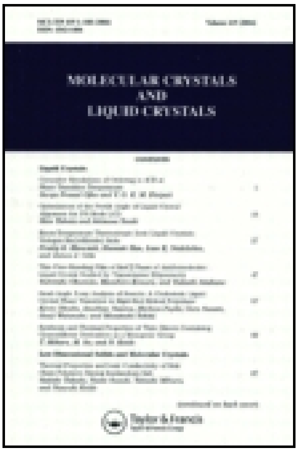

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Mesomorphic Properties of Four-Ring Systems Bearing No Terminal Substituent

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MESOMORPHIC PROPERTIES OF FOUR-RING SYSTEMS BEARING NO TERMINAL SUBSTITUENT

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Abstract Temperatures of the solid-nematic and nematic-isotropic transitions have been measured for forty-eight diverse compounds bearing no terminal substituent. Four benzene rings are connected to each other by single carbon-carbon bond(s) and/or by carbonyloxy, azomethine, and azo groups. The consequence of any linking group placed centrally in a quaterphenyl molecule is a drastic suppression of the solid state stability. The nematic-isotropic transition is hardly affected by the introduction of an azo linkage and also by an azomethine one, whereas it is significantly depressed by a carbonyloxy linkage. The presence of two or three linking groups yields generally complex effects on the thermal behavior because of the marked interdependence of the effects of the linking groups. No efficiency order in promoting a nematic phase applicable to all the compounds could be established.

INTRODUCTION

On the basis of examinations of the effects of linking groups between ring systems with various terminal substituents on the mesomorphic properties, it has been concluded that the nematic-isotropic (N-I) transition temperature changes with the nature of linking group in a fairly predictable manner determined by the effect of the group on the anisotropy of the molecular polarizability and the stereochemistry.[1] We worked earlier on three-ring systems carrying only one terminal substituent.[2] Employing two asymmetric linkages which preserve conjugative interactions and molecular rigidity, -CH=N- and -COO-, sets of eight isomeric compounds carrying cyano, nitro, methoxy, and ethoxy groups respectively were studied in order to clarify the interdependence of the effects of terminal and linking groups. The N-I transition temperatures found for the above-mentioned four sets are widely separated from each other, indicating that they are more significantly affected by the nature of terminal substituents than that of the linkages. Moreover, the variation in temperature by the arrangement of linking groups is appreciably reduced by the introduction of the second terminal substituent. If one hopes to gain some insights into the relationship between linking group and mesophase stability, it is clearly desirable to work on substances free from such influential terminal substituents. To be nematogenic, the molecule must involve, at least, four rings as manifested by numerous examples.[3] The interdependence of the effects of linking groups is evidently unavoidable when two or three groups are employed.

EXPERIMENTAL

Carbonyloxy linkage was incorporated by esterification following the procedure of Hassner and Alexanian,[4] azomethine linkage by the condensation reaction between an aniline and an aldehyde, and azo linkage by employing 4-hydroxyazobenzene, azobenzene-4-carboxylic acid, and 4-formylazobenzene as precursors. The transition temperatures and associated enthalpies were determined by a Rigaku Thermoflex differential scanning calorimeter at a heating rate of 5 K min^{-1}.

RESULTS

The thermodynamic data for newly-examined forty-eight compounds with those of the five compounds taken from the literatures are listed in Table I. Here, K, N, and I denote the crystalline, nematic, and isotropic liquid states, respectively. The compounds are represented by linking groups, X, Y, and Z.

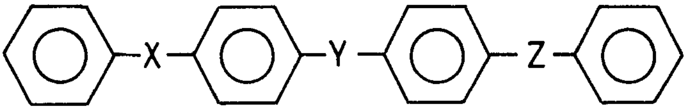

Table I Linking groups, transition temperatures and associated enthalpies of four-ring systems

