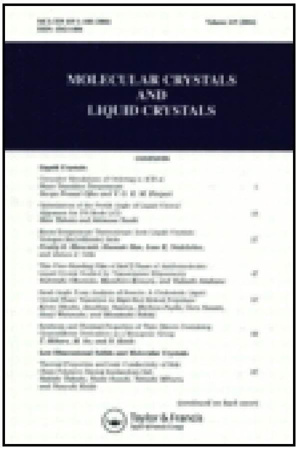

Molecular Crystals and Liquid Crystals

Molecular Parameters of Glass Forming Disc-Like Mesogens

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MOLECULAR PARAMETERS OF GLASS FORMING DISC-LIKE MESOGENS

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With the help of the HyperChem Pro 6.0 program we have constructed and optimized the models for a new series of molecular structures, that comprise 43 non-mesogenic and mesogenic disc-like, glass-forming and non-glass-forming compounds of known structure with the domination of glass-forming, disc-like mesogens. We have calculated the molecular parameters for all the compounds of the series. Later, with the help of these parameters, the possibility of selection of the next two series was analyzed: 1) the class of disk-like mesogens; 2) the sub-class of glass-forming, disc-like mesogens in the disc-like mesogen class. It has been defined that in this series of compounds the disc-like mesogen class can be selected the probability within a 90% probability range, while the sub-class of glass-forming disc-like mesogens was selected within the 60% probability range.

Keywords: columnar mesomorphism; disc-like mesogens; glass-forming; mesogenic compounds; mesomorphic behaviour prediction; structure-property relations

INTRODUCTION

The directed synthesis of discotic mesomorphic compounds, including those which have a glass transition, is an important task for the physics and chemistry of liquid crystals as well as for practical applications [1].

Recent research [2] points to a certain similarity of liquid crystal and glass-like states. In each of them there can be observed characteristic structural elements, polymorphism, micro-heterogenity of the media and other properties. The very process of turning a liquid crystal into a

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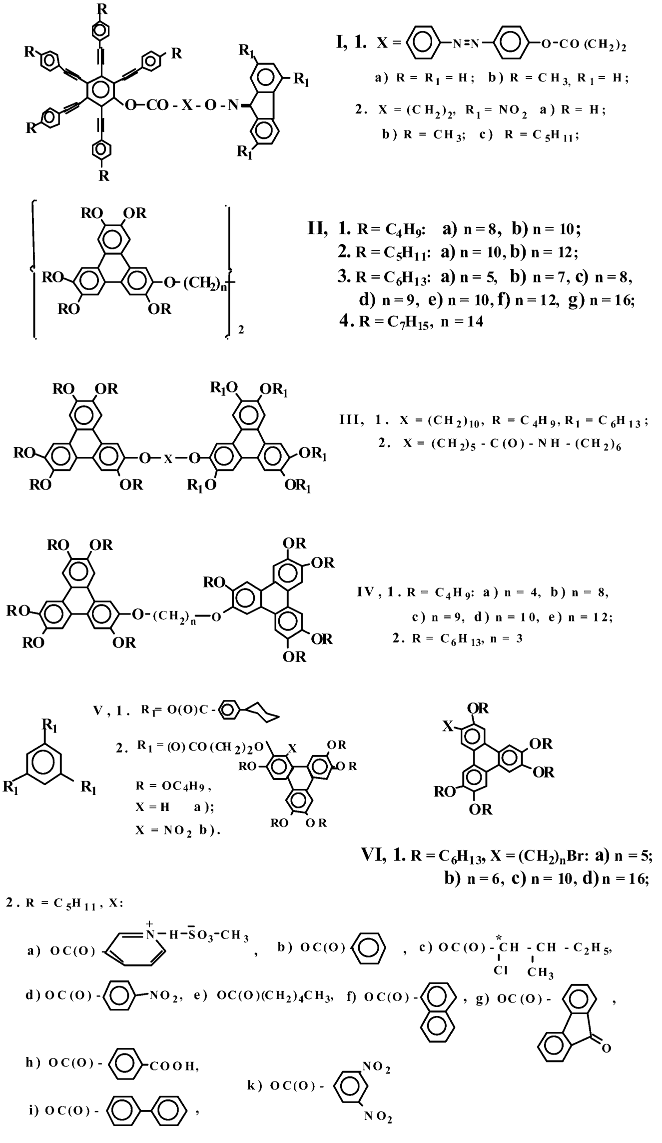


