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Effect of intermolecular hydrogen-bonding and terminal substituents on the mesophase behavior of binary mixtures of dissimilarly-substituted benzoic acids

Refaat I. Nessim [a,*], Maher I. Nessim [b]

[a] Department of Chemistry, Faculty of Science, Cairo University, Cairo 00202, Egypt
[b] Department of Analysis and Evaluation, Egyptian Petroleum Research Institute, Egypt

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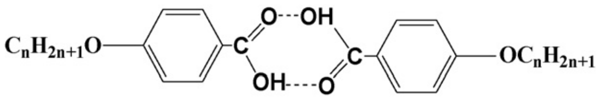
ABSTRACT

Binary mixtures of two types of 4-substituted benzoic acids, covering the whole composition range, were prepared by melting both components together, stirring to give an intimate blend, and then cooling to room temperature. The mixtures prepared were characterized for their mesophase behavior by differential scanning calorimetry (DSC) and polarized-optical microscopy (POM). The first type of the acid is substituted with a small compact polar group that cover a wide range of polarity. The other type of the acid is 4-alkoxy benzoic acid bearing an alkoxy (OC_nH_{2n+1}) group with varying chain length ($n = 6–16$). Binary phase diagrams were constructed whereby all phases observed were identified by POM. The smectic C (SmC) mesophase was observed in all mixtures investigated, while the nematic phase (N) was observed, together with the SmC phase, only in mixtures possessing the acid homologues with $n \leq 12$ carbons.

Complex formation was also supported by FT-IR spectroscopic measurements.

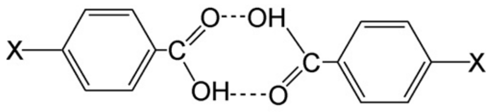
1. Introduction

Usually, at least two rings are required to enable the generation of liquid crystal phases; however, 4-alkoxy (or alkyl) benzoic acids are the only examples of one-ring mesogens. In a single molecule, the actual molecular species is certainly not long or lath-like; however, dimerization through hydrogen-bonding creates a long lath-like structure **(1)** with a three-ring core and two flexible terminal chains [1].



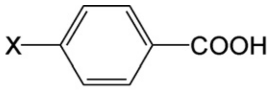
Dimer A-A (**1**)

Benzoic acid derivatives were the most frequently employed components for the formation of LC materials through such hydrogen–bonding interaction [2]. Wing polar groups are usually used in the modification of a liquid crystal material. Since calamitic (rod-like) molecule has two ends, the wing groups may be similar or different. Many terminal units have been employed in the generation of liquid crystals, but the most successful route [3] is to use either a fairly long, straight hydrocarbon (usually alkyl or alkoxy), or small polar substituent (e.g. CH_3, CH_3O, CN, NO_2, Cl, etc.). The role of these groups is to act either as a flexible extension to the core or as a dipolar moiety to introduce anisotropy in physical properties. The option to choose dissimilar wing groups in the case of 4-substituted benzoic acids is not allowed, since we come with either an acid B, ($\mathbf{I}_{a-f}$), substituted with a small compact polar terminal group (X) to give the non-mesomorphic dimer **(2)**,



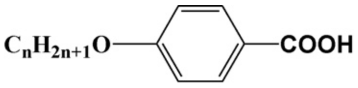
Dimer B-B (**2**)

Or the mesomorphic benzoic acid (**I***n*) substituted with 4-alkoxy group **(1)**.



$\mathbf{I}_{a\text{-}f}$

Acid B. . .$\mathbf{I}_a$, X = CH_3O; $\mathbf{I}_b$, X = CH_3; $\mathbf{I}_c$, X = Cl; $\mathbf{I}_d$, X = Br; $\mathbf{I}_e$, X = CN; $\mathbf{I}_f$, X = NO_2.



I*n*

Acid A. . .**I**6, $n = 6$; **I**8, $n = 8$; **I**10, $n = 10$; **I**12, $n = 12$; **I**16, $n = 16$.