No.	Linking groups			t_m	ΔH_m	t_{NI}	ΔH_{NI}	Δt
	X	Y	Z	/°C	/kJmol^{-1}	/°C	/kJmol^{-1}	/°C
1[a]	-	-	-	320	--	[250]	--	-70
2	-	-COO-	-	222	42	[213][c]	--	-9
3	-	-CH=N-	-	250	39	251	0.43	1
4[b]	-	-N=N-	-	256	--	[255][c]	--	-1
5	-	-OOC-	-COO-	243	49	[233][c]	--	-10
6	-	-OOC-	-OOC-	210	43	224	0.41	14
7	-	-COO-	-COO-	186	45	228	0.29	42
8	-	-COO-	-OOC-	214	51	233	0.53	19
9[b]	-OOC-	-	-COO-	213	--	245	--	32
10	-COO-	-	-OOC-	251	48	[232][c]	0.46	-19
11[b]	-CH=N-	-	-N=CH-	234	--	260	--	26
12	-	-N=CH-	-COO-	199	44	258	0.47	59
13	-	-N=CH-	-OOC-	200	47	252	0.49	52
14	-	-CH=N-	-COO-	211	46	245	0.43	34
15	-	-CH=N-	-OOC-	200	36	251	0.32	51

(Table I continued)

16	-	-OOC-	-CH=N-	208	44	243	0.32	35
17	-	-OOC-	-N=CH-	201	43	226	0.36	25
18	-	-COO-	-CH=N-	192	36	242	0.46	50
19	-	-COO-	-N=CH-	220	44	233	0.55	13
20[b]	-	-N=N-	-OOC-	194	--	240	--	46
21	-	-OOC-	-N=N-	211	37	229	0.46	18
22	-	-COO-	-N=N-	212	41	230	0.20	18
23	-OOC-	-COO-	-COO-	223	51	255	0.48	32
24	-OOC-	-COO-	-OOC-	238	51	253	0.39	15
25	-COO-	-COO-	-COO-	178	44	254	0.59	76
26	-COO-	-COO-	-OOC-	226	40	251	0.68	25
27	-OOC-	-CH=N-	-COO-	191	39	268	0.27	69
28	-OOC-	-CH=N-	-OOC-	189	44	271	0.60	82
29	-COO-	-CH=N-	-COO-	215	46	274	0.08	59
30	-COO-	-CH=N-	-OOC-	202	40	268	1.2	66
31	-OOC-	-OOC-	-CH=N-	192	42	259	0.22	67
32	-OOC-	-OOC-	-N=CH-	216	48	251	0.26	35
33	-OOC-	-COO-	-CH=N-	219	56	259	0.32	40
34	-OOC-	-COO-	-N=CH-	211	50	250	0.32	39
35	-COO-	-OOC-	-CH=N-	189	42	266	0.53	77
36	-COO-	-OOC-	-N=CH-	201	37	247	0.31	46
37	-COO-	-COO-	-CH=N-	209	49	255	0.48	46
38	-COO-	-COO-	-N=CH-	186	36	252	0.48	66
39	-N=N-	-OOC-	-COO-	220	53	246	0.38	26
40	-N=N-	-OOC-	-OOC-	180	40	252	0.54	72
41	-N=N-	-COO-	-COO-	185	49	254	0.27	69
42	-N=N-	-COO-	-OOC-	224	45	256	0.40	32
43	-N=CH-	-COO-	-CH=N-	191	33	273	0.71	82
44	-N=CH-	-COO-	-N=CH-	196	45	293	--	97
45	-CH=N-	-COO-	-CH=N-	178	45	277	--	99
46	-CH=N-	-COO-	-N=CH-	197	43	256	1.1	59

(Table I continued)

47	-N=N-	-COO-	-N=N-	214	51	252	0.25	38
48	-N=N-	-N=CH-	-COO-	205	38	268	0.19	63
49	-N=N-	-N=CH-	-OOC-	188	40	267	0.29	79
50	-N=N-	-OOC-	-CH=N-	211	52	256	0.34	45
51	-N=N-	-OOC-	-N=CH-	185	40	249	0.35	64
52	-N=N-	-COO-	-CH=N-	190	44	265	0.26	75
53	-N=N-	-COO-	-N=CH-	206	45	251	0.44	45

a. Taken from ref. 5.

b. Taken from ref. 3.

c. Monotropic transition.

