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Supramolecular Liquid Crystals Induced by Hydrogen-Bonding Interactions Between Non-Mesomorphic Compounds. I. 4-(4′-Pyridylazo phenyl)-4″-Substituted Benzoates and 4-Substituted Benzoic Acids

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Equimolar binary mixtures of the title compounds were prepared to investigate the effect of different polar substituents, either on the pyridine-based derivatives or on the acid component, on the extent and stability of the supramolecular liquid crystal phases induced by intermolecular hydrogen bonding. None of the pyridine-based derivative or the acid complement is mesomorphic, but the hydrogen-bonded complexes are. The mixtures prepared were characterized for their mesophase behavior by differential scanning calorimetry, DSC, and polarized light microscopy, PLM. Five azo pyridine-based derivatives ($\mathbf{I}_{a-e}$*), with molecular formula X-*$C_6H_4COOC_6H_4$*-N=N-*C_5H_4N*, were prepared that differ from each other by the substituent X. The latter varies between* CH_3O, CH_3, H, Br, and NO_2. *Six 4-substitutedbenzoic acids (Y-*C_6H_4COOH, $\mathbf{II}_{a-f}$*) were used; the substituent Y varies between* CH_3O, CH_3, H, Br, CN, and NO_2. *Nematic mesophase is induced in most of the binary mixtures investigated.*

Keywords: 4-(4′-pyridylazophenyl)-4″-substituted benzoates; 4-substituted benzoic acids; binary mixtures; supramolecular LCs

1. INTRODUCTION

In recent years, several classes of supramolecular liquid crystals, formed via hydrogen-bonding interaction of complementary molecules, have been recognized and characterized for their mesophase behavior [1,2]. A single hydrogen bond between the pyridyl nitrogen and a carboxylic

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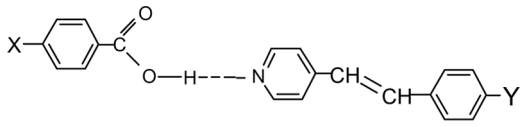
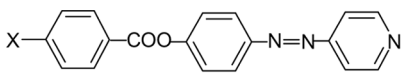
proton was found [2] to be fruitful in generating novel liquid crystals. Generally, hydrogen bonding leads to an elongation of the rigid-rod segment of the individual components. Complementary components may be either mesomorphic or non-mesomorphic; in both cases, however, novel liquid crystals can be obtained. For instance, carboxylic acids, substituted with a small compact polar group, when interacted with 4-cyano- or 4-nitro-4′stilbazole afforded complexes of the general formula **1** [3].



(**1**)

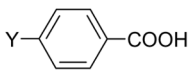
X=CH_3, CN, NO_2; Y=CN, NO_2.

Although none of the two complementary components bears an alkyl chain, most of the complexes examined proved to exhibit nematic mesomorphism with high clearing temperatures. The nature of the terminal substituents (X or Y) was found to have crucial effect upon mesomorphism. These results have encouraged us to widen our previous study [4,5] to test the possibility of liquid crystal formation between the non-mesomorphic 4-(4′-pyridylazophenyl)-4″-substituted benzoates ($\mathbf{I}_{a–e}$) and 4-substituted benzoic acids ($\mathbf{II}_{a–f}$). Using two terminal groups (X and Y) of variable polarities may affect the stability or the type of the mesophase to variable extents. The goal of the present study is to investigate the possibility of mesophase formation between the two non-mesomorphic components. So, it is planned to prepare supramolecular complexes (in the 1:1 molar proportions) in order to monitor the effect of similar and/or different polar substituents on mesophase formation.



