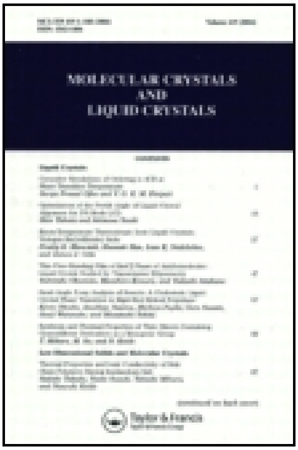

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On the Intermolecular Forces Operating in Induced Smectics

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On the Intermolecular Forces Operating in Induced Smectics

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Molecular interaction between induced smectics components was studied, i.e. between *p,p'*-cyano-*n*-pentylbiphenyl (PCB) on the one hand and *p-,p'*-dialkylazoxybenzenes (CnAX), where alkyl was CH_3, n-C_4H_9, n-C_5H_{11} and n-C_6H_{13}, on the other. With the Few-Smith's dielectric method[12,13] the stability constant and dipole moment of the formed 1:1 complex were determined and discussed as regards the spatial structure.

INTRODUCTION

Mixtures of nematic liquid crystals with similar chemical structures exhibit the nematic—isotropic transition temperatures, T_{NI}, varying linearly with composition.[1] Furthermore, other physical properties of the mixtures correspond to the average values of the components.

The mixtures show usually eutectic behavior in their solid-nematic phase transition, which results in extending nematic phase temperature range.

In contrast, if the intermolecular interactions in the mixture differs considerably from those in the pure components, very complicated phase boundaries can be obtained. Besides large deviations in T_{NI}, a strong enhancement in the stability of smectic phases or even the formation of smectic phases from non-smectic liquid crystals have been found e.g.[2,3] It seems that Dave, Patel, and Vasanth were the first who observed[4] the smectic phase formation on mixing two non-smectic materials. The phases which are usually very stable thermally are called induced smectic phases ISP's. In general these ISP's are of an A type. But S_B and S_E types can also be found,[3] whereas S_C, S_I, and S_G phases of the pure components are not enhanced in the area of the ISP's. In no case an ISP with a tilted director was found.[3,5] The molecular origin of the ISP formation has caused a dispute in the literature. Park *et al.*[6] basing on a positive deviation of T_{NI} from the additivity, a shift in the UV absorption bands, and a non-linear Δ H solid-nematic composition curve have suggested that the two mixed compounds form a charge-transfer complex. This model was challenged by Oh,[1] who has proposed a dipole induced lamellar structure. Recently both models were strongly criticized by Schneider *et al.*[7] as incompatible with their X-ray data. In an attempt of a better understanding of intermolecular interactions taking place between compounds forming an ISP we have decided to examine them in binary systems consisting of cyclohexane solutions of *p*-,*p*′-cyano-*n*-pentylbiphenyl (PCB) with *p*-,*p*′-dialkylazoxybenzenes (CnAX), where the alkyl used was: methyl (C1AX), *n*-butyl (C4AX), *n*-pentyl (C5AX), and *n*-hexyl (C6AX). The ISP formation in these binary systems was described elsewhere.[8] Cyclohexane was chosen as the solvent because it is quite inert with respect to the intermolecular interactions taking place in it, e.g.[9] For this study two dielectric measurement procedures were used—Job's continuous variation method for determining stoichiometry of the presumed molecular complex formed[10,11] and Few and Smith's method[12,13] for determining the stability constant, K, and the dipole moment $\mathbf{p}_{e,C}$, of the molecular complex.

EXPERIMENTAL

Materials. The preparation and purification of the nematics PCB, C1AX, C4AX, C5AX, C6AX were described in Refs. 14 and 15. The purification of cyclohexane, p.a. POCh, Gliwice, Poland, was the same as reported in Ref. 16.

Physical measurements. The apparatus and procedures were described in Refs. 17 and 18. All measurements were carried out at 298.15 K.

