

The InfraRed Spectra of pBenzened 2 and pBenzened 4

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with d representing the interaction. If we denote the secular equations for the separate blocks (setting $d=0$) by

$$0 = A(\lambda) = \sum_{i=0}^m a_i \lambda^{m-i}, \quad (\text{A2})$$

$$0 = B(\lambda) = \sum_{j=0}^n b_j \lambda^{n-j}, \quad (\text{A3})$$

and their product by

$$0 = C(\lambda) = A(\lambda) \cdot B(\lambda) = \sum_{k=0}^{m+n} c_k \lambda^{m+n-k}, \quad (\text{A4})$$

$$c_k = \sum_{i=0}^k a_i b_{k-i},$$

then the secular equation with $d \neq 0$ is simply obtained from $C(\lambda)$: wherever the product $g_m^m g_{m+1}^{m+1}$ appears, one has only to substitute therefor $(g_m^m g_{m+1}^{m+1} - d^2)$.

This is easily seen. For, of all possible minors of the \mathbf{G} matrix (A1) containing d , those which do not obviously vanish will be of the same form as (A1)—i.e., will have d 's "bridging" the principal diagonal—or will be of the form

$$\left[\begin{array}{cccc|c} g_1^1 & \cdots & g_1^k & g_1^m & \\ \cdots & \cdots & \cdots & \cdots & \\ g_1^k & \cdots & g_1^k & g_1^k & X \\ 0 & \cdots & 0 & d & \\ \hline & & & 0 & X \end{array} \right], \quad (\text{A5})$$

or of the form

$$\left[\begin{array}{ccc|c} g_k^k & \cdots & g_m^k & 0 \\ \cdots & \cdots & \cdots & \\ g_k^m & \cdots & g_m^m & \\ \hline 0 & \cdots & d & \\ \cdots & \cdots & \cdots & \\ 0 & \cdots & 0 & X \end{array} \right]. \quad (\text{A6})$$

The determinants of the form (A6) will clearly not contain d , while determinants of the form (A5) will correspond to vanishing minors of the \mathbf{F} matrix; hence no contribution from d will arise in either of these cases. So we need consider only minors of the form (A1). Such a determinant may be expanded, by Laplace's development, in the second minors of second-order determinants based on the m th and $(m+1)$ th columns. To be non-vanishing, these second minors must be obtained by striking out one of the first m rows and one of the last n ; this restricts the second-order determinants which will actually contribute to those of the types

$$\begin{vmatrix} X & 0 \\ 0 & X \end{vmatrix}, \quad \begin{vmatrix} X & 0 \\ d & X \end{vmatrix}, \quad \begin{vmatrix} X & d \\ d & X \end{vmatrix}.$$

There is but one of this last type, and it will contribute the term $(g_m^m g_{m+1}^{m+1} - d^2)$ —the only way in which d can appear in the final secular equation.

Similar considerations can be applied if more than one interaction couples two blocks, but the increased complexity makes it scarcely worth while.

The Infra-Red Spectra of p -Benzene- d_2 and p -Benzene- d_4

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INTRODUCTION

IN a paper by the authors which appears in this issue¹ reference is made to some experimental work on the infra-red spectrum of p -benzene- d_2 . The purpose of this note is to present the data on this compound, together with that on p -benzene- d_4 , in detail sufficient for the above-mentioned paper. The work was originally undertaken for the purpose of locating ν_{14} and ν_{15} and for completing the analysis of the vibrational spectrum of benzene. This aspect will be discussed in a later report.

PREPARATION OF SAMPLES

The deuterium compounds were prepared by

¹ F. A. Miller and B. L. Crawford, Jr., *J. Chem. Phys.* **14**, 282 (1946).

the method of Langseth and Klit,² which involves the continuous formation of a Grignard reagent and its decomposition with deuterium chloride. The last step is the separation of the deuterio-benzene from the great excess of diethyl ether solvent by distillation. In the case of the p -benzene- d_4 an unknown intermediate fraction boiling at 70–75° was obtained in addition to the desired p -benzene- d_4 fraction at 76.3–77.0°.³ On exposure to air this intermediate fraction

² A. Langseth and A. Klit, *Kgl. Danske Vid. Sels. Math. fys. Medd.* **15**, No. 13 (1938).

