INFRARED SPECTRUM OF BENZENE

Work done by John Flanagan, R. Gardner,
Frances McKee and Richard Schlegel

Written by Richard Schlegel

ABSTRACT

Benzene shows weak absorption bands in the 3 aliphatic C-H region of the spectrum. The peaks of these bands are at 3.439, 3.459, 3.504, and 3.545.

In connection with the study of the infrared spectrum of irradiated benzene an intensive study was made of the spectrum of pure benzene in the 3 aliphatic C-H region. It was found that pure benzene shows some absorption in that region. "Aliphatic" peaks were found at wave-lengths 3.439, 3.459, 3.504, 3.545. (See Fig. 1) The absorption coefficients* of the very strong benzene bands around 3.26 (the aromatic C-H region) compare with those of the "aliphatic" peaks shown below.

TABLE 1

ABSORPTION COEFFICIENTS OF BENZENE BANDS

"Aromatic" Region		"Aliphatic" Region	
Wave Length	Absorp. Coeff.	Wave Length	Absorp. Coeff.
3.232	43.8	3.439	0.4
3.253	36.5	3.459	1.2
3.290	54.2	3.504	0.3
...	...	3.545	0.9

*The absorption coefficient k is here defined by the expression $I = I_0 \text{ expt. } (-kcd)$ where c is the concentration in moles per 1000 g of carbon tetrachloride and d is the path-length in cm.

At first it was assumed that the absorption bands in the aliphatic region were the result of aliphatic impurities in the benzene. Cyclohexane, with freezing and boiling points close to those of benzene, seemed a possible impurity. However, the frequencies of the 3 cyclohexane bands are sufficiently different from the observed benzene bands to eliminate the chance that the latter arise from cyclohexane. An actual study of a mixture of benzene and cyclohexane corroborated this conclusion.

Next a study of samples of benzene of extremely high purity was made. One sample was prepared by the method of Richards and Shipley[1], which is now in general use for the preparation of benzene for thermodynamic and physical studies. The method involves various chemical washings, and is completed with six recrystallizations and fractional distillation. With this very pure sample (derived from Baker's C. P. thiophene-free reagent) no decrease in infrared absorption in the aliphatic region was found. Benzene was also prepared from benzoic acid and calcium oxide, CaO. This benzene was recrystallized four times and fractionally distilled. Again, no decrease in the aliphatic absorption was found.

Finally carbon disulfide was used in place of carbon trachloride, the solvent in which the benzene absorption is usually studied. The possible effect of a glyptal glue (used in the cell and normally impervious to the solvents used) on the dilute solutions of benzene was also studied. None of these studies indicated that the absorption was caused by materials extraneous to benzene. It was concluded that the bands observed are proper to the benzene spectrum.

These investigations were made with the University of Illinois echelette type grating spectrometer, ruled 3600 lines to the inch, which was made available through the courtesy of Professor W. H. Rodebush.

The only previous work found on the presence of benzene absorption bands in the aliphatic C-H region is that of Barnes[2], done with the Johns Hopkins grating in 1930. There seem to have been uncertainties, however, in Barnes's method; he does not report the bands in later papers.

BIBLIOGRAPHY

(1) Richards, T. W., and J. W. Shipley, J. Am. Chem. Soc., 36, 1825 (1914).

(2) Barnes, H. B., Phys Rev., 35, 1525 (1930); and 36, 296 (1930).

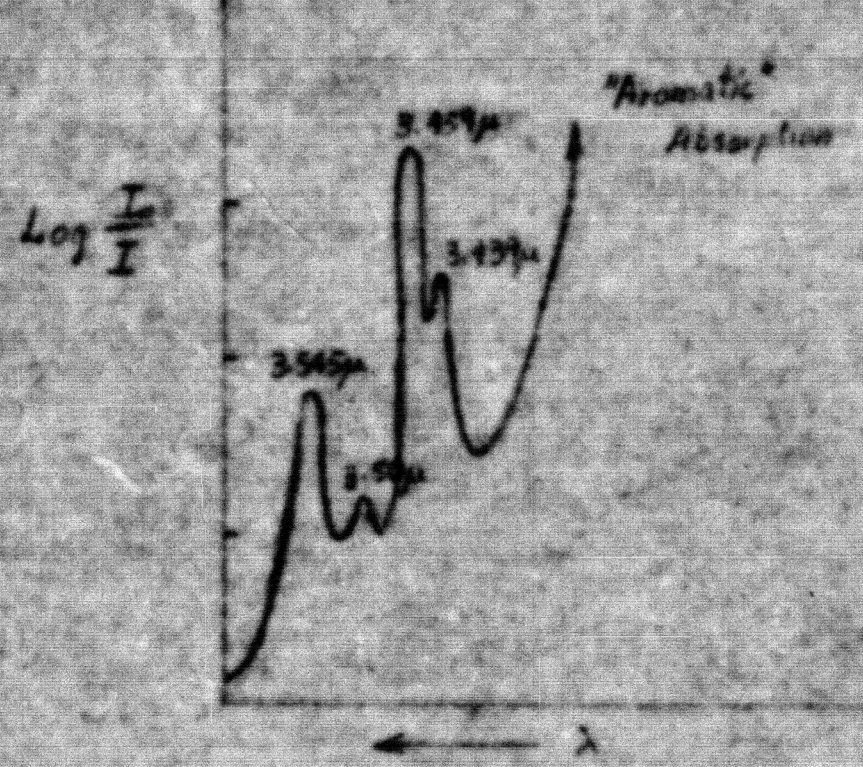

Fig. 1. Infrared absorption in benzene