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## RELATIONS BETWEEN GAS CHROMATOGRAPHIC BEHAVIOUR AND CHEMICAL STRUCTURE

## III. THE NATURE OF INTERNAL ROTATION IN METHYL DERIVATIVES OF BENZENE\*

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## SUMMARY

The absence of a large isotope effect in the gas chromatographic behaviour of methyl derivatives of benzene indicates that the methyl rotation is not free in our model compounds, but corresponds to rotation-oscillation.

An incremental value in  $\log \alpha$  is found whenever one methyl group is in *ortho* position with respect to another. Additional absorption bands, which are the expected overtones of methyl non-symmetric deformations in the infrared spectra of such compounds, suggest that this "*ortho*-shift" effect in gas chromatography is due to perturbation of the methyl rotation-oscillation.

Conversely, it is suggested that the "*ortho*-shift" effect in gas chromatography may be exploited as an additional or a complementary technique in the investigation of configuration and conformation of isomers in organic chemistry.

## INTRODUCTION

There is a growing interest in the correlation of chemical structure with behaviour of compounds in gas-liquid chromatography (GLC). The most general statistical mechanical approach, taking into account the effects of the kinetic energy and the configurational potential energy of the molecule in the liquid phase, is, at present, too complicated for practical calculations. No such approach has been reported. The statistical methods, proposed so far, concentrate on the contributions of the configurational potential energy which is only possible however, with the simplifying assumption of hard sphere molecules<sup>3,4</sup>. With the latter methods some fundamental molecular details get lost and it is therefore difficult to account for many of the structural variations of organic chemistry.

In this study the effects of the kinetic energy are investigated and an attempt

\* For parts I and II, see refs. 1 and 2.

is made to eliminate the effects of the configurational potential energy by extreme simplification of the experimental conditions with regard to the liquid phase.

The sensitivity of the energy functions to slight variations of chemical structure and the precision of the additivity rules have been demonstrated in a preliminary investigation<sup>10</sup>.

A direct relation<sup>1</sup> was shown between the partition coefficient in GLC and the ratio of partition functions of statistical mechanics. Extreme simplifications of the mathematical expressions were obtained when the relative retention  $\alpha$ , instead of the absolute retention, were studied. Applying the analysis of variance<sup>1,5</sup> to discriminate between a number of hypotheses postulated, it was found that the separation of benzene and its methyl derivatives on a nonpolar liquid stationary phase corresponds to energy contributions due to translation and internal rotation, the contributions of other types of energy cancel. Under normal GC conditions<sup>1</sup>:

$$\log \alpha = \Delta \log [M^{3/2} \cdot Q_f] \quad (1)$$

where  $M$  is the molecular weight, and  $Q_f$  is its contribution of the internal rotation.

Analysis of the mathematical expressions for the free and the hindered internal rotational energies suggests that the nature of the methyl rotation can be conveniently determined by introducing hydrogen isotopes at strategic positions\* in the model compounds.

#### THEORY

Two types of internal rotation are theoretically considered in our model compounds. They represent special cases according to the height of the potential barrier hindering internal rotation, for which mathematical expressions have been developed.

##### *Free internal rotation*

The height of the potential barrier is small compared to the kinetic energy associated with torsional momentum. For molecules with a number of *light* symmetric tops attached to a *heavy* rigid frame, as described by PITZER AND GWINN<sup>7</sup>, as a good approximation each top contributes a factor  $Q_f$  to the partition function

$$Q_f = \frac{(8\pi^{3/2} k_B T)^{3/2}}{hn} \cdot I_m^{3/2} \quad (2)$$

where

$k_B$  = Boltzmann's constant

$h$  = Planck's constant

$T$  = absolute temperature

$n$  = symmetry factor of top

$I_m = I_m^0$  = moment of inertia of a light symmetric top. This simplification is a good approximation in the case of our model compounds.

Substituting a trideuterated methyl in the place of a methyl group in our model compounds will double the value of  $I_m$ .

\* The mixed trideuteromethyl and methyl derivatives of benzene in this investigation are a type of compound which have not been described in literature before. Their synthesis, purification and identification is described elsewhere<sup>9</sup>.

Therefore according to eqns. 1 and 2 a contribution of approximately

$$\Delta \log a = \log \sqrt{2}$$

is to be expected for every trideuterated methyl group in the case of free internal rotation

#### *Hindered internal rotation*

The height of the potential barrier is high compared to the kinetic energy associated with torsional momentum, frequency of tunnelling through the barrier is negligible in comparison to the rotation-oscillation frequency.