RESULTS AND DISCUSSION

Job's plot shown in Figure 1 for the PCB-C5AX system in cyclohexane indicates the formation of a fairly distinct molecular complex with stoichiometry of 1 : 1. The permittivity deviations $\Delta\epsilon$ from additivity are mainly determined by the complex stability constant, K, and to a less extent by the change, $\Delta\mathbf{p}_e$, in the average molecular dipole moment due to the complex formation.[17,18] Hence from the Job's plot one can infer that the K value should be fairly large. Moreover the positive sign of the $\Delta\epsilon$ value shows that the component (i.e. PCB and C5AX) dipoles enhance each other in the complex molecule, at least partly. To elucidate the complexation process more closely the complex dipole moment, $\mathbf{p}_{e,C}$, and the stability constant, K, have been measured with the Few and Smith's procedure.[12,13] The appropriate data for the systems studied, i.e. PCB-C5AX as well as for its homologues: PCB-C1AX, PCB-C4AX, and PCB-C6AX are listed in Tables I–IV. For all the systems the same solvent was

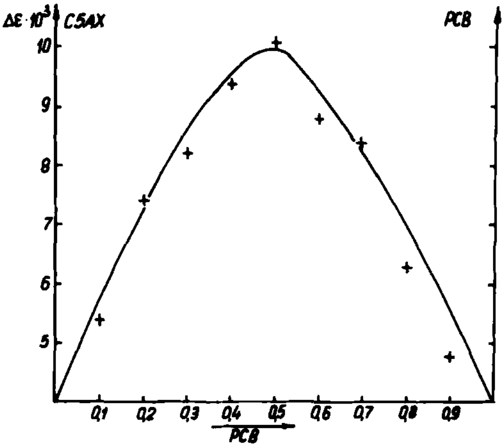

FIGURE 1 Job's continuous variation curve for the *p*-,*p*′-cyano-*n*-pentylbiphenyl (PCB)-*p*-,*p*′-di-*n*-pentylazoxybenzene (C5AX)-cyclohexane system. Total molar concentration $c = 0.25$ mol/dm^3.

used—cyclohexane. The measurements were carried out for solutions with an excess of CnAX over PCB, to minimize the antiparallel self-dimerization of PCB molecules.

In contrast to PCB, CnAX do not dimerize in cyclohexane solutions as it was found out by dielectric studies of pure PCB and pure CnAX solutions, respectively.[19] If a system studied complies with the assumption made by Smith and his co-workers[13] then the dependence $1/\Delta_T P^*$ versus $1/w_{BS}\rho_{BS}$ should be linear and its slope and intercept give us the K value and the molar polarizibility change $(\Delta_T P^\infty)_S$ due to the complex formation. The $(\Delta_T P^\infty)_S$ value together with the molar polarizibilities of PCB—$_T(P_A{}^\infty)_S$ and of CnAX—$_T(P_B{}^\infty)_S$, see Tables V and VI, enable us to calculate the molecular complex dipole moment, $p_{e,C}$. But the graphs of the $1/\Delta_T P^*$ versus $1/w_{BS}\rho_{BS}$ dependence for the system studied here, were only partly linear, see e.g. Figure 2. Hence, in the systems, other molecular processes have also taken place than that taken into account by the afore-mentioned assumptions. The side-processes prevail for the solutions represented by the points lying outside the linear part. The possible side-processes can be specified as, e.g., the formation of complexes with other than the 1:1 stoichiometry or with other arrangements of the components in the complex, and the PCB dimerization not fully suppressed by the excess CnAX in the solution. The question is under investigation, just now. The competition of the side-processes with that of the main 1:1 complex formation indicates that the energy change in connection with the side processes is of similar magnitude to that of the complex formation. The 1:1 complexes studied here, are much less energetically stable than the ordinary H- and CT-molecular complexes. Then the complex formation proc-

TABLE I

Results for the system: *p*-,*p*′-cyano-*n*-pentylbiphenyl (PCB)—*p*-,*p*′-dimethylazoxybenzene (C1AX) in cyclohexane at 298.15 K

