

A likely explanation is that the downfield shifts result from electrostatic interactions<sup>9</sup> between the -OH and -CH(CH<sub>3</sub>)<sub>2</sub> groups, which also affect the average rotational conformation of the isopropyl group with respect to the plane of the benzene ring. Thus, the stable form of the 2-isopropylphenol probably is that in which the C-H of the isopropyl group is in the plane of the ring and *cis* to the phenol oxygen. In the 2,6-diisopropylphenol one of the isopropyl groups could have this configuration, but the other would be rotated so that the C-H was *trans* to the oxygen. The latter

C-H has an environment similar to that in the two equivalent rotational forms of isopropylbenzene, which accounts for the intermediate shift.<sup>22</sup>

**Acknowledgment.**—We wish to thank the Ethyl Corporation for providing the samples of hindered phenols and to acknowledge many helpful discussions with G. R. Miller.

(22) This model is similar to that proposed to explain the CF<sub>3</sub> shifts and the F-CF<sub>3</sub> coupling constants in substituted 2-fluorobenzotrifluorides; see H. S. Gutowsky and V. D. Mochel, *J. Chem. Phys.*, in press.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, N. J.]

## Infrared and Nuclear Magnetic Resonance Hydrogen-Bonding Study of Dioxane and Pyridine in Aqueous Mixtures

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An infrared study of the spectral behavior of all components of dioxane-water and pyridine-water mixtures was carried out. The frequency location of absorption bands studied for these components all exhibited a concentration dependence. High frequency shifts were observed for the -OH stretching band upon dilution in either solvent, indicating a reduction of the hydrogen bonding present in pure water. The low frequency shift noted for the C-O stretching mode of dioxane in aqueous mixtures was attributed to the occurrence of hydrogen bonding at the oxygen sites. High frequency displacement observed for the C-H stretching modes in both dioxane and pyridine in their aqueous mixtures could not be unambiguously interpreted. An attempt was made to correlate the infrared data with the results of nuclear magnetic resonance studies of these systems.

### Introduction

Recent nuclear magnetic resonance studies<sup>2</sup> on dioxane-water and pyridine-water mixtures revealed a marked concentration dependence of the proton chemical shift of all the species involved. This indicated the presence of strong solvent interactions, interpreted as hydrogen bonding. Previous spectroscopic studies of these mixtures include infrared investigations of the water spectrum in dioxane<sup>3,4a,b</sup> and pyridine<sup>4a,b</sup> mixtures and extensive Raman investigation of the dioxane-water system.<sup>5</sup>

An infrared study of the spectral behavior of the organic components as well as the water in these mixtures was undertaken in an attempt to assign the interactions occurring to specific groups, particularly in the dioxane system for which the n.m.r. results could not unambiguously differentiate between interactions taking place at the dioxane oxygen or hydrogen sites.

### Experimental

A Perkin-Elmer Model 421 grating spectrometer was used in this study. The abscissa scale was mechanically expanded 4X to increase the accuracy of the frequency determinations except when determining the position of the broad water -OH band, which was recorded at 1X. All solutions were studied in a 0.015-mm. CaF<sub>2</sub> cell.

### Results

**Dioxane.**—The portion of the pure dioxane infrared spectrum which we investigated consists of three groups of absorptions: four bands which arise from the C-H stretching modes appear at ~2900 cm.<sup>-1</sup>, four bands centered at ~1350 cm.<sup>-1</sup> result from C-H deformations, and three absorptions due to the C-O stretching in the 1100 cm.<sup>-1</sup> region.

Band position was determined as a function of concentration for all the absorptions mentioned above. For a series of solutions, ranging in concentration from 100 to

12% dioxane in water, all the spectra were recorded on the same chart thereby permitting direct measurement of the absorption shifts. This is illustrated in Fig. 1a and 1b, wherein the band positions of the C-H and C-O stretching modes are shown for a 25% dioxane in water mixture and for 100% dioxane.