($\mathbf{I}_{a-e}$)

$\mathbf{I}_a$, X=CH_3O, $\mathbf{I}_b$, X=CH_3, $\mathbf{I}_c$, X=H, $\mathbf{I}_d$, X= Br, $\mathbf{I}_e$, X=NO_2



($\mathbf{II}_{a-f}$)

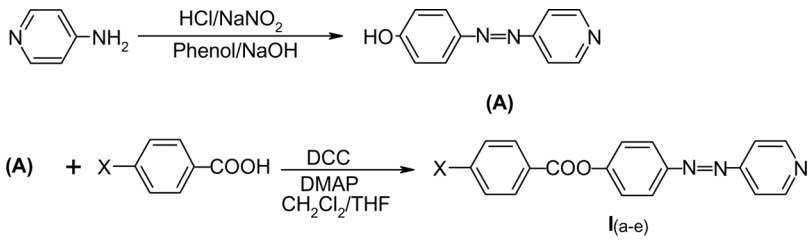
$\mathbf{II}_a$, Y=CH_3O, $\mathbf{II}_b$, Y=CH_3, $\mathbf{II}_c$, Y=H, $\mathbf{II}_d$, Y= Br, $\mathbf{II}_e$, Y=CN, $\mathbf{II}_f$, Y= NO_2

2. EXPERIMENTAL

Chemicals are of pure grades that were purchased from the following Companies: Fluka, Buchs, Switzerland; MP Biomedicals, Inc., Illkirch, France; BDH, Poole, England; Aldrich, Wisconsin, USA; and E. Merck, Darmstadt, Germany.

2.1. Preparation of Materials

The pyridine-based azo dyes ($\mathbf{I}_{a-e}$) were prepared, by the method described previously [4], according to the following scheme:



The solids obtained were found to be TLC pure and possess sharp melting temperatures, given in Table 1, that agree with those reported before [4].

2.2. Physical Characterization

For the investigation of the supramolecular complexes (**I**/**II**), binary mixtures of any two complimentary components, were prepared in a 1:1 molar ratio by melting the appropriate amounts of each component, stirring to give an intimate blend, and then cooling with stirring to room temperature.

Calorimetric measurements were carried out using a PL-DSC of Polymer Laboratories, England. The instrument was calibrated for temperature, heat, and heat flow according to the method recommended by Cammenga *et al*. [6]. DSC measurements were carried out on small samples (2–3 mg) placed in sealed aluminum pans. All of the thermograms have been achieved at a heating rate of 10°C/min in inert atmosphere of nitrogen gas (10 ml/min).

Transition temperatures were checked and types of mesophases identified for adducts prepared with a standard polarized light microscope PLM (Wild, Germany) attached to a home made hot-stage.

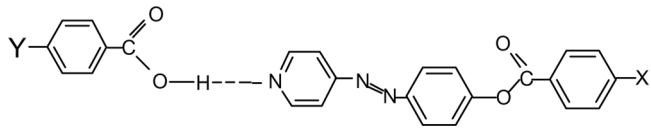
The temperatures obtained for the prepared blends, as measured by both DSC and PLM, agreed within 2–3°C.

TABLE 1 Phase Transition Temperatures (°C), Enthalpies ($\Delta \boldsymbol{H}$, kJ/mole), and Entropies ($\Delta \boldsymbol{S}_c$, J/mole/K) of the 1:1 Supramolecular Hydrogen-bonded Complexes of the Systems **I**/**II**

