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.[11] The observed effect in the opposite direction might be ascribed to "back double bonding"[22] in the case of 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.[23]

Copper and nickel mesoporphyrin IX dimethyl esters were prepared and purified by the method of Fischer and Stangler.[24]

Alkali metal porphyrins were prepared and studied essentially by the methods of Dorough, Miller, and Huennekens.[18]

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.

(22) L. E. Orgel, "An Introduction to Transition-Metal Chemistry Ligand-Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 134.

(23) H. Fischer, M. Goldschmidt, and W. Nussler, *Ann.*, **486**, 5 (1931).

(24) H. Fischer and G. Stangler, *ibid.*, **459**, 73 (1927).

[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[1] 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).

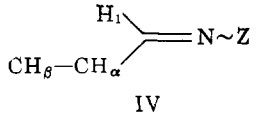
$$R_1R_2C{=}NZ$$
I

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

$$R_1R_2C{=}NNHC_6H_5 \qquad R_1R_2CHN{=}NC_6H_5$$
II III

reported[3] 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. 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.



IV

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 ±0.03 p.p.m.; relative values between *cis*- and *trans*-hydrogens ($\delta_{cis} - \delta_{trans}$) are accurate to ±0.006 p.p.m. Assignments of hydrogens as *cis* and *trans* are based on arguments given previously.[1] Figure 1 shows the spectra of the phenylhydrazones of acetone, methyl ethyl ketone, methyl isopropyl ketone, and methyl *t*-butyl ketone.

(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).

TABLE I

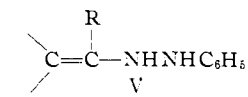
CHEMICAL SHIFTS (τ-VALUES) OF PHENYLHYDRAZONES

$R_1R_2C{=}NNHC_6H_5$			——H_1——		$H_\alpha(CH)$	——$H_\alpha(CH_2)$——		——$H_\alpha(CH_3)$——		——$H_\beta(CH_3)$——			Aro-
R_1	R_2	Solvent[a]	*cis*	*trans*	*trans*[b]	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	NH[c]	matic[d]
H	Me	CCl_4	[e]	3.59				8.29	8.12				3.1
H	Me	CH_2Br_2	[e]	..				8.25	8.12				3.0
H	Me	Acetone	[e]	3.50				8.18	8.13				3.1
H	Me	DMSO[f]	[e]					8.17	8.13				3.1
H	Me	CH_3OH	[e]	3.51				8.18	8.13				3.1
H	Me	C_6H_6	[e]	3.80				8.92	8.37				
H	Et	Neat	3.55	3.80		8.28	7.93			9.21	9.08		3.1
H	Et	CCl_4	[e]	3.78			7.87			9.02	9.00		3.1
H	Et	CH_2Br_2	[e]	3.68			7.83			8.98	8.98		3.1
H	Et	CH_3OH	[e]	3.68			7.80			8.95	8.95	1.25	3.1
H	Et	C_6H_6	3.67	3.79		8.52	7.95			9.30	9.08		
H	*i*-Pr	Neat	3.68	3.90	7.72					9.21	9.03		3.1
H	*i*-Pr	CCl_4	3.52	3.88	7.67					9.05	8.98		3.1
H	*i*-Pr	CH_2Br_2	[e]		7.58					8.98	8.93		3.0
H	*i*-Pr	CH_3OH	[e]		7.58					8.98	8.93	1.60	3.1
H	*i*-Pr	C_6H_6	3.75	3.97	7.70					9.28	9.03		
Me	Me	CCl_4						8.36	8.08				3.1
Me	Me	CH_2Br_2						8.22	8.02				3.0
Me	Me	DMSO[f]						8.15	8.07				3.1
Me	Me	CH_3OH						8.23	8.07				3.0
Me	Me	C_6H_6						8.72	8.16				
Me	Et	Neat				8.18	7.88	8.62	8.22	9.22	9.00		3.2
Me	Et	CCl_4				7.97	7.78	8.40	8.12	9.03	8.93		3.2
Me	Et	CH_2Br_2					7.75	8.30	8.07	8.97	8.92		3.1
Me	Et	CH_3OH					7.73	8.22	8.08	8.97	8.92	2.28	3.1
Me	Et	C_6H_6				8.33	7.90	8.77	8.20	9.30	8.97		
Me	*i*-Pr	Neat			7.63			8.63	8.27	9.20	9.00		3.1
Me	*i*-Pr	CCl_4			7.55			8.43	8.18	9.03	8.93		3.1
Me	*i*-Pr	CH_2Br_2			7.50			8.30	8.12	8.97	8.90		3.1
Me	*i*-Pr	CH_3OH			7.48			8.23	8.13	8.97	8.90	2.32	3.1
Me	*i*-Pr	C_6H_6			7.63			8.77	8.23	9.28	8.97		
Me	*i*-Pr	$C_6H_5CO_2Me$			7.55			8.35	8.15	9.11	8.93		
Me	*t*-Bu	Neat						8.63			8.93	3.53	3.1
Me	*t*-Bu	CCl_4						8.40			8.88		3.1
Me	*t*-Bu	CH_2Br_2						8.30			8.87		3.0
Me	*t*-Bu	CH_3OH						8.25			8.87	2.42	3.0
Me	*t*-Bu	C_6H_6						8.75			8.92	3.55	
Me	*i*-Bu	Neat						8.58	8.17	9.22[g]	9.15[g]		3.2
Me	*i*-Bu	CCl_4						8.40	8.10	9.08[g]	9.08[g]		3.2
Me	*i*-Bu	CH_2Br_2						8.30	8.05	9.12[g]	9.08[g]		3.1
Me	*i*-Bu	CH_3OH						8.20	8.05	9.08[g]	9.08[g]	2.22	3.1
Me	*i*-Bu	C_6H_6						8.73	8.15	9.27[g]	9.13[g]		
Me	C_6H_5	CCl_4						8.00					
Me	C_6H_5	CH_2Br_2						8.03				3.17	
Me	C_6H_5	Acetone						7.80				3.22	
Me	C_6H_5	DMSO[f]						7.77				3.22	
Me	C_6H_5	CH_2OH						7.83					
Me	C_6H_5	C_6H_6						8.53					
Me	$CH_2C_6H_5$	CCl_4				6.58	6.52	8.40	8.07				
Me	$CH_2C_6H_5$	CH_2Br_2				6.72	6.47	8.33	8.03				
Me	$CH_2C_6H_5$	C_6H_6				6.93	6.58	8.82	8.18				