The band shifts measured in this way are listed in Table I and plotted in Fig. 2a, b, and c as a function of dioxane concentration. These shifts, designated by

TABLE I  
DIOXANE FREQUENCY SHIFT DATA AT 25°

Dioxane, %	C-O stretching, $\nu$ (cm. <sup>-1</sup> )			$\Delta\nu$
	1048 $\Delta\nu$	1083 $\Delta\nu$	1122 $\Delta\nu$	
75	-2.9	-1.8		-0.6
50	-3.3	-1.8		-4.7
25	-3.3	-2.7		-5.8
12	-3.3	-3.0		-5.7

Dioxane, %	C-H bending, $\nu$ (cm. <sup>-1</sup> )			
	1253 $\Delta\nu$	1288 $\Delta\nu$	1365 $\Delta\nu$	1453 $\Delta\nu$
75	+0.7	+1.8	+1.9	+1.1
50	1.9	4.0	4.2	1.3
25	2.8	5.9	5.5	2.7
12	2.7	6.5	6.1	~2

Dioxane, %	C-H stretching, $\nu$ (cm. <sup>-1</sup> )			
	2853 $\Delta\nu$	2892 $\Delta\nu$	2915 $\Delta\nu$	2961 $\Delta\nu$
75	+6.3	+4.0	+4.0	+6
50	10	6.3	6.8	11
25	13	10	14	19
12	13	9	16	20

$\Delta\nu$ , were obtained by subtracting the frequency location of the pure dioxane band from that of dioxane in an aqueous mixture. Thus, the high frequency shift is indicated by  $\nu\uparrow$  and a low frequency shift by  $\nu\downarrow$  in Fig. 2. Noticeable in Table I is the shift to lower frequency of the absorptions due to the C-O group upon dilution with water, whereas the bands arising from C-H stretching and bending shift to higher frequency.

Some of the observed shifts were very small, amounting to a few wave numbers, but in no case did the

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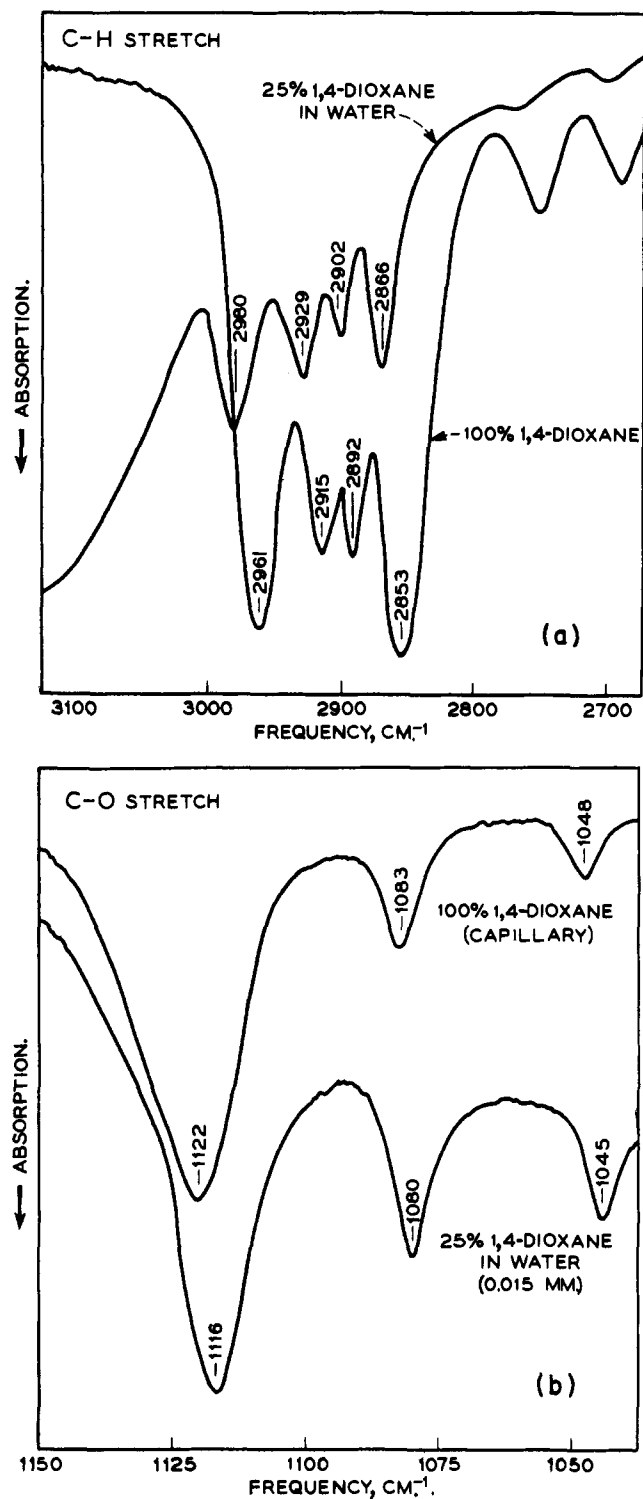


Fig. 1a,b.—C-H and C-O vibrational modes for pure dioxane and a 25% aqueous mixture.

experimental uncertainty, usually 10–20% of the shift, exceed the  $\Delta\nu$ .

