A study of the structure of some cyclic molecules by chromatostructural analysis

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Abstract - Some geometric parameters characterizing non-planarity of
the molecules of cyclobutane, bicyclo[3.3.0]-oct-1,5-ene and bicyclo-
[4.4.0]-dec-1,6-ene are determined by comparing the results of gas chro-
matographic measurements and molecular statistical calculation of the
Henry constant of adsorption equilibrium on GTCB.

INTRODUCTION

Chromatostructural analysis (chromatoscopy) was developed by Kiselev and Poshkus
as a method of evaluating structural parameters of molecules from their adsorption charac-
teristics (Ref. 1,2). A convenient adsorbent for such use is graphitized thermal carbon
black (GTCB), with its homogeneous surface, highly sensitive to the geometry of adsorbed
molecules.

The Henry constant of adsorption equilibrium K_1 measured by gas chromatography (the
retention volume at zero sample size) is compared with the K_1 values obtained by
molecular statistical calculation in atom-atom approximation for a number of mole-
cular models with geometry being varied. In this way certain structural parameters were
evaluated for the molecules of tetralin, hexamethylbenzene, indane and its methyl deriva-
tives, good agreement with the data of other methods being observed (Ref. 1,2).

The series of chromatoscopic investigations of quasi-rigid molecules is continued by the de-
termination of geometric parameters of cyclobutane (Ref. 3), bicyclo[3.3.0]-oct-1,5-ene
(BCO) and bicyclo[4.4.0]-dec-1,6-ene (BCD). Chromatostructural analysis is especially sen-
sitive to variation of those parameters which determine non-planarity of the molecule. In
cyclobutane such parameter is the dihedral angle β of the four-membered cycle, in BCO
the dihedral angle α of the five-membered cycle, in BCD the height h of deviation of
carbon atoms 3,4,8 and 9 from the plane 5-6-7-10-1-2 upwards and downwards (see Fig. 1).

CALCULATIONS

The Henry constants were calculated by the following formula (Ref. 1,2):

$$K_1 = (1/4\pi) \iint (2\pi k T/\varphi'')^{1/2} exp(-\varphi_0/kT) \sin\theta \, d\theta \, d\psi ,$$

where $\Phi = \sum\sum \varphi_{ij}$ is the potential energy of interaction between the molecule and the adsor-
bent. The calculations were carried out with the atom-atom potential functions φ of
interaction H...C(GTCB) (1), $C(sp^3)$...C(GTCB) (2) and $C(sp^2)$...C(GTCB) (3).

Geometric parameters of a cyclobutane molecule were taken from electron diffraction data
(Ref. 4). The models of molecules of BCO and BCD were constructed by joining two cyclo-
pentene rings and two cyclohexene rings, respectively, along the double bond, electron dif-
fraction data on the molecular geometry of cyclopentene (Ref. 5) and cyclohexene (Ref. 6)
being used. Gas adsorption chromatography on GTCB and C^{13}-NMR spectroscopy at room tempera-
ture have detected no difference in respective characteristics of cis- and trans-forms of
BCO and BCD, therefore in chromatostructural analysis only trans-forms were considered.

EXPERIMENTAL

Adsorbent: graphitized thermal carbon black Sterling MT-D4 (7.6 m^2/g).

Chromatographs: a) Varian–Mat–3700, a flame ionization detector, a glass column 40 cm x 0.18 cm, GTCB grains fraction 0.25 - 0.5 mm; b) Tsvett-I, a flame ionization detector, a stainless steel column 50 cm x 0.25 cm, GTCB grains fraction 0.3 - 0.5 mm.

Experimental temperature dependences of K_1 (cm^3/m^2) are expressed by following equations: for cyclobutane $\ln K_1 = -9.48 + 2758/T$, for BCO $\ln K_1 = -12.86 + 5737/T$, for BCD $\ln K_1 = -12.12 + 6190/T$.

CHROMATOSTRUCTURAL ANALYSIS

Figure 1 shows calculated K_1 values for the three molecules in the range of variation of their geometric parameters. In the calculations for BCD the atom-atom potentials (1), (2) and (3) were used. A considerable strain in the molecule of cyclobutane (the strain energy is 111.2 kJ/mol) makes one expect poor results when using the potential (2), which was obtained for non-strained saturated hydrocarbons (Ref. 7). Therefore the calculations for cyclobutane were made both with the potentials (1) and (2) (the lower curve) and with the potentials (1) and (3) (the upper curve), as in the case of cyclopropane (Ref. 8).
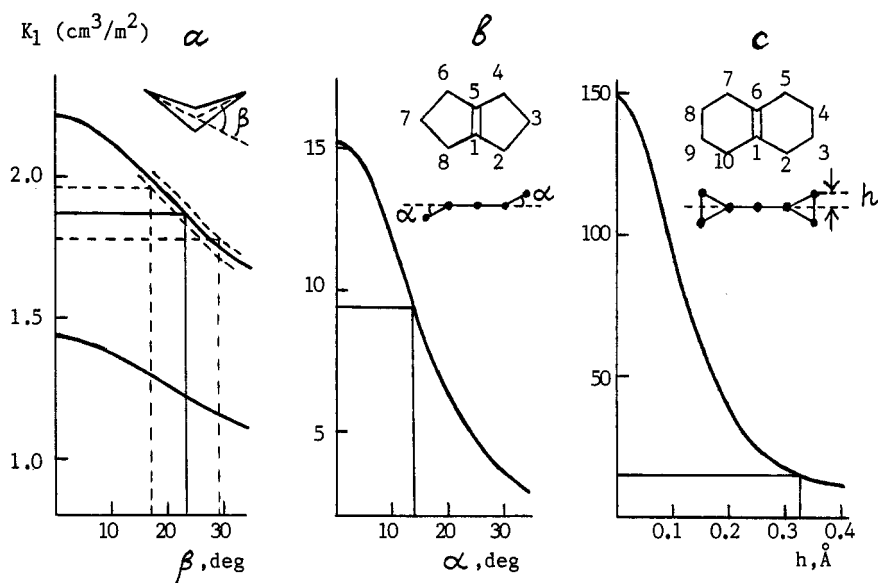

Fig. 1 . The dependence of calculated K_1 on dihedral angles in cyclobutane at 273 K (a) and BCO at 380 K (b) and on the height of deviation in BCD at 420 K (c). Solid horizontal lines represent experimental gas chromatographic values, dashed lines denote the limits of errors in experiment and calculation.

The comparison of the calculated curves and the experimental K_1 values (horizontal lines) leads to the following conclusions: 1) The atom-atom potential of the interaction $C(sp^3)...C(GTCB)$ is not applicable to cyclobutane; the calculations with the potential of interaction $C(sp^2)...C(GTCB)$ gives for the dihedral angle β the value $23^\circ \pm 6^\circ$, which is within the range of estimates by other methods; 2) The dihedral angle α in BCO is $13.6^\circ \pm 1.7^\circ$ (electron diffraction gives 17°); 3) The height h in BCD is 0.325 ± 0.040 Å (molecular mechanics gives 0.405 Å).

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