No	$w_B \times 10^2$	ϵ_{BS}	n^2_{BS}	α	$v_{BS} \times 10^3$ [m^3 kg^{-1}]	$\beta \times 10^3$ [m^3 kg^{-1}]	$\frac{M_B}{\rho_{BS} w_{BS}} 10^6$ [m^3 mol^{-1}]	$({}_TP_A{}^\infty)_{BS}\ 10^6$ [m^3 mol^{-1}]	$\frac{1}{\Delta_T P^*} 10^{-6}$ [mol m^{-3}]
1	1.0356	2.0312	2.03754	8.33	1.2913	−0.251	28209	561.53	−0.130
2	1.8369	2.0439	2.04134	8.44	1.2883		15867	561.56	−0.130
3	2.6342	2.0574	2.04494	8.54	1.2845		11032	565.80	−0.292
4	3.3236	2.0688	2.04845	8.61	1.2819		8726	566.35	−0.347
5	4.2997	2.0850	2.05303	8.40	1.2783		6726	551.39	−0.056

w_B–the weight fraction of C1AX in the mixed solvent B-S: C1AX—cyclohexane.

ϵ_{BS}–the electric permittivity of the mixed solvent B-S.

$\alpha = \partial\epsilon/\partial w_A$–the slope of the linear part of the dependence of the electric permittivity ϵ of PCB solutions in the mixed solvent B-S versus the weight fraction of PCB—w_A.

n_{BS}–the sodium D-line refractive index of the mixed solvent B-S.

$v_{BS} = 1/\rho$–the specific volume of the solvent B-S.

$\beta = \partial v/\partial w_A$–the slope of the specific volume v vs. w_A.

$({}_TP_A{}^\infty)_{BS} = 3\alpha v_{BS} M_B/(\epsilon_{BS} + 2)^2 + M_B\,(v_{BS} + \beta)\epsilon_{BS} - 1/\epsilon_{BS} + 2$—the total molar polarizability of PCB in B-S extrapolated to $w_A = 0$.

$\Delta_T P^* = ({}_TP_A{}^\infty)_{BS} - ({}_TP_A{}^\infty)_S$.

$({}_TP_A{}^\infty)_S$–the total molar polarizability of PCB in cyclohexane extrapolated to $w_A = 0$.

TABLE II

Results for the system: *p-,p'*-cyano-*n*-pentylbiphenyl (PCB)—*p-,p'*-di-*n*-butylazoxybenzene (C4AX) in cyclohexane at 298.15 K

No	$w_B \times 10^2$	ϵ_{BS}	α	n^2_{BS}	$v_{BS} \times 10^3$ [m^3 kg^{-1}]	$\beta \times 10^3$ [m^3 kg^{-1}]	$\frac{M_B}{\rho_{BS} w_{BS}} 10^6$ [m^3 mol^{-1}]	$({}_TP_A^\infty)_{BS} 10^6$ [m^3 mol^{-1}]	$\frac{1}{\Delta_T P^*} 10^{-6}$ [mol m^{-3}]
1	0.8671	2.0227	8.13	2.03559	1.2912	−0.24	46219	550.26	−0.053
2	1.7171	2.0354	8.29	2.03836	1.2885		23291	555.13	−0.071
3	2.4120	2.0439	8.41	2.04116	1.2865		16555	562.45	−0.148
4	3.0830	2.0534	8.50	2.04424	1.2834		12921	561.39	−0.128
5	3.6902	2.0613	8.53	2.04662	1.2816		10777	563.76	−0.183

The meaning of the symbols is correspondingly the same as those in Table I.