**Pyridine.**—Although the frequency shifts of the various nonequivalent protons of pyridine are easily distinguishable using n.m.r. techniques, the infrared results are much less specific owing to the uncertainty of the band assignments required. The assignments required are the specific C—H group absorptions, the C=N and the C=C absorptions, and the hydrogen deformation modes. However, the absorptions at  $\sim 3000$  cm<sup>-1</sup> (C—H stretching),  $\sim 1500$  cm<sup>-1</sup> (double bond), and near  $\sim 1100$  cm<sup>-1</sup> (hydrogen deformation or

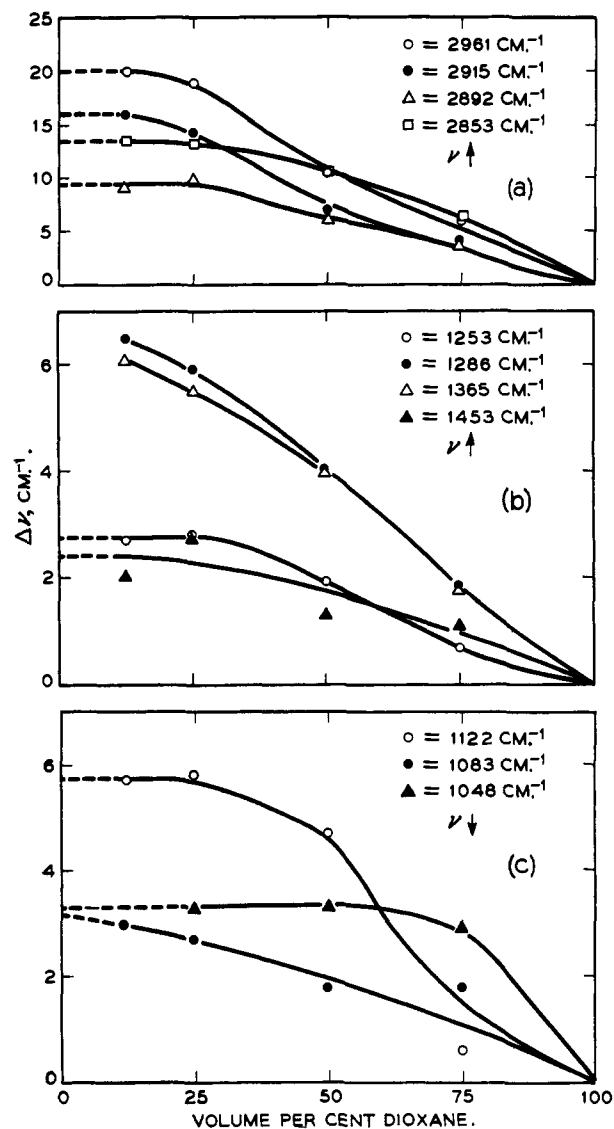


Fig. 2a,b,c.—Dioxane infrared frequency shifts as a function of concentration in aqueous mixtures.

ring vibrations) were used to measure the frequency shifts, since they were unambiguously distinguished.

In Table II it can be seen that all these absorptions shift to higher frequencies upon dilution with water; D<sub>2</sub>O was used to avoid obliteration of the C—H bands by the broad —OH band in this region.