System	X	Y	$\boldsymbol{T}_m$	$\Delta \boldsymbol{H}_m$	$\boldsymbol{T}_C$	$\Delta \boldsymbol{H}_C$	$\Delta \boldsymbol{S}_C$	$\sqrt{\boldsymbol{T}_C}$
$\mathbf{I}_a/\mathbf{II}_a$	CH_3O	CH_3O	163.7	5.34	220.5	1.03	2.09	22.20
$\mathbf{I}_a/\mathbf{II}_b$		CH_3	138.0	5.64	218.0	0.35	0.71	22.16
$\mathbf{I}_a/\mathbf{II}_c$		H	170.1	4.08	193.3	0.10	0.47	21.60
$\mathbf{I}_a/\mathbf{II}_d$		Br	156.5	9.83	221.4	0.09	0.18	22.45
$\mathbf{I}_a/\mathbf{II}_e$		CN	177.3	6.98	229.7	0.12	0.24	22.42
$\mathbf{I}_a/\mathbf{II}_f$		NO_2	170.4	4.00	241.4	1.74	3.38	22.68
$\mathbf{I}_b/\mathbf{II}_a$	CH_3	CH_3O	166.3	12.68	205.6	0.54	1.13	21.87
$\mathbf{I}_b/\mathbf{II}_b$		CH_3	179.2	7.91	206.4	0.42	0.88	21.90
$\mathbf{I}_b/\mathbf{II}_c$		H	133.7	2.63	181.0	0.31	0.68	21.30
$\mathbf{I}_b/\mathbf{II}_d$		Br	179.4	5.19	219.5	0.29	0.56	22.20
$\mathbf{I}_b/\mathbf{II}_e$		CN	168.9	4.32	232.2	2.04	4.04	22.47
$\mathbf{I}_b/\mathbf{II}_f$		NO_2	178.4	4.35	238.4	0.23	0.45	22.60
$\mathbf{I}_c/\mathbf{II}_a$	H	CH_3O	170.1	10.94	198.7	0.14	0.30	21.71
$\mathbf{I}_c/\mathbf{II}_b$		CH_3	163.7	3.30	180.9	0.12	0.26	21.31
$\mathbf{I}_c/\mathbf{II}_c$		H	125.8	4.57	161.3	0.09	0.21	20.84
$\mathbf{I}_c/\mathbf{II}_d$		Br	161.6	6.68	173.4	0.36	0.81	21.13
$\mathbf{I}_c/\mathbf{II}_e$		CN	162.0	8.40	217.9	0.93	1.89	22.16
$\mathbf{I}_c/\mathbf{II}_f$		NO_2	200.6	7.07	214.4	0.92	1.89	22.08
$\mathbf{I}_d/\mathbf{II}_a$	Br	CH_3O	172.9	11.73	218.4	0.27	0.55	22.16
$\mathbf{I}_d/\mathbf{II}_b$		CH_3	173.9	7.70	200.1	0.14	0.30	21.75
$\mathbf{I}_d/\mathbf{II}_c$		H	189.6	7.02	174.2	0.08	0.18	21.15
$\mathbf{I}_d/\mathbf{II}_d$		Br	177.9	11.45	216.0	0.27	0.55	21.12
$\mathbf{I}_d/\mathbf{II}_e$		CN	181.9	8.05	234.5	0.44	0.87	22.53
$\mathbf{I}_d/\mathbf{II}_f$		NO_2	211.3	6.72	241.1	0.46	0.89	22.68
$\mathbf{I}_e/\mathbf{II}_a$	NO_2	CH_3O	154.7	6.40	179.4	0.31	0.68	21.27
$\mathbf{I}_e/\mathbf{II}_b$		CH_3	141.4	4.52	178.3	0.24	0.53	21.25
$\mathbf{I}_e/\mathbf{II}_c$		H	154.8	6.88	190.2	0.11	0.23	21.53
$\mathbf{I}_e/\mathbf{II}_d$		Br	187.3	18.15	221.2	0.83	1.68	22.23
$\mathbf{I}_e/\mathbf{II}_e$		CN	194.9	15.23	224.2	0.95	1.91	22.3
$\mathbf{I}_e/\mathbf{II}_f$		NO_2	155.3	28.42	–	–	–	–

3. RESULTS AND DISCUSSION

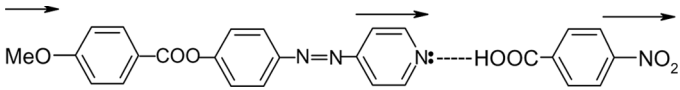
Supramolecular hydrogen-bonded liquid crystals are frequently induced between aromatic carboxylic acids as proton donor and the pyridine nitrogen, in a pyridine-based derivative, as proton acceptor. In such cases, neither of the two complementary components should disturb the alignment of the other. However, each component in the mixture may be either mesomorphic, or non-mesomorphic, or both; in each case, novel liquid crystals can be obtained. For our investigated systems, hydrogen bonding leads to an elongation of the individual components and represented by formula **2**.