FIGURE 1 Presentation of the structures of disc-like molecules, **I–VI**, [10–16].

glass-like state after having being strongly supercooled is a frequent phenomenon. For instance, in ref. [2] there have been given the data on the systematic research of such transition in calamitic carboxylate salts which are ionic liquid crystals [3]. For them the authors of [4] found some numerical criteria of the mesogenity, these are defined by the cation charges and the radius of the cations and anions, for the constituents of these salts. In such a way, the structure of matter, being defined on the micro-level, leads to its transition to the mesomorphic state on the macro-level. The transition of metallomesogens into the isotropic or anisotropic glass-like state, according to ref. [2], depends on the value of T_g. Undoubtedly, glass-formation is mainly defined by the kinetics of the phase transition. But at comparable rates of cooling of the mesogens as well as other external conditions, as we suppose, to the foreground comes the characteristic structure of the molecules, which determines, in most cases, the transition of matter into the glass-like state.

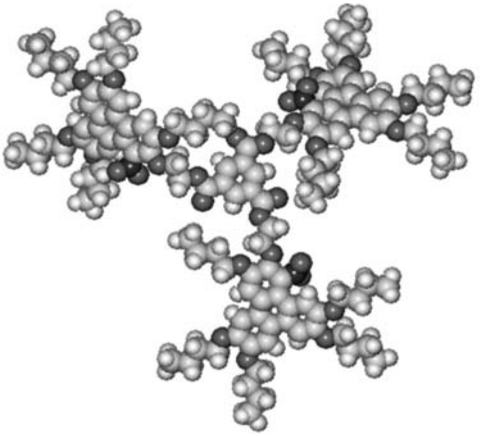
While for calamitic liquid crystals, as we have seen, there have been some attempts to define the qualitative and quantitative interdependence of the mesomorphic compounds glass-formation process and their molecular structure. However, for disc-like mesogens such interdependency has not been investigated. Earlier [5] we have evaluated only qualitative peculiarities of the molecular structure of the compounds, predominantly with a disc-like form, that influence the glass-formation of the mesophases. In this paper we have attempted to find the quantitative molecular parameters of the glass-forming disc-like mesogens based on their molecular structure. In our efforts we have relied on our experience in the definition of the mesogenic state of disc-like compounds through the analysis of the quantitative properties calculated from the molecular structure [6]. The appropriateness and the heuristicity of this method are supported by numerous data on the prediction of columnar and nematic mesomorphism of the new disc-like compounds of various structures and by comparison with the experimental results [7–9]. This method has not yet been applied for compounds with glass-forming mesophases. In order to explore its relevance, we have reviewed the behaviour of a new series of compounds **I–VI,** shown in Figure 1.

METHODS AND MATERIALS

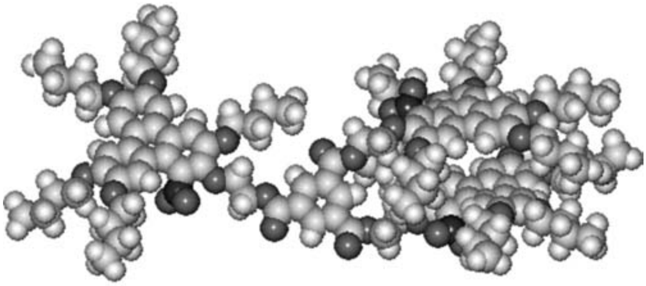
The preferred approach to solve the formulated problem is first calculation and then analysis of the molecular parameters. The calculation technique does not differ from that proposed earlier [7–9]. The molecular structures were optimized by a molecular-mechanics method (force field MM+) with the help of the *HyperChem Pro 6.0* program. Optimization of the molecular geometry was finished at a gradient of 0.01 kcal/mol.

