

Yields of the saturated ( $E_\infty$ ) and unsaturated ester were determined on samples in which peroxide decomposition was complete.

**Carbon Dioxide and Acid Yields.**—The appropriate solutions were prepared and degassed in flasks constructed to allow later sweeping with nitrogen by breaking sealed-tip side arms. The flasks were immersed in a thermostated bath at 80°, and remained for 48–50 hr. Where water had been added, the flask

made, can be written  $E = C(A_0 - A)/k$ . As  $t \rightarrow \infty$ ,  $A \rightarrow 0$ , so that  $E_\infty = CA_0/k$ . Substituting this expression for  $CA_0/k$  into eq. 8 gives  $E = E_\infty(1 - e^{-kt})$  which can be expressed in logarithmic form as  $\ln(E_\infty - E) = -kt + \ln E_\infty$ . Thus, a plot of  $\ln(E_\infty - E)$  against  $t$  should give  $k$ , the rate constant for disappearance of peroxide. We wish to acknowledge and thank Dr. Robert C. Lamb for calling this feature to our attention. We have plotted  $\log(E_\infty - E)$  against  $t$  for the two runs in cyclohexene and one run in cyclopentene for which  $E_\infty$  was known. The results were, for cyclohexene,  $k = 6.93$  and  $8.41 \times 10^{-4}$  sec $^{-1}$ , and for cyclopentene,  $k = 8.1 \times 10^{-4}$  sec $^{-1}$ . Considering the fact that values of  $E$  were obtained from peak areas after a somewhat cumbersome work-up procedure, these values of  $k$  are in fairly good agreement with those obtained by direct measurement and given in Table I.

was shaken vigorously during the whole of the heating period in a bath constructed for this purpose. Earlier it was found that magnetic stirring of the sealed contents did not give reproducible results. The flask was cooled and placed in the nitrogen sweep train. The nitrogen was passed through a bed of solid sodium hydroxide before entering the flask. After breaking the tips of the flask side arms, the carbon dioxide was swept out through a Dry Ice trap, concentrated sulfuric acid, quinoline, magnesium perchlorate, and into an Ascarite tube. The nitrogen sweep was continued until the Ascarite tube no longer gained weight. This time period also included finally allowing the Dry Ice trap to warm to 0°.

The acid content was determined by titrating all or part of the flask contents. The per cent acid listed in the tables refers to the appropriate carboxylic acid equivalent to the standard base used, and does not distinguish between HCl and carboxylic acid if the former was present (*i.e.*, in carbon tetrachloride experiments).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MD.]

## Steric Effects on the Near-Ultraviolet Absorption (Soret Band) of Porphyrins<sup>1</sup>

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Earlier observers recorded that the formation of an octahedral complex of a metalloporphyrin with a nitrogenous base caused the appearance of a new absorption peak in the near-ultraviolet (Soret) region with a shift from a maximum at 390–400  $m\mu$  to one at 410–420  $m\mu$ . This effect is now ascribed to steric interference between the ligand and the  $\pi$ -electron system of the porphyrin ring, similar to that observed upon N-methylation. The same phenomenon occurring with the alkali metals and with Ag<sup>+</sup> is ascribed to the interferences between alkali metal atoms above and below the ring and the porphyrin  $\pi$ -electron system.

The coordination of iron porphyrins with bases has been studied by many investigators,<sup>1,4</sup> primarily because of the importance of these complexes with respect to the chemistry of hemoglobin. Miller and Dorough<sup>5</sup> showed, through a study of visible spectra, that magnesium, zinc, cadmium, mercury, copper, and cobalt porphyrins also form pyridinate complexes comparable in some respects to those formed by iron porphyrins. Erdman, Ramsey, Kalenda, and Hanson<sup>6</sup> extended the observation to vanadyl complexes and pointed out that complexing of the metalloporphyrin with pyridine caused the formation of a second near ultraviolet (Soret) peak at a longer wave length. Caughey, Deal, McLees, and Alben<sup>7</sup> have shown that the coordination of pyridine to nickel in nickel porphyrins also causes a shift of the Soret band to longer wave lengths. This effect has also been observed by Whitten, Corwin, and Baker<sup>1</sup> in cobalt and iron porphyrins. Loach and Calvin<sup>8</sup> have observed a similar shift with a manganese porphyrin and McCartin<sup>9</sup> with hydrated chlorophylls. The present paper records parallel observations on a variety of other porphyrin derivatives and advances an explanation of these phenomena on steric grounds similar to those proposed by Brunings and Corwin.<sup>10</sup>

**Transition Metal Derivatives.**—In the case of nickel mesoporphyrin, the findings of Caughey, *et al.*,<sup>7</sup> were verified and extended. In the presence of very strong ligands, two Soret peaks were observed, as shown in Table I.