(**2**)

For the formation of liquid crystalline materials through hydrogen bonding interactions, the nature of the interacting components coupled with the directionability of hydrogen-bonds are the main (but not the sole) factors contributing to the exhibition of liquid crystallinity. The appropriate shape and stability of the hydrogen bonded supramolecular complexes are also required. All possible 1:1 supramolecular complexes, made from each of the five pyridine-based derivatives ($\mathbf{I}_{a-e}$) with each of the substituted benzoic acids ($\mathbf{II}_{a-f}$) were investigated for their mesophase behavior by DSC and PLM, and the results are collected in Table 1.

Since the mesophase is not shown by either of the two interacting components, the mesophase stabilization of the 1:1 complex is attributed to the formation of the new and elongated mesogen, obtained through a single intermolecular hydrogen bond which allows the complex to behave as a single liquid crystalline compound. Complex formation was supported by FTIR measurements, according to which the initial dimeric acid is replaced by the heterodimeric complex [7]. Certainly, the relative acid (or basic) strength of the two complementary components of the complex has a crucial effect upon mesomorphism. This in turn, is influenced by the nature of the terminal substituents on both the pyridine-based component (**X**) and/or on the acid complement (**Y**) of the supramolecular complex. Thus, electron-donating substitution on the pyridine side is expected to increase electron-density on the nitrogen of the pyridine ring that leads to strengthening the resulting hydrogen-bond. On the other hand, electron-withdrawing substituent on the acid side will enhance acidity of the acid-proton, and consequently adds extra stability to the hydrogen-bond.



That is, the methoxy (and less effectively the methyl) substitution on the pyridine side, together with the nitro or cyano (and less effectively the bromo) groups on the acid partner of the complex, will

furnish the most mesophasically stable adducts. Recalling Table 1, this was found to be true. The clearing temperature ($\boldsymbol{T}_C = 241.4\ ^\circ C$) of the complex containing the substituents ($\mathbf{X}$=CH_3O and $\mathbf{Y}$=NO_2) is considerably higher than that of the complex ($\boldsymbol{T}_C$=179.4 °C) bearing opposite substitution, i.e., X=NO_2 and Y=CH_3O. Also, the entropy change associated with the clearing transition (ΔS_C) showed an analogous behaviour ($\Delta S_C = 3.38$ and $0.68\,J/mol/K$, respectively). That is the mesophase stability, $\boldsymbol{T}_C$, of the adducts formed from the methoxy or the methyl-substituted pyridine-based derivatives ($\mathbf{I}_a$ or $\mathbf{I}_b$) with the variously substituted acids ($\mathbf{II}_{a-f}$) decreases in the order:

$$NO_2 > CN > Br > CH_3O > CH_3 > H,$$

whereas, $\boldsymbol{T}_C$ of the adducts, formed from the cyano- (or nitro-) substituted acids ($\mathbf{II}_e$ or $\mathbf{II}_f$) with the variously substituted pyridine-based compounds, decreases in the order:

$$CH_3O > Br > CH_3 > CH > NO_2.$$

It can be also concluded that, for the systems containing proton-acceptor bearing an electron-releasing group, hydrogen-bonding complexation with acids substituted with electron-withdrawing group, not only enhances liquid crystallinity, but also increases the degree of molecular ordering.

