

[CONTRIBUTION FROM THE DEPARTMENTS OF PHYSICS AND CHEMISTRY, THE UNIVERSITY OF TEXAS]

**Molecular Orbital Theory and Spectra of Monosubstituted Benzenes. VI. Styrene, Phenylacetylene and Phenylcycloalkanes**BY W. W. ROBERTSON, J. F. MUSIC<sup>1</sup> AND F. A. MATSEN**Introduction**

The spectra of monosubstituted benzenes provide an excellent medium for the study of the electronic characteristics of functional groups. The near ultraviolet spectrum of benzene itself is unique among the electronic spectra of polyatomic molecules both from the standpoint of its discreteness and more importantly from the standpoint of its unambiguous interpretation. Further, most substituent groups perturb only slightly the benzene nucleus and, consequently, it maintains most of its characteristics.

On substitution, the benzene spectrum is modified, and the amount of the modification is a measure of the extent of perturbation by the substituent group. This, in turn, provides for an electronic characterization of the group. Directing power, hyperconjugation, ring strain and steric hindrance are a few of the phenomena which may be studied by means of these spectra.

A slowly, almost continuously, varying perturbation may be imposed on the benzene ring by a proper choice of substituents. This permits a unified interpretation of many different spectra which increases one's confidence in the interpretation. Further, this feature permits extrapolation to relatively complicated molecules. A slowly increasing perturbation is here presented in the series, isopropylbenzene, phenylcyclohexane, phenylcyclopentane, phenylcyclopropane, phenylacetylene and styrene.<sup>2</sup>

**Instrumental**

The vapor spectra were obtained on a three-meter grating and scanned with a Leeds and Northrup microphotometer. Spectra of styrene were taken at a number of different reservoir temperatures so that accurate measurements could be made on all bands. The plates were measured on a Gaertner 20-inch comparator. The solution spectra were obtained in cyclohexane on a Beckman quartz spectrophotometer. The isopropylbenzene was Phillips research grade. The styrene, phenylacetylene and phenylcyclohexane were obtained from Eastman Kodak Co. and were redistilled before use. The phenylcyclopentane and phenylcyclopropane were synthesized for this work by Dr. S. H. Lee<sup>3</sup> using the method suggested by Rogers.<sup>4</sup>

**Ring Strain**

There are three features of the spectra of mono-

(1) du Pont Fellow, The University of Texas, 1949-1950.

(2) Previously published spectra of the compounds include: isopropylbenzene in solution American Petroleum Institute Ultraviolet Spectrograms, Serial No. 18, 22, 59, 160; as vapor see ref. 7. Phenylcyclopropane in solution, see reference 4. Phenylacetylene and styrene in solution and as vapor, Horio, *Mem. Coll. Eng. Kyoto Imp. Univ.*, **7**, 177 (1933). Styrene in solution, American Petroleum Institute Ultraviolet Spectrograms, Serial Nos. 23, 33, 93, 168.

(3) Department of Chemistry, Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma.

(4) Rogers, *THIS JOURNAL*, **69**, 2544 (1947), and private communication.

substituted benzenes which give a measure of the interaction, or resonance, of the substituent with the benzene ring: position, intensity and internal distribution of intensity. A large interaction moves the absorption of the monosubstituted benzene to longer wave lengths, intensifies the spectrum and changes the internal intensity distribution away from that of benzene. For example, the strong bands in the benzene spectrum are at  $0 + 520 \text{ cm.}^{-1}$  (called A + B),  $0 + 520 + 930$  (A + B + C),  $0 + 520 + 2 \times 930$  (A + B + 2C), etc. In the monosubstituted benzene these benzene bands still appear and, in addition, there occur 0-0 (A) and  $0 + 930$  (A + C) bands (see Fig. 1). The ratio of the intensity of (A + C) to (A + B) increases with an increasing interaction between substituent and the ring. From Table I and Figs. 1, 2 and 3, it will be seen that phenylcyclopropane is between isopropylbenzene and styrene, in its position,

TABLE I

Compound	Position of the 0-0 band, $\text{cm.}^{-1}$
Benzene	38,089
Isopropylbenzene	37,601
Cyclohexylbenzene	37,590
Cyclopentylbenzene	37,435
Cyclopropylbenzene	36,861
Phenylacetylene	36,370
Styrene	34,761

intensity and (A + C) to (A + B) intensity ratio. The interaction of the phenyl group with the isopropyl group is characterized as second order conjugation (hyperconjugation) while with the vinyl group, as first order conjugation. It is to be concluded, then, that with the cyclopropyl group, because of the ring strain, there is, in addition to the second order conjugation, an appreciable amount of first order conjugation.<sup>5</sup> A more quantitative description was given in the preceding paper,<sup>6</sup> in which it was shown that  $p\pi$  orbitals account for the observed first order conjugation.