TABLE I  
SORET SPECTRA OF NICKEL MESOPORPHYRIN IX DIMETHYL ESTER

Solution	Soret 1, $m\mu$	Soret 2, $m\mu$	O.D. <sub>1</sub> /O.D. <sub>2</sub> <sup>b</sup>
Pyridine, 27.5°	417	391	0.22
–11°	417	391	.60
Piperidine, 27.5°	417	393	1.24
–10°	417	393	3.31
Pyrrrolidine, 27.5°	418	392	3.58
–9°	418	392	9.5
2-Methylpiperidine, 27.5°	..	392	..
DABCO <sup>a</sup> in benzene, 27.5°	417	393	0.67
<i>n</i> -Butylamine, 27.5°	415	389	.53
Ethylenimine, 27.5°	415	388	.75

<sup>a</sup> Diazabicyclooctane, saturated solution. The authors wish to thank the Houdry Process and Chemical Co. for this material.

<sup>b</sup> Ratio of optical densities.

With copper complexes in weak ligand fields, only one Soret band was observed. In the presence of very strong ligands, however, two peaks were found. Cooling intensified the long wave length peak at the expense of the short where strong ligands were present. It was notably more difficult to produce the formation of two peaks for copper mesoporphyrin than for nickel mesoporphyrin. Only by cooling solutions of the copper compound in pyrrolidine or piperidine could we make the long wave length peak predominate. The results are summarized in Table II.

In contrast to the nickel and copper derivatives, zinc mesoporphyrin gives only a single Soret band. In fur-

(1) Porphyrin Studies XXVIII: paper XXVII, D. G. Whitten, E. W. Baker, and A. H. Corwin, *J. Org. Chem.*, **28**, 2363 (1963). This work was supported in part by Research Grant A-2877 from the National Institutes of Health.

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(3) Du Pont Fellow, 1962–1963.

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(7) W. S. Caughey, R. M. Deal, B. D. McLees, and J. O. Alben, *ibid.*, **84**, 1735 (1962).

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(10) K. J. Brunings and A. H. Corwin, *J. Am. Chem. Soc.*, **64**, 593 (1942).

TABLE II

## SORET SPECTRA OF COPPER MESOPORPHYRIN IX DIMETHYL ESTER

Solution	Soret 1, m $\mu$	Soret 2, m $\mu$	O.D. <sub>1</sub> /O.D. <sub>2</sub> <sup>a</sup>
Cyclohexane		396	
Toluene		398	
Tetrahydrofuran		396	
Acetic acid		392	
2-Methylpiperidine		396	
N,N-Dimethylformamide		394	
Pyridine, 27.5°		398	
-11.5°	408	398	0.72
-41.5°	408	398	.89
Piperidine, 27.5°	409	397	.92
-9.5°	409	397	1.48
Pyrrolidine, 27.5°	412	398	0.73
-12.5°	412	398	1.27
Ethylenimine, 27.5°	408	393	0.39

<sup>a</sup> Ratio of optical densities.

ther contrast, however, the position of this band varies through a relatively wide range with the coordinating power of the ligand, showing a shift to the red as the ligand field strength increases, as shown in Table III.

TABLE III

## SORET SPECTRA OF ZINC MESOPORPHYRIN IX DIMETHYL ESTER

Solution	Soret, m $\mu$	Solution	Soret, m $\mu$
Cyclohexane	397	Pyridine	411
1,2-Dichloroethane	400	2-Methylpiperidine	411
Acetic acid	401	2-Picoline	412
Toluene	402	1% pyrrolidine in N,N-dimethyl- formamide	412
Ethyl acetate	402		
Methyl ethyl ketone	403	1% pyrrolidine in cyclohexane	412
Dioxane	404		
Tetrahydrofuran	404	4-Picoline	413
Methanol	404	4-Pyridylaldehyde	413
N-Methylformamide	406	Piperidine	413
N,N-Dimethyl- formamide	407	Pyrrolidine	414
Ethylenimine	411		