The total rotational energy of the molecule according to TOWNES AND SCHAWLOW<sup>8</sup> is given by

$$W = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I\dot{\chi}^2 + \frac{1}{2}\frac{I_1I_2}{I}\dot{\theta}^2 + \frac{1}{2}V_0(1 - \cos 3\theta) \quad (3)$$

The first three terms in eqn. 3 correspond to the rotational contributions in the case of "rigid rotation" which drop out of GLC relations<sup>1</sup>. The fourth and fifth terms are the contributions of internal rotation-oscillation, being the kinetic and the potential energy, respectively. For the rotation-oscillation  $\dot{\theta}$  should be proportional to the frequency  $\nu$ , thus

$$\dot{\theta}^2 \sim \nu^2 = \frac{k}{4\pi^2} \cdot \frac{I}{I_1I_2} \quad (4)$$

where

$k$  = a force constant, independent of isotope substitution

$\omega$ ,  $\dot{\chi}$  and  $\dot{\theta}$  are angular velocities

$\theta$  = angle of rotation of substituent relative to the frame

$I$  = moment of inertia

$V_0$  = potential barrier hindering internal rotation.

Therefore the moments of inertia cancel out for the kinetic energy of internal rotation, which is the fourth term in eqn. 3.

In the last term of eqn. 3 the energy is controlled by the potential field effects,  $V_0$ . The gravitational constant being extremely small means that by good approximation mass effects do not contribute to  $V_0$ . Substituting a trideuterated methyl in the place of a methyl group in our model compounds therefore has no influence on the last two terms of eqn. 3. In contrast to the case of free internal rotation, a much smaller contribution

$$\Delta \log a \ll \log \sqrt{2}$$

should be expected for every trideuteromethyl group in the case of hindered internal rotation.

#### *Higher order terms of hindered internal rotation*

The shape of the potential barrier in eqn. 3 is not given perfectly by the  $\cos 3\theta$  variation, but more generally should be written as a Fourier series<sup>8</sup>

$$V = \sum_p (a_p \cos 3p\theta + b_p \sin 3p\theta) \quad (5)$$

where

$V$  = potential barrier hindering internal rotation

$p = 1, 2, \dots, p$  indicates the order of the terms

Eqn. 3 is a good approximation for isolated methyl groups. Studying Stuart-Briegleb molecular models it is seen that the presence of another methyl group in the *ortho* position will interfere with the rotation-oscillation movements of the methyl groups. This will cause higher order terms to appear in eqns. 3 and 5. In GC this means an additional contribution to  $\log \alpha$  which is the "*ortho*-shift" effect in our model compounds.

At the same time the appearance of additional absorption bands, overtones (higher order terms of the Fourier series) associated with methyl vibrations, should be expected in the IR spectra of such molecules.

## RESULTS

### Nature of methyl rotation

As is shown in Table I a contribution of the isotope effect was found experimentally for every trideuterated methyl group, amounting to

$$\Delta \log \alpha = -0.0205 \pm 0.0009$$

This value is much less than  $\log \sqrt{2}$  and clearly points to the case of hindered internal rotation with a high potential barrier (eqn. 3) and not to the case of free internal rotation (eqn. 2).

The experimental values of  $\Delta \log \alpha$  are too small to allow the assumption of an intermediate height of the potential barrier. On the other hand, considering the relatively high values of  $Q_f$  that were found in an earlier investigation<sup>1</sup>, the extreme case of a very high potential barrier corresponding to stiff molecules with methyl

TABLE I

RETENTION OF TRIDEUTEROMETHYL ANALOGUES RELATIVE TO NORMAL METHYL DERIVATIVES OF BENZENE ON APIEZON L AT 95°

The relative retention  $\alpha$  of perdeuterobenzene is given for comparison.