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* Corresponding author. Tel.: +20 101649558; fax: +20 24591403.
E-mail address: refaat_nessim@hotmail.com (R.I. Nessim).

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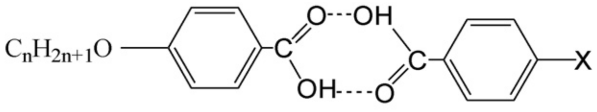
The goal of the present investigation is to allow hydrogen bond formation between two dissimilar acids (**I***n* and $\mathbf{I}_{a-f}$) aiming to form a new type of mesogen **(3)** that bears two dissimilar wing groups (X and $C_nH_{2n+1}O$).



Dimer A-B (**3**)

The idea can be realized simply by investigating, first, the binary phase behavior through binary phase diagrams of two differently substituted benzoic acids; the first bears a small compact group of different polarity and the other bears a terminal alkoxy group of varying chain length.

The study aims further to investigate the mesomorphic characteristics of the all possible supramolecular complexes that could be formed alternatively between each of the acids $\mathbf{I}_{a-f}$ and **I***n*.

2. Experimental

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

Infrared spectroscopic measurements were recorded at room temperature in a Nicolet, model Magna 560 FT-IR spectrometer at a resolution of 2 cm^{-1}.

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. [4]. DSC measurements were carried out for 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 an inert atmosphere of nitrogen gas (10 ml/min).

Transition temperatures were checked and type of mesophase identified for the mixed derivatives (**I***n*), and the binary associates of the acids (**I***n* and $\mathbf{I}_{a-f}$), using a standard polarized-optical microscope POM (Wild, Germany) attached to a home- made hot-stage where the temperature is measured by a thermocouple attached to Brookfield temperature controller, England.

2.1. Preparation of supramolecular complexes

For the preparation of the supramolecular acid complexes (**I***n*/$\mathbf{I}_{a-f}$), binary mixtures of any two complimentary acids, were prepared in a 1:1 molar ratio of samples, (acid A:acid B = 1:1), by melting the appropriate amounts of each component, stirring to give an intimate blend, and then cooling with stirring to room temperature.

For the construction of binary phase diagrams, the mixtures of the two components were prepared to cover the whole range of composition. Transition temperatures obtained for all prepared blends, as measured by both DSC and POM, agreed within 2–3 °C. In the phase diagrams constructed by plotting the transition temperatures versus mixture composition, the symbol "○" denotes solid-mesophase, "□" mesophase-isotropic transitions, "●" mesophase-another mesophase, and, "△" eutectic temperature.

3. Results and discussion

3.1. Characterization of hydrogen-bonded complexes

Hydrogen-bonded complex formation was confirmed by:

Table 1
Acid carbonyl frequencies (in cm^{-1}) in their homo and hetero substituted states for some selected examples of the complexes.

Compound	X	Y	Homo acid	Hetero acid
I12	$C_{12}H_{25}O$	$C_{12}H_{25}O$	1682	–
$\mathbf{I}_e$	CN	CN	1720	–
$\mathbf{I}_a$	CH_3O	CH_3O	1682	–
I12/$\mathbf{I}_a$	$C_{12}H_{25}O$	CH_3O	–	1682
I12/$\mathbf{I}_e$	$C_{12}H_{25}O$	CN	–	1702

3.1.1. Infrared spectra

Complex formation was supported by FT-IR measurements, according to which the initial dimeric acid, A–A or B–B, is replaced by the heterocomplex dimer, A–B [2]. Certainly, the relative acid strength of the two complementary components of the complex has a crucial effect upon the strength of newly formed hydrogen-bond, and consequently upon mesomorphism. This in turn, is influenced by the nature of the terminal substituents on both acids. Thus, for instance, electron-withdrawing substituents are expected to enhance acidity of the acid-proton, and consequently add extra stability of the hydrogen-bonding. Generally, the hydroxyl stretching vibration band appears in the region 3400–3600 cm^{-1}, however, the resolution is so poor that it is not possible to discern between free and hydrogen-bonded ones. Therefore, only the carbonyl stretching region is used to confirm hydrogen-bond formation [5]. Table 1 summarizes the acid carbonyl frequencies in their similar and dissimilar states, for some selected examples of the heterocomplexes that show extremes in polarities.