The spectral characteristics of phenylcyclohexane seem to indicate that the cyclohexyl group is essentially aliphatic in character. The fact that the frequency of its 0-0 band is slightly lower than that of isopropylbenzene probably had no significance since among the alkyl benzenes there is a slight drop in frequency with increasing molecular weight of the substituent.<sup>7</sup> For example, the

(5) Rogers, ref. 4, has compared the solution spectra of propylbenzene, phenylcyclopropane and styrene. He obtained the intensity relations and more qualitatively the relations between positions described above. The conclusions which he drew are essentially the same as those given here.

(6) Music and Matsen, *THIS JOURNAL*, **72**, 5256 (1950).

(7) Matsen, Robertson and Chuoke, *Chem. Revs.*, **41**, 273 (1947).

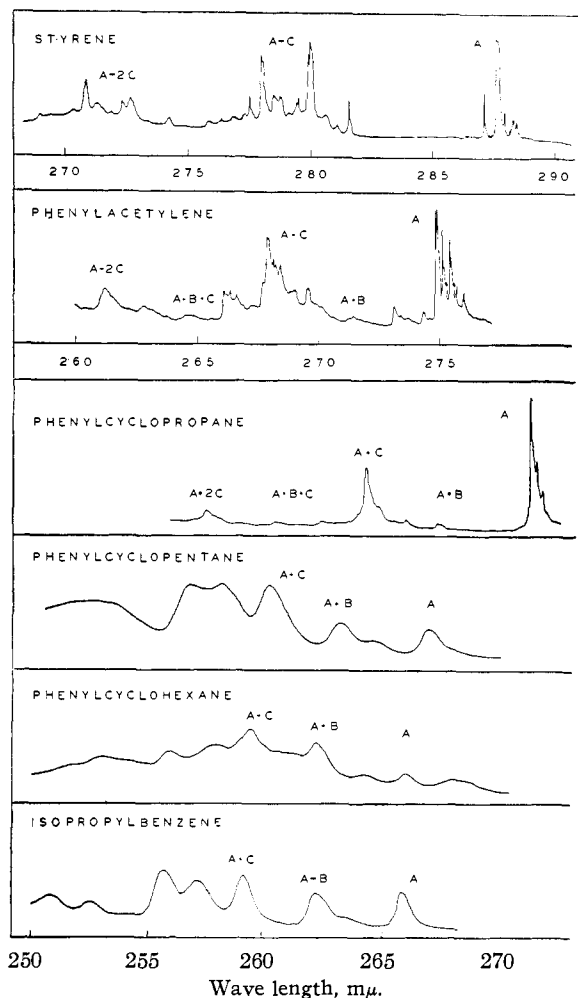


Fig. 1.—Microphotometer tracings of the near ultraviolet absorption spectra of the vapors of styrene, phenylacetylene, phenylcyclopropane, phenylcyclopentane, phenylcyclohexane and isopropylbenzene.

frequency of the 0-0 band of *s*-butylbenzene is 32  $\text{cm}^{-1}$  less than that of isopropylbenzene. However, by the same argument the drop of 155  $\text{cm}^{-1}$  from cyclohexylbenzene to cyclopentylbenzene becomes even more significant and is taken to indicate that in the cyclopentyl group there is enough ring strain to generate some  $\pi$ -orbital character in the bond functions. Further evidence for the ring strain is given by the higher intensity and the larger (A + C) to (A + B) intensity ratio for phenylcyclopentane than for phenylcyclohexane and isopropylbenzene.

The substituents in phenylacetylene and styrene are both unsaturated which makes each molecule simultaneously an analog of butadiene and a monosubstituted benzene. Therefore, one should consider whether the long wave length transition is similar to the  $N \rightarrow V_1$  transition of butadiene or whether it is an  $A_{1g} \rightarrow B_{2u}$  type transition of a monosubstituted benzene. The series of spectra in Fig. 1 range from molecules in which the transition is certainly  $A_{1g} \rightarrow B_{2u}$  to the spectra in question. The regularities in the series—discussed previously—offer strong evidence that for styrene and phenylacetylene the transition is of the  $A_{1g} \rightarrow B_{2u}$  type. Further evidence for this interpretation comes from a comparison of the excited state vibrational frequencies (see Table II).

