

Short Communication

High-performance liquid chromatographic study of acenaphthaleno[1,2-*e*]pyrene, phenanthro[9,10-*e*]pyrene and their dihydro derivatives

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ABSTRACT

The high-performance liquid chromatographic study of acenaphthaleno[1,2-*e*]pyrene, phenanthro[9,10-*e*]pyrene and their dihydro derivatives is reported. The main factor which determines the retention order is the degree of staggering of the two *ortho*-fused moieties. The degree of staggering in the fully unsaturated systems is dependent on the bay-region steric interactions and that in the dihydro derivatives is determined by the geometric demand of the saturated bridge.

INTRODUCTION

The polycyclic aromatic compounds (PACs) are now routinely analysed by chromatographic methods [1,2]. High-performance liquid chromatography (HPLC), for example, is most useful for the analysis of the higher benzenoids with low volatility. Results reported previously indicate that effective HPLC separations of PACs depend on the number of rings and shape as well as the degree of planarity [3-5] of the PACs. The deviation from planarity studied so far is mainly the result of intramolecular steric strain arising from interaction between aromatic protons in various bay regions. We have recently prepared [6-8] acenaphthylene[1,2-*e*]pyrene (**1**), phenanthro[9,10-*e*]pyrene (**2**)

and their respective dihydro derivatives (**3** and **4**). The spectral data of **3** and **4** indicated a large deviation from planarity of the two fused moieties in each molecule. There are no detailed reports on comparative chromatographic studies of PACs and their corresponding dihydro derivatives and thus it would be interesting to investigate the chromatographic behaviour of **1-4** collectively. The PACs are environmental pollutants that perhaps represent the largest class of suspected chemical carcinogens. However, the chemical analysis of large PACs has sometimes been limited owing to lack of standard reference compounds. Our study was aimed at providing some analytical data for the PACs (**1-4**) concerned.

EXPERIMENTAL

Syntheses of the investigated PACs, **1** [6], **2** [7], **3** [6] and **4** [8], have been achieved in our laboratory.

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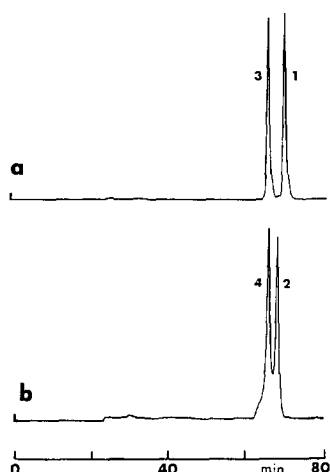
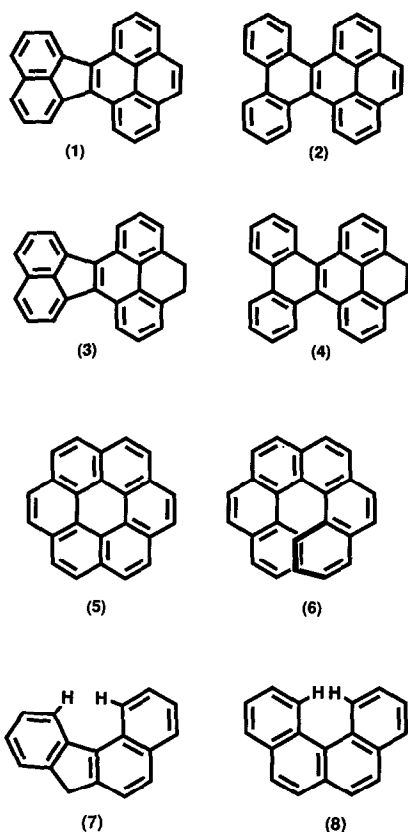


Fig. 1. High-performance liquid chromatograms of (a) **1** and **3**; (b) **2** and **4**. The approximate concentration of each sample was 0.5 mg/ml in dichloromethane.

study. In the chromatographic study [9] of the planar coronene **5** and the non-planar phenanthro[3,4-*c*]phenanthrene **6** a slot model of retention was used to account for the retention order. In each pair of **1** and **3** or **2** and **4**, the dihydro derivative was always eluted first. Observation from appropriate molecular models suggests that the geometric demand of the saturated bridge in **3** and **4** leads to more severe

Chromatographic studies were performed on a Shimadzu LC-6A binary gradient liquid chromatograph equipped with a Shimadzu SPD-6AV UV-Vis spectrophotometric (254 nm) detector and a Shimadzu SCL-6A system controller. A Partisil 5 ODS-3 reversed-phase C_{18} column (30 cm \times 3.9 mm I.D.) was used for chromatographic separations. HPLC-grade acetonitrile and dichloromethane were purchased from Fisher Scientific and J. T. Baker, respectively. Water was purified with a Milli-Q system (Millipore, Bedford, MA, USA).

The chromatographic condition employed was a linear gradient of 40–100% acetonitrile in water at 0.5%/min and 1 ml/min with a maximum pressure of 500 kgf/cm².