[a] Concentrations of 3 to 6 mole % phenylhydrazone were used. [b] Because of the low concentrations of the *anti* isomers the *cis* protons could not be detected. [c] In most solvents the NH is masked by the aromatic protons. [d] Values represent centers of complex multiplets. [e] Masked by the aromatic protons. [f] Dimethyl sulfoxide. [g] Values for γ-hydrogens.

From the data we conclude that H_1 resonates at lower magnetic fields (deshielded) when *cis* than when *trans* to the anilino group, while H_α and H_β (methyl and methylene) resonate at higher magnetic fields (shielded).

Phenylhydrazone solutions that are pale yellow when freshly prepared develop a dark red color on prolonged standing at room temperature. The color change is rapid in carbon tetrachloride and slow in benzene. In the early stages of decomposition the spectra of freshly prepared and dark red solutions are virtually identical. After standing for several days, carbon tetrachloride solutions decompose extensively. We were unable to detect any azo compound or any resonance in the vinyl region. In solution or as pure liquids, therefore, phenylhydrazones exist in the hydrazone form II. If the azo (III) or the ene-hydrazine (V) forms are present their concentrations must be less



V

than 3%. When oxygen is bubbled through phenylhydrazone solutions the spectra change; *e.g.*, in benzene the doublet (τ = 8.16, 8.72) of acetone phenylhydrazone is replaced by a singlet at τ = 8.53; the singlet (τ = 8.53) of acetophenone phenylhydrazone is replaced

