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Letter to the Editor

Correlation between retention on liquid crystalline phases and chemical structure

Sir,

In a recent paper concerning the correlations between retention on liquid crystalline phases and the chemical structure of dimethylnaphthalenes (DMNs), Suprynowicz *et al.*[1] concluded that the so-called shape parameter, η, previously proposed[2,3] by us had little, if any, relevance to chromatographic distribution. We believe that this conclusion resulted from a misunderstanding of our idea. We would emphasize:

(1) The shape parameter, η, must be defined unequivocally. We expressed η as the ratio of the longer to the shorter sides of the smallest rectangle which can enclose the structure, drawn proportionally to the atomic dimensions (see Fig. 1). The criterion of the smallest rectangle is the decisive one for reproducibility. It is not clear what criterion was applied by Suprynowicz *et al.*[1] to obtain their b/l values.

(2) Obviously, the molecular shape may not be the only factor governing the retention. Contrary to that one may expect to detect the influence of molecular shape on the retention of a series of solutes mainly in cases when the prevailing "bulky" properties (ability to participate in Van der Waals interaction) of the compounds studied are similar. Thus, for the series of DMNs considered both the shape parameter and, *e.g.*, the connectivity index of the individual compounds should be considered together.

Bearing the above conditions in mind, we have reconsidered the experimental data discussed by Suprynowicz *et al.*[1]. As there is a generally regular dependence of the retention index on temperature, we will examine exemplary data obtained by the authors[1] at 129.4°C. These data, $I_{obsd.}$, together with those calculated by us, $I_{cald.}$, and the structural parameters, *i.e.*, the shape parameter, η, determined according to Fig. 1 and the connectivity index, $^1\chi$, calculated by Suprynowicz *et al.*[1], are given in Table I. The two-parameter equation relating the retention index, $I_{obsd.}$, to both η and $^1\chi$ has the form

$$I_{obsd.} \cdot 10^{-3} = 1.465 + 0.116\eta + 3.514\,(^1\chi - 4.200) \quad (1)$$

$$n = 8,\ R = 0.9408,\ \sigma = 0.0097,\ p = 0.02$$

where n is the number of derivatives considered, R is the multiple correlation coefficient, σ is the standard deviation from regression and p is the significance level. To facilitate the calculations, the numerical values of the retention index were divided by 1000 and a constant number, 4.200, was substracted from the $^1\chi$ values.

In fact, for 2,7-DMN the experimental retention index given by Suprynowicz *et al.*[1] deviates significantly from eqn. 1 and has not been included in the statistics.

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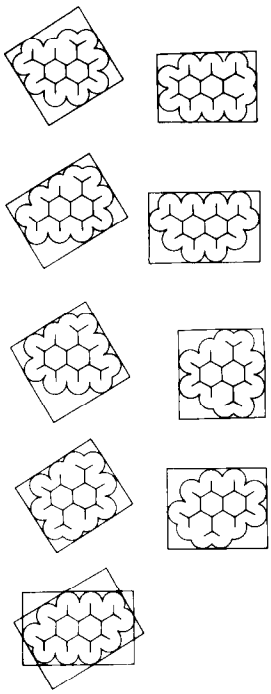

Fig. 1. Smallest rectangular envelopes for DMNs. For different bond types the following interatomic distances (Å) were used: 1.4 (C–C aromatic); 1.5 (C–C aromatic to aliphatic); 1.1 (C–H single bond) and 1.2 (Van der Waals radius of hydrogen atom).

There is nothing unusual in one solute out of a group of nine deviating from a statistical relationship. What is peculiar, however, is that this is the only solute of the group studied by Suprynowicz *et al.*[1] which shows irregular behaviour on I *vs.* T plots (see Fig. 6 in ref. 1). As is evident from Table I, the elution order calculated

TABLE I

STRUCTURAL PARAMETERS AND RETENTION INDICES OBSERVED[1] AND CALCULATED BY EQN. 1 FOR DIMETHYLNAPHTHALENES (DMNs)

DMN	η	$^1\chi$	$I_{obsd.}$	$I_{calc.}$
1,7	1.00	4.232	1692	1694
1,3	1.03	4.232	1704	1697
1,4	1.03	4.238	1715	1718
2,7	1.60	4.226	1716	–
1,6	1.32	4.232	1723	1731
1,5	1.20	4.238	1728	1738
2,6	1.58*	4.226	1738	1740
2,3	1.42	4.232	1748	1742
1,2	1.26	4.238	1756	1745

* Two smallest envelopes may be drawn for the same surface. The η value for the more compact (less elongated) one would be 1.42.

by us for the remaining eight DMNs is exactly that experimentally found by Suprynowicz *et al.*[1]. Thus, in addition to previous reports[4–6], the results discussed here provide further support of our approach to the structure–retention relationships in selected series of solutes.

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