TABLE III

Results for the system: *p-,p'*-cyano-*n*-pentylbiphenyl (PCB)—*p-,p'*-di-*n*-pentylazoxybenzene (C5AX) in cyclohexane at 298.15 K

No	$w_B \times 10^2$	ϵ_{BS}	α	n^2_{BS}	$v_{BS} \times 10^3$ [m^3 kg^{-1}]	$\beta \times 10^3$ [m^3 kg^{-1}]	$\frac{M_B}{\rho_{BS} w_{BS}} 10^6$ [m^3 mol^{-1}]	$({}_TP_A^\infty)_{BS} 10^6$ [m^3 mol^{-1}]	$\frac{1}{\Delta_T P^*} 10^{-6}$ [mol m^{-3}]
1	0.8453	2.0239	8.46	2.0229	1.2913	−0.22	51708	570.10	1.150
2	1.7013	2.0335	8.52	2.0383	1.2890		25642	577.08	0.127
3	3.2295	2.0514	8.66	2.0443	1.2845		13461	579.41	0.098
4	4.0390	2.0629	8.62	2.0629	1.2816		10739	562.12	−0.141
5	4.6956	2.0708	8.63	2.0701	1.2801		9226	571.62	0.418

The meaning of the symbols is correspondingly the same as those in Table I.

TABLE IV

Results for the system: *p-,p'*-cyano-*n*-pentylbiphenyl (PCB)—*p-,p'*-di-*n*-hexylazoxybenzene (C6AX) in cyclohexane at 298.15 K

No	$w_B \times 10^2$	ϵ_{BS}	α	n^2_{BS}	$v_{BS} \times 10^3$ [m^3 kg^{-1}]	$\beta \times 10^3$ [m^3 kg^{-1}]	$\frac{M_B}{\rho_{BS} w_{BS}} 10^6$ [m^3 mol^{-1}]	$({}_TP_A^\infty)_{BS} 10^6$ [m^3 mol^{-1}]	$\frac{1}{\Delta_T P^*} 10^{-6}$ [mol m^{-3}]
1	0.7401	2.0219	8.62	2.03735	1.2910	−0.21	63935	578.87	0.104
2	1.4062	2.0299	8.77	2.03475	1.2893		33607	584.93	0.064
3	2.0371	2.0358	8.95	2.03855	1.2880		23175	592.58	0.043
4	2.6440	2.0427	8.55	2.04201	1.2868		17839	572.32	0.324
5	3.2877	2.0506	8.47	2.04402	1.2847		14410	560.92	−0.120

The meaning of the symbols is correspondingly the same as those in Table I.

TABLE V

Total molar polarizability $({}_TP_A^\infty)_S$, and dipole moment, $\mathbf{p}_{e,A}$, of PCB in cyclohexane at 298.15 K

ϵ_S	α	$v_S \times 10^3$ [m$^3 \cdot$kg^{-1}]	$\beta \times 10^3$ [m^3 kg^{-1}]	$({}_TP_A^\infty)_S \cdot 10^6$ [m^3 mol^{-1}]	n^2_S	γ	$(R_A^\infty)_S 10^6$ [m^3 mol^{-1}]	$\mathbf{p}_{e,A} 10^{30}$ [C·m]
2.0136	8.41	1.2935	−0.27	569.23	2.03185	0.37	86.78	16.20

The meaning of the symbols is correspondingly the same as those in Table I.

$(R_A^\infty)_S$–the molar refraction of PCB in cyclohexane extrapolated to infinite dilution, i.e., $w_A = 0$.

$\gamma = (\partial n^2/\partial w_A)$–the slope of the dependence of square of refractive index of PCB solutions in cyclohexane, S, on the weight fraction of PCB.

TABLE VI

Total molar polarizability $({}_{\mathrm{T}}P_{\mathrm{B}\infty})_{\mathrm{S}}$, and dipole moment, $\mathbf{p}_{\epsilon,\mathrm{B}}$, of *p*-,*p*′-di-*n*-alkylazoxybenzenes, CnAX, in cyclohexane at 298.15 K