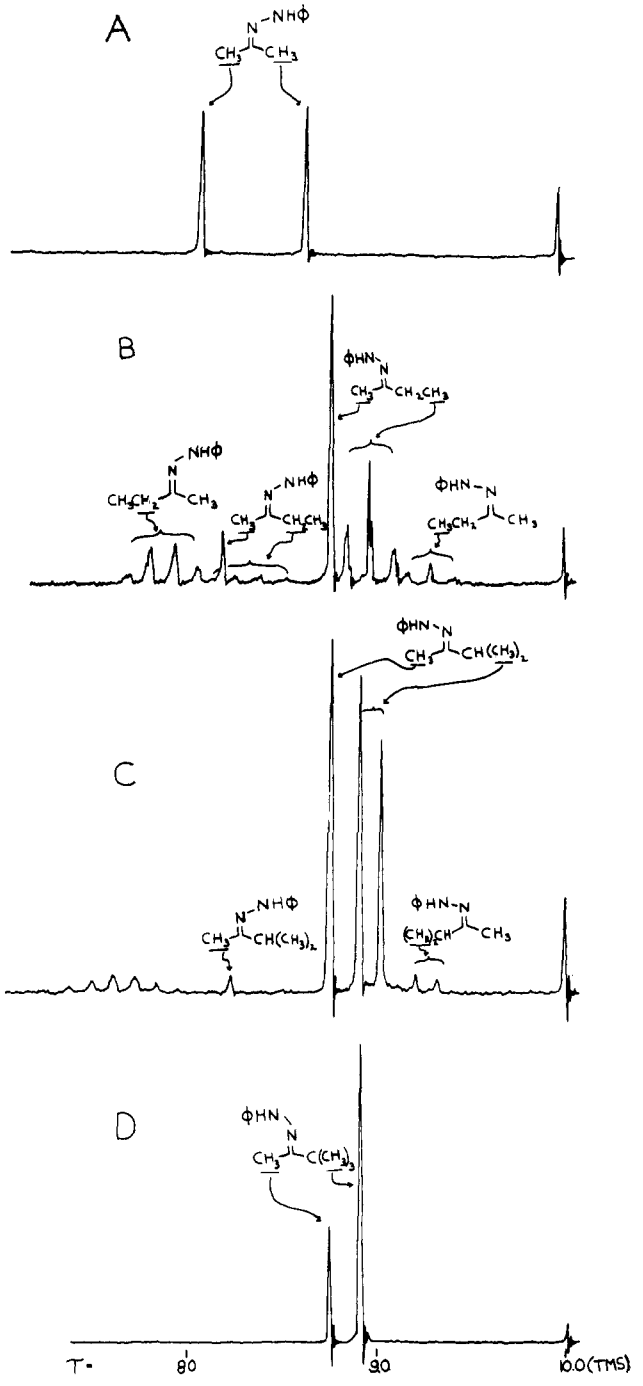


Fig. 1.—N.m.r. spectra of the phenylhydrazones of acetone (A), butanone (B), methyl isopropyl ketone (C), and methyl *t*-butyl ketone (D) in benzene, at concentrations of 5 mole % phenylhydrazone.

by a new singlet at $\tau = 8.10$. (These singlets are not those of the ketones.) It is known[4] that phenylhydrazones are converted to hydroperoxides (VI) by

$$R_1R_2C(OOH)-N=NC_6H_5 \qquad R_1R_2C=N-N(OOH)C_6H_5$$

VI VII

facile oxygen absorption. Our data are in accord with structure VI, and exclude the unlikely structure VII.

Solvent Effects.—Both *cis*- and *trans*-hydrogens (H_1, H_α, H_β, H_γ) of phenylhydrazones resonate at higher magnetic fields in benzene than in aliphatic solvents. The upfield shift of the *cis*-hydrogens is three to six times larger than that of the corresponding

(4) K. N. Pausacker, *J. Chem. Soc.*, 3478 (1950); R. Criegee and G. Lohaus, *Chem. Ber.*, **84**, 219 (1951).