As can be seen from Table 1, Carbonyl groups of the homo acids of the type A–A, that bearing either the alkoxy group e.g. $C_{12}H_{25}O$ in I12 or the methoxy group in $\mathbf{I}_a$ of the homo acid, both absorb at the same frequency (1682 cm^{-1}) revealing that the length of the alkoxy group does not affect the polarizability of the carbonyl group. On the other hand, the electron-withdrawing cyano group, located in the para position with respect to the carbonyl group in $\mathbf{I}_e$ increases its double bond character and a red-shift is observed in the carbonyl-absorption frequency that appeared at 1720 cm^{-1}. With respect to the complex **I**12/$\mathbf{I}_a$, that is substituted on both sides with two different alkoxy groups (CH_3O and $C_{12}H_{25}O$), it absorbs at the same frequency as that of the pure components, namely 1682 cm^{-1}. Alternatively, the complex **I**12/$\mathbf{I}_e$ that is terminally substituted with the electron-donating $C_{12}H_{25}O$ on one side and the electron-withdrawing CN group on the other side, proved to exhibit one absorption band at intermediate frequency, 1702 cm^{-1}.

3.1.2. Constructing the binary phase diagrams covering the whole range of composition for any two dissimilar acid components

It is well known that 4-substituted benzoic acids form dimmer via hydrogen-bonding as given by the formulae **1** (**A**–**A**) and **2** (**B**–**B**). Upon mixing two different acids, one from each group ($\mathbf{I}_{a-f}$ and **I***n*), there are two possibilities to arrange the molecules of one component within the molecular arrangement of the other. The first possibility is that long-lath dimers (**A**–**A** and **B**–**B**) will be arranged side-by-side without being ruptured during mixing. In such case, a solid solution is expected either to from both components with melting temperature changes regularly from that of the first component to that of the other, or at least pass through one eutectic composition. Also in such case, the mesophase stability of the alkoxy component **(1)** will be gradually disrupted by the gradual addition of the non-mesomorphic component **(2)**, and consequently linear composition dependence is expected for mixed mesophase stability.

The other possibility for molecular arrangement in mixed systems may take place by rupturing the hydrogen bonds in both dimmers resulting in the formation of a new unsymmetrical dimmer **(3)**.

To investigate which type of molecular arrangement actually takes place in our system, let us first construct the binary phase diagrams for selected representative examples composed from both types of acids. Two homologous of extreme chain length (**I**8 and **I**16) were chosen from the acid 1 that bears 8 and 16 carbons, respectively. The longer homologue is smectogenic, possessing the smectic C (SmC) phase as the only mesophase, while the shorter one is dimorphic, possessing both the SmC and nematic (N) mesophases. On the other hand, two extremes of the acid **(2)** were selected where one ($\mathbf{I}_a$) bears the strong electron-donating CH_3O group and the other ($\mathbf{I}_e$) is substituted with the strong electron-withdrawing CN group.

3.2. Binary phase behavior

Fig. 1 represents the two binary phase diagrams of the electron-donating substituted acid ($\mathbf{I}_a$) with the two homologues of 4-alkoxy benzoic acid (**I**8 and **I**16). As can be seen from Fig. 1, independent of the length of the alkoxy chain (8 or 16 carbon atoms), supramolecular complexes are produced in both systems. Complex formation in the solid phase is evidenced by the two eutectic points, one preceding and the other following the 1:1 molar ratio (50 mol%). The hydrogen-bonded complex is retained in the mesophase as confirmed by the enhanced stability of the mesophase. These results revealed that the second possibility of molecular rearrangement, as given by formula **3**, most probably prevails.

