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DETERMINATION OF SOME MOLECULAR STRUCTURE PARAMETERS FOR HYDROCARBONS FROM THE RETENTION VOLUMES ON GRAPHITIZED CARBON BLACK

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SUMMARY

It has been found that some molecular structure parameters of hydrocarbons can be determined on the basis of their retention volumes on graphitized thermal carbon black as measured by gas chromatography and calculated by semiempirical molecular statistical methods. The potential barriers to internal rotation of the ethyl group with respect to the benzene ring in ethylbenzene and of the benzene rings with respect to each other in biphenyl, the equilibrium torsional angle and the potential barriers to internal rotation of the benzene rings around the central C–C bond in 2,6-dimethylbiphenyl, and the angle of alternate displacement of methyl carbons from the benzene ring plane in hexamethylbenzene were determined.

INTRODUCTION

In gas adsorption chromatography, the retention volumes of hydrocarbons on graphitized thermal carbon black (GTCB) are strongly dependent on the geometric structure of the adsorbate molecules[1,2]. A semiempirical molecular statistical method for the calculation of retention volumes of hydrocarbons for zero sample size, $V_{A,1}$, on GTCB has been developed[1,3]. The values of $V_{A,1}$ calculated by this method are in good agreement with the corresponding experimental values. Moreover, the calculations showed that $V_{A,1}$ is strongly dependent on the equilibrium angles and potential barriers to internal rotation of the molecules. Thus it is possible to determine some molecular structure parameters, in particular, the equilibrium angles and potential barriers to internal rotation, on the basis of experimental $V_{A,1}$ values for hydrocarbons obtained on GTCB and from molecular statistical calculations of $V_{A,1}$.

In this paper the potential barriers to internal rotation of the ethyl group with respect to the benzene ring in ethylbenzene and of the benzene rings with respect to each other in biphenyl, as well as the equilibrium torsional angle and potential barriers to internal rotation of the benzene rings around the central C–C bond in 2,6-dimethylbiphenyl and the angle of alternate displacement of methyl carbons from the benzene ring plane in hexamethylbenzene, are determined by this method.

THEORETICAL

The equilibrium torsional angles and the potential barriers to internal rotation of the molecules are determined from the experimental $V_{A,1}$ values at various temperatures by the following procedure. First, the dependence of $V_{A,1}$ on the torsional angle α is calculated from

$$V_{A,1}(\alpha) = (1/4\pi) \iint (2\pi kT/\Phi_z^{''})^{1/2} \exp\left(- \Phi_0/kT\right) \sin\theta \, d\theta d\varphi \tag{1}$$

where Φ_0 and $\Phi_z^{''}$ are the potential energies of the molecule–adsorbent interaction and its second derivative with respect to the distance z between the centre of masses of the molecule and the surface at fixed α and the Euler angles θ and φ at the corresponding equilibrium distance z_0.

The potential function Φ is calculated using the atom–atom approximation and the following semiempirical atom–atom potential functions obtained previously[3,4]:

$$\varphi_{H\cdots C(graphite)} = -0.498\cdot 10^{-3}r^{-6} - 0.950\cdot 10^{-5}r^{-8} + 3.60\cdot 10^4 \exp\left(-35.7\,r\right) \tag{2}$$

$$\varphi_{C(alkane)\cdots C(graphite)} = -1.386\cdot 10^{-3}r^{-6} - 2.148\cdot 10^{-5}r^{-8} + 1.89\cdot 10^5 \exp\left(- 35.7r\right) \tag{3}$$

$$\varphi_{C(aromatic)\cdots C(graphite)} = - 1.48\cdot 10^{-3}r^{-6} - 2.30\cdot 10^{-5}r^{-8} + 2.03\cdot 10^5 \exp\left(- 35.7r\right) \tag{4}$$

where the distance r between the atoms is expressed in nm, and φ in kJ mol^{-1}.