**Rationalization of Results.**—The results obtained for the three metalloporphyrins can be rationalized with the use of ligand field theory. The results and explanation are a logical extension of phenomena previously observed with cobalt and nickel porphyrins. With nickel mesoporphyrin IX we have extended the findings of Caughey, *et al.*,<sup>7</sup> by using stronger ligands (pyrrolidine, piperidine, and DABCO). The stronger ligands allow observation of the transition to the octahedral complex with mesoporphyrin, whereas Caughey used porphyrins which incorporated electron-withdrawing groups to accomplish the same transition.

Copper porphyrin complexes ordinarily exist in the tetragonal form without bonding to additional ligands. For this reason, the spectra of copper porphyrin complexes should be solvent invariant. This we found to be true with copper mesoporphyrin in solvents producing weak to moderate ligand fields. In pyrrolidine and piperidine, which produce very strong ligand fields, we observed two Soret peaks, one at 408–410 m $\mu$ , the other "normal" peak at about 396 m $\mu$ . We attribute the peak at longer wave length to a new species in which the copper exists in an octahedral configuration such that the ligands along the "z" axis perturb the porphyrin  $\pi$ -electron system in the same way as in other octahedral complexes. The change from the normal peak to the new species is a discontinuous one, as evidenced by the presence of two Soret peaks rather than a gradual migration of a single peak. The change in configura-

tion for copper occurs at higher ligand field thresholds than the corresponding change for nickel complexes. In turn, the change for nickel occurs at much higher thresholds than those for the change of cobaltous to cobaltic porphyrins. If we accept Caughey's hypothesis that the change in the nickel porphyrins is due to electron rearrangement in the nickel atom such that the nickel can bond with two additional ligands, an analogous change can be postulated for the copper in copper porphyrin complexes (Table IV). That the copper should not accept additional ligands as readily as nickel seems reasonable. In the case of nickel, as the electron is transferred to the  $d_{x^2-y^2}$  orbital, the release of energy from the unpairing of electrons should help to offset the unfavorable interaction with the porphyrin. In the case of copper, there is no such compensation.

TABLE IV

## ELECTRONIC CONFIGURATIONS OF COPPER AND NICKEL COMPLEXES

Geometry	3d-Orbitals				
	$d_{xy}$	$d_{xz}$	$d_{yz}$	$d_z^2$	$d_x^2-y^2$
Tetragonal Ni	"	"	"	"	"
Cu	"	"	"	"	"
Octahedral Ni	"	"	"	"	"
Cu	"	"	"	"	"

Cooling solutions of copper mesoporphyrin IX dimethyl ester in piperidine and pyrrolidine increased the absorption at the longer wave length band dramatically. In pyridine, this complex showed only one Soret peak, the short wave length absorption, at room temperature. When this solution was cooled to -40°, the second peak was observed and its intensity almost equalled that of the short wave length peak. This effect of cooling supports our hypothesis that the long wave length peak indicates a more highly ordered (octahedral) complex than that attributed to the short wave length band (tetragonal).

The contrasting behavior of the zinc mesoporphyrin IX dimethyl ester in different solvents was also predicted. Here no appreciable barrier to the formation of an octahedral complex should exist at the zinc atom, since this requires acceptance of two ligands along the "z" axis. The spherically symmetrical electron cloud about the zinc needs to undergo no great change in configuration with the acceptance of these ligands. The formation of progressively tighter octahedral complexes can be observed spectrally due to the increasing perturbation of the porphyrin  $\pi$ -electron system in such complexes. Taking zinc mesoporphyrin IX dimethyl ester in cyclohexane as the standard for a tetragonal complex, it is interesting to note that even such non-polar solvents as toluene, methyl ethyl ketone, and tetrahydrofuran interact sufficiently with the complex to alter its spectrum. Zinc mesoporphyrin IX dimethyl ester shows a Soret peak varying continuously in wave length from 397 to 414 m $\mu$ .