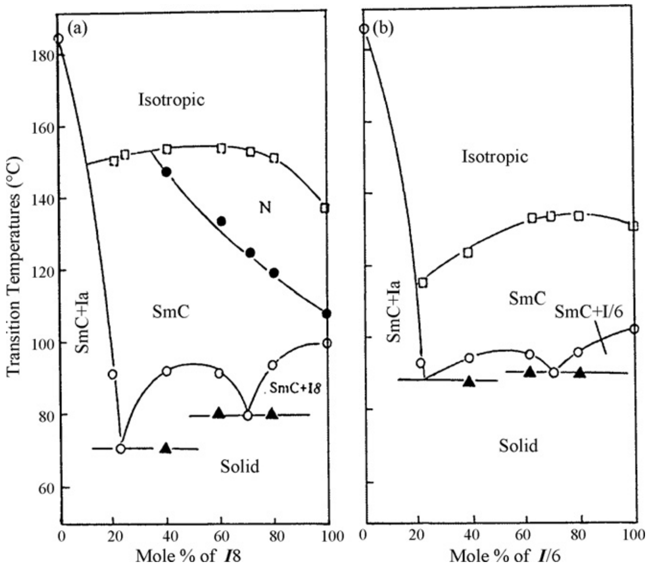


Fig. 1. Binary phase diagrams of the 4-methoxy benzoic acid ($\mathbf{I}_a$) with: (a) octyloxy benzoic acid, and (b) hexadecyloxy benzoic acid.

To test if complex formation is restricted by the polarity of the substituent X, we are going to investigate the binary phase behavior of the other extreme in polarity, where X is the strong electron-withdrawing CN group, in $\mathbf{I}_e$. Fig. 2 describes the binary phase behavior of $\mathbf{I}_e$ when mixed with the same homologues of acid **I**8 and **I**16. As can be seen from Fig. 2, hydrogen bonded complexes are again observed in either the solid or mesophases, independent of the alkoxy-chain length. These results revealed that the affinity of individual acids towards hydrogen bond formation with each other is much greater than that occurring within molecules of the same acid. This may be ascribed to the dual electronic effect of the polar substituent on the individual members of the group $\mathbf{I}_{a-f}$. That is, electron-donating group will increase the electron density on the carbonyl group of the acid, thus enhances the strength of the hydrogen bond. Alternatively, electron-withdrawing group lead to an increase of the acidity of hydrogen, leading to increased probability for hydrogen bond formation.

Being confirmed, all possible supramolecular complexes **(3)** were prepared using each of the 4-substituted benzoic acids $\mathbf{I}_{a-f}$, alternatively with each of the homologues **I***n* in a 1:1 molar ratio and their mesophase behavior investigated by DSC and phases detected by POM. The results are collected in Table 2.

Table 2
Phase transition temperatures (°C) of the 1:1 complexes of the system $\mathbf{I}n/\mathbf{I}_{a-g}$.