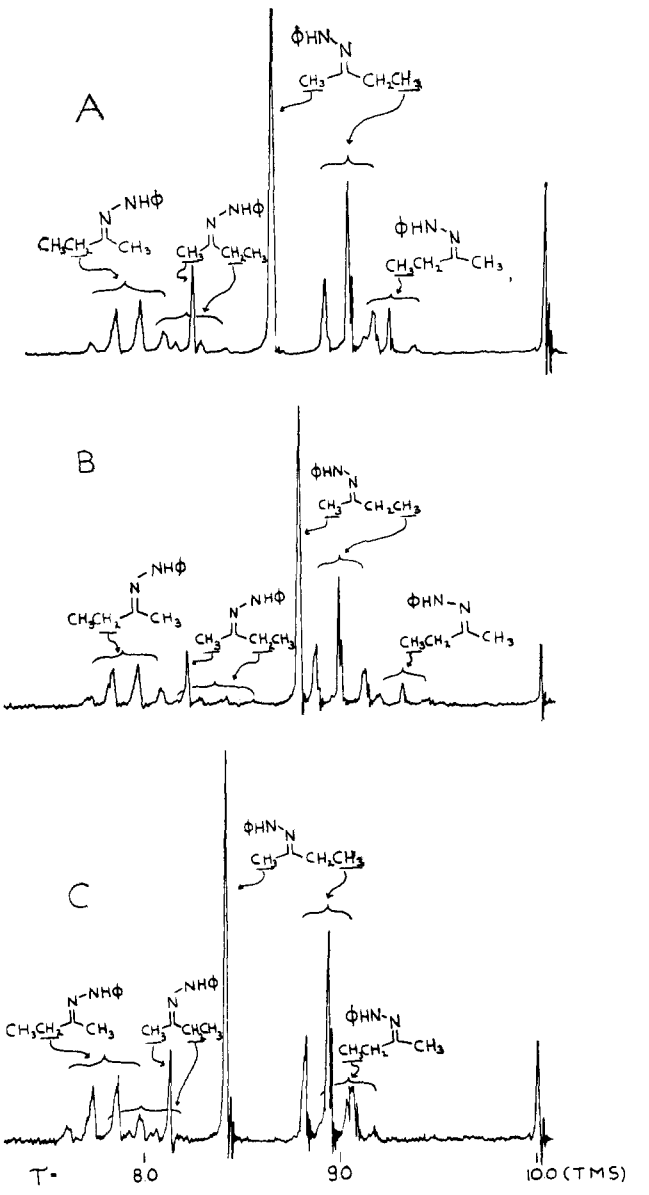


Fig. 2.—N.m.r. spectrum of butanone phenylhydrazone: A, *neat*; B, 5 mole % in benzene; C, 5 mole % in carbon tetrachloride.

trans. A comparison of the spectra of butanone phenylhydrazone, neat, in benzene and in carbon tetrachloride is shown in Fig. 2. Table II summarizes $\Delta\nu$ values

TABLE II

COMPARISON OF THE CHEMICAL SHIFTS OF PHENYLHYDRAZONES IN BENZENE AND CARBON TETRACHLORIDE

$R_1R_2C{=}NNHC_6H_5$		$\Delta\nu^a$(α-CH_3)		$\Delta\nu$(α-CH_2)		$\Delta\nu$(α-CH)	$\Delta\nu$(β-CH_3)	
R_1	R_2	*cis*	*trans*	*cis*	*trans*	*trans*	*cis*	*trans*
H	Me	37.8	15.0					
H	Et				4.8		18.8	4.8
H	*i*-Pr					1.8	13.8	3.0
Me	Me	21.6	4.8					
Me	Et	22.2	4.8	21.6	7.2		16.2	2.4
Me	*i*-Pr	20.4	3.0			4.8	15.0	2.4
Me	*t*-Bu	21.0						2.4
Me	*i*-Bu	19.8	3.0				11.4[b]	3.0[b]
Me	$CH_2C_6H_5$	25.2	6.6	21.0	3.6			
Me	C_6H_5	31.8						

[a] $\Delta\nu = \nu_{\text{in benzene}} - \nu_{\text{in carbon tetrachloride}}$; for convenience the differences are expressed in c.p.s. [b] Values for γ-CH_3.

($\Delta\nu = \nu_{\text{in benzene}} - \nu_{\text{in carbon tetrachloride}}$) compiled from the data of Table I. Use of ν values in other aliphatic solvents instead of those in carbon tetrachloride gives similar results. We recommend the use of this in-

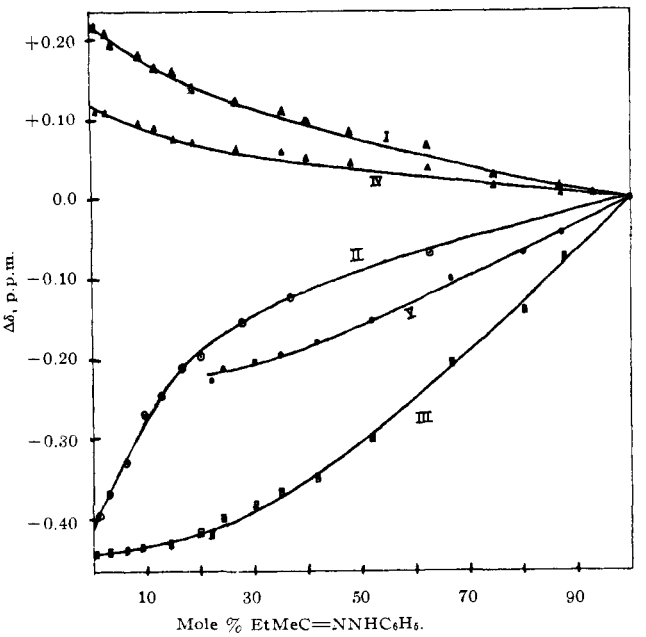


Fig. 3.—Effect of dilution on the chemical shifts of butanone phenylhydrazone: I, *cis*, α-methyl in benzene; II, *cis*, α-methyl in carbon tetrachloride; III, *cis*, α-methyl in dimethyl sulfoxide; IV, *cis*, β-methyl in benzene; V, *cis*, β-methyl in dimethyl sulfoxide.