TABLE II  
PYRIDINE FREQUENCY SHIFT DATA AT 25°

Pyridine, %	1100 cm <sup>-1</sup> region, $\nu$ (cm <sup>-1</sup> )				
	985 $\Delta\nu$	1025 $\Delta\nu$	1065 $\Delta\nu$	1145 $\Delta\nu$	1215 $\Delta\nu$
50	+9	+4	0	+4	
25	12	5	+2	4	0
Pyridine, %	Double bond region, $\nu$ (cm <sup>-1</sup> )				
	1435 $\Delta\nu$	1480 $\Delta\nu$	1580 $\Delta\nu$		
50	+4.0	0	+11		
25	4.9	+3	13		
Pyridine, %	C—H stretching region, $\nu$ (cm <sup>-1</sup> )				
	3000 $\Delta\nu$	3030 $\Delta\nu$	3060 $\Delta\nu$	3080 $\Delta\nu$	
50	0		+8	+6.8	
25	0		13	14	
12	+6	0	13	14	

**Water.**—The —OH vibration of water shifts to higher frequency when mixed with each of the two organic

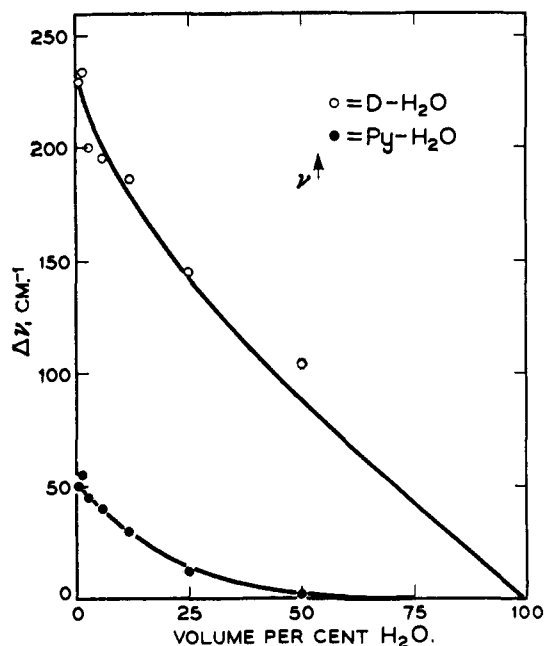


Fig. 3.—Water infrared frequency shifts ( $-OH$  stretching) as a function of concentration in dioxane and pyridine mixtures.

solvents, over the concentration range 100–0.8% water. These results are given in Table III and plotted as a function of concentration in Fig. 3. At high water concentrations (75%) the water band was very broad,  $\sim 500$   $cm^{-1}$  and, consequently, the center was determined by assuming the band to be reasonably symmetrical. At lower concentrations, the profile of the  $-OH$  absorption bands were much sharper and frequency position could be determined with greater accuracy. Although the pure water  $-OH$  band was broad, it can be seen in Fig. 3 that satisfactory precision was attained, amounting to 10 to 20% of the shift.

TABLE III  
WATER FREQUENCY ( $-OH$ ) SHIFT DATA AT 25°

Dioxane-water			Pyridine-water		
Water, %	$\nu$	$\Delta\nu$	Water, %	$\nu$	$\Delta\nu$
100	3320		100	3320	
50		104	50		2
25		145	25		12
12		186	12		30
6		195	6		40
3		200	3		45
1.5		234	1.5		55
1.8		230	0.8		50

The profiles of the  $-OH$  absorptions at low concentrations (<6%) in dioxane and pyridine were noted to be quite different. In dioxane the water  $-OH$  absorption band appeared as a doublet, whereas in pyridine it appeared as a broad single band. This is in agreement with the observations of other workers,<sup>4a,b</sup> particularly Greinacher, *et al.*,<sup>3,4a</sup> who studied water at low concentrations in a variety of solvents.

#### Discussion

**Water.**—In general it has been established that vibrational spectra are significantly influenced by hydrogen bond formation. This is particularly noticeable for stretching modes, which are displaced to lower frequencies upon association. This displacement to lower frequency is believed to be due to a decrease in the force constant of the bond involved, arising from the bond length increase expected upon association.<sup>6</sup> Therefore, in the water mixtures studied here, one can