Seven different, non-dimensional molecular parameters were calculated, using the program module *ChemCard* [9]: K, K_c, K_s, K_p, K_{ar} M_m, and M_r [8]. We now describe in detail these parameters:

1. Parameters connected with the anisometric properties of a molecule or its constituent parts ($K = L_{max}/s$, L_{max} – maximum length of the molecule, s – thickness of the molecule in the stable conformation; $K_c = l_c/b_c$,, l_c – length of the centre, b_c – width of the centre including the adjoining heteroatoms; $K_p = l_c/\ 2l_p$, where $2l_p$ the length of the periphery, hydrocarbon moieties being in their all-trans conformation).



(a) **IIIb** (X= NO_2, R=C_4H_9) [9], *star* conformation
E = 195.8 kcal/ mol; ***MP***: $\boldsymbol{M_m}$= 1.08, $\boldsymbol{M_r}$ = 0.61,
$\boldsymbol{K_c}$ = 1.02, $\boldsymbol{K_p}$ = 0.35, ***K*** = 2.19, $\boldsymbol{K_{ar}}$ = 0.464.
Prediction with ***KM*** is (+).



(b) **IIIb**, X= NO_2, R=C_4H_9 [9], *swallow-tail* conformation
E = 163.18 kcal/mol; ***MP***: $\boldsymbol{M_m}$= 1.08, $\boldsymbol{M_r}$ = 0.61, $\boldsymbol{K_c}$ = 2.21,
$\boldsymbol{K_p}$ = 1.64, ***K*** = 5.74, $\boldsymbol{K_{ar}}$ = 0.184.
Prediction with ***KM*** is (–).

FIGURE 2 (a–c) Models of the optimized molecular structures (**IIIb**) in their stable conformations.

(c) **IIIb**, X= H, R=C_4H_9 [9], *swallow-tail* conformation
E = 143.2 kcal/ mol; ***MP***: $\boldsymbol{M_m}$= 1.24, $\boldsymbol{M_r}$ = 0.62, $\boldsymbol{K_c}$ = 1.97,
$\boldsymbol{K_p}$ = 1.63, $\boldsymbol{K}$ = 5.02, $\boldsymbol{K_{ar}}$ = 0.177.
Prediction with ***KM*** is **(–)**.

FIGURE 2 (Continued).

The parameter based on the ratio of the real number of peripheral substituents in the molecule to the maximum possible number of such substituents ($K_s = N/N_{max}$, N– number of the substituents in the molecule, N_{max}– the maximum possible number of substituents);

2. Parameters based on the ratio of the central fragment weights to the weights of the peripheral substituents ($M_m = M_c/\ M_p$, where M_c is the molecular mass of the central fragment, including heteroatoms, attached to it, M_p is the molecular mass of the periphery; $M_r = M_m K_s$ is the transformed molecular-mass parameter considering the degree of central fragment substitution by the peripheral substituents).
3. In addition to K_s, another parameter K_{ar} was introduced [7]. It made it possible to estimate the density of the peripheral substituents and so the packing of mesogenic or non-mesogenic compounds. It was calculated by using the formula: $K_{ak} = N_p/\pi(l_p^{2} + l_p^{*}\ l_c)$, N_p is the number of carbon, hydrogen and other atoms surrounding the central fragment.

The numeral values presented earlier [6–9,16] in the analysis of more than 600 non-mesogenic or mesogenic compounds serve as a mesogenic (disc-like compounds) criterion for the molecules studied. These values are as follows: $K = 2.00 - 8.50$, $K_c = 1.00 - 2.60$, $K_s = 0.25 - 1.00$, $K_p = 0.25 - 0.70$, $M_m = 0.30 - 0.80$, $M_r = 0.15 - 0.80$, $K_{ar} = 0.08 - 0.30$ **(1)** [10]. The structures, which have parameters with values in these ranges, are potentially discotic mesogens. It is necessary to emphasize that the closer the boundaries of the ranges are the less reliable the mesophase prediction is. It has been revealed that when one of the parameters falls outside the limits of this series, the probability of columnar mesomorphism for such structures is very small.