Further, the statistical average values of $V_{A,1}$ are calculated from

$$V_{A,1} = \frac{\int \exp\left[- W(\alpha)/kT\right] V_{A,1}(\alpha)\, d\alpha}{\int \exp\left[- W(\alpha)/kT\right] d\alpha} \tag{5}$$

where $W(\alpha)$ is the potential function of hindered internal rotation of an isolated molecule.

For the potential function W of hindered internal rotation of the ethyl group with respect to the benzene ring in ethylbenzene, the following form is assumed

$$W = (W_0/2)\,(1 - \cos 2\alpha) \tag{6}$$

where W_0 is the potential barrier for a planar conformation of the molecule, α is the angle of internal rotation of the ethyl group with respect to the benzene ring, assumed to be zero when the ethyl group lies on a plane perpendicular to the benzene ring. For the potential function $W(\alpha)$ in the isolated biphenyl and 2,6-dimethylbiphenyl molecules the following form is assumed for $0° \leqslant \alpha \leqslant \alpha_{min}$.

$$W = (W_{01}/2)\,[1 + \cos\left(180\alpha/\alpha_{min}\right)] \tag{7a}$$

and for $\alpha_{min.} \leqslant \alpha \leqslant 90°$

$$W = (W_{02}/2) \cdot \{1 - \cos [180 (\alpha - \alpha_{min.})/(90 - \alpha_{min.})]\} \tag{7b}$$

where W_{01} and W_{02} are the potential barriers for the planar $(\alpha = 0)$ and the perpendicular arrangements of the benzene rings in the molecules, and $\alpha_{min.}$ is the equilibrium angle between the planes of benzene rings, i.e., the angle of internal rotation at the potential minimum of the isolated molecule.

Calculations of $V_{A,1}$ are carried out at various possible values of the potential barriers W_0, W_{01}, W_{02} and of the equilibrium angle $\alpha_{min.}$, and at several temperatures. The results may be approximated by:

$$\ln V_{A,1} = A + B/T + C \ln T \tag{8}$$

The parameters of this equation are determined from the calculated $V_{A,1}$ values by the least-squares method.

Then the r.m.s. deviations δ of the experimental ln $V_{A,1}$ values at various temperatures from those calculated at different values of the molecular structure parameters are calculated from

$$\delta = \sqrt{ 1/n^2 \sum_{i=1}^{n} [\ln V_{A,1}^{exptl.}(T_i) - \ln V_{A,1}^{calc.}(T_i)]^2 } \tag{9}$$

where $V_{A,1}^{exptl.}(T_i)$ and $V_{A,1}^{calc.}(T_i)$ are the experimental and the calculated $V_{A,1}$ values at temperature T_i, respectively, and n is the number of experimental values of $V_{A,1}$.

Finally, the values of the molecular structure parameters are found at which the calculated $V_{A,1}$ values best fit the experimental ones, i.e., at which δ is minimum.

RESULTS

Fig. 1 shows the results of the calculations for ethylbenzene. In calculating δ, the experimental $V_{A,1}$ values for ethylbenzene on GTCB obtained by Vidal-Madjar et al[4] are used. It follows from the figure that the best agreement between the calculated and experimental $V_{A,1}$ values for ethylbenzene is obtained when $W_0 \approx 2$ kJ
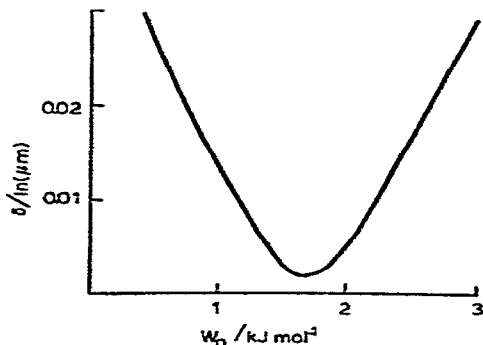

Fig. 1. The dependence of δ on W_0 for ethylbenzene.

mol^{-1}. The assumed form for the potential function W (a) and the experimental data used in calculating δ have a slight effect on the value of W_0 determined by this method (Table I). The value of W_0 for ethylbenzene obtained

TABLE I

EFFECT OF THE FORM OF THE FUNCTION $W(a)$ AND OF THE EXPERIMENTAL VALUES OF $V_{A,1}$ ON THE DETERMINED VALUES OF W_0 FOR ETHYLBENZENE

Function $W(a)$	W_0 $(kJ\,mol^{-1})$	
	Experimental $V_{A,1}$ values from ref. 4	Experimental $V_{A,1}$ values from ref. 5
Cosinusoidal	1.7	2.0
"Saw-tooth" shape	2.1	2.5
Rectangular	1.4	1.6

from $V_{A,1}$ is about half of that obtained recently from calorimetric data[6].