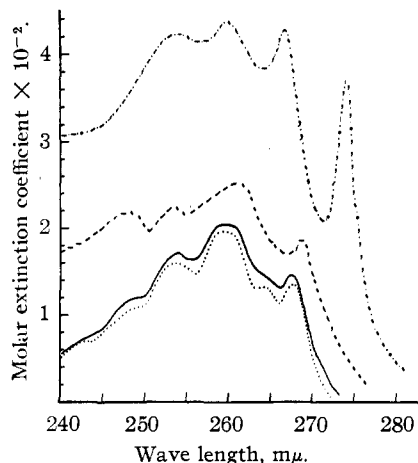


Fig. 2.—The solution spectra in cyclohexane of isopropylbenzene (.....), phenylcyclohexane (—), phenylcyclopentane (---) and phenylcyclopropane (-·-·-).

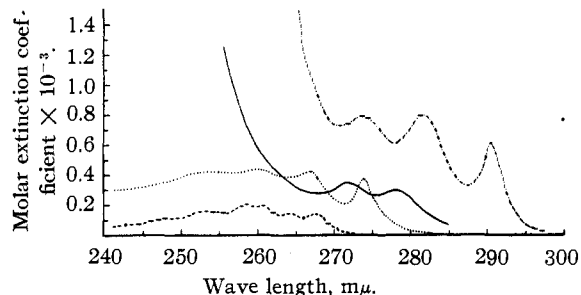


Fig. 3.—The solution spectra in cyclohexane of styrene (-·-·-), phenylacetylene (—), phenylcyclopropane (.....) and isopropylbenzene (---).

TABLE II

Isopropylbenzene	Phenylcyclohexane	Phenylcyclopentane	Phenylcyclopropane	Phenylacetylene	Styrene
0 + 353	0 + 315	0 + 330			
0 + 516	0 + 526	0 + 525	0 + 524	None	None
			0 + 707	0 + 716	0 + 746
0 + 944	0 + 939	0 + 945	0 + 948	0 + 950	0 + 948
			0 + 957	0 + 970	0 + 959
0 + 1234	0 + 1187	0 + 1235	0 + 1203	0 + 1190	0 + 1209

The smaller frequency and lower intensity in phenylacetylene as compared to styrene is attributed to the larger resonance integral of the acetylene bond. A more quantitative description of these transitions is given in the preceding paper.<sup>6</sup> The solution spectra show a large absorption at 2500 Å. for styrene and phenylacetylene. This appears to be due to the  $N \rightarrow V_1$  type transition which would be superimposed on the  $A_{1g} \rightarrow B_{1u}$  transition.

#### Discreteness of the Spectra

The spectra of styrene, phenylacetylene, toluene and benzene are discrete; while those of cyclohexyl-, cyclopentyl-, butyl-, propyl- and ethylbenzene are diffuse. An electronic state becomes diffuse when it is either overlapped by or interacts with another electronic state. For the compounds considered here an interfering state, whose presence is indicated by actual absorption, is not the cause of the diffuseness, since only the discrete styrene and phenylacetylene spectra show absorption in the same region. No statement can be made concerning states not involved in absorption.

