CHROM. 17 895

CORRELATIONS BETWEEN RETENTION ON LIQUID CRYSTALLINE STATIONARY PHASES AND CHEMICAL STRUCTURE

I. DIMETHYLNAPHTHALENES

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(First received December 12th, 1984; revised manuscript received May 14th, 1985)

SUMMARY

    The chromatographic behaviour of isomeric dimethylnaphthalenes on a capillary column with a liquid crystalline stationary phase was studied. The liquid crystal used was 4-ethyl-4'-(p-methylbenzoyloxy)azobenzene, the mesophase of which is stable at temperatures ranging from 119 to 232°C. A simple interpretation of retention data based on the concept of shape parameter and the connectivity parameter does not lead to a satisfactory description of the retention mechanism. A model of retention is proposed that explains the behaviour of dimethylnaphthalenes and that may also be applicable to other systems involving alkyl-substituted aromatic rings.

INTRODUCTION

    Increasing interest in liquid crystals as stationary phases for gas chromatography (GC) is due to their high resolving power towards isomeric substances[1-5]. It is commonly accepted[3,6] that the separation mechanism in chromatographic systems with liquid cryustalline stationary phases is based on differences in the shapes of solute molecules. This unique solvent property of nematic liquid crystalline stationary phases results from the long-range parallel alignment of their rod-like molecules; similar, rod-like solute molecules are often observed to show higher retention times owing to preferential accommodation among the molecules of the stationary phase. On the other hand, bulky solute molecules, which are unable to penetrate the liquid crystalline stationary phase so deeply, usually elute before their more rod-like isomers.

    The purpose of this study was to establish correlations between chromatographic behaviour and geometrical structure of dimethylnaphthalenes (DMNs). An earlier study[7] on the chromatographic behaviour of DMNs with a conventional isotropic liquid stationary phase (Carbowax 20M) led to the conclusion that their retention indices could be represented by the following equation:

$$I_X = I_{AR} + k\Delta I_{\alpha\text{-CH}_3} + l\Delta I_{\beta\text{-CH}_3} + n\Delta I_0 + \Delta I_S \tag{1}$$

where $k + l = 2$, k and $l = 0$, 1 or 2 and $n = 0$ or 1; I_{AR} is the retention index of naphthalene, $\Delta I_{\alpha\text{-CH}_3}$ and $\Delta I_{\beta\text{-CH}_3}$ are the contributions due to methyl groups located in the α and β position, respectively, ΔI_0 is the contribution due to the presence of two methyl groups on adjacent carbon atoms of the aromatic ring and ΔI_S is the contribution connected with the shape of the solute molecule X. Numerical analysis of experimental retention indices for naphthalene and mono-, di- and multi-substituted methylnaphthalenes led to the following relationship between ΔI_S and the breadth-to-length ratio, b/l:

$$I_S = A_1(b/l)^3 + A_2(b/l)^2 + A_3(b/l) + A_4 \tag{2}$$

where A_i ($i = 1$, 2, 3, or 4) are constants. The ratio b/l is the so-called shape parameter[6] and is equal to the ratio of the shorter to longer sides of a rectangle encompassing a molecule. The above relationship was surprizing as it was found for an isotropic liquid phase. Therefore, we decided to investigate whether the retention indices of DMNs chromatographed on a liquid crystalline phase also give a well defined relationship between ΔI_S and the shape papameter.

EXPERIMENTAL

The chromatograph used was a Chrom-5 equipped with a flame-ionization detector (Laboratory Instruments, Prague, Czechoslovakia). The injector and detector temperatures were 150.0°C. The column was a glass capillary (21 m × 0.3 mm I.D.). The retention times were determined electronically with an accuracy of 0.2 sec. The dead time was measured with methane. Helium was used as the carrier gas. The sample volume was 0.5 μl and was introduced using a 1-μl Hamilton syringe. The injected samples were solutions of a mixture of naphthalene (N), α- and β-methylnaphthalenes (MNs) and dimethylnaphthalenes (DMNs) in benzene.