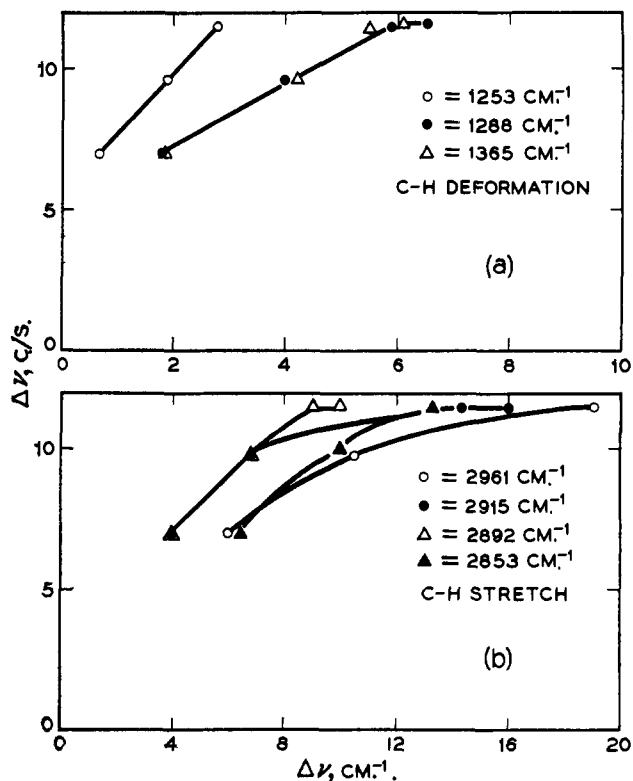


Fig. 4.—Nuclear magnetic resonance vs. infrared shifts for dioxane-water mixtures.

assume that the addition of a less polar solvent would bring about a decrease in the over-all water association. The shift to higher frequency of the  $-OH$  stretching band upon addition of the organic component confirms this expectation. Furthermore, the less polar dioxane, whose predominant effect would be a reduction of the association of the water molecules, should produce the greater shift to higher frequency, which is observed. In the pyridine-water mixture the  $-OH$  shift is less because of partial compensation by the interaction between water and the relatively more polar pyridine. These observations are in agreement with the n.m.r. results<sup>2</sup> obtained previously. In the latter case also the expected upfield frequency shift of the water signal at infinite dilution was about five times as great with dioxane as solvent.

Significant also is the fact that in the pyridine mixtures the water proton resonance signal was displaced to a lower field at  $\sim 50\%$  pyridine, and then to higher fields as the organic component concentration was increased. The minimum was again indicative of the strong interactions occurring in this system. Similarly, the shift observed in the infrared spectrum is essentially zero at  $50\%$  pyridine, and it is conceivable that if greater precision were attainable, a low frequency displacement might be observed.

Finally, the water spectrum at low concentration may be considered. The doublet observed in dioxane mixtures was previously attributed<sup>4</sup> to complex formation with the organic component, resulting in two non-equivalent water protons producing the two absorption bands. However, more extensive interactions are occurring in the pyridine mixtures wherein the water  $-OH$  stretching absorption was a broad singlet at low water concentrations. At high dilutions in solvents more inert than dioxane, and in which interactions can be neglected, the water stretching absorption was a doublet.<sup>4a</sup> This indicates that intermolecular inter-

(6) D. Hadzi, "Hydrogen Bonding," Pergamon Press, New York, N. Y., 1959, p. 85.

actions broaden rather than double the band in water at high dilutions.

**Dioxane.**—The displacement to lower frequency of the C–O stretching mode in the dioxane spectrum upon the addition of water would indicate that hydrogen bond formation is occurring at this site. This is reasonable since the dioxane molecule has large dipole moments at the oxygen nuclei, even though it has essentially an over-all moment of zero. The reason for the high frequency shift of the modes involving the protons (C–H stretch and deformation) is not clear at this time. Since the shift to a higher frequency of the C–H stretching band is in an opposite direction to that expected as a result of hydrogen bonding, another phenomenon is apparently responsible. It may be a change in the ionic character of the C–H bond as dioxane becomes solvated, or coupling between the various vibrational modes may cause a disturbance of the C–H frequency when solvation occurs at the neighboring dioxane oxygen.

The infrared displacement curves in Fig. 2 show a sharp decrease in slope at high water concentrations. This is similar to the n.m.r. concentration dependent curve of the chemical shift for dioxane, which also leveled off and remained constant at dioxane concentrations less than  $\sim 30\%$ . As stated previously,<sup>2</sup> this points to a local dioxane environment which is undergoing little or no change at high water concentrations.

Since the concentration dependence of the infrared

and n.m.r. solvent shifts were somewhat similar, an attempt was made to correlate the results of the two techniques. The n.m.r. shifts were plotted *vs.* the infrared shifts observed at the same concentrations. Only vibrational modes involving the dioxane protons were used. These plots are illustrated in Fig. 4. In the case of the C–H bending modes, reasonably linear plots are obtained for all lines, whereas smooth curves are observed for the stretching frequencies. It is conceivable that a dipole moment change in a dioxane C–H bond, as well as a disturbance of the shielding of the proton involved, could result from a change in the electronic charge distribution of the C–H bond brought about by solvent interactions.