Quaterphenyl (no.1) is the logical starting point for a discussion of the effects of any structural change in four-ring systems on mesomorphic properties but is known to be nonmesogenic. Fortunately, its virtual N-I transition temperature has been estimated to be 250 ± 5°C on the basis of phase diagrams of the binary systems with mesogenic higher polyphenyls,[5] so this hydrocarbon offers a unique reference substance devoid of possible vitiating effects of terminal substituents. The carbonyloxy group placed centrally in a molecule lowers substantially both the clearing and melting points, generating a monotropic nematic phase (see no.2). As to azomethine and azo groups placed similarly, only a marginal change in the clearing point is observed, whereas the depression of the melting point is so pronounced that these two compounds can provide an enantiotropic nematic phase.

The presence of two linking groups in the system gives rise to a broadening of the temperature range of the nematic phase with the exception of compounds 5 and 10. Compounds 5 to 8 containing two carbonyloxy links at the Y and Z positions clear at temperatures higher by 11 to 20°C than compound 2 possessing only one carbonyloxy link inserted centrally. The direction of linking groups is an important factor in determining the mesomorphic behavior. Thus, the mesophase appearing in compound 5 is metastable due to a stabilization of solid. On the other hand, compound 6 displays a mesophase thermodynamically stable over 14℃ even though its clearing point is the lowest among these four isomeric compounds. In the case of compound 7 which has the second lowest clearing point, the mesophase is stable over 42℃ because of a considerable depression of the melting point. Nevertheless, it must be pointed out that none of the observed N-I transition temperatures is located above the value estimated for quaterphenyl, 250±5℃.

The mesomorphic behavior is also subjected to a great change by the direction of two carbonyloxy linkages placed terminally. Compound 9 has a nematic phase stable over 32℃, whereas compound 10 has a monotropic mesophase. The N-I transition temperature of the latter compound is located close to that of compound 5 exhibiting also a metastable nematic phase. However, the direction of carbonyloxy linkages in these two compounds is opposite to each other. Two azomethine groups placed terminally increase the clearing point and decrease the melting point in contrast to the case of no.3 (see no.11), broadening further the nematic temperature range.

The clearing point of the isomeric compounds 12 to 19 is scattered in a relatively wide range, 226 to 258℃. The nematic temperature range varies also greatly; namely, from 13℃ for compound 19 to 59℃ for compound 12. While the average clearing point for compounds 12 to 15 having an azomethine group inserted centrally (252℃) agrees nearly with that given by compound 3, the average for compounds 16 to 19 with a carbonyloxy group placed similarly (236℃) is lower than the former one but is appreciably higher than that given by compound 2. Comparing the clearing points of the latter four with those for compounds 5 to 8 (230℃ on average), one might say that the promotion of the nematic phase by an azomethine linkage at the Z position is larger but only slightly than that by a carbonyloxy one placed at the same position. This proposition is in accordance with the observations made for compounds 9 to 11. If one divides compounds nos.12 to 19 into two groups, the first four members and the second four members, compounds 12 and 16 have the highest clearing point and compounds 14 and 17 the lowest in each group. The reversal of the carbonyloxy linkage in compound 12 results in a decrease of the clearing point by 6℃ and that in compound 14 results in an increase by the same amount. When the azomethine linkage at the Z position in compounds 16 and 18 is inverted, the transition temperature is diminished as much as by 17 and 9℃ respectively (compare nos.16 with 17 and nos.18 with 19).

Compound 20 exhibits an N-I transition temperature higher by about 10℃ than compounds 21 and 22 suggesting that the central linkage is more important in promoting the temperature than the terminal one. It may be of interest to note the effect of direction of the azomethine group at the Z position; that is, the clearing points of compounds 21 and 22 are close to those of compounds 17 and 19, 230℃ on average, but distinctly lower than those of compounds 16 and 18, 243℃ on average.