The stationary phase was a 4-ethyl,4'-(p-methylbenzoyloxy)azobenzene liquid crystal (Fig. 1). Its mesophase is stable at temperatures ranging from 119 to 232°C. The measurements were carried out at 123.0, 125.0, 129.4, 130.3 and 137.4°C. The stationary phase film thickness was 0.15 μm and it was assumed that adsorption effects could be ignored.
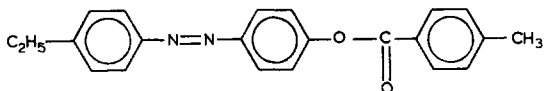

Fig. 1. Structure of the liquid crystal.

RESULTS AND DISCUSSION

The results of the chromatographic measurements are given in Table I.

From the shape parameter (b/l) considerations[6] it follows that the more rod-like a solute molecule is, the longer is its retention time. Hence, the elution order for DMNs, predicted solely on the basis of b/l values, would be as follows: 1, 1,4-DMN and 1,5-DMN; 2, 1,7-DMN, 1,3-DMN and 1,6-DMN; 3, 2,7-DMN; and 4, 2,6-DMN. The positions of 1,2- and 2,3-DMN have not been predicted, as the above

TABLE I

RETENTION INDICES OF NAPHTHALENE DERIVATIVES

N = naphthalene; MN = methylnaphthalene; DMN = dimethylnaphthalene.

No.	Substance	I				
		$T = 123.0°C$	$T = 125.0°C$	$T = 129.4°C$	$T = 130.4°C$	$T = 137.4°C$
1	N	1464.10	1466.97	1474.62	1474.87	1486.59
2	α-MN	1582.04	1585.83	1594.04	1595.64	1607.72
3	β-MN	1590.24	1593.41	1600.54	1601.97	1613.18
4	1,7-DMN	1680.15	1683.98	1691.80	1693.39	1705.93
5	1,3-DMN	1692.71	1696.64	1704.39	1706.26	1718.68
6	1,4-DMN	1702.21	1706.38	1714.71	1716.53	1729.68
7	2,7-DMN	1705.60	1708.88	1716.2	1717.70	1729.43
8	1,6-DMN	1711.20	1715.13	1722.94	1724.76	1736.79
9	1,5-DMN	1715.96	1719.86	1728.21	1729.88	1742.91
10	2,6-DMN	1727.10	1730.88	1738.13	1739.59	1750.70
11	2,3-DMN	1736.35	1740.25	1747.73	1749.71	1761.60
12	1,2-DMN	1743.48	1747.62	1755.58	1757.67	1770.51

model does not allow an estimate of the *ortho*-effect, which certainly affects reten-tion[8,9]. The values of b/l for all DMNs are given in Table II.

The observed elution order of DMNs chromatographed on the liquid crystal-line stationary phase used in this work is, however, completely different to that in-dicated above, being 1, 1,7-DMN; 2, 1,3-DMN; 3, 1,4-DMN at temperatures below 135.5°C, 2,7-DMN at temperatures above 135.5°C; 4, 2,7-DMN at temperatures be-low 135.5°C, 1,4-DMN at temperatures above 135.5°C; 5, 1,6-DMN; 6, 1,5-DMN; 7, 2,6-DMN; 8, 2,3-DMN; and 9, 1,2-DMN. The positions of 1,2- and 2,3-DMNs show that *ortho*-effects are strong.

The concept of the shape parameter, b/l, fails in predicting the elution order

TABLE II

SHAPE PARAMETERS AND CONNECTIVITY PARAMETERS FOR NAPHTHALENE DERIV-ATIVES

No.	Substance	b/l	χ
1	N	0.76	3.405
2	α-MN	0.90	3.821
3	β-MN	0.65	3.815
4	1,7-DMN	0.76	4.232
5	1,3-DMN	0.76	4.232
6	1,4-DMN	0.92	4.238
7	2,7-DMN	0.59	4.226
8	1,6-DMN	0.76	4.232
9	1,5-DMN	0.92	4.238
10	2,6-DMN	0.57	4.226
11	2,3-DMN	0.65	4.232
12	1,2-DMN	0.76	4.238

of DMNs and therefore another explanation for the retention mechanism is needed.