For the analysis of and search for quantitative structure-property relations for disc-like mesogens exhibiting glass-forming mesophases, we considered a new series of compounds **I–VI** (See Figure 1) with the different variants of mesomorphism being revealed [10–16]. The choice of the compounds was defined by the peculiarities of their molecular structure, they are, on a qualitative level, inherent in the glass-forming, disc-like mesogens [5]. In the series investigated there were included compounds with: i) bulky substituents, including electron acceptors, both homogeneous and heterogeneous, on the molecular perimeter; ii) asymmetric and symmetric substitution of the central nucleus and iii) the presence of flexible ethyleneoxide or olefinic chains.

RESULTS AND DISCUSSION

The 43 compounds were sub-divided into five classes: a) non-mesogenic and non-glass forming (*NM–NG*), b) non-mesogenic, but glass forming (*NM–G*), c) mesogenic, but non-glass forming (*M–NG*), d) mesogenic and glass forming (*M–G*), e) mesogenic and glass forming ($M\text{–}G_A$) materials. The groups (d) and (e) were combined, because there were only two compounds in the last group.

The first stage of the work was the selection, with the help of the molecular parameters, of the class of mesogens from the whole series of disc-like compounds. The most stable conformations of the molecules were analyzed from the optimization of the molecular structures. For the subsequent analysis we used the stable conformations that, based on their molecular properties, made it possible to make predictions that correlated with the experimental data. This approach can be illustrated with the following examples.

The models of the optimized structures of the two stable conformations: 1 – *star*, 2 – *swallow tail* for the derivatives of benzene with triphenylene fragments on the molecule perimeter [11] are shown in Figure 2. These molecular models are the basis for the calculations of the properties. The values for these properties, which exceed the limits of the numerical series (**1**), are coloured gray (See Fig. 1). It must be pointed out, that the mesomorphism prediction for compound **V, 2b (X = $\mathbf{NO_2}$)**, is negative, although we used the more energetically favourable *swallow-tail* conformation (Fig. 2b). The s*tar* conformation (Fig. 2a) of this compound is more favourable for columnar mesophase formation. Recently, it has been shown [11], that compound **V, 2b,** (**X = $\mathbf{NO_2}$**) exhibits a hexagonal columnar phase from 161.1°C to 181.3°C. The mesophase transforms into an anisotropic glass below 158.8°C, it remains in this state down to −50°C. Probably, it is connected with the *star* conformation of the molecule in the mesophase.