Comparison of the earlier results obtained for cobalt mesoporphyrin IX<sup>1</sup> with those reported here for zinc, copper, and nickel mesoporphyrin IX dimethyl esters shows that both discontinuous and continuous changes occur with cobalt. The change from cobaltous mesoporphyrin IX (tetragonal) to cobaltic mesoporphyrin IX (distorted octahedral) is a discontinuous one as evidenced by the presence of two Soret peaks. The change in cobaltic mesoporphyrin IX from solutions in moderate ligands (distorted octahedral or tetragonal pyramid) to solutions in strong ligands (regular octahedral) is continuous, reflected in a single Soret band varying from 410 to 420 m $\mu$ .

**Origin of the Spectral Shifts.**—Brunings and Corwin<sup>10</sup> found that the steric deformation caused by the substitution of methyl groups for a hydrogen in dipyrromethenes caused a shift in the visible spectrum toward longer wave length. This conclusion was critically examined and confirmed by Brooker,<sup>11</sup> who had shown previously that the effect to be expected from the inductive influence of the methyl groups would have been in the opposite direction. Erdman and Corwin<sup>12</sup> extended this steric argument to the effect of N-methyl groups in the porphyrins. The genesis of the observed spectral shift lies in the fact that the ground state of the  $\pi$ -bond system is smaller than the excited state, due to weaker bonding in the latter. Thus the energy of deformation of the ground state by a bulky group would be greater than that of the excited state, bringing the two energy levels closer together and resulting in a shift toward the lower energy region of the spectrum.

Corwin, Walter, and Singh<sup>13</sup> deduced from models that the methyl group in an N-methylporphyrin would cause a "wrist action" of one pyrrole ring out of the plane of the porphyrin ring with compensating distortion of the other rings. This effect was analyzed and confirmed experimentally by a study of the n.m.r. spectra by Caughey and Iber.<sup>14</sup> They showed that interference exists between the hydrogens of the N-methyl and the  $\pi$ -bond electron system of the porphyrin ring and that in the case of an N-ethylporphyrin, the terminal methyl of the ethyl group has passed the peak of interference by the  $\pi$ -bond system, tending to emerge above it. These observations may reasonably be interpreted as due to a doughnut-shaped  $\pi$ -electron system above and below the plane of the porphyrin ring with diminished electron density in the center but with sufficient field strength at the radius of the methyl group to cause the observed interference. It would be a logical inference that other groups inserted into this field should cause a distortion similar to that observed with the methyl group.

The formation of octahedral complexes of nickel, copper, and zinc porphyrins would require the insertion of a ligand molecule into the space in the center of the  $\pi$ -electron system of the metalloporphyrin occupied by the methyl group in N-methyl etioporphyrin. This should cause resistance to the insertion of the ligand and distortion of the  $\pi$ -electron cloud. This resistance would explain the relative stability of the tetragonal complexes in the zinc system as contrasted to other zinc chelates in which octahedral complexes are the normal form. In addition, the distortion of the  $\pi$ -electron cloud would be greater in the ground state than in the excited state here as in the N-methyl case, giving rise to the observed shift to the red.

**Alkali Metal Derivatives.**—We now wish to report additional cases of the phenomenon recorded above which differ in detail from those previously observed. A red shift of the Soret band is found in the alkali metal derivatives of the porphyrins.<sup>15-18</sup> Because this is probably not due to octahedral complex formation, another explanation must be sought. We have examined the Li, Na, K, Rb, and Cs derivatives of tetra-

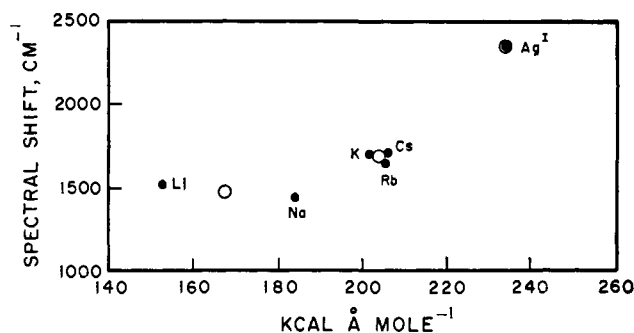


Fig. 1.—Plot of Soret band shifts against the product of atomic radius and ionization energy in metalloporphyrins: Li, Na; K, Rb, Cs; Ag<sup>1</sup>. O: averages (see text).