The factor that is often used to correlate retention data and solute chemical structure is the connectivity parameter[10,11], χ, defined by

$$\chi = \sum_{i,j} (\delta_i \delta_j)^{-1/2} \tag{3}$$

where the summation covers all pairs of adjacent carbon atoms in a molecule and δ_i is the number of carbon atoms bonded to the ith carbon atom. With DMNs we have three different values of χ corresponding to three possible mutual positions of methyl groups, (α,α), (α,β) and (β,β) (see Table II). The connectivity parameter for 1,2-DMN is the same as for α,α-substituted isomers, whereas for 2,3-DMN we have the same value of χ as for α,β-substituted isomers. Fig. 2 shows the dependence of retention indices for DMNs at 129.4°C on χ. It can be seen that there is no direct correlation, but we can trace some regularities if we first consider idealized DMNs. We consider that all isomeric DMNs can be grouped according to their χ values, then we assume that the retention indices corresponding to these groups can be calculated using the additivity principle, *i.e.*,

$$I_{X(id)} = I_{AR} + k\Delta I_{\alpha\text{-}CH_3} + l\Delta I_{\beta\text{-}CH_3} \tag{4}$$

where $k + l = 2$, k and $l = 0, 1, 2$. The increments $\Delta I_{\alpha\text{-}CH_3}$ and $\Delta I_{\beta\text{-}CH_3}$ are assumed to be equal to

$$\Delta I_{\tau\text{-}CH_3} = I_{\tau\text{-}MN} - I_N \tag{5}$$
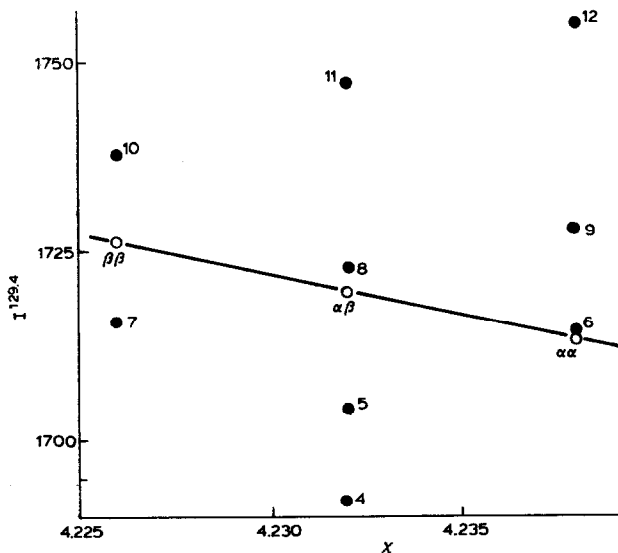
where $\tau = \alpha$ or β.

Fig. 2. Dependence of the retention indices of DMNs on the connectivity factor, χ, at 129.4°C. The numbers correspond to the compounds listed in Table I. ●, Experimental data; O, results for idealized DMNs.

TABLE III

RETENTION INDICES AND RETENTION INDEX INCREMENTS FOR IDEALIZED DMNs

Parameter	T (°C)				
	123.0	125.0	129.4	130.4	137.4
$\Delta I^{id}_{\alpha\text{-CH}_3}$	117.94	118.86	119.42	120.77	121.13
$\Delta I^{id}_{\beta\text{-CH}_3}$	126.14	126.44	125.92	127.10	126.59
$I_{(\alpha,\alpha)}$-DMN	1699.98	1704.69	1713.46	1716.41	1728.85
$I_{(\alpha,\beta)}$-DMN	1708.18	1712.27	1719.96	1722.74	1734.31
$I_{(\beta,\beta)}$-DMN	1716.38	1719.85	1726.46	1729.07	1739.77