3.1. Thermal Mesophase Stability and Polarizability Anisotropy of C_{ar}-X and/or C_{ar}-Y Bonds

As we concluded above, in hydrogen-bonded liquid crystal complexes, phase behavior is related to the strength of the hydrogen bonds involved [8]. In the pyridine/acid complexes, the association is primarily affected by the acidity of the proton-donor, the acid, as well as the basicity of the pyridine derivative. The relationship between the stability of the mesophase, expressed as the clearing temperature, $\boldsymbol{T}_C$, and the anisotropy of polarizability ($\Delta\alpha_X$) of bonds to the small compact terminal substituent (C_{ar}-X), was studied by van der Veen [9]. The relationship has the form

$$\boldsymbol{T}_C \alpha (\Delta\alpha_M + \Delta\alpha_X)^2, \tag{1}$$

where $\boldsymbol{T}_C$ is measured in Kelvin. Equation (1) can be put in the form [10]

$$\boldsymbol{T}_C^{1/2} \alpha (\Delta\alpha_M + \Delta\alpha_X) = a \cdot \Delta\alpha_M + a \cdot \Delta\alpha_X. \tag{2}$$

The term $\Delta\alpha_M$ is the polarizability anisotropy of all the molecular structure except the terminal substituent, X, and "*a*" is the proportionality constant. Thus, if, $T_C^{1/2}$ of any of our investigated hydrogen-bonded series bearing one and the same acid substituent "**Y**" but of

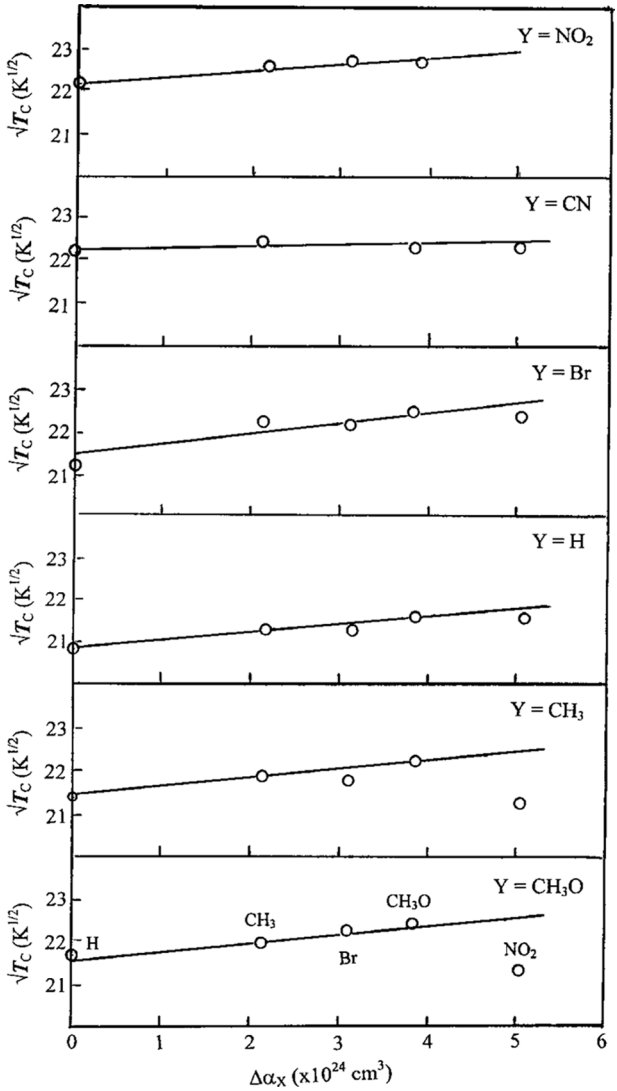


FIGURE 1 Dependence of the mesophase stability (T_C) of the investigated 1:1 adducts on the polarizability anisotropy ($\Delta\alpha_X$) of the pyridine-based substituent (X).

varying base substitution "**X**", is plotted against the polarizability anisotropy to the bond X, $\Delta\alpha_X$, a straight line is expected with a slope "$a_{(X)}$", and intercept equals "$a_{(X)} \cdot \Delta\alpha_{M(Y)}$", where "$a_{(X)}$" is the slope of the of $(T_C^{1/2} - \Delta\alpha_X)$ dependency, and "$\Delta\alpha_{M(Y)}$" is the polarizability anisotropy of the remainder of the molecular structure except the substituent (**X**), but still including the substituent (**Y**). Figure 1 illustrates the correlations between the $T_C^{1/2}$ values and $\Delta\alpha_X$ of the bonds to X in the pyridine-based component of the supramolecular complex, individually, with the variously substituted acids ($\mathbf{II}_a - \mathbf{II}_f$).