Benzene derivative	$\alpha$	$\Delta \log \alpha$	$\Delta \log \alpha$ per $CD_3$
1- $CD_3$	0.9810 $\pm$ 0.0010	-0.0192	-0.0192
1- $CD_3$ -2- $CH_3$	0.9805 $\pm$ 0.0010	-0.0197	-0.0197
1- $CD_3$ -3- $CH_3$	0.9792 $\pm$ 0.0010	-0.0210	-0.0210
1- $CD_3$ -4- $CH_3$	0.9808 $\pm$ 0.0007	-0.0194	-0.0194
1- $CD_3$ -2,3-di- $CH_3$	0.9791 $\pm$ 0.0004	-0.0211	-0.0211
2- $CD_3$ -1,3-di- $CH_3$	0.9808 $\pm$ 0.0004	-0.0194	-0.0194
1- $CD_3$ -2,4-di- $CH_3$	0.9801 $\pm$ 0.0004	-0.0201	-0.0201
2- $CD_3$ -1,4-di- $CH_3$	0.9786 $\pm$ 0.0004	-0.0216	-0.0216
4- $CD_3$ -1,2-di- $CH_3$	0.9786 $\pm$ 0.0005	-0.0216	-0.0216
2- $CD_3$ -1,3,5-tri- $CH_3$	0.9793 $\pm$ 0.0005	-0.0209	-0.0209
1,2-di- $CD_3$	0.9602 $\pm$ 0.0004	-0.0406	-0.0203
1,3-di- $CD_3$	0.9573 $\pm$ 0.0006	-0.0436	-0.0218
1,4-di- $CD_3$	0.9605 $\pm$ 0.0008	-0.0402	-0.0201
2,4-di- $CD_3$ -1,3,5-tri- $CH_3$	0.9590 $\pm$ 0.0002	-0.0418	-0.0209
1,2,4-tri- $CD_3$	0.9354 $\pm$ 0.0007	-0.0667	-0.0222
$C_6D_6$	0.9786 $\pm$ 0.0010	-0.0216	

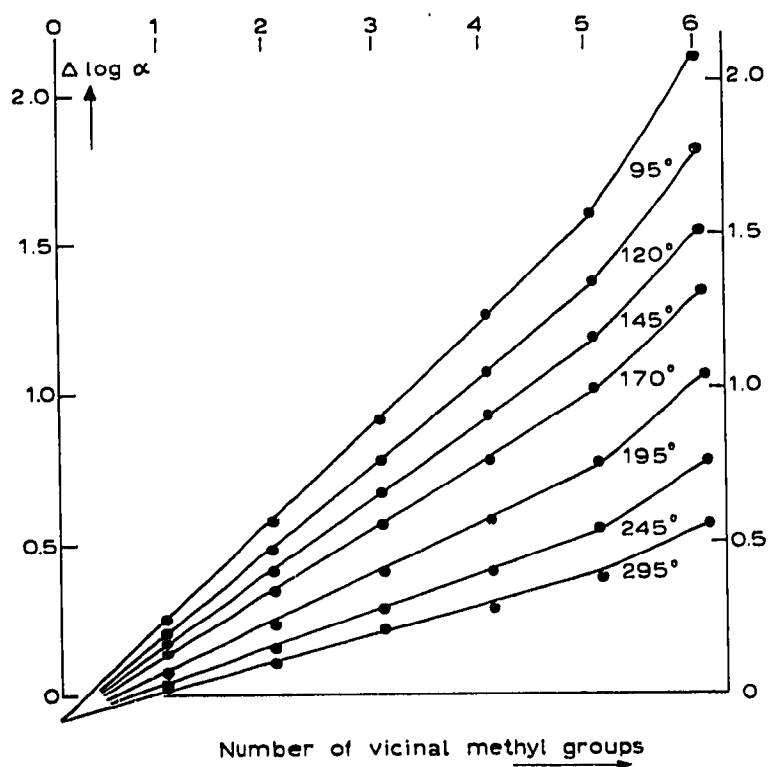


Fig. 1. Contribution of  $\Delta \log \alpha$  of isolated and vicinal methyl groups (M1 through M6) of the methyl derivatives of benzene on Apiezon-L at 95–295°. Data reported in ref. 1.

rotation frozen, can be excluded in our temperature range. It is therefore concluded that methyl rotation in our model compounds corresponds to rotation-oscillation with occasional tunnelling through a high potential barrier.

#### Higher order terms of hindered internal rotation

Every addition of one methyl group in a position *ortho* to another causes perturbation of rotation-oscillation in both of the methyl groups every time. By approximation the same incremental value for the "ortho-shift" in GLC should therefore be expected in the series M1 through M5 (an isolated methyl group is indicated as M1, a string of vicinal methyl groups is treated as one substituent indicated as M2 through M6). In Fig. 1 experimental  $\Delta \log \alpha$  of M1 through M5, by good approximation, indeed show a linear relationship.