Table III gives the values of $\Delta I_{\alpha\text{-CH}_3}$, $\Delta I_{\beta\text{-CH}_3}$ and $I_{X(id)}$ obtained from experimental data in Table I. Fig. 2 also shows the dependence of $I_{X(id)}$ on χ at 129.4°C. Now, it can be seen that we select the group of DMNs (2,6-, 1,6- and 1,4-isomers) that exhibit the same dependence on χ as $I_{X(id)}$. In addition, we have the groups of DMNs [(a) 2,6-, 2,3- and 1,2-isomers, (b) 2,7-, 1,6- and 1,5-isomers and (c) 1,3- and 1,4-isomers] that exhibit a linear dependence between their retention indices and χ, but the slopes of these lines are positive whereas $I_{X(id)}$ decreases with increasing χ. The dependence of the retention indices for DMNs on b/l is qualitatively the same because we have a linear dependence between χ and b/l for DMNs (see Fig. 3).

In order to establish the thermodynamic characteristics of the interaction between solutes and the stationary phase we determined the partial molar enthalpies and entropies of solution for the investigated DMNs and also the values corresponding to our idealized systems. In the calculations we used the relationship
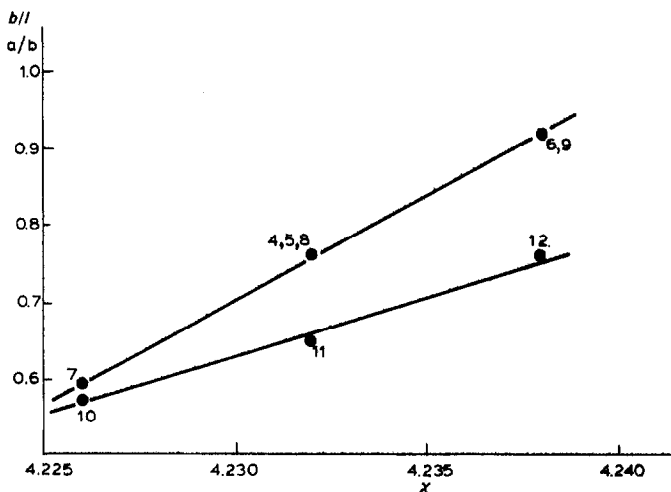
$$\ln k' = -\Delta H/RT + C \qquad (6)$$

Fig. 3. Relationships between the shape parameter, b/l, and the connectivity factor, χ, for DMNs. The numbers correspond to the DMNs listed in Table I.

TABLE IV

PARTIAL MOLAR ENTHALPIES AND ENTROPIES OF SOLUTION FOR NAPHTALENE DE-
RIVATIVES (AND IDEALIZED SYSTEMS)

No.	Substance	$-\Delta H$ (kJ/mole)	$-C$	r^*
4	1,7-DMN	48.63	11.88	0.999962
5	1,3-DMN	49.05	11.93	0.999953
6	1,4-DMN	48.62	11.75	0.999969
7	2,7-DMN	50.61	12.33	0.999951
8	1,6-DMN	49.97	12.10	0.999976
9	1,5-DMN	49.39	11.90	0.999977
10	2,6-DMN	51.65	12.51	0.999986
11	2,3-DMN	51.15	12.31	0.999960
12	1,2-DMN	50.47	12.06	0.999954
(α,α)-DMN$_{id}$		51.10	12.56	0.999878
(α,β)-DMN$_{id}$		52.72	13.00	0.999947
$(\beta,\beta$-DMN$_{id}$		54.57	13.52	0.999545

 * r is the correlation coefficient of the ln (t_R/t_M) *vs.* $1/T$ plot.