Fig. 2 shows the results of analogous calculations for biphenyl. On the ordinate axis in Fig. 2a are given the minimum values of the r.m.s. deviations, $\delta_{min.}$, of the experimental $\ln V_{A,1}$ values for biphenyl[5] from those calculated at various equilibrium angles $a_{min.}$ and at the corresponding potential barriers for a planar benzene ring arrangement, W_{01} (shown in Fig. 2b), and for a perpendicular one, W_{02} (shown in Fig. 2c). Fig. 2a shows that the equilibrium angle $a_{min.}$ in biphenyl cannot be determined unambiguously from $V_{A,1}$ on GTCB. Nevertheless, we can conclude that $a_{min.} \geqslant 20°$ and $W_{01} \geqslant 6$ kJ mol^{-1}. If, however, one uses the value $a_{min.} = 42°$ obtained by the electronographic method[7] then both values of the potential barriers can be determined from the experimental $V_{A,1}$ values. It follows from Fig. 2 that at $a_{min.} = 42°$, $W_{01} \approx 7$ kJ mol^{-1} and W_{02} is close to zero.
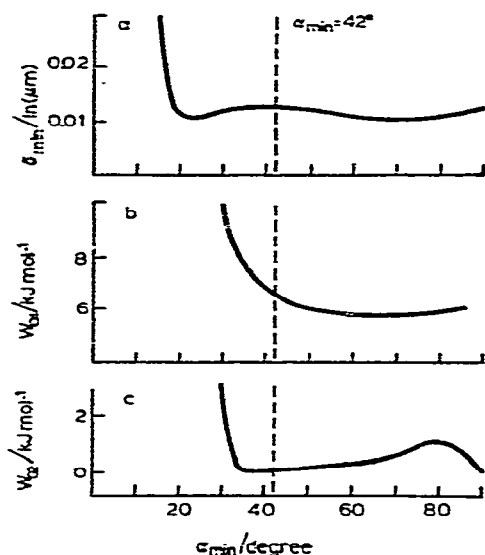

Fig. 2. Values of $\delta_{min.}$ for biphenyl obtained at various fixed values of $a_{min.}$ (a) and at the corresponding values of W_{01} (b) and W_{02} (c).

As in the case of ethylbenzene, the form of $W(\alpha)$ for biphenyl as well as the slight changes in the form of dependence of $V_{A,1}$ on α have little effect on the potential barriers W_{01} and W_{02} determined from $V_{A,1}$. However, the errors in the experimental $V_{A,1}$ values can have a significant effect on those values. The W_{01} value obtained by us is close to that determined with the use of spectral data[8] and lies in the middle of the range of values calculated by various theoretical methods. W_{02} determined from chromatographic data is apparently less accurate than W_{01}.