Introduction of the sixth methyl group closes the ring of methyl groups causing extra perturbations. The  $\Delta \log \alpha$  of M6 therefore should be higher than would be expected from the linear relationship of M1 through M5 (see Fig. 1).

It can be concluded therefore that, on applying perturbation theory, the GC behaviour of twelve out of thirteen model compounds can be correlated by means of eqns. 1, 3 and 5 and the values of Fig. 1; hexamethyl-benzene is the only exception.

#### Supporting evidence from IR spectra

All the deuterated model compounds of Table I show strong  $\text{CD}_3$  stretching bands at  $2232 \pm 5$ ,  $2210 \pm 5$ ,  $2132 \pm 6$  and  $2060 \pm 10 \text{ cm}^{-1}$  in their IR spectra.

As these bands are sharper and are situated at much larger distance from each other in comparison to those of  $\text{CH}_3$ , it is convenient to study the appearance of overtones in this region: overtones of  $\text{CD}_3$  non-symmetric deformation might be expected here (calculated from the  $\text{CH}_3$  vibrations<sup>0</sup> of propene using  $\bar{\nu}_D/\bar{\nu}_H = 0.73$ ). A number of additional absorption bands of medium strength are indeed found in the IR spectra of 1,2-di- $\text{CD}_3$ -benzene (2158, 2130, 2118 and 2080  $\text{cm}^{-1}$ ) and 1,2,4-tri- $\text{CD}_3$ -benzene (2170, 2110, 2075 and 2055  $\text{cm}^{-1}$ ).

Correspondingly, inspection of the IR spectra of all normal methyl derivatives of benzene showed that the absorption bands in the region between 2960 and 2850  $\text{cm}^{-1}$  have a more complicated pattern when vicinal methyl groups are present in the molecule. When the vicinal methyl groups are not identical, that is  $\text{CD}_3$  *ortho* to  $\text{CH}_3$ , no additional absorption bands are found in both the regions 2230–2050 and 2960–2850  $\text{cm}^{-1}$  or 2600–2450  $\text{cm}^{-1}$ . This suggests that combination bands of  $\text{CD}_3$  and  $\text{CH}_3$  non-symmetric deformations are absent or extremely weak, and the additional bands observed are the overtones expected.

It is suggested therefore that addition of one methyl group in a position *ortho* to another causes perturbation in methyl group non-symmetric deformation vibrations. The resulting overtones are spectroscopically strongly active when the vicinal methyl groups are identical. When the vicinal methyl groups are mixed ( $\text{CD}_3$  *ortho* to  $\text{CH}_3$ ) perturbation is still present, causing the same "*ortho*-shifts" in GC, however because of in-phase and out-of-phase coupling of the vibrations ( $\bar{\nu}_D/\bar{\nu}_H = 0.73$ ) these overtones are, by chance, spectroscopically non-active.

There is no reason to believe that perturbation, whenever it occurs, should be limited to one type of methyl vibration only. It is therefore concluded that, applying perturbation theory, the "*ortho*-shift" effect in our model compounds in GC is related to the appearance of additional absorption bands in their IR spectra. Conversely, this suggests that the "*ortho*-shift" effect in GC may be exploited as a new technique in the investigation of configuration and conformation of isomers in organic chemistry. This will be of particular convenience in those cases where internal rotation is spectroscopically not active in IR, Raman and microwave spectrometry.

## EXPERIMENTAL

The mixed trideuteromethyl and methyl derivatives\* of benzene<sup>0</sup> were obtained by the Wurtz-Fittig synthesis, purified by GLC and identified by IR\*\* and NMR\*\*\* spectrometry. The NMR spectra showed a high isotopic purity for the methyl groups; this was confirmed by mass spectrometry. Perdeuterobenzene was commercially available.

### IR spectra

Double beam grating IR spectrophotometer, Perkin-Elmer Model 337; 2–10 mg sample in 0.3 ml carbon tetrachloride, 0.5 mm KBr cell.

\* Synthesis and purification were performed with the assistance of Miss M. C. HAZELEGER.

\*\* IR spectra were measured by Mrs. M. A. G. DEN DULK-BARENS.

\*\*\* NMR spectra were measured by Miss L. A. MARS.