where k' is the capacity ratio, ΔH is the partial molar enthalpy of solution and C is
a constant proportional to the partial molar entropy of solution. The results obtained
are summarized in Table IV. Fig. 4 shows the relationship between $-\Delta H$ and $-C$.
From the shape parameter considerations[12] it follows that the enthalpy and entropy
of solution for more rod-like molecules should be greater (more regative) than for
more compact isomers. In the present instance we observe that the above rule is
satisfied but only within groups of isomers with different χ values. Also, we observe
a well defined linear dependence between $-\Delta H$ and $-C$ for substances with the
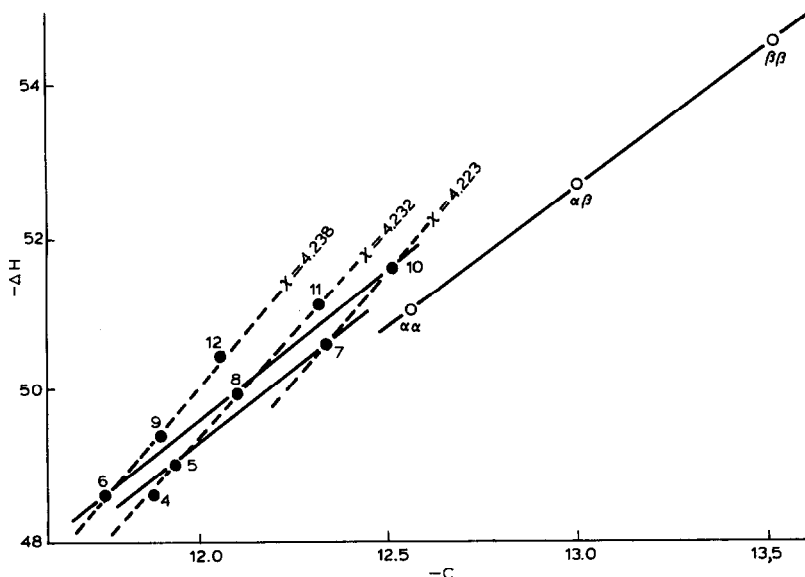

Fig. 4. Relationship between $-\Delta H$ and $-C$ for experimental systems (●) and idealized DMNs (O).

same χ (broken lines in Fig. 4). On the other hand, the dependence between enthalpy and entropy for idealized systems agrees very well with the rule derived from the shape parameter considerations. It is noteworthy that the slopes of the lines corresponding to idealized systems and the selected groups of isomers (solid lines in Fig. 4) are nearly the same. It is also interesting that there are groups of isomers with increasing retention indices and decreasing enthalpies and entropies (2,6-, 2,3- and 1,2-DMN; 2,7-, 1,6- and 1,5-DMN).

From the above discussion it follows that the retention mechanism of DMNs is complex and cannot be explained by using solely the model based on the correspondence between elongations of solute molecules and their retention. In fact, Chow and Martire[13] have suggested that the above model is not valid at all and its predictions are misleading.

We shall now present a model of retention of DMNs that seems to explain their behaviour in contact with a liquid crystalline stationary phase. We assume that the main factor determining the retention of isomeric DMNs is the symmetry of substitution. By this term we understand the mutual arrangement of methyl groups relative to each other and to the aromatic skeleton. Hence we assume that the retention index of any DMN can be represented by

$$I_X = I_{X(id)} + \Delta I_{ex} \tag{7}$$

where ΔI_{ex} is the increment due to symmetry of substitution and $I_{X(id)}$ is the retention index for an idealized DMN with the same connectivity parameter, χ, as the considered compound X. The basic hypothesis of our model is that when both methyl groups are located on the same side of the aromatic skeleton, as in 1,3- and 1,7-DMN, then their presence prevents a solute molecule from penetrating deeply into the ordered phase of the liquid crystal. On the other hand, when methyl groups are located on opposite sides of the aromatic skeleton, they are assumed to act as "hooks" that impede the movement of solute molecules from the stationary phase, after the solute has penetrated the ordered structure of the liquid crystal. Now, the question arises of why methyl groups situated on the same side of aromatic skeleton act differently from those situated on opposite sides. We propose the following answer. In the former instance two methyl groups are too large an obstacle for a molecule to overcome so that only part of aromatic skeleton can penetrate the liquid crystalline phase. In the later instance, however, the methyl groups are separated by aromatic rings. Therefore, these methyl groups act separately and the interaction between the solute and solvent may force the substance being chromatographed into the stationary phase despite the presence of methyl groups. When a molecule is already inside the layer of liquid crystal, then the methyl groups hinder its movement out to the mobile phase. Of course, the above argument is purely hypothetical and only experimental results can confirm it. Also, we are not able, at present, to derive any expressions connecting the positions of methyl groups with their effects on retention. Nevertheless, using the above model we can predict the elution order for DMNs, namely 1, 1,7-DMN; 2, 1,3-DMN [1,7-DMN is expected to elute before the 1,3-isomer because it cannot penetrate the liquid crystalline ordered phase as deeply as 1,3-DMN (see Fig. 5)]; 3, 1,4- and 2,7-DMN [in this instance our purely qualitative model does not allow any distinction to be made between these isomers; it should be