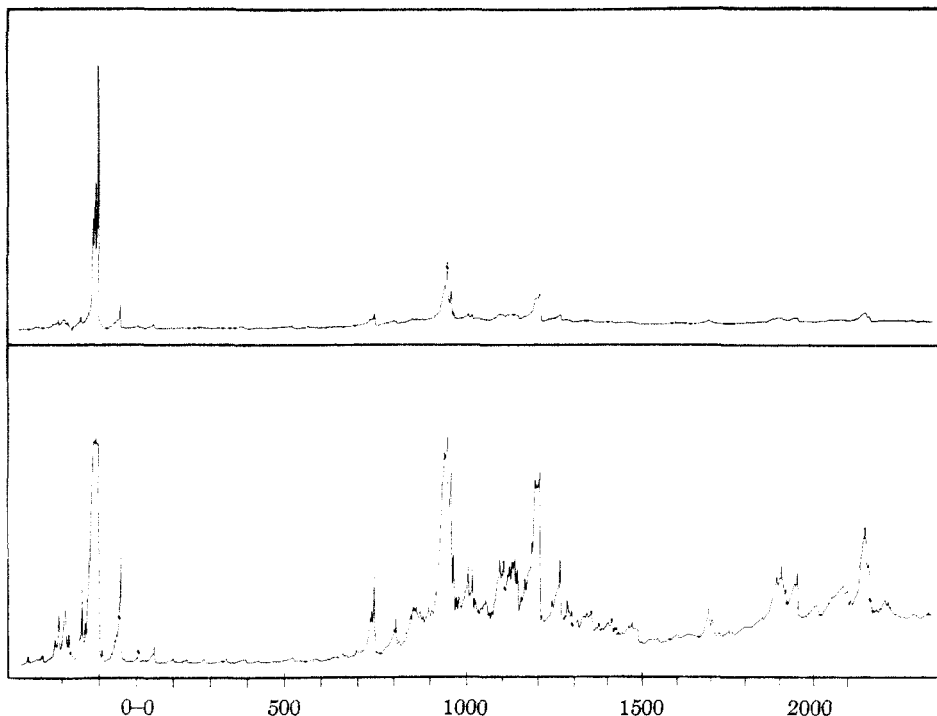


Fig. 4.—Microphotometer tracings of the near ultraviolet absorption spectrum of the vapor of styrene.

Diffuseness may also be caused by internal conversion. In this effect the bands are broadened as a result of the shortening of the lifetime of the vibronic states by conversion of the energy to other forms, *e. g.*, torsional and other vibrations. The observation may be made, that, in the discrete group above, the molecular orbitals extend rather completely over the entire molecule. Thus, although the transition is of the benzene type, it utilizes orbitals which extend well into the substituent. On the other hand, in the diffuse group the MO's extend only over the benzene ring and around the alpha carbon atom. In this case energy conversion could be made to degrees of freedom which are not directly involved in the vibronic state, thus decreasing the lifetime of these states.

In terms of the preceding discussion, it is interesting to note that the cyclopropylbenzene spectrum is only moderately discrete.

### Spectroscopic Bond Order

The position of the near ultraviolet absorption of a monosubstituted benzene is to a great extent determined by the  $\pi$  character of the substituent group. Since the  $\pi$  character of individual bonds is generally described by a bond order, it is useful to define a spectroscopic bond order as

$$SBO_X = 1 + \frac{\nu_B - \nu_X}{\nu_B - \nu_S}$$

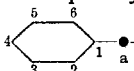
where  $\nu_B$ ,  $\nu_S$  and  $\nu_X$  are the frequencies of the 0-0 bands for benzene, styrene and a monosubstituted benzene with substituent X. The SBO is set up so as to give a bond order of two for the vinyl group in styrene and one (no  $\pi$  character) for non-substituted benzene (see Table III). These bond orders refer to the linkage between the alpha carbon atom and the atom or atoms in the beta position. For the first

two groups the  $\pi$  character arises from the hybrid sigma bonds, and the interaction is called hyperconjugation. For the third group, the  $\pi$  character comes from ring strain. It is interesting to note that a bond order of 1.12 has been calculated<sup>8</sup> for the carbon-carbon bond in ethane.

TABLE III

Group	SBO
Ethyl	1.17
Methyl	1.18
Cyclopropyl	1.67
Vinyl	2.00

It will be recognized that the SBO is crude and less well defined than the regular bond order. No allowance is made for the observation that the frequency of the 0-0 band decreases with the increasing molecular weight of the substituent (see above). Moreover, the frequency of absorp-

tion for the type molecule  is a com-

plicated function of the resonance integrals  $\beta_{a1}$  and  $\beta_{ab}$ . However, since it can be assumed that the resonance integrals are proportional to the respective bond orders (see the preceding paper<sup>6</sup>) there does exist a quasi-theoretical relationship between bond order and frequency.

**Vibrational Analysis of Styrene.**—The near ultraviolet absorption spectrum of styrene, in two stages of development, is presented in Fig. 4. A rather large portion of the more intense fea-

(8) Mulliken, Rieke and Brown, *THIS JOURNAL*, **63**, 41 (1941).

tures of the spectrum<sup>9</sup> may be analyzed on the basis of the following band types: (I) 0-0, (II) 0 -  $\nu$ , (III) 0 +  $\nu'$ , (IV) 0 +  $\nu'_i + \nu'_j$ , (V) 0 + 2 $\nu'$ , (VI) 0 -  $\nu_L$ , (VII) 0 +  $\nu'_L$ , (VIII) 0 +  $\nu' + \nu'_L$ , (IX) 0 +  $\nu' - \nu_L$ . Here  $\nu$  is a ground state fundamental;  $\nu'$  is an excited state fundamental;  $\nu_L$  and  $\nu'_L$  are rather intense low frequency bands. Table IV gives the particular  $\nu$ ,  $\nu'$ ,  $\nu_L$  and  $\nu'_L$  values used in this analysis.