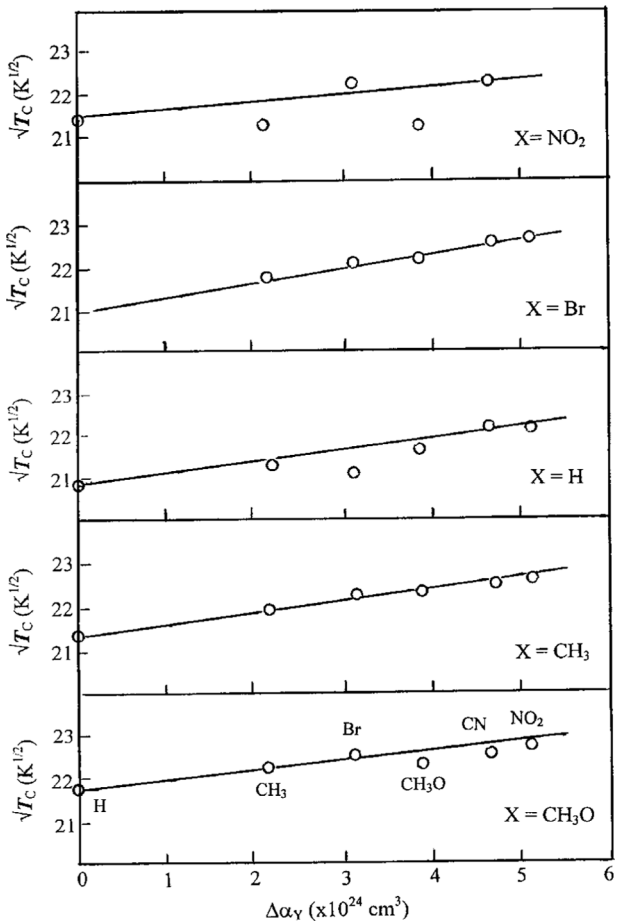


FIGURE 2 Dependence of the mesophase stability (T_C) of the investigated 1:1 adducts on the polarizability anisotropy ($\Delta\alpha_Y$) of the acid substituent (Y).

Alternatively, if $T_C^{1/2}$ values of any series bearing the same pyridine-based substituent (**X**), whereas the acid component bears different substituent (**Y**), is plotted against the polarizability anisotropy ($\Delta\alpha_Y$) of the substituent (**Y**), a straight line is again expected, but in this case the slope is "$a_{(Y)}$" and the intercept is "$a_{(Y)} \cdot \Delta\alpha_{M(X)}$", where "$\Delta\alpha_{M(X)}$" is the polarizability anisotropy of the remainder of the molecular structure comprising the substituent (**X**). The $T_C^{1/2}$ values are again plotted, individually, for each series bearing one and the same substituent **X**, as a function of $\Delta\alpha_Y$ and depicted in Fig. 2. As can be seen from Figs. 1 and 2, fairly linear dependencies were observed in nearly all series investigated, except for the system where X=NO_2 (Fig. 2). This is expected, since electron-withdrawing substitution on the base-side of the complex decreases electron-density on the pyridine-nitrogen and, consequently, destabilizes the complex formed resulting in irregularity of data. It would be worthy mentioning here that the bromo-substituted derivatives behave, more or less, as the unsubstituted analogues, where its electron-withdrawing inductive power is counterbalanced by its mesomeric character, resulting in an increased mesophase stability of the resulting complex as evidenced by their relatively high T_C values (see Table 1, where **X**=Br while **Y** is varied).