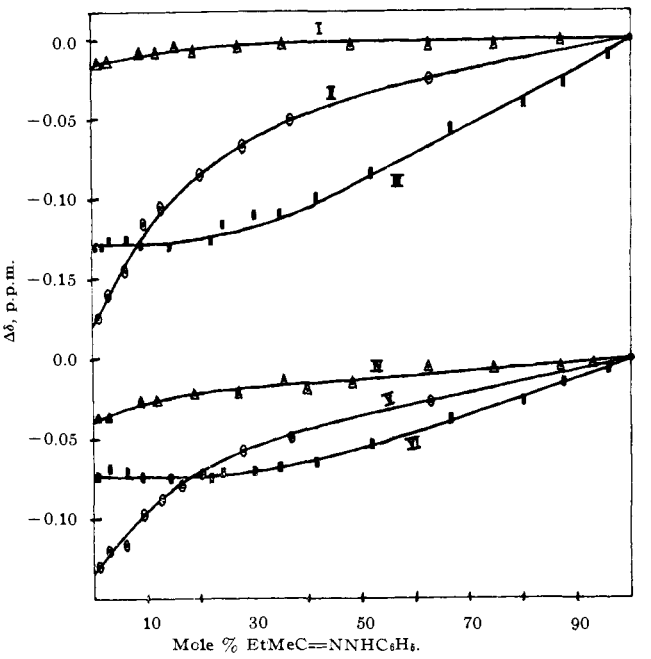


Fig. 4.—Effect of dilution on the chemical shifts of butanone phenylhydrazone: I, *trans*, α-methyl in benzene; II, *trans*, α-methyl in carbon tetrachloride; III, *trans*, α-methyl in dimethyl sulfoxide; IV, *trans*, β-methyl in benzene; V, *trans*, β-methyl in carbon tetrachloride; VI, *trans*, β-methyl in dimethyl sulfoxide.

equality between $\Delta\nu(cis)$ and $\Delta\nu(trans)$ as a convenient and accurate method for assigning *syn* and *anti* structures to phenylhydrazone isomers. From the magnitude of $\Delta\nu$ (31.8 c.p.s.) we have assigned the *syn*-methyl configuration to acetophenone phenylhydrazone, m.p. 104–106°.

Table III summarizes the effect of several solvents on the chemical shifts of butanone phenylhydrazone. Methyl benzoate, nitrobenzene, pyridine, and 2,6-dimethylpyridine behave as the nonaromatic solvents acetone, dimethyl sulfoxide, and methanol.

TABLE III

SOLVENT EFFECTS[a] ON THE CHEMICAL SHIFTS OF BUTANONE PHENYLHYDRAZONE

Solvent	α-CH3		β-CH3	
	cis	*trans*	*cis*	*trans*
Benzene	8.77	8.20	9.30	8.97
Toluene	8.73	8.20	9.25	8.97
o-Xylene	8.72	8.22	9.22	8.97
m-Xylene	8.72	8.22	9.22	8.97
p-Xylene	8.70	8.20	9.22	8.95
Isodurene	8.65	8.22	9.18	8.95
Anisole	8.62	8.13	9.19	8.96
N,N-Dimethylaniline	8.72	8.22	9.24	8.98
Fluorobenzene	8.55	8.14	9.14	8.95
Chlorobenzene	8.55	8.15	9.17	8.97
Bromobenzene	8.55	8.15	9.16	8.96
Iodobenzene	8.52	8.14	9.14	8.96
m-Dichlorobenzene	8.44	8.12	9.19	8.95
Methyl benzoate	8.30	8.05	9.14	8.86
Nitrobenzene	8.17	8.00	8.93	8.88
Pyridine	8.27	8.04	9.11	8.91
Dimethyl sulfoxide	8.22	8.10		8.95
Acetone	8.20			8.91
Benzene–chlorobenzene (1:1, m./m.)	8.65	8.19	9.23	8.89
Benzene–acetone (1:1, m./m.)	8.35			8.93
Benzene–pyridine (1:1, m./m.)	8.43	8.10	9.24	8.94
Benzene–dimethyl sulfoxide (1:1, m./m.)	8.24	8.09	9.01	8.94
Benzene–nitrobenzene (1:1, m./m.)	8.41	8.08	9.19	8.94
Benzene–isodurene (1:1, m./m.)	8.74		9.23	8.97

[a] Concentrations of 5 mole % phenylhydrazone were used; all values are in τ.