Alkyl	ϵ_{S}	α	$v_{\mathrm{S}} \times 10^3$ [m^3 kg^{-1}]	$\beta \times 10^3$ [m^3 kg^{-1}]	$({}_{\mathrm{T}}P_{\mathrm{B}\infty})10^6$ [m^3 mol^{-1}]	n_{S}^2	γ	$(R_{\mathrm{B}\infty})_{\mathrm{S}}10^6$ [m^3 mol^{-1}]	$\mathbf{p}_{\epsilon,\mathrm{B}}10^{30}$ [C·m]
methyl	2.0136	1.652	1.2935	−0.40	140.84	2.03185	0.48	77.17	5.78
n-butyl	2.0136	1.665	1.2935	−0.36	197.65	2.03185	0.40	103.58	7.13
n-pentyl	2.0136	1.230	1.2935	−0.28	186.79	2.03185	0.39	119.54	6.03
n-hexyl	2.0136	1.120	1.2935	−0.25	196.04	2.03185	0.32	127.26	6.10

The meaning of the symbols is correspondingly the same as those in Table V.

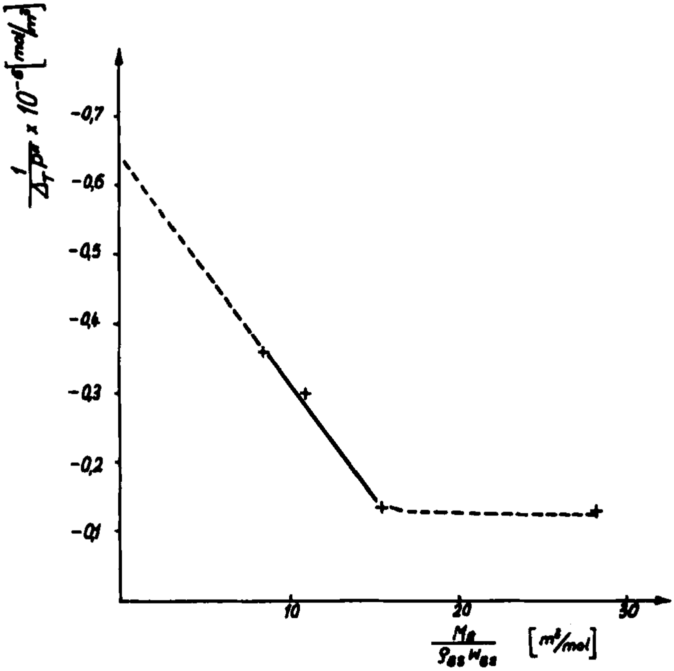

FIGURE 2 Dependence of $1/\Delta_T P^* = 1/_T(P_A^\infty)_{BS} - {}_T(P_A^\infty)_S$ versus $M_B/\rho_{BS}w_{BS}$ for the *p*-,*p*'-cyano-*n*-pentylbiphenyl, A,-*p*-,*p*'-dimethylazoxybenzene, B,-cyclohexane system.

ess differ only a little in energy from the ordinary non-specific van der Waals interaction.

The linear part of the $1/\Delta_T P^*$ versus $1/w_{BS}\rho_{BS}$ plot for all the systems studied made it possible to evaluate $(\Delta_T P^\infty)_S$ and K's for the 1 : 1 complexes. The data as well as the dipole moment of the complexes, $p_{e,C}$ are summarized in Table VII. The first three systems, viz., those with C1AX, C4AX and C5AX have exhibited fairly large K values 20–30 dm^3/mol, while the corresponding $(\Delta_T P^\infty)_S$ values are only a little smaller (for C1AX and C4AX) or larger (for

TABLE VII

The stability constant, K, the change $(\Delta_T P^\infty)_S$ in the system molar polarizability due to the complex formation, the complex dipole moment, $p_{e,C}$, the angle θ, between the PCB and CnAX dipole moments in the complex and $\Delta\theta = 90° - \theta$

Alkyl	K [dm^3 mol^{-1}]	$(\Delta_T P^\infty)_S 10^6$ [m^3 mol^{-1}]	$p_{e,C} \times 10^{30}$ [C m]	θ [°]	$\Delta\theta$ [°]
methyl	20.9	−1.5	17.20	90.0	−0.0
n-butyl	32.5	−3.6	17.63	90.6	−0.6
n-pentyl	28.7	15.2	17.50	87.8	2.2
n-hexyl	8.3	84.0	18.56	76.8	13.1