Fig. 3 shows the results of analogous calculations for 2,6-dimethylbiphenyl. In this case, both the equilibrium angle $\alpha_{min.}$ and the potential barriers W_{01} and W_{02} can be determined from $V_{A,1}$. It follows from Fig. 3 that $\alpha_{min.} \approx 68°$, $W_{01} > 200$ and $W_{02} \approx 5$ kJ mol.$^{-1}$. The obtained $\alpha_{min.}$ value is close to that obtained by the electronographic method for 4-fluoro-2,4,6-trimethylbiphenyl[9] which has also two methyl groups in *ortho* positions. To our knowledge, there are no literature data on the potential barriers to internal rotation in 2,6-dimethylbiphenyl.
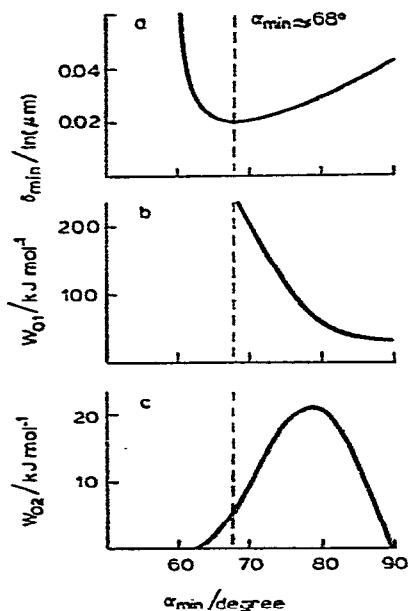

Fig. 3. Values of $\delta_{min.}$ for 2,6-dimethylbiphenyl obtained at various fixed values of $\alpha_{min.}$ (a) and at the corresponding values of W_{01} (b) and W_{02} (c).

Fig. 4 shows the calculated dependence of $\ln V_{A,i}$ for hexamethylbenzene at 500 K on the angle β of the deviation of C–CH$_3$ bonds to different sides of the plane of the benzene ring. The horizontal dashed line shows the experimental $V_{A,1}$ value for hexamethylbenzene at this temperature[5] and the vertical dashed line shows the corresponding β value, equal to *ca.* 10°. The latter value is close to that determined by the electronographic method[10].

Thus the retention volumes of hydrocarbons on GTCB can be used to determine some important structural parameters, in particular the equilibrium angles and the potential barriers to internal rotation of molecules, which for many molecules are not yet known.
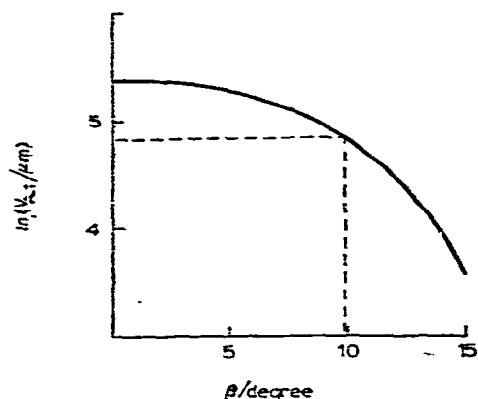
Fig. 4. The dependence of ln $V_{A,1}$ on β for hexamethylbenzene calculated at 500° K (solid curve) and the corresponding experimental ln $V_{A,1}$ value (horizontal dashed line).

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REFERENCES

1 N. N. Avgul, A. V. Kiselev and D. P. Poshkus, *Adsorptsiya gazov i parov na odnorodnykh poverkhnostyakh (Adsorption of Gases and Vapours on Homogeneous Surface)*, Khimya, Moscow, 1975.
2 E. V. Kalashnikova, A. V. Kiselev, R. S. Petrova and K. D. Shcherbakova, *Chromatographia*, 4 (1971) 495.
3 A. V. Kiselev and D. P. Poshkus, *J. Chem. Soc., Farad. Trans. II*, 72 (1976) 950.
4 C. Vidal-Madjar, M.-F. Gonnord and G. Guiochon, *J. Colloid Interface Sci.*, 52 (1975) 102.
5 E. V. Kalashnikova, A. V. Kiselev and K. D. Shcherbakova, *Chromatographia*, 7 (1974) 22.
6 A. Miller and D. W. Scott, *J. Chem. Phys.*, 68 (1978) 1317.
7 A. A. Almenningen and O. Bastiansen, *Kgl. Nor. Vidensk. Selsk. Skr.*, No. 4 (1958) 1.
8 J. E. Katon and E. R. Lippincott, *Spectrochim. Acta*, (1959) 627.
9 K. Zeitz, H. Oberhammer and G. Häfelinger, *Z. Naturforsch.*, *B*, 32 (1977) 420.
10 R. R. Kare, U. C. Wang and S. H. Bauer, *J. Mol. Struct.*, 25 (1975) 17.