Figure 3 shows the effect of dilution on the chemical shifts of *cis*-α-methyl and *cis*-β-methyl hydrogens of butanone phenylhydrazone. The chemical shift of the α-methyl is more sensitive to dilution than that of the β-methyl. In benzene, decrease in phenylhydrazone concentration shifts the resonances to higher fields, in carbon tetrachloride and dimethyl sulfoxide to lower. The curves in dimethyl sulfoxide are concave downward, in carbon tetrachloride convex downward, in benzene concave upward. Figure 4 shows the effect of dilution on the *trans*-α-methyl and *trans*-β-methyl hydrogens. These hydrogens are less affected by dilution than the *cis*. (Note their unusual behavior in benzene, *i.e.*, decrease in phenylhydrazone concentration shifts their resonances to *lower* magnetic fields.) Figure 5 shows the effect of dilution on the chemical shifts of the hydrogens of methyl *t*-butyl ketone phenylhydrazone. Note that these chemical shifts are less sensitive to dilution than those of butanone phenylhydrazone.

syn/anti **Ratios.**—Table IV summarizes *syn/anti* ratios of phenylhydrazones in several solvents. The

TABLE IV

syn/anti RATIOS OF PHENYLHYDRAZONES IN SOLUTION

$R_1R_2C{=}NNHC_6H_5$		% *syn/anti*	
R_1	R_2	(initial)	% *syn/anti* (equilibrium)
H	Me	0/100[b,c,f]	64/36[b]; 63/37[c]; 65/35[d,g]; 61/39[e]
H	Et	[h]	89/11[a]; 82/18[c]
H	*i*-Pr	[h]	95/5[a,d]; 96/4[c]; 94/6[f,g]
Me	Et	[h]	80/20[a]; 86/14[c]; 90/10[d]; 87/13[f]; 83/17[g]
Me	*i*-Pr	[h]	94/6[a]; 95/5[c,f,g]; 97/3[d]
Me	*i*-Bu	[h]	~82/18[c]
Me	*t*-Bu	100/0[a–h]	100/0[a–g]
Me	$CH_2C_6H_5$	100/0[b–g]	84/16[c]; 85/15[d]; 88/12[g]
Me	C_6H_5	100/0[b–g]	100/0[b–g]

[a] Neat. [b] Acetone. [c] Benzene. [d] Carbon tetrachloride. [e] Dimethyl sulfoxide. [f] Methanol. [g] Methylene bromide. [h] These compounds are liquids having equilibrated during or before distillation.

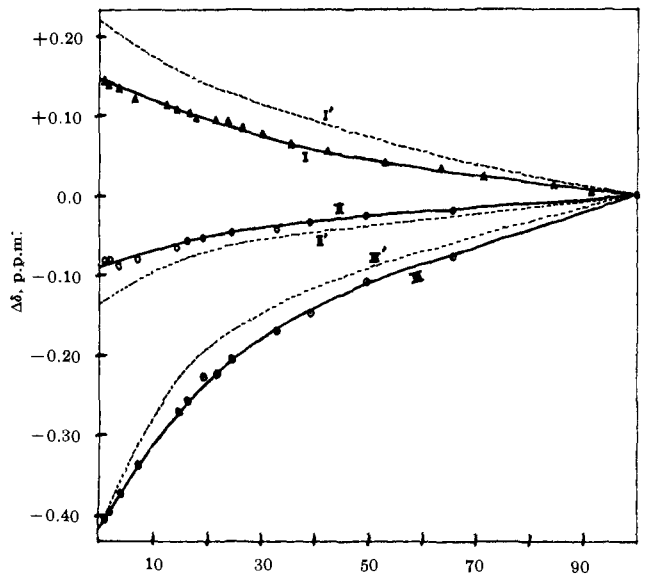
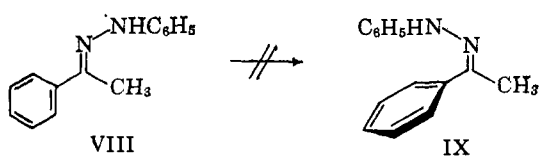


Fig. 5.—Effect of dilution on the chemical shifts of methyl *t*-butyl ketone phenylhydrazone: I, *cis*, α-methyl in benzene; II, *trans*, β-methyl in carbon tetrachloride; III, *cis*, α-methyl in carbon tetrachloride; I′, *cis*, α-methyl of butanone phenylhydrazone in benzene; II′, *trans*, β-methyl of butanone phenylhydrazone in carbon tetrachloride; III′, *cis*, α-methyl of butanone phenylhydrazone in carbon tetrachloride.

values were determined from integration of peak areas and are accurate to ±5%. The results agree reasonably well with previous findings[1a,b] on 2,4-dinitrophenylhydrazones and semicarbazones.

The reaction of acetaldehyde with phenylhydrazine led to an oil from which we isolated the thermodynamically less stable *anti* isomer, m.p. 81–82°. In solution *syn–anti* equilibration is reached within a few hours, the equilibration being faster in carbon tetrachloride and methylene bromide than in benzene, methanol, and acetone.