System	*n*	X	T_{Cr-C}	T_{C-N}	T_{C-I}	T_{N-I}	$\sqrt{T_C}$ ($K^{1/2}$)
$\mathbf{I6/I_a}$	6	CH_3O	95.2	144.3	–	155.3	20.7
$\mathbf{I6/I_b}$		CH_3	96.5	120.7	–	143.0	20.4
$\mathbf{I6/I_c}$		Cl	100.6	132.2	–	147.1	20.5
$\mathbf{I6/I_d}$		Br	93.5	132.5	–	151.2	20.6
$\mathbf{I6/I_e}$		CN	99.5	144.0	–	163.7	20.9
$\mathbf{I6/I_f}$		NO_2	107.7	122.0	–	172.1	21.1
$\mathbf{I8/I_a}$	8	CH_3O	94.2	140.1	–	155.3	20.7
$\mathbf{I8/I_b}$		CH_3	106.2	123.2	–	143.0	20.4
$\mathbf{I8/I_c}$		Cl	95.1	136.2	–	151.2	20.6
$\mathbf{I8/I_d}$		Br	96.5	131.4	–	147.1	20.5
$\mathbf{I8/I_e}$		CN	80.0	144.8	–	172.1	21.1
$\mathbf{I8/I_f}$		NO_2	89.6	140.1	–	176.3	21.2
$\mathbf{I10/I_a}$	10	CH_3O	94.4	–	147.1	–	20.5
$\mathbf{I10/I_b}$		CH_3	89.5	130.3	–	138.9	20.3
$\mathbf{I10/I_c}$		Cl	87.7	–	143.0	–	20.4
$\mathbf{I10/I_d}$		Br	86.5	–	147.1	–	20.5
$\mathbf{I10/I_e}$		CN	108.2	–	159.5	–	20.8
$\mathbf{I10/I_f}$		NO_2	88.9	–	–	167.9	21.0
$\mathbf{I12/I_a}$	12	CH_3O	108.7	–	140.8	–	20.4
$\mathbf{I12/I_b}$		CH_3	97.0	–	133.9	–	20.2
$\mathbf{I12/I_c}$		Cl	96.6	–	140.6	–	20.3
$\mathbf{I12/I_d}$		Br	100.0	–	142.6	–	20.4
$\mathbf{I12/I_e}$		CN	95.7	–	160.5	–	20.8
$\mathbf{I12/I_f}$		NO_2	99.1	–	164.0	–	20.9
$\mathbf{I16/I_a}$	16	CH_3O	95.8	–	129.7	–	20.1
$\mathbf{I16/I_b}$		CH_3	93.5	–	126.0	–	19.9
$\mathbf{I16/I_c}$		Cl	86.5	–	130.9	–	20.1
$\mathbf{I16/I_d}$		Br	87.5	–	129.7	–	20.2
$\mathbf{I16/I_e}$		CN	86.2	–	147.8	–	20.5
$\mathbf{I16/I_f}$		NO_2	95.3	–	142.9	–	20.4

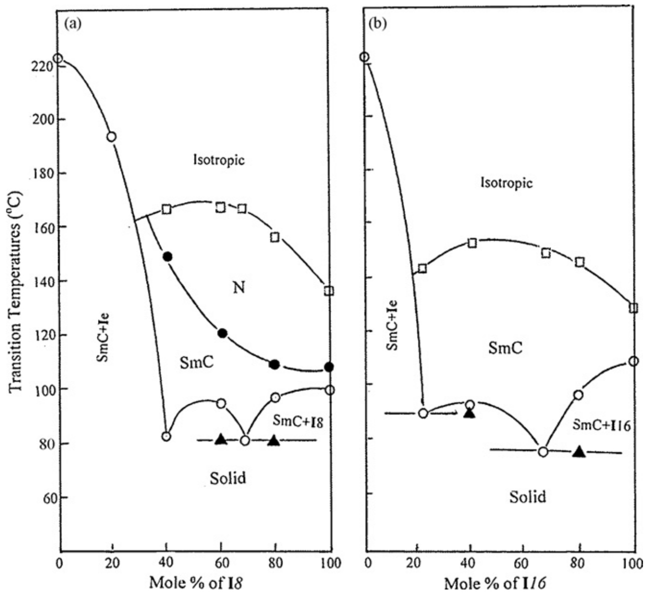


Fig. 2. Binary phase diagrams of the 4-cyano benzoic acid ($\mathbf{I}_g$) with: (a) octyloxy benzoic acid, and (b) hexadecyloxy benzoic acid.

3.2.1. *Effect of alkoxy-chain length on complex formation*

In order to investigate the effect of the alkoxy-chain length on complex **3**, on the liquid crystalline properties of the supramolecular complexes, the dependences, on the acid alkoxy-chain length (n), of transition temperatures of the supramolecular complexes are depicted in Fig. 3. As can be seen from Fig. 3, polar substituent, whether it is electron-donating or electron-withdrawing, are effective in promoting the smectic C mesophase. Irrespective of the substituent, X, the stability of the SmC phases decreases slightly with the increase of the length of the alkoxy chain. The nematic phase appears only with the shorter homologues (**I**6 and **I**8) and remains up to the homologue **I**10 with 4-methyl benzoic acid ($\mathbf{I}_b$). The greatest nematic temperature range is observed with the 4-nitro analogue, while the smallest range is exhibited by the 4-methoxy substituted complex. As usual the melting point of the complexes does not change regularly with chain length.