*GC conditions*

Chromatograph, Hewlett-Packard/F & M, Model 5750.

Detector, hydrogen flame ionisation detector.

Recorder, Hewlett-Packard,  $-0.05-1$  mV, 1 sec.

Carrier gas, He at 100 ml/min measured at the exit at  $20^\circ$  and 1 atm.

Sample size, 0.01 to 0.10 mg per component.

Analysis temperature,  $95^\circ$ .

*Column K47*: 9 m  $\times$  0.5 cm I.D. coiled copper tube filled with Apiezon L (5:95) on Chromosorb P DMCS (100/120 mesh), efficiency *ca.* 12,000 theoretical plates; analysis time 550 min for pentamethylbenzene.

*Column K56*: 4 m  $\times$  0.5 cm I.D. coiled stainless steel tube filled with Apiezon L (5:95) on Chromosorb P DMCS (100/120 mesh), efficiency *ca.* 6,000 theoretical plates. Other conditions and correction factors are given in ref. 10.

*Evaluation of retention data from partially resolved pairs*

Evaluation of partially resolved normal peak pairs has been studied by VANDENBELT AND HENRICH<sup>11</sup>.

Peak pairs that have 50% or better separation have their apparent maxima at the same positions as the maxima of the component peaks<sup>11</sup>. No corrections are therefore needed for the peak positions of the di-CD<sub>3</sub> and the tri-CD<sub>3</sub> derivatives relative to their fully protonated analogues. Representative chromatograms are shown in Fig. 2, showing separations on column K56.

On the high resolution column K47 some separations (not shown) were obtained that were even better than 90%.

The mono-CD<sub>3</sub> derivatives, even with the high resolution column K47, have a separation of approximately 10% relative to their fully protonated analogues. In such cases the apparent peak maxima are shifted relative to the maxima of the component peaks. The corrections are most conveniently evaluated<sup>11</sup> when the com-

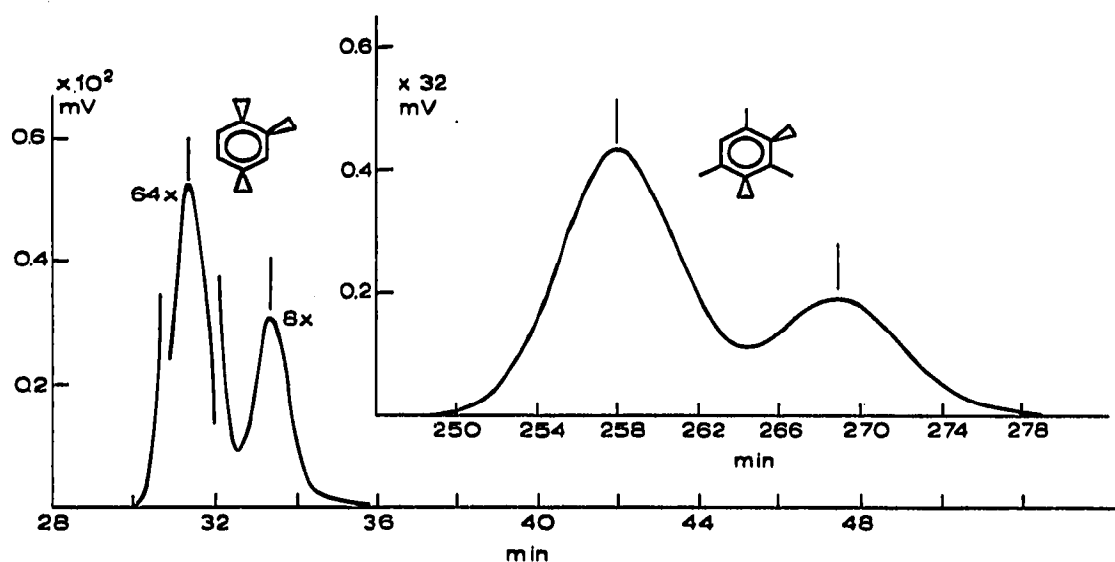


Fig. 2. Separations of 2,4-di-CD<sub>3</sub>-1,3,5-tri-CH<sub>3</sub>-benzene and 1,2,4-tri-CD<sub>3</sub>-benzene from their fully protonated analogues on an Apiezon L GC column K56 at  $95^\circ$ .