The clearing points of compounds 23 to 26 incorporating three carbonyloxy linkages are located in a narrow range of 251 to 255℃. The nematic behavior is certainly enhanced by an additional carbonyloxy linkage placed at the X position of compounds 5 to 8 or the Y position of compounds 9 and 10. Note that the difference in N-I transition temperature between the last-mentioned two, 13℃, is diminished by the presence of the third carbonyloxy linkage to 4℃ (see nos.23 and 26). On the other hand, the variation of melting point is enlarged by the presence of three carbonyloxy groups; that is, the highest is 238℃ of compound 24 and the lowest 178℃ of compound 25, producing widely different nematic temperature ranges, 15 to 76℃. The narrowest range is given by compound 24 possessing the neighboring linking groups in different direction, whereas the widest range is given by compound 25 with all the carbonyloxy linkages incorporated in the same direction.

The nematic thermal stability is promoted by 13 to 20℃ by replacement of the central carbonyloxy linkage with an azomethine one (compared nos.27 to 30 with nos.23 to 26). The crystalline state stability is diminished by this structural modification except for compound 25, which has the lowest melting point; therefore, the nematic temperature range is obviously broadened; namely, 66 to 82℃. Note that the difference in clearing point between compounds 9 and 10 is completely lost by the incorporation of this linking group (see nos.27 and 30). Comparing the present four compounds with compounds 12 to 15, one may say that the clearing point is generally raised by a carbonyloxy linkage inserted into the X position, 18℃ on average, and the melting point becomes more diversified. As a result, the nematic temperature range becomes broader in all the cases.

An azomethine group replacing a carbonyloxy group located at the Z position is not so efficient to enhance the nematic behavior as that at the Y position. The clearing points of compounds 31 to 38 are in a little wider range of 247 to 266℃ compared with 251 to 255℃ of compounds bearing three carbonyloxy groups (nos.23 to 26). The former temperature range does not overlap the range covered by compounds 27 to 30 with an azomethine group placed centrally, 268 to 274℃. The melting point is found in the range of 186 to 219℃ and is less variable than that for compounds 23 to 26; nevertheless, the temperature range of stable existence of the mesophase remains broad, 35 to 77℃. Comparison of the behavior of the present eight compounds with that of compounds 5 to 8 and also with that of 16 to 19 reveals that both the additional azomethine and carbonyloxy linkages contribute to the enhancement of the mesophase stability and also that the former linkage is a little more efficient.

Compounds 39 to 42 with one azo and two carbonyloxy linkages exhibit a clearing point in the range of 246 to 256℃ which is located at lower temperature than that for compounds 31 to 38. However, the situation is not straightforward if one takes the direction of carbonyloxy groups into the consideration. While compounds 39 and 41 show temperatures lower by a few degrees than compounds 34 and 32, compounds 40 and 38 exhibit the same temperature as each other and compound 42 gives a temperature higher by 9°C than compound 36. The temperature range of stable existence of the nematic phase is wide when the two carbonyloxy linkages are in the same direction, 69 and 72°C in compounds 40 and 41, respectively, because of the low melting point. In the other cases, the range is distinctly narrower, 26 and 32°C for compounds 39 and 42 respectively. It may be added that compounds 31, 32, 37, and 38 carrying an azomethine group instead of an azo group in compounds 40 and 41 have two carbonyloxy linkages in the same direction but cannot show such a distinct difference in the nematic temperature range relative to the other four because the N-I transition temperature is more sensitive to the reversal of the azomethine group.

Compounds 43 to 46 with two azomethine groups placed terminally clear in a fairly wide temperature range; that is, 256 to 293°C, indicating the marked interdependence between linking groups and their direction. It must be noted that compounds 44 and 45 display the highest and the second highest clearing points and also the widest and second widest temperature range of stable existence of the mesophase in the present work.

The clearing point given by compound 47 bearing two azo links is lower than any of compounds 43 to 46. Thus, the azo linkages in this particular compound are not so effective in promoting the mesophase as azomethine linkages. Compounds 48 and 49 with three different linkages show essentially the identical clearing point. Their transition temperatures are lower, by 5°C on average, than those given by compounds 28 and 29; therefore, the azo linkage in the present two is less efficient compared even with the carbonyloxy linkage in sharp contrast with the tendency shown by compounds 2 to 4 with much simpler molecular structure. Moreover, comparison of compounds 50 with 43 or 44, 51 with 45 or 46, 52 with 43 or 45, and also 53 with 44 or 46 discloses definitely that the azo linkage in these compounds is also less efficient in promoting the mesophase than the azomethine linkage in compounds 43 to 46.