TABLE IV

Raman and infrared <sup>a</sup>	$\nu$	This research		$\nu'$
		$\nu_L$	$\nu'_L$	
240	244	7	59	746
510	514	43	107	948
622	621	86	148	959
777	774	102		1209
999	1001			

<sup>a</sup> Pitzer, Guttman and Westrum, THIS JOURNAL, 68, 2209 (1946).

Five fundamentals appearing in type II bands are correlated with the Raman and infrared data. In the excited state the four fundamentals (III) are assigned on the basis of position, intensity and appearance in combinations of type (IV). The prominent excited state frequencies at 1694, 1705, 1907, 1955, 2157 and 2168 (see Fig. 4) are accounted for in this manner. The

(9) A total of some 402 bands were measured. The complete table together with the specific assignments may be obtained in mimeographed form upon request.

relatively strong band at 0 + 940 is not assigned to a fundamental because it fails to combine with the 746 and 1208. Instead, it is taken as arising from a type (IX) combination in which  $\nu_L$  is 7. It should be noted that no band in the 500 cm.<sup>-1</sup> region is of sufficient intensity to test as a fundamental. The significance of this is discussed in a previous section. With reasonable allowances for anharmonicity, assignments are made for type (VI) for each of the fundamentals.

One feature of the spectrum is the appearance of many low frequency bands, some of which combine with the fundamentals. These may be rotation bands, difference frequencies, or excited state low frequency fundamentals. Because of the lack of a basis for sorting out their origin, those which combine are grouped with the subscript L. All those listed in Table IV, combine in forms (VIII) and (IX).

### Summary

The vapor and solution spectra of phenylisopropane, phenylcyclohexane, phenylcyclopentane, phenylcyclopropane, phenylacetylene and styrene are presented. From them, it is concluded that the cyclopentyl and cyclopropyl groups exhibit ring strain and that the long wave length spectrum of styrene is a monosubstituted benzene spectrum. A vibrational analysis of the styrene spectrum is also given.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## The Effect of Traces of Oxygen on the Reaction of Aluminum Borohydride with Ethylene<sup>1</sup>

BY RICHARD S. BROKAW AND ROBERT N. PEASE

In studying the induced combustion of hydrocarbon-oxygen mixtures with aluminum borohydride<sup>2</sup> it was found that only with unsaturated hydrocarbons did explosion occur in the absence of water vapor. This led to a study of the reaction between olefins and aluminum borohydride.<sup>3</sup> The kinetics of this reaction were determined; the reaction is first order with respect to the aluminum borohydride concentration and zero order with respect to the olefin. It was shown that

(1) (a) Taken from a thesis submitted by Richard S. Brokaw in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University. (b) The work described in this paper was done in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coordinated by the Applied Physics Laboratory, The Johns Hopkins University; and Contract N6-ori-105 with the Office of Naval Research and Office of Air Research as coordinated by Project Squid, Princeton University. (c) We wish to acknowledge the assistance of Dean H. S. Taylor, who has general supervision of this project. (d) Reproduction in whole or in part permitted for any purpose of the United States Government.

(2) Brokaw, Badin and Pease, THIS JOURNAL, 72, 1793 (1950).

(3) Brokaw and Pease, *ibid.*, 72, 3237 (1950).

boron alkyls are among the reaction products.

The object of the research described in this paper has been to investigate the effect of oxygen on the reaction between aluminum borohydride and ethylene.

### Experimental

The apparatus used for the kinetic studies has previously been described.<sup>3</sup> As before, spherical reaction bulbs were of 6.6 cm. inside diameter. It was found necessary to seal a clean reaction flask to the apparatus for each experiment. Aluminum borohydride was obtained from the Naval Research Laboratory and ethylene from U. S. Industrial Chemicals, Inc.

Experiments were carried out in the same manner as those in the absence of oxygen,<sup>3</sup> except that small amounts of oxygen (measured with a McLeod gage) were premixed with the ethylene.

A few explosion limit experiments were performed. For this purpose the apparatus was altered to the type used by Badin, Walters and Pease<sup>4</sup> in studying the ignition of *n*-butane with zinc dimethyl. Experiments were performed in the same fashion as in the induced combustion of butene-1.<sup>3</sup>

(4) Badin, Walters and Pease, *ibid.*, 69, 2586 (1947).