The reaction of acetophenone and phenylacetone with phenylhydrazine led to the thermodynamically more stable *syn* isomers. In solution the *syn* isomer of phenylacetone phenylhydrazone equilibrates with the *anti* within a day; that of acetophenone phenylhydrazone resists isomerization. Nonbonded interactions (more severe in IX than in VIII) and resonance interac-

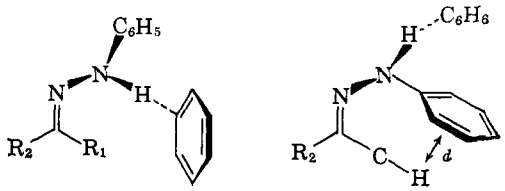


VIII IX

tions (more favorable in VIII than in IX) are apparently sufficient to shift the equilibrium completely in favor of VIII.

Discussion

The large differences between $\Delta\nu(cis)$ and $\Delta\nu(trans)$, and the dependence of the chemical shifts on the concentration of phenylhydrazone in benzene, suggest specific and reversible association between benzene and phenylhydrazone. A hydrogen-bonded complex[5] of conformation X adequately accommodates all the data, *e.g.*, as a consequence of R_1 being closer to the ring



X XI

center $\Delta\nu(cis) > \Delta\nu(trans)$; because of steric interactions between benzene and R_1, *cis*-β-methyl will assume conformations in which *cis*-H_β is farther away from the ring than is *cis*-H_α, hence $\Delta\nu(cis\text{-}H_\alpha) > \Delta\nu(cis\text{-}H_\beta)$. In conformation XI the distance d between the center of the phenyl ring and the hydrogen in the position shown—assuming a trigonal nitrogen—is about 2.1 Å. We can exclude, therefore, XI as energetically unfavorable. Furthermore, if XI were a significant contributor, in all other solvents hydrogen bonding with the NH *cis*-H_α(methyl) and *trans*-H_α(methyl) should be shielded by the phenyl by 0.3 p.p.m. and 0.1 p.p.m., respectively,[6] a prediction contradicted by the results. The several other conformations available by rotation about the nitrogen–nitrogen bond, in addition to having lost partially or totally the π-sp^3 overlap, do not accommodate the large $\Delta\nu(cis) - \Delta\nu(trans)$ values.

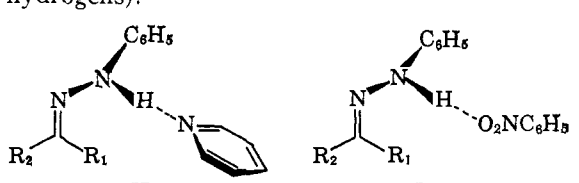
Successive substitution of toluene, xylenes, or isodurene for benzene progressively decreases the upfield shift of *cis*-hydrogens[7] (Table III). This trend, consistent with structure X, is explicable in terms of successive decreases in the stability of the complexes, *e.g.*, the equilibrium constant for (1) is greater than that for (2). The data support this explanation; *e.g.*, the

$$R_1R_2C{=}NNHC_6H_5 + C_6H_6 \rightleftharpoons R_1R_2C{=}NNHC_6H_5{\cdot}C_6H_6 \quad (1)$$

$$R_1R_2C{=}NNHC_6H_5 + \text{isodurene} \rightleftharpoons R_1R_2C{=}NNHC_6H_5{\cdot}\text{isodurene} \quad (2)$$

resonance of *cis*-H_α in a 1:1 (mole/mole) mixture of benzene–isodurene (8.74) is closer to that in benzene (8.77) than to that in isodurene (8.65).

In solvents having two basic sites the question arises as to which site hydrogen bonds to the NH. Nitrobenzene, methyl benzoate, and pyridine, behaving similarly to acetone, dimethyl sulfoxide, and methanol, and competing more effectively than benzene for the NH, must hydrogen bond through the lone pairs of electrons on the hetero atoms (structures XII and XIII predict no shielding effect by the aromatic ring on the *cis*-hydrogens).