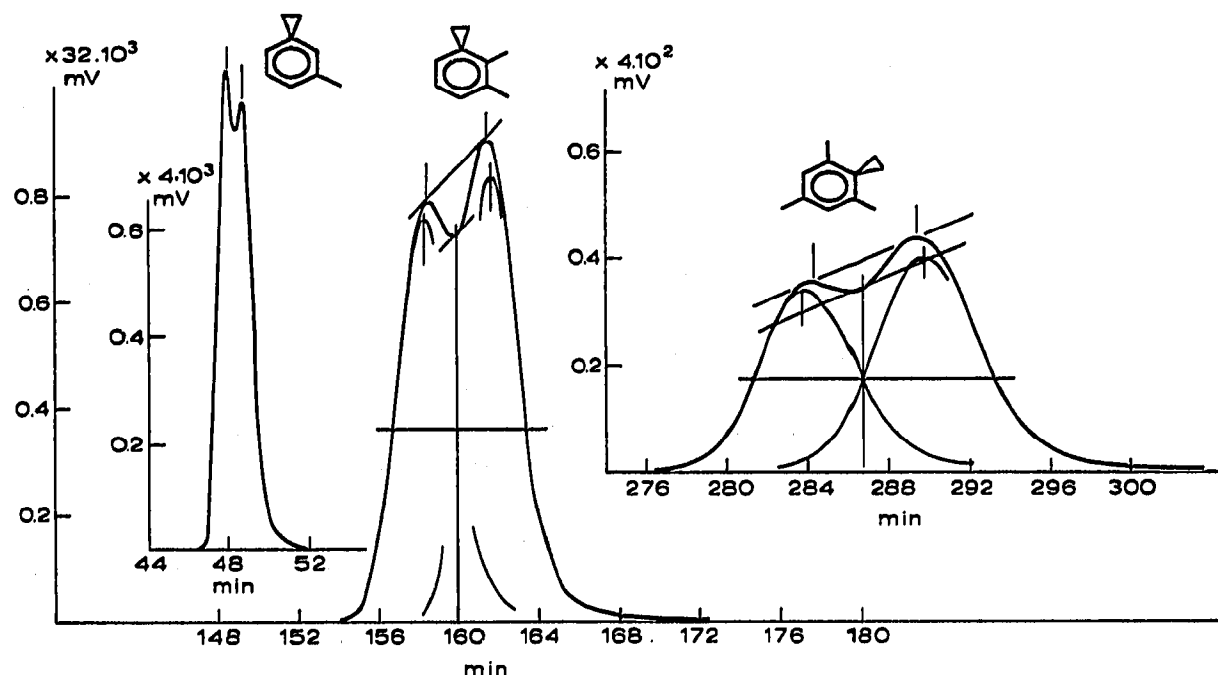


Fig. 3. Separations of 1- $\text{CD}_3$ -3- $\text{CH}_3$ -benzene, 1- $\text{CD}_3$ -2,4-di- $\text{CH}_3$ -benzene and 2- $\text{CD}_3$ -1,3,5-tri- $\text{CH}_3$ -benzene on an Apiezon L GC column K47 at  $95^\circ$ .

ponents have equal peak height. Sample composition\* was adjusted with this in mind.

Alternatively, corrections to the position of the peak maxima were obtained by the following approach as demonstrated in Fig. 3. A straight line joining the two apparent peak maxima is drawn. The tangent to the valley is drawn parallel to the first line. Its point of contact is, by approximation, the point where both components contribute equally to the amplitude of the detector signal. The point at half height is a common point of the two component peaks (see Fig. 3). The lower front part of the second component is drawn through the common point parallel to the lower front part of the first component (which coincides with the lower front part of the apparent peak for separation of 10% or better). The amplitudes for the top part of the first component peak are found by computation. The top part of the second component peak is constructed in an analogous way. The two methods produce practically the same corrections for the location of the peak maxima. Representative gas chromatograms are shown in Fig. 3.

Trideuteromethyl benzene and perdeuterobenzene are eluted very rapidly and they are, therefore, more difficult to separate from their fully protonated analogues. They were injected separately with a number of internal standards. Repeat experiments were performed until the required accuracy was attained.

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\* There is a large difference of detector response in several cases. The signal of an equal weight of 1,4-di- $\text{CD}_3$ -benzene is approximately a factor 10 less than that of the corresponding *para*-xylene. A detailed investigation of this effect is in progress.



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