**Pyridine.**—The nuclear magnetic resonance results on pyridine–water mixtures<sup>2</sup> revealed that in addition to the interactions occurring at the nitrogen site, the  $\beta$ - and  $\gamma$ -protons also showed marked activity, indicated by their chemical shift concentration dependence. Unfortunately, the contributions from the chemically nonequivalent protons of pyridine cannot be distinguished in the infrared. The observed shifts were all toward higher frequencies as water was added. As with dioxane, the cause of the shifts to higher frequencies is uncertain, but similar phenomena may be operative in this molecule.

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[CONTRIBUTION NO. 1080 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, IND.]

## Electron Diffraction Determination of the Molecular Structure of the Butyl Halides. III. *t*-Butyl Chloride in the Gas Phase<sup>1</sup>

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The structure of gaseous *t*-butyl chloride has been determined by the sector-microphotometer method of electron diffraction. The experimental molecular parameters were found to be:  $r_g(\text{C–H}) = 1.104 \text{ \AA.}$ ,  $r_g(\text{C–C}) = 1.532 \text{ \AA.}$ , and  $r_g(\text{C–Cl}) = 1.828 \text{ \AA.}$ ;  $l_m(\text{C–H}) = 0.075 \text{ \AA.}$ ,  $l_m(\text{C–C}) = 0.056 \text{ \AA.}$ , and  $l_m(\text{C–Cl}) = 0.054 \text{ \AA.}$ ;  $\angle \text{C–C–Cl} = 107.4^\circ$  and  $\angle \text{C–C–H} = 110.0^\circ$ . An approximate value of 4 kcal./mole was obtained for the barrier to rotation of the methyl groups about the C–C single bonds.

The structure of *t*-butyl chloride is of special interest because of the possibility that structural abnormalities might occur. In a previous study of *t*-butylacetylene and *t*-butyl cyanide, Nugent, Mann, and Lide<sup>2</sup> found a lengthening of the C–C bond connected to the *t*-butyl group of about 0.035  $\text{\AA.}$  Lide and Mann have also shown similar lengthenings in bonds connected to *t*-butyl groups in the cases of isobutane and *t*-butyl fluoride.<sup>3</sup>

The structure of *t*-butyl chloride has been worked out previously by a number of other investigators,<sup>4–7</sup> but none of these determinations has been of sufficient accuracy to give really definitive answers to the possibility of distortions in the structural parameters. It is also of interest to attempt to determine the barrier to rotation of the methyl groups about the carbon–carbon single bonds.

(1) The authors wish to thank the National Science Foundation and the Atomic Energy Commission for their financial support of this work.

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### Experimental

A sample of *t*-butyl chloride was obtained from the Columbia Chemical Co. and was purified by vacuum column distillation. Boiling point and index of refraction measurements indicated the sample used for diffraction measurements was at least 99% pure. The sample of *t*-butyl chloride was purified immediately prior to the taking of the electron diffraction photographs in order to avoid any possible contamination. Electron diffraction photographs were obtained with an  $r^3$  sector, using the sector electron diffraction camera in L. S. Bartell's laboratory at Iowa State University. Specimen pressures of 20 to 80 mm. with exposure times of 1 to 4 sec. were used at a temperature of 298°K. The beam current was 0.3  $\mu\text{a.}$  and the accelerating voltage was 40 kv. Four research grade plates at each of two camera distances were obtained. The photographic plates were microphotometered in Professor L. O. Brockway's laboratory at the University of Michigan.

The microphotometer traces of the electron diffraction photographs were read, at 0.25-mm. intervals, to four significant figures in the optical density with the aid of a Bausch and Lomb 7-power measuring magnifier. The photographic emulsion was calibrated by a procedure developed by Bartell and Brockway.<sup>8</sup> The indices of resolution were found to be 0.90 for the 21.35-cm. camera distance and 1.00 for the 10.66-cm. camera distance. It was felt that the near unity values of the indices of resolution indicated the absence of any serious extraneous scattering effects.

**Structure Analysis.**—The experimental data were analyzed according to numerical schemes outlined in detail elsewhere.<sup>9–12</sup>

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