3.2.2. *Transition temperatures and polarizability anisotropy of the C_{ar}-X*

The relationship between the stability of the mesophase, expressed as the clearing temperature, 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 [6]. The relationship is expressed as:

(1)$T_C \alpha (\Delta\alpha_M + D\alpha_X)^2$where T_C is measured in Kelvin. Eq. (1) can be put in the form [7]:

(2)$T_C^{1/2} \alpha (\Delta\alpha_M + \Delta\alpha_X) = \alpha\Delta\alpha_M + a\Delta a_X$

The term $\Delta\alpha_M$ is the polarizability anisotropy of the whole molecular structure except the terminal substituent, X, and “a” is

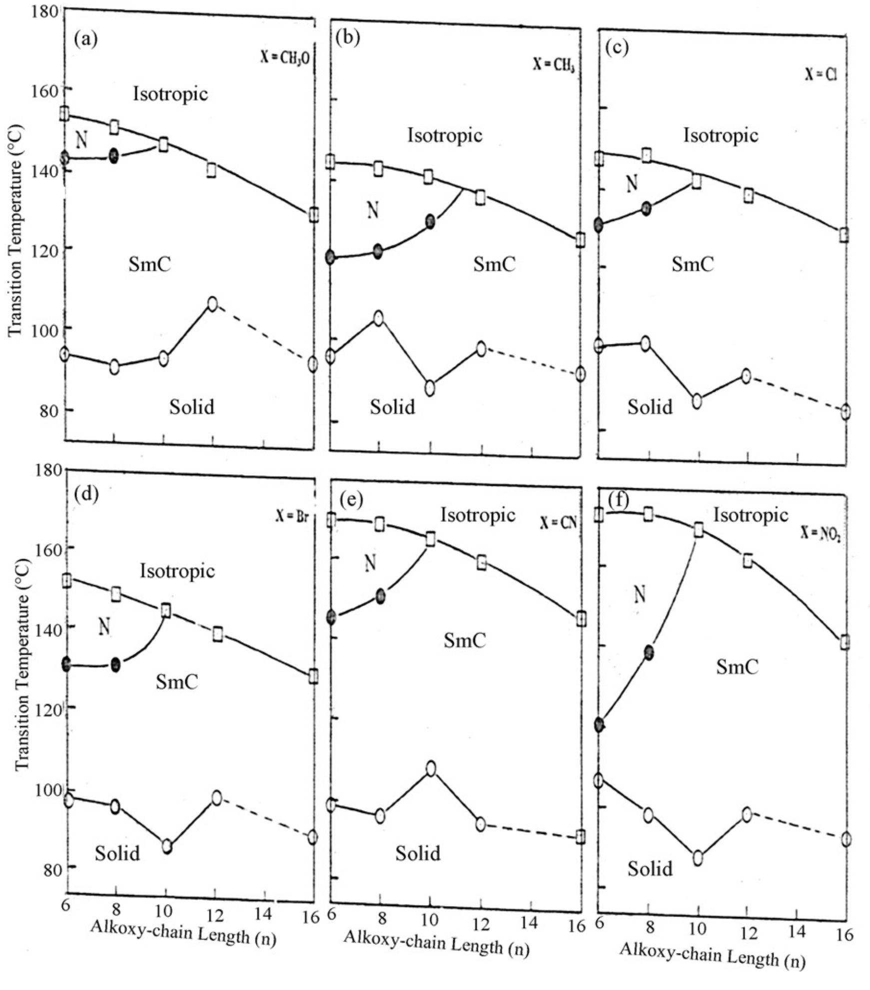


Fig. 3. Effect of the alkoxy-chain length (n) on the mesophase behavior of the supramolecular complexes $\mathbf{I}n/\mathbf{I}_{a-g}$.