RESULTS AND DISCUSSION

Satisfactory resolution (Fig. 1) of both pairs of compounds, **1** and **3** or **2** and **4**, was observed under the chromatographic conditions employed in our

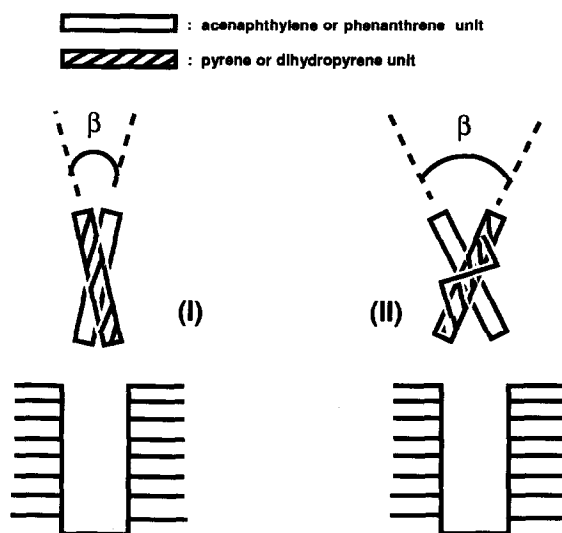


Fig. 2. Representation of the slot model of retention showing the differences in case of fitting into the gaps in the stationary phase.

(Fig. 2; larger angle β) puckering of the dihydropyrene ring and the staggering of the two fused moieties as represented in Fig. 2 (II), compared with that of the corresponding parent PACs as shown in Fig. 2 (I). The less planar **3** and **4** thus could not fit readily into the “gaps” of the stationary phase, resulting in a weaker interaction with the bonded phase, and they eluted earlier than **1** and **2**, respectively.

In the chromatographic study (Fig. 3) of a mixture of acenaphthylene, phenanthrene, pyrene and compounds **1–4**, the higher benzenoids, **1–4**, eluted much more slowly, as expected. However, the separation of **1** and **2** could be affected by several factors. Based on the number of π electrons or double-bond equivalents [10–12], acenaphthylenopyrene **1** (with 13 pairs of π electrons) is expected to elute before phenanthropyrene **2** (with 14 pairs of π electrons). Differences in retention owing to the shape of the molecules [9,13,14] have been described in terms of the length-to-breadth ratio (L/B). Approximate measurements from molecular modelling (Fig. 4) gave **1** a slightly larger L/B ratio than **2**, again suggesting that **1** would elute before **2**. The result from our work (Fig. 3) however clearly indicates that **1** eluted after **2**, in contrast to the prediction made from the above-mentioned factors. It is believed that the governing factor is in fact the

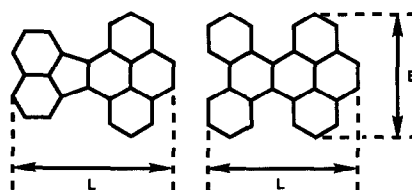


Fig. 4. The longest axis, L , and its longest perpendicular axis, B , for the consideration of the L/B ratio.

degree of staggering [see Fig. 2 (I)] of the two fused moieties in **1** and **2**. The steric interactions experienced in **1** and **2** are expected to be similar to those of the corresponding four-sided bay regions in benzo[*c*]fluorene **7** and benzo[*c*]phenanthrene **8**, with the latter known to deviate more significantly from planarity. A similar argument would suggest a larger angle β in **1** (Fig. 3) for **2** than for **1**. Based on the permeation effect, **1** would then penetrate more readily into the “slots”, interact more strongly with the stationary phase and thus elute after **2**.

The dihydro compounds, **3** and **4**, unexpectedly were not resolved in our study (Fig. 3). With the introduction of the saturated bridges, steric interactions in bay regions in **3** and **4** are no longer significant because of molecular puckering. However, the degree of staggering of the two fused moieties is governed mainly by the geometric demand of the bridge. Thus a similar angle β in Fig. 2 (II) is expected of both **3** and **4** resulting in similar retention and no separation of the two compounds as described in our chromatographic study.

CONCLUSIONS

The PACs investigated in this work have a unique structural feature in having two smaller benzenoid units *ortho* fused. Retention of these PACs seems to depend largely on the degree of staggering of these two fused moieties. In fact, this is the main factor involved, making others such as the double-bond equivalent and the L/B ratio less important. This staggering effect determined by the geometric demand of the saturated bridge is more significant in the dihydro derivatives but it results in less satisfactory separation of the dihydro-PACs with similar dihydro bridges.

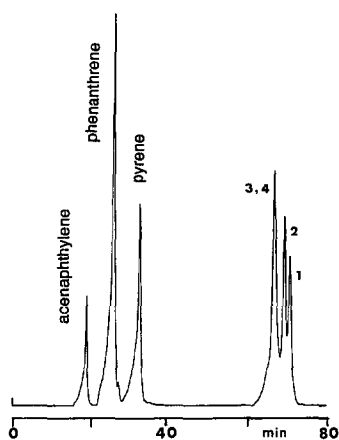


Fig. 3. High-performance liquid chromatogram of a mixture of **1–4** and three reference PACs. Approximate concentrations in dichloromethane: acenaphthylene, 2.0 mg/ml; phenanthrene, 0.75 mg/ml; pyrene, 1.5 mg/ml; **1–4**, 0.25 mg/ml. Retention times observed in order are 19.1, 26.2, 33.0, 68.0, 68.0, 70.7 and 72.2 min, respectively.

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