methyltetracarboxyporphyrin III, as well as its argentous derivative. Each of these has two atoms of the metal to one molecule of the porphyrin. From an initial value of 427  $m\mu$  in the free base, the red shift in the cases of Li and Na averages 1515  $cm^{-1}$ ; K, Rb, and Cs 1713  $cm^{-1}$ ; and Ag<sup>1</sup> 2370  $cm^{-1}$ . If we assume that in each of these complexes one metal atom occupies a position slightly above the porphyrin ring and one a corresponding position slightly below the ring, the metal atoms would then be in positions roughly analogous to those occupied by ligand molecules in the octahedral complexes discussed above. To estimate the extent of the interference to be expected in these cases, we must include in our computation not only the radius of the atom in question<sup>19a</sup> but also its "hardness." We estimate the latter to be proportional to the first ionization potential,<sup>19b</sup> as a first approximation. Accordingly, the interfering powers of the atoms should be the products of the radii and the ionization potentials. The pertinent data are given in Table V.

TABLE V  
SPECTRAL SHIFTS OF THE SORET PEAK OF ALKALI METAL PORPHYRINS

(1) Atom	(2) MH radius, Å.	(3) Ionization energy, kcal./mole	(4) Prod. (2) × (3)	(5) $\lambda_{max}$ , $m\mu$	(6) Spectral shift, $cm^{-1}$
Li	1.23	124.3	152.9	457	1540
Na	1.57	118.4	185.9	456	1490
K	2.03	100.0	203.0	461	1730
Rb	2.16	96.3	208.0	460	1680
Cs	2.33	89.7	209.1	461	1730
Ag <sup>1</sup>	1.34	174.6	234.0	475	2370

Figure 1 shows a plot of the individual points and of the averages of the groups (I) Li and Na; (II) K, Rb, and Cs; and (III) Ag<sup>1</sup>. The trend of the curve indicates that increasing interference with the  $\pi$ -electron cloud by monovalent metals above and below the porphyrin ring causes increasing shifts of the near-ultraviolet peak toward the red.

### Discussion

It has been assumed<sup>18-20a</sup> that the richness of the visible spectra of porphyrin free bases is due to vibrational components of the electronic transitions. These additional components are assumed to be forbidden in the symmetrical metalloporphyrins but allowed in the less symmetrical free bases. Platt<sup>20b</sup> and others<sup>21</sup> have taken the position that the excited state in symmetrically substituted metalloporphyrins should be doubly degenerate so that substitutions causing de-

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partures from symmetry could split the electronic transitions into  $x$ - and  $y$ -components. It might be argued that the "extra" Soret band observed in the base complexes is due either to an extra vibrational component or, alternatively, to a departure from symmetry causing the appearance of  $x$ - and  $y$ -splitting. Neither of these sources of extra bands has yet been demonstrated with certainty to exist in the Soret region, although most Soret bands have at least one hump on the high energy side which may be ascribed to either.

Examination shows that neither of these alternative explanations can be applied to the "extra" band in the Soret region formed by base complexes. Both theories would predict that both Soret peaks would appear simultaneously in the same molecule, while the observation is that the two absorptions are associated with different molecules. In addition, both of these theories would predict only discontinuous shifts, when any appeared. In fact, we observe continuous shifts with solvent changes in the cases of cobalt and zinc.

On electronic grounds, we should expect the substitution of an electron-donating base to shift the absorption spectrum toward shorter wave lengths.<sup>11</sup> The observed effect in the opposite direction might be ascribed to "back double bonding"<sup>22</sup> in the case of

(22) L. E. Orgel, "An Introduction to Transition-Metal Chemistry

pyridine but hardly so in the cases of secondary bases such as pyrrolidine and piperidine nor in the cases of the monovalent alkali metals.

We conclude that the explanation of the observed shifts based on a steric effect, advanced above, is the most reasonable method for correlating the diverse substituents causing the shifts—that is, *N*-methyl, secondary, and tertiary bases and alkali metals—with the uniform effect of these substituents in bringing about the change to lower energy transitions.