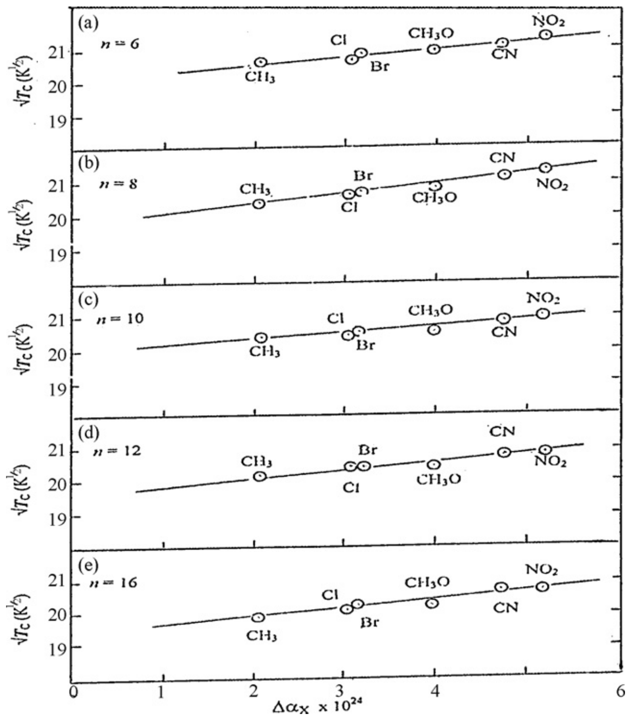


Fig. 4. Dependence of the mesophase stability ($T_C^{1/2}$) of the investigated supramolecular complexes on the polarizability anisotropy ($\Delta\alpha_X$) of the acid substituent (X).

the proportionality constant. The values of $\Delta\alpha_X$ were [4] calculated from the data given by Le Fevre and co-workers [8–10]. Thus, if, $T_C^{1/2}$ of any of the investigated hydrogen-bonded dimmer bearing one and the same acid alkoxy substituent "C_nH_{2n+1}" but of varying polar substituent "X", is plotted against $\Delta\alpha_X$, a straight line is expected with a slope "a" and intercept equals "$a\Delta\alpha_M$". Where "$\Delta\alpha_M$" is the polarizability anisotropy of the whole of the molecular structure except the substituent (X). Fig. 4 illustrates the dependency of the $T_C^{1/2}$ values on the polarizability anisotropy of the bonds to X in the polar substituted benzoic acid component of the supramolecular complex, individually, with different substituted acids (**I**$_a$–**I**$_f$).

As can be seen from Fig. 4, fairly linear dependencies were observed in nearly all series investigated. This indicates that polarity and/or polarizability on one side of the complex play a main role in stabilizing the mesophase of the resulting unsymmetrical dimmer. It would be worth mentioning here that the chloro- and bromo- substituted acid derivatives are more effective, than the unsubstituted analogue, in stabilizing the hydrogen-bonded associates. The electromeric releasing power of the halogen is completely counterbalanced by its electron-withdrawing inductive character, resulting in an increased mesophase stability of the resulting associate, as evidenced by their relatively high T_C values. Unsubstituted benzoic acid was tested but the mixtures do not show a mesophase.

Table 3
Regression analyses data for the van der Veen correlations for supramolecular complexes investigated.

System	N	X	Slope × 10^{-23}	Intercept	$\Delta\alpha_M \times 10^{23}$
I6/**I**$_{a-g}$	6	Varies	1.8	20.05	11.13
I8/**I**$_{a-g}$	8	Varies	3.15	19.61	6.23
I10/**I**$_{a-g}$	10	Varies	1.75	19.94	11.39
I12/**I**$_{a-g}$	12	Varies	2.47	19.61	7.94
I16/**I**$_{a-g}$	16	Varies	2.10	19.55	9.31

Fig. 4 was used to calculate the slope and intercept of each of their regression lines from which $\Delta\alpha_M$ are calculated. The results of the computation are given in Table 3 which shows that the polarizability anisotropy $\Delta\alpha_M$ of the whole complex, except the substituent X, decreases according to n in the order:

$10 > 6 > 16 > 12 > 8$.

This order reveals that the polarizability anisotropy of the whole molecular structure, expect the substituent X, is independent on the length of the molecule.

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