Figures 1 and 2 were used to calculate the slope and intercept of each of their regression lines from which $\Delta\alpha_{M(X)}$ and $\Delta\alpha_{M(Y)}$ are calculated. The results of the computation are given in Table 2. Table 2 shows that the polarizability anisotropy $\Delta\alpha_{M(Y)}$ of the complex except the substituent **X** decreases, according to **Y**, in the order

$$NO_2 > CH_3O \approx CH_3 > H \approx Br.$$

TABLE 2 Regression Analyses Data for the van der Veen Correlations

System	X	Y	Slope × 10^{23} Cm^3	Intercept	$\Delta\alpha_{M(X)}$ × 10^{24} Cm^3	$\Delta\alpha_{M(Y)}$ × 10^{24} Cm^3
I/**II**$_a$		CH_3O	1.89	21.68	–	11.50
I/**II**$_b$		CH_3	1.91	21.34	–	11.17
I/**II**$_c$		H	1.94	20.72	–	10.52
I/**II**$_d$		Br	2.09	21.85	–	10.45
I/**II**$_f$		NO_2	1.62	22.14	–	13.67
I$_a$/**II**	CH_3O		2.11	21.64	10.12	–
I$_b$/**II**	CH_3		2.16	21.35	9.88	–
I$_c$/**II**	H		2.57	20.72	8.06	–
I$_d$/**II**	Br		2.16	20.97	9.71	–
I$_e$/**II**	NO_2		1.26	21.37	16.96	–

The high anisotropy of polarizability of the nitro-substituted complex may be ascribed to the high molecular ordering observed in the pure solid component ($\Delta S = 65.9 \times 10^3/(205 + 273) = 137.8$ J/mol/K).

On the other hand, as can also be deduced from Table 2, $\Delta\alpha_{M(X)}$ of the complex, except the substituent **Y** decreases, according to **X,** in the order

$$NO_2 > CH_3O > CH_3 > Br \approx H.$$

This nearly similar order, again ensures the similarity between the unsubstituted and bromo derivatives, either in the acid or pyridine sides of the complex.

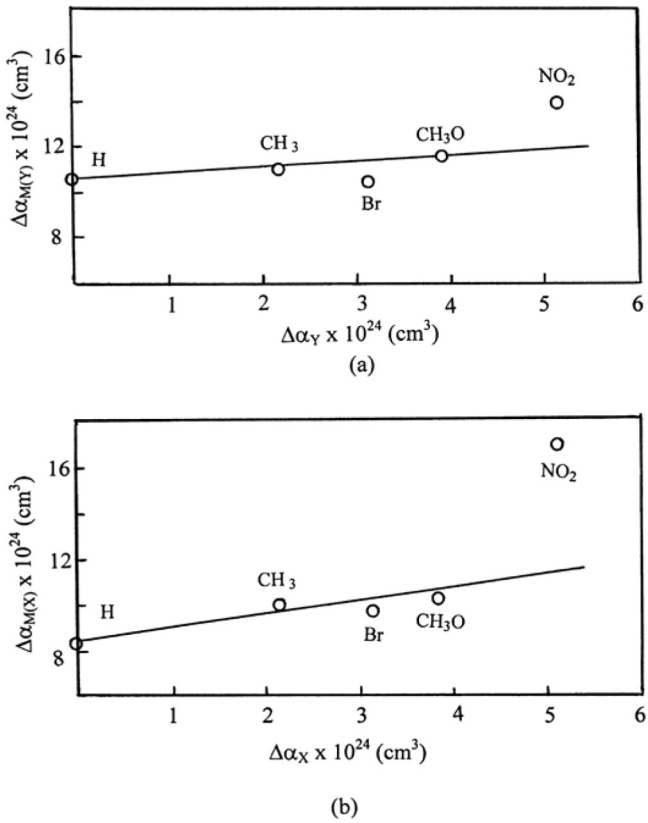


FIGURE 3 (a) Dependence of the polarizability anisotropy ($\Delta\alpha_{M(Y)}$) of the investigated 1:1 adducts, except the substituent (X), on the polarizability anisotropy ($\Delta\alpha_Y$). (b) Dependence of the polarizability anisotropy ($\Delta\alpha_{M(X)}$) of the investigated 1:1 adducts, except the substituent (Y), on the polarizability anisotropy ($\Delta\alpha_X$).