³ Because these temperatures are uncorrected for atmospheric pressure (745 mm) and for errors in calibration of the thermometer (at least 1.2°), they have only relative significance. The boiling point of benzene was observed to be 77.0° under the same conditions, although the correct value is 80.1°.

gradually turned pink. To eliminate any absorption bands in the spectrum of the *p*-benzene-*d*₄ sample which may be due to this impurity, the spectrum of the 70–75° fraction was obtained under identical conditions. It was found that all absorption bands but one in the spectrum of the 70–75° fraction were of the same order of intensity as those in the spectrum of the *p*-benzene-*d*₄ sample. They were therefore thought to be due to *p*-benzene-*d*₄, since the 70–75° fraction is certainly rich in this. The one exception (1213 cm⁻¹) was very intense in the 70–75° fraction, but was weak in the *p*-benzene-*d*₄ sample. Consequently it was considered to originate with the impurity and was rejected from the spectrum of the deuterobenzene. The diminution of intensity was so great that there is little likelihood of having overlooked any other such interferences.

SPECTROSCOPIC PROCEDURES

The spectrum of *p*-benzene-*d*₂ was obtained on two different spectrometers: (1) one constructed at the University of Minnesota, using fluorite (CaF₂), rocksalt, and KBr prisms. (2) a

TABLE I.

<i>p</i> -benzene- <i>d</i> ₂ cm ⁻¹	Int.	<i>p</i> -benzene- <i>d</i> ₄ cm ⁻¹	Int.
594	<i>vs</i>	780	<i>w</i>
657	<i>w</i>	817	<i>vs</i>
693	<i>m</i>	832	<i>s</i>
766	<i>m</i>	865	<i>s</i>
778	<i>vs</i>	925	<i>vs</i>
792	<i>m</i>	938	<i>s</i>
815	<i>s</i>	1058	<i>m</i>
829	<i>m</i>	1122	<i>m</i>
873	<i>vs</i>	1180	<i>w</i>
924	<i>s</i>	1207	<i>m</i>
1034	<i>m</i>	1281	<i>w</i>
1097	<i>vw</i>	1301	<i>w</i>
1227	<i>w</i>	1341	<i>w</i>
1325	<i>vw</i>	1396	<i>vw</i>
1416	<i>s</i>	1447	<i>vs</i>
1473	<i>vs</i>	1563	<i>m</i>
1609	<i>w</i>	~1722	<i>vw</i>
1719	<i>m</i>	1831	<i>vs</i>
1814	<i>s</i>	2283	<i>vs</i>
1924	<i>s</i>	~2320	<i>m</i>
2101	<i>vw</i>		
2194	<i>w</i>		
2276	<i>vs</i>		
2314	<i>m</i>		
2866	<i>w</i>		
2992	<i>m</i>		
3044	<i>m</i>		
3083	<i>vs</i>		
3279	<i>w</i>		

TABLE II.

	<i>p</i> -benzene- <i>d</i> ₂ Calc.	Obs.	<i>p</i> -benzene- <i>d</i> ₄ Calc.	Obs.
ν_{11}	600	594	549	
ν_{16b}	360		377	
ν_{17b}	868	873	918	925

Perkin-Elmer instrument with rocksalt optics at the University of Illinois. Results agreed well, so only averaged or preferred values will be tabulated here.

The spectrum of *p*-benzene-*d*₄ was obtained in the rocksalt region with the Perkin-Elmer instrument only.

All the spectra were measured in the gas phase with a vapor pressure of 85 mm of mercury. The cell length of the Minnesota spectrometer was 20 cm; that of the Perkin-Elmer instrument 10 cm.

RESULTS AND COMMENT

The results are tabulated in Table I.

Several assignments can immediately be made to the non-planar vibrations which are infra-red-active. These are indicated in Table II.⁴

There is little doubt that the absorptions of 873 and 925 cm⁻¹ originate from the same vibration, for both are very intense and the band contours are similar. Even if calculated values were not already at hand, one would probably want to assign the two bands to ν_{17b} because the frequency in *p*-benzene-*d*₂ is *lower* than that in *p*-benzene-*d*₄. It is nevertheless noteworthy that the value of ν_{17b} can be calculated so precisely. This provides convincing support for the assignment of ν_{17} advanced by the authors in the accompanying paper, and leads one to feel that force constants σ , θ , and ω cannot be far wrong.

More complete experimental details and an analysis of the remainder of the spectra will be presented in a later paper.

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⁴ The calculated values are taken from Table VII of reference 1.