C5AX) than zero. These values were expected assuming that: (1) there is no charge redistribution in the system due to the molecular complex formation, and (2) that the component molecular dipoles are oriented at right angle. Thus the $(\Delta_T P\infty)_S$ data show that, in the case of the complexes of C1AX, C4AX, and C5AX with PCB, the dipole moments of the component molecules are disposed nearly perpendicularly. The measured $p_{e,C}$ together with the determined $p_{e,\mathrm{PCB}}$ and $p_{e,\mathrm{CnAX}}$ values enabled us to calculate the angle, θ, between the PCB and CnAX dipole moment directions in the complex. The data as well as $\Delta\theta = 90° - \theta$ are listed in Table VII. For the arrangement, the molecular dipole-dipole interaction is negligible hence it does not contribute to the system over-all stability. The angle, θ, between the PCB and CnAX dipole moments in the complex was calculated from the measured, $p_{e,C}$, value assuming no charge redistribution due to the complex formation.[20] The θ values are listed in Table VII. The dipole direction for PCB is parallel and that for CnAX is approximately perpendicular to their respective molecular long axis. The θ values obtained show that the above two molecules are nearly parallel in the complex. Thus it seems that the molecular planes are disposed in a "sandwich type" manner as shown in Figure 3.† Such a type of the arrangement, on the one hand, indicates no molecular dipole-dipole interaction due to $\theta \sim 90°$ and, on the other hand, suggests a contribution of the charge-transfer forces to the stability of the complex in solution. The situation differs in the case of the PCB-C6AX system, (see Table VII), presumably due to a steric effect caused by the longer alkyl group attached to both ends of the molecular long axis. Here, the complex stability constant, is lower (8.3 dm^3/mol). But the complex formation is accompanied by a higher $(\Delta_T P\infty)_S$ value (84 · 10^{-6} m^3/mol). The $\Delta\theta$ value is 13.1°, which indicates that the alignment of the molecular long axes is decreased as compared with the other systems studied. The dipole-dipole interaction is increased as evidenced by the $(\Delta_T P\infty)_S$ value which may even lead to a higher interaction energy than in the case of the other systems. It seems that the mutual positions of the interacting molecules is of considerable importance for the complex stability. In the case of the PCB-C6AX system a little change in its molecular arrangement as compared with the three other systems causes a pronounced increase in the $(\Delta_T P\infty)_S$ value.

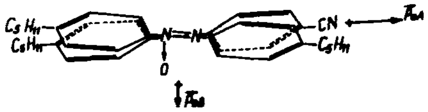

FIGURE 3 The arrangement of the PCB and CnAX molecules in the complex.

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† But the θ value of ~90° is also in conformity with a complex structure with the component molecular planes at right angle.

CONCLUSIONS

The data obtained for cyclohexane solutions of mixtures of PCB with CnAX strongly suggest the 1 : 1 molecular complex formation taking place in the solutions. Despite the pronounced magnitude of the component dipole moments $p_{e,PCB} = 16.20 \times 10^{-30}$ Cm and $p_{e,CnAX} = (5.78–7.13) \times 10^{-30}$ Cm the molecular dipole-dipole forces do not contribute significantly to the complex energy. It seems that besides the van der Waals interactions (dipole-induced dipole and dispersive) an intermolecular charge transfer makes a contribution to the over-all complex stability. This latter effect seems to be evidenced by the presumable sandwich-like structure of the complexes. The formation of the ISP is promoted by originating the complex molecules due to their increased molecular weight and then the decreased mobility as compared with the uncomplexed (single) molecules. Thus the induced smectic phase formed consists of the complex molecules (PCB-CnAX). The intermolecular forces responsible for the ISP formation operate between these molecular entities. The ISP structure considered here seems to be quite similar to the interdigitated structure proposed for some one-component smectics to explain the unusal X-ray data obtained for them.[21]

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