### Experimental

**Zinc mesoporphyrin IX dimethyl ester** was prepared by a slight modification of the method of Fischer, Goldschmidt, and Nussler.<sup>23</sup>

**Copper and nickel mesoporphyrin IX dimethyl esters** were prepared and purified by the method of Fischer and Stangler.<sup>24</sup>

**Alkali metal porphyrins** were prepared and studied essentially by the methods of Dorough, Miller, and Huennekens.<sup>18</sup>

**Spectra.**—All spectra were taken on a Beckman DK-2 recording spectrophotometer. The spectra were taken in matched quartz cells. Temperature studies were made using a Beckman cell compartment heating unit and an Aminco refrigeration unit. The cell compartment was flushed with dry nitrogen in the low temperature studies. The wave length calibration of the instrument was checked with a mercury source.

Ligand-Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 134.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

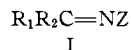
## Structural Studies by Nuclear Magnetic Resonance. V. Phenylhydrazones

BY GERASIMOS J. KARABATSOS AND ROBERT A. TALLER

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In solution or as pure liquids phenylhydrazones exist in the hydrazone form. Hydrogens *cis* or *trans* to the anilino group resonate at higher magnetic fields in benzene than in aliphatic solvents. The upfield shift of *cis*-hydrogens, however, is three to six times larger than that of the corresponding *trans*, and this difference can be used as a convenient and accurate method of assigning *syn* and *anti* structures to phenylhydrazone isomers. Solvent and dilution studies indicate hydrogen bonding between phenylhydrazone and solvent. From these studies information is obtained on the relative strength of the hydrogen bonds and the structures of the association complexes.

We reported<sup>1</sup> n.m.r. studies on *syn-anti* structural and conformational assignments, equilibrium concentrations of *syn* and *anti* isomers, and anisotropic effects of *Z* and solvent on the protons of  $R_1$  and  $R_2$  (I).



From spectroscopic studies it was concluded<sup>2</sup> that in solution phenylhydrazones (II) isomerize readily to the azo form III. In contrast, several authors have



reported<sup>3</sup> that the hydrazone form is the more stable of the two. Disregarding resonance contributions, the hydrazone form is favored over the azo form by 9 kcal. (C=N, 147 kcal./mole; N=N, 38 kcal./mole; N-H, 93 kcal./mole; N=N, 100 kcal./mole; C-N, 70 kcal./mole; C-H, 99 kcal./mole).

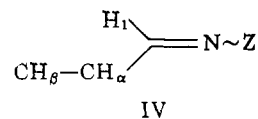
We will discuss in this paper the results of n.m.r. studies on phenylhydrazones. Some aspects of these studies are relevant to hydrazone-azo tautomerism.

(1) (a) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Am. Chem. Soc.*, **84**, 753 (1962); (b) G. J. Karabatsos, B. L. Shapiro, F. M. Vane, J. S. Fleming, and J. S. Ratka, *ibid.*, **85**, 2784 (1963); (c) G. J. Karabatsos, R. A. Taller, and F. M. Vane, *ibid.*, **85**, 2326, 2327 (1963).

(2) R. O'Connor, *J. Org. Chem.*, **26**, 4375 (1961).

(3) (a) R. H. Wiley and C. H. Jarboe, Jr., *J. Am. Chem. Soc.*, **77**, 403 (1955); (b) C. H. DePuy and P. R. Wells, *ibid.*, **82**, 2909 (1960); (c) H. C. Yao and P. Resnick, *ibid.*, **84**, 3514 (1962).

Throughout the text we will use the following conventions: The *syn* isomer has *Z* *cis* to the smaller R group, e.g., the *syn* isomer of butanone phenylhydrazone has the methyl and anilino groups *cis* to each other. The notation used to distinguish the various protons of the R groups is shown in IV; each proton is referred to as *cis* or *trans* with respect to *Z*.



### Results

The n.m.r. spectra of undegassed solutions of three aldehyde and seven ketone phenylhydrazones were examined at 60 Mc. The probe temperature was maintained at about 36°.

**Chemical Shifts.**—Table I summarizes the chemical shifts of phenylhydrazones in several solvents. The values are accurate to  $\pm 0.03$  p.p.m.; relative values between *cis*- and *trans*-hydrogens ( $\delta_{cis} - \delta_{trans}$ ) are accurate to  $\pm 0.006$  p.p.m. Assignments of hydrogens as *cis* and *trans* are based on arguments given previously.<sup>1</sup> Figure 1 shows the spectra of the phenylhydrazones of acetone, methyl ethyl ketone, methyl isopropyl ketone, and methyl *t*-butyl ketone.