In order to investigate the relative effectiveness of the substituents (**X** with **Y**) on the mesophase stability, the polarizability anisotropy of the whole molecular structure except either of the substituents **X** or **Y** (i.e., $\Delta\alpha_{M(X)}$ and $\Delta\alpha_{M(Y)}$) are plotted as a function of $\Delta\alpha_X$ and $\Delta\alpha_Y$, respectively, in Figs. 3a, b. Figure 3 showed acceptable linear dependencies of the polarizability of anisotropy $\Delta\alpha_{M(X)}$ or $\Delta\alpha_{M(Y)}$ on $\Delta\alpha_X$ or $\Delta\alpha_Y$, respectively, except for the nitro substituent. This is again in accordance with the irregular results obtained before.

CONCLUSIONS

Five pyridine-based azo derivatives of the type 4-(4′-pyridylazo phenyl)-4″-substituted benzoates, $\mathbf{I}_{a-e}$, were prepared in which the substituent varies between CH_3O, CH_3, H, Br, and NO_2 groups, respectively. The effect of the electron donating or electron withdrawing character of the substituent on both sides of the supramolecular hydrogen-bonded complexes with six differently substituted benzoic acids, $\mathbf{II}_{a-f}$, on the possibility of formation, and stability of the mesophase of the resulting adducts was investigated via differential scanning calorimetry and polarized-optical microscopy. The study revealed that:

1. Most of the mixtures, in their 1:1 molar ratio, proved to exhibit a nematic mesophase.
2. The stability of the mesophase, expressed as the clearing temperature, is found to be greatly influenced by the nature of the substituent on either side of the new elongated mesogen.
3. Electron-donating substituents on the pyridine side, together with electron-withdrawing substitution on the acid side of the complex, were found to be most effective on mesophase stability.
4. Acceptable linear correlations, between $\sqrt{T_C}$ and the polarizability anisotropy of bonds to substituent on either side of the complexes, were obtained.
5. Except for the nitro substituent, the polarizability anisotropy of the whole molecular structure except one of the two substituents was almost linearly related to those of the bond with the substituent remained, indicating a strong dependency of the stability of the mesophase upon substitution on either side of the complex.

REFERENCES

[1] Lehn, J. M. (1988). *Angew. Chem. Int. Ed. Engl.*, *27*, 89.
[2] Constantinos, M. P., & Dimitris, T. (2001). *Liq. Cryst.*, *28*, 1127.

[3] Price, D. J., Adams, H., & Bruce, D. W. (1999). *Mol. Cryst. Liq. Cryst.*, *289*, 127.
[4] Naoum, M. M., Fahmi, A. A., & Alaasar, M. A. (2008). *Mol. Cryst. Liq. Cryst.*, *482*, 57.
[5] Naoum, M. M., Fahmi, A. A., & Alaasar, M. A. (2008). *Mol. Cryst. Liq. Cryst.*, *487*, 74.
[6] Cammenga, H. K., Eysel, W., Gmelin, E., Hemmiger, W., Hoehne, G. W. H., & Sagre, S. M. (1993). *Thermochim. Acta*, *219*, 333.
[7] Paleos, C. M., & Tsiourvas, D. (2001). *Liq. Cryst.*, *28*, 1128.
[8] Bernhardt, H., Weissflog, W., & Kresse, H. (1996). *Angew. Chem. Int. Ed. Engl.*, *35*, 874.
[9] van der Veen, J. (1975). *J. Phys. Colloq. C1*, *36*, 375.
[10] Naoum, M. M., Saad, G. R., Nessim, R. I., & Abdel Aziz, T. A. (1998). *Liq. Cryst.*, *25*, 73.