TABLE 1 Calculated Values of the Molecular Parameters of the Series **I–VI**

Compound	E/calmol^{-1}	K	K_p	M_m	M_r	P on (**1**)	**E**
I, 1a	62.97	2.51	0.47	0.72	0.72	+	N_{col} [14]
I, 1b	78.73	3.70	0.26	0.82	0.82	+	N_{col}
I, 2a	52.17	6.72	0.31	0.84	0.84	+	*Col*
I, 2b	73.17	7.61	0.33	0.74	0.74	+	*Col*
I, 2c	88.94	4.70	0.31	0.65	0.65	+	*Col*
II, 1a	134.40	7.04	0.84′	0.93′	0.47	±	Col_p [12]
II, 1b	135.24	7.59	0.68	0.89	0.45	+	Col_p
II, 2a	125.71	8.57	0.69	0.75	0.37	+	Col_h
II, 2b	128.06	6.50	0.62	0.72	0.36	+	Col_h
II, 2c	129.30	6.38	0.53	0.70	0.35	+	Col_h
II, 3a	132.39	6.92	0.53	0.69	0.34	+	*NM*
II, 3b	133.65	7.30	0.52	0.67	0.33	+	*NM*
II, 3c	135.97	7.00	0.59	0.66	0.33	+	Col_h
II, 3d	135.53	6.74	0.59	0.65	0.33	+	Col_h
II, 3e	136.37	6.64	0.59	0.64	0.32	+	Col_h
II, 3f	144.49	6.98	0.58	0.62	0.31	+	Col_h
II, 3g	146.73	7.39	0.48	0.59	0.30	+	Col_h
II, 4	153.69	6.86	0.51	0.54	0.27	+	Col_h
III, 1	127.56	6.82	0.59	0.64	0.32	+	Col_h
III, 2	132.87	5.51	0.53	0.62	0.31	+	Col_h
IV, 1a	120.73	5.16	0.84′	1.02′	0.51	–	*NM* [13]
IV, 1b	135.36	6.66	0.76	0.93′	0.47	±	Col_p
IV, 1c	142.82	5.64	0.76	0.91′	0.46	±	Col_p
IV, 1d	144.62	5.66	0.79′	0.89′	0.45	±	Col_p
IV, 1e	152.33	7.48	0.62	0.86′	0.43	±	Col_p-Col_h
IV, 2	124.75	7.32	1.44′	0.72	0.36	–	*NM*[12]
V, 1	64.49	4.10	0.37	0.44	0.22	+	N_D [16]
V, 2a	143.18	5.02	1.63′	1.24′	0.62	–	*NM*[11]
V, 2b	195.69	2.19	0.35	1.08′	0.61	±	Col_h
VI, 1a	72.80	3.27	0.59	0.55	0.28	+	*Col*[12]
VI, 1b	72.04	4.72	0.53	0.54	0.27	+	*NM*
VI, 1c	74.35	5.72	0.32	0.49	0.25	+	*NM*
VI, 1d	85.17	6.96	0.21′	0.44	0.22	±	*NM*
VI, 2a	86.79	2.30	1.00′	1.46′	0.73	–	*NM* [10]
VI, 2b	62.07	2.27	0.75′	0.80	0.40	±	*NM*
VI, 2c	69.76	3.30	0.58	0.65	0.33	+	Col_{Ch}^{*}
VI, 2d	68.98	2.30	0.67	0.73	0.36	+	Col_h
VI, 2e	60.47	6.52	0.70	0.81′	0.41	±	Col_{ho}
VI, 2f	74.09	2.09	0.69	0.72	0.36	+	Col_h
VI, 2g	90.57	2.14	0.69	0.65	0.32	+	Col_h
VI, 2h	68.98	2.32	0.61	0.73	0.36	+	Col_{ho}
VI, 2i	77.63	2.60	0.56	0.68	0.34	+	Col_h
VI, 2k	70.84	2.33	0.68	0.66	0.33	+	Col_{ho}

Note: ′ – indicates parameters, falling outside the limits of established boundary values; $\boldsymbol{K_c}$ = 1,0–1,97, 2,79; $\boldsymbol{K_s}$ = 0.5 end 1,0 – for this series; ***P*** – the prediction of ***M***; ***E*** – experimental data; $\boldsymbol{N_{col}}$ – columnar nematic phase, $\boldsymbol{N_D}$ – discotic nematic; *Col* – columnar phase; ***NM*** – the compound is non-mesogenic; Disagreement of the predicted results with the experimental data is highlighted in grey.