TABLE V

VALUES OF ΔI_{ex} FOR NAPHTHALENE DERIVATIVES

No.	Substance	T (°C)				
		123.0	125.0	129.4	130.3	137.4
4	1,7-DMN	−28.03	−28.29	−28.16	−29.35	−28.38
5	1,3-DMN	−15.47	−15.63	−15.57	−16.48	−15.63
6	1,4-DMN	2.23	1.69	1.25	0.12	0.87
7	2,7-DMN	−10.78	−10.97	−10.26	−11.37	−10.34
8	1,6-DMN	3.02	2.86	2.98	2.02	2.48
9	1,5-DMN	15.98	15.17	14.75	13.47	14.06
10	2,6-DMN	10.72	11.03	11.67	10.52	10.93

noted that experimental results for these two isomers are nearly the same (see Table I)]; 4, 1,6-DMN; 5, 1,5-DMN; and 6, 2,6-DMN (2,6-DMN is more rod-like than 1,5-DMN and hence the latter is expected to elute first).

The above sequence agrees very well with the observed elution order of DMNs. We could not predict, however, the positions of the 2,3- and 1,2-isomers because we cannot estimate the influence of *ortho*-effects on the retention of these compounds. One can speculate that the *ortho*-effect should be greater with 1,2-DMN owing to the greater stiffening of the methyl group at position 1 caused by the presence of a hydrogen atom at position 8. Table V gives the values of I_{ex} obtained from experimental data. It can be seen that for the isomers for which we expect a weakening of retention (relative to idealized DMNs) the values of ΔI_{ex} are negative, whereas for other isomers the values of ΔI_{ex} are positive.

One should note an interesting dependence between the connectivity parameter and the values of $\partial I/\partial T$. Fig. 6 shows the relationships between retention indices and temperature for DMNs. It can be seen that in the range of temperatures (I) at which our measurements were performed, the retention indices vary linearly with T. The slopes of these lines ($\partial I/\partial T$) are summarized in Table VI, together with the values predicted for idealized DMNs. Fig. 7 shows the relationships between $\partial I/\partial T$ and χ for real and idealized DMNs. In both instances a nearly linear dependence is observed. Finally, Fig. 8 shows the relationship between $\partial I/\partial T$ and the shape parameter, b/l. As expected, there is a linear relationship, but with deviations for 1,2- and 2,3-isomers. The above results are surprising because the retention indices were found
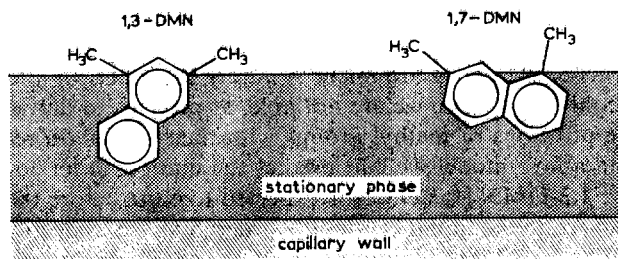

