel and antiparallel orientations differ significantly, amounting to -2.2 kcal/mole and -1.3 kcal/mole, respectively, and E_{es} additionally stabilizes the parallel orientation.

TABLE V

The coordinates and angles Ψ ($\phi = 0°$) for the configurations shown in Figure 6. (Explanation in the text).

Configuration	Y	Z	Ψ
A	3.0	−5.2	150°
B	−5.2	−3.0	90°
C	6.0	0.0	270°
D	0.0	6.0	90°

Basing on the results summarized in Table IV, some remarks relating to steric effects can be made. Both for parallel and antiparallel molecular orientations of the $(MBBA)_2$ system the configurations with $\psi = 90°$ and $\psi = 270°$ are characterized by high values of E_{rep}. This means that some atoms belonging to different molecules approach each other incidentally. The situation is clearly visualized in Figure 6 where the YZ projection of two BA molecules is drawn. The solid lines limit Van der Waals repulsion regions of the peripheral atoms. The forms A, B, C and D represent different localizations of the molecule, whose centre may occupy different sites on a circle of 6 Å radius around the central molecule. The coordinates (in the YZ plane) of this molecule centre in the configurations A, B, C and D, together with the ψ angles of its

TABLE VI

Interaction energy of the $(BA)_2$ system for the configurations shown in Figure 6.

Translation d[a]	Type of Configuration	E_{es}	E_{ind}	E_{dis}	E_{rep}	E_{int}
0.00	A	0.2	−0.03	−2.1	0.4	−1.5
	B	−0.2	−0.03	−1.8	0.3	−1.8
	C	0.1	−0.03	−2.1	0.4	−1.6
	D	0.4	−0.1	−2.1	1.2	−0.7
3.25	A	0.1	−0.03	−1.6	0.2	−1.3
	B	−0.3	−0.05	−1.9	0.3	−1.9
	C	0.2	−0.02	−1.2	0.1	−0.8
6.50	A	−0.1	−0.01	−1.2	0.3	−1.1
	B	−0.2	−0.03	−2.0	0.6	−1.6
	C	0.1	−0.01	−0.5	0.01	−0.4
9.75	A	−0.03	0.0	−0.5	0.1	−0.4
	B	−0.1	−0.01	−0.7	0.1	−0.7
	C	−0.01	0.0	−0.2	0.0	−0.2

[a] d is the distance of translation in the +X direction.

rotations are gathered in Table V. The orientations A, B and C reveal no overlap of the Van der Waals regions of the central and second molecules. Orientation D reveals a significant overlap. The energy terms relating to the mentioned orientations are presented in the first part of Table VI, referring to the translation d = 0.0 Å. The energetical difference between the nonoverlapping A, B, C configurations and overlapping D is evident. This suggests that the rotation of the molecules around their long axes has jump-like rather than diffuse-like character.

An additional conclusion can be deduced from the data of Table V as a whole. The subsequent parts of the table refer to the relative longitudinal translations of the interacting molecules in the direction perpendicular to the plane of Figure 6. The step of this translation is about one-third of the length of the BA molecule. Evidently the interaction energy E_{int} decreases with increasing translation path. However it is easy to see that the longitudinal translation of one molecule along a chain of linearly arranged molecules is nearly free, i.e. passes without significant change of E_{int}.

4 CONCLUDING REMARKS

The results obtained in this work show that our method allows us to estimate the values and relative significance of the various contributions to the interaction energy of the considered nematogenic molecules.

The reasonable minimum values of the total interaction energy E_{int} = (1 – 3) kcal/mole have been found. The statement concerning the predominant role of the dispersion interaction and negligible role of the induction interaction in the region of intermolecular attraction supports the assumptions made in the majority of statistical theories.[3,4,9] It also seems to be worthwhile to note the role of electrostatic interaction which energetically distinguishes configurations of approximately the same dispersion interaction. Moreover it appeared possible to give a semiquantitative support to the intuitive model of the rotation and longitudinal translation of the molecules considered. We must admit however that our calculations do not reveal the difference between the interaction of the nematogenic MBBA molecules and the BA molecules which do not form the nematic phase. Nevertheless we think that the above described method and the results obtained can serve as a starting point for further studies of the problems considered here.

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