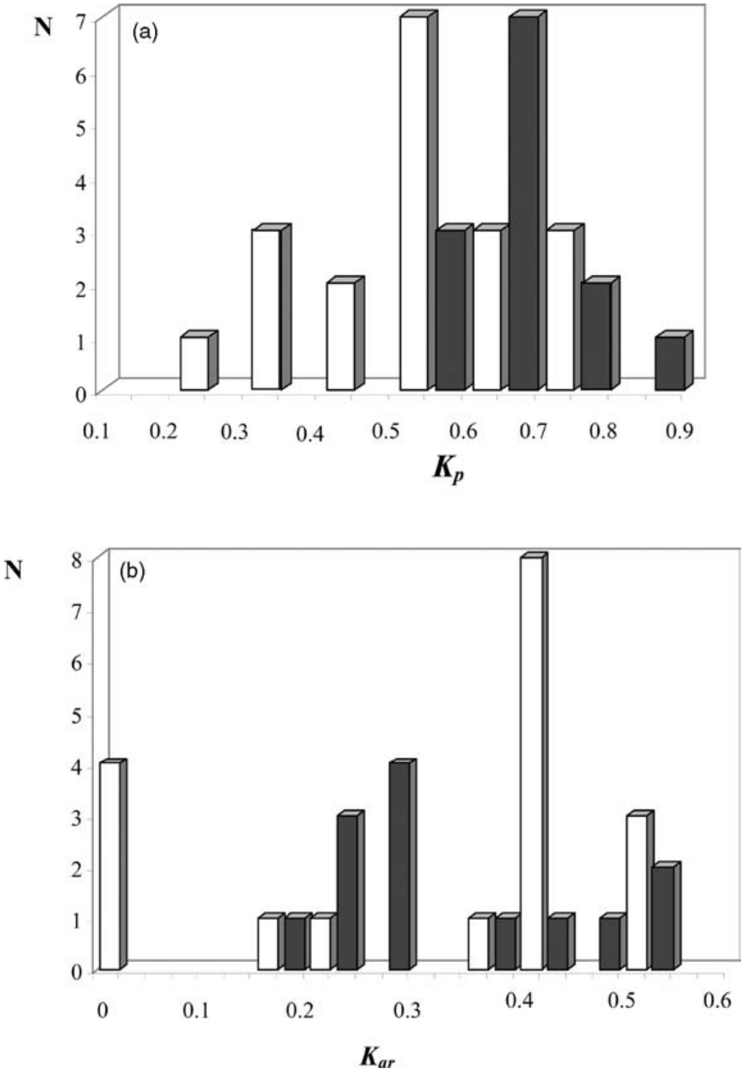


FIGURE 3 Histograms showing the distribution of glass forming (□) and non-glass forming (■), disc-like mesogens according to ***MP***: a) $\boldsymbol{K_p}$ and b) $\boldsymbol{K_{ar}}$; **N** is the number of compounds with a definite magnitude of ***MP***.

On the other hand, according to the prediction, as well as the experimental datacompound **V, 2a** (**X** = **H**) is non-mesogenic: it melts into isotropic phase below 185°C. sw*allow-tail* conformation is possibly the reason for the non-mesogenity in this case.

The construction of models of other compounds in the series **I–VI** in their stable conformations, and further calculations and the analyses of calculated properties with the help of the classificationrow (**1**), gave a sufficiently good correlation between the mesomorphism predictions and the experimental data (Table 1). For 93% of the compounds the prediction of the presence or absence of columnar mesophases coincided with the experimental results. Included in the percentage are those compounds for which the prediction of the presence or absence of the mesophases has an even probability.

Another step in the solution of this problem was the isolation of the glass-forming liquid crystal sub-class in the class of discotic mesogens using the given parameters. Unfortunately, parameters such as M_m and M_r did not make it possible for us to expose the predominant areas of their values which correspond to sub-classes *M–NG* and *M–G* and, then, apply them to the prediction of glass-forming mesophases. Indeed, we found differences in their values for the sub-classes of glass-forming and non-glass-forming mesogens for parameters K_p and K_{ar} (see Figures 3a, b).

On the histograms shown in Figures 3a, and b we can see areas of predominant values of the molecular properties for glass-forming and non-glass-forming mesogens, which are, however, partially overlayed. As a result, the use of the latter two parameters made it possible to us to select the glass-forming representatives in the discotic mesogen class with a probability of 60%.

CONCLUSION

While accepting that the formation of the glass-like state of the disc-like mesogens is connected with the kinetics of the phase formation, we have shown that, according to the molecular property, it is possible, with a certain level of probability, to identify the molecular feature which is favourable for the formation of glass-like state. Probably, the difficulties in prediction of the glass-forming sub-class are connected with the similar values of the energy in their optimised conformations compared to the non-glass-forming analogues. According to our calculations, such differences amounts, in some cases, to 0.15 kcal/mol [17].

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