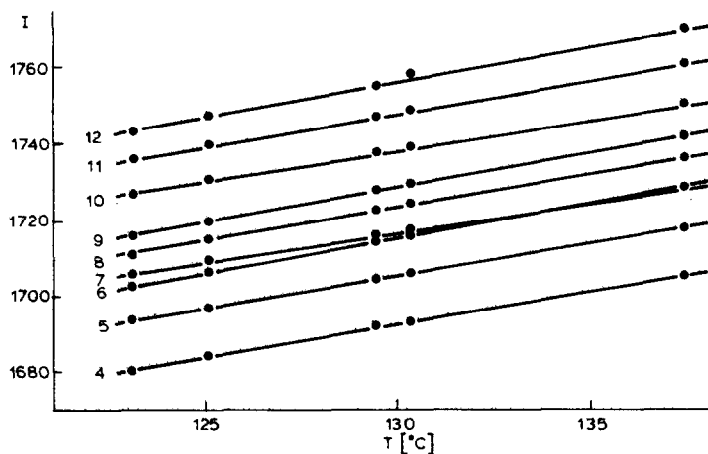Fig. 5. Interaction between solute molecules and the liquid crystal.

Fig. 6. Dependences of retention indices of DMNs on temperature. The numbers correspond to the compounds listed in Table I.

TABLE VI

THE VALUES OF $\partial I/\partial T$ FOR NAPHTHALENE DERIVATIVES

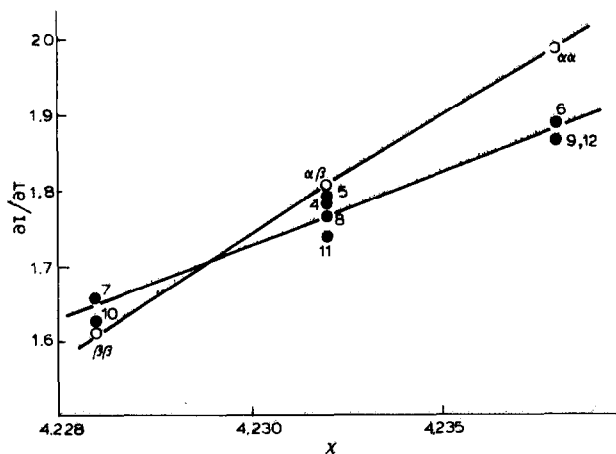| No.	Substance	$\partial I/\partial T$
4	1,7-DMN	1.78
5	1,3-DMN	1.79
6	1,4-DMN	1.90
7	2,7-DMN	1.66
8	1,6-DMN	1.77
9	1,5-DMN	1.87
10	2,6-DMN	1.63
11	2,3-DMN	1.74
12	1,2-DMN	1.87
(α,α)-DMN$_{id}$		1.99
(α,β)-DMN$_{id}$		1.81
(β,β)-DMN$_{id}$		1.61

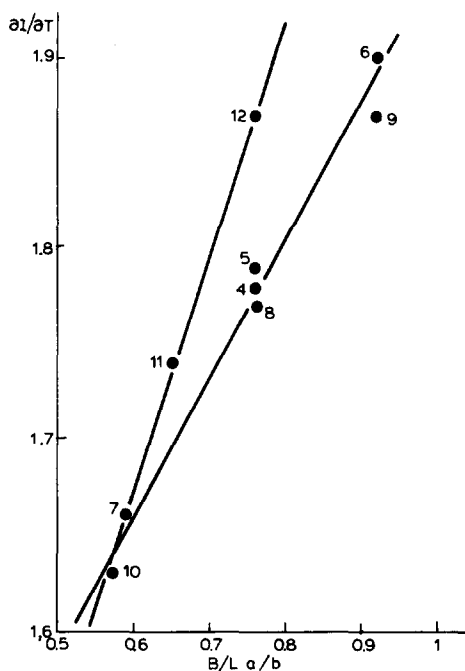Fig. 7. Relationships between $\partial I/\partial T$ and χ for real (●) and idealized (○) DMNs.

Fig. 8. Relationship between $\partial I/\partial T$ and the shape parameter, b/l, for DMNs.

to be only very loosely connected with χ. Also, we cannot find any connection between the observed values of $\partial I/\partial T$ and the predictions of our retention model. It is possible, however, that further studies of other groups of isomeric multi-substituted aromatic systems will lead to clearer relationships between the structures of solute molecules and their retention.

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