DISCUSSION

Gray constructed the following average order of linking group efficiency in promoting a nematic phase; -CH=CH- > -N=NO- > -C=C- > -N=N- > -CH=N- > -COO- > none,[1] whereas Coates obtained a rather different one; -N=NO- > -N=N- > -CH=CH- > -COO- > -C=C- > -CH=N- > none.[6] Anyhow, the incorporation of a linking group to the system is regarded conducive to enhance the nematic thermal stability. This is not the case, and our results concerning compounds 1 to 4 may be summarized as follows; -N=N- ~ none ~ -CH=N- > -COO-. Thus, the carbonyloxy group inserted centrally in quaterphenyl molecule does not stabilize the nematic phase but destabilizes it. Even the azo group gives rise to a very little promotion of the clearing point. The emergence of a nematic phase in compounds 2 to 4 is almost exclusively attributed to the reduced intermolecular lateral attraction in the crystalline state. Apparently, it would be very difficult, if not impossible, to carry out similar works on biphenyl and terphenyl derivatives and find out whether the above-mentioned trends are observable or not.

The effects of two or three linking groups are more complex. Thus, the incorporation of the second carbonyloxy linkage does not necessarily destabilize the solid state. While the additional carbonyloxy group introduced to the Z position of compound 3 results in a decrease or no change in mesophase stability (see nos.14 and 15), the group placed to the X position of the same compound leads to an increase (see nos.12 and 13). On the other hand, the nematic phase in compounds 7 and 8 is stabilized relative to that in compound 2 regardless of the direction of the second carbonyloxy linkage.

Nonetheless, the clearing points of compounds 5 to 10 and also compounds 16 to 22 are lower than that of the reference substance.

There are several compounds bearing three linking groups which exhibit a wide nematic temperature range and have the clearing point not higher than that of the parent hydrocarbon (see nos.34, 36, 39, and 51). The mesophase in compounds 23 to 26 is invariably stabilized by the third carbonyloxy group but only to an extent that their clearing points approach that of quaterphenyl.

The variation in clearing point is large for compounds 12 to 19 which may be considered as phenyl analogues of the eight three-ring systems employed formerly for a study on the effects of terminal substituents.[2] Indeed one find close resemblance between a plot of the transition temperatures against the number assigned to the present compounds and that given by the corresponding methoxy derivatives. The clearing point in the methoxy derivatives is in the range from 158 to 187°C and the temperature range of stable existence of the nematic phase from 5°C to 61°C. The difference between the two series is merely a shift of the transition temperature by replacement of the methoxyl group with a phenyl group. The trend shown by compounds 12 to 15 is different from that shown by compounds 16 to 19, implying that polarity has little effect on this behavior. In agreement with the proposition made by Dewar and Riddle,[7] the dominant factor in promoting the nematic behavior of the methoxy compounds appeared to be rigidity as discussed in our earlier paper.[2] Comparison of isomeric pairs with the azomethine linkage inverted showed that a phenyliminomethyl end group is more favorable to the nematic stability than a benzylideneamino end group. This empirical rule appears to be applicable to a number of pairs in this paper; nos.31 and 32, 33 and 34, 35 and 36, 37 and 38, 43 and 46, 50 and 51, and 52 and 53 but not to the pair of 43 and 44. Another pairwise comparison showed that a benzoyloxy group is more favorable to the nematic stability as an end group than a phenyloxycarbonyl group. The behavior of compounds listed in Table I is mostly in disagreement with this earlier observation, presumably because carbonyloxy linkage is inferior to azomethine linkage in retaining the conjugative interactions and the molecular rigidity and its stereochmistry is more amenable by the presence of the third linkage.

Summarizing the present results, one has to conclude that the constitution of the whole molecular system has meaningful influence on how linking group affects the nematic phase stability. No identifiable efficiency order of linking groups in promoting the mesophase stability is obtainable from the present results.

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