XII XIII

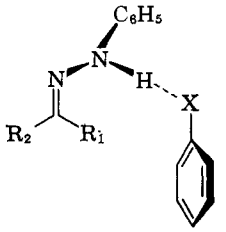
Halobenzenes also compete more effectively than benzene for the NH, *e.g.*, the resonance of *cis*-Hα in a 1:1 (mole/mole) benzene–chlorobenzene mixture (8.65) is closer to that in chlorobenzene (8.55) than to that in benzene (8.77), and consequently hydrogen bonding must involve the unshared electrons of the halogen atoms rather than the π-electrons of the ring. At the same time halobenzenes, like benzene, exert

(5) For evidence that the association complex involves hydrogen bonding between NH and benzene see ref. 1c. In addition it has been shown, ref. 1b, that the NH of 2,4-dintrophenylhydrazones hydrogen bonds with various solvents. We will assume in our arguments a pyramidal anilino nitrogen in view of recent evidence favoring a pyramidal configuration for the nitrogen of aniline and N-substituted anilines: *e.g.*, J. C. Evans, *Spectrochim. Acta*, **16**, 428 (1960); A. T. Bottini and C. P. Nash, *J. Am. Chem. Soc.*, **84**, 734 (1962); also see B. M. Wepster in "Progress in Stereochemistry," Vol. II, edited by W. Klyne and P. B. D. de la Mare, Academic Press, Inc., New York, N. Y., 1958, Chapter 4. Our data, however, can be explained equally well by assuming a trigonal nitrogen.

(6) These values were calculated by Dr. F. M. Vane according to the procedure of C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(7) We will use the resonance of *cis* α-methyl, because of its greater sensitivity to solvent changes.

strong shielding effects on the *cis*-hydrogens. Considering the directional properties of the unshared electrons the data can be rationalized in terms of XIV. Several conformations of the halobenzene are obviously possible by rotation about the axis of the hydrogen

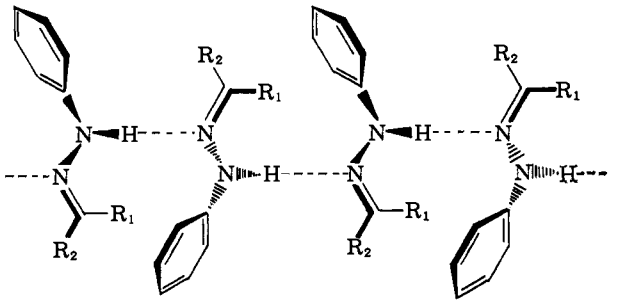


XIV

bond and the over-all effect will depend on the weighted average of all these conformations.

Because of the unusually strong solvent dependence of *cis*-H_α the data in mixed solvents, when compared with those in the pure solvents, afford a sensitive test of the relative abilities of bases to hydrogen bond with the NH of phenylhydrazones. From the data (Table III) the relative strengths of these hydrogen bonds for the solvents examined are: dimethyl sulfoxide > acetone > pyridine > nitrobenzene > chlorobenzene > benzene > isodurene.

On the basis of the dilution results (Fig. 3–5) and the data already discussed, we propose XV as a general structure for liquid phenylhydrazones.[8] Structure XV accommodates the larger upfield shift of *cis*-hydrogens over *trans* and of *cis*-H_α over *cis*-H_β as the concentration of phenylhydrazone in aliphatic solvents increases (the explanation rests on the arguments invoked with X to rationalize the relative magnitudes of $\Delta\nu$ values). It can also accommodate the unusual downfield shift of *trans*-hydrogens with decrease in concentration of phenylhydrazone in benzene, on the assumption that the two phenyls—one on each side—in XV will exert a stronger shielding effect than the single benzene ring in X. It is possible, however, for the shielding effect in XV to be equal to or smaller than it is in X and at the same time *trans*-hydrogens to resonate at higher magnetic field in neat than in benzene solutions, provided the ratio associated/unassociated phenylhydrazone is larger in the neat liquid state than in benzene. We have no way to distinguish between these two possibilities.



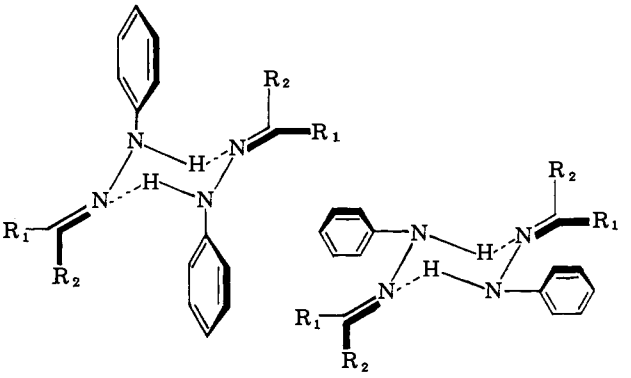
XV

(8) As with all other complexes suggested in this work an equilibrium is implied here between associated and unassociated molecules.

From the shapes of the dilution curves we conclude that hydrogen bonding between dimethyl sulfoxide and phenylhydrazone is stronger than phenylhydrazone self-association, and that hydrogen bonding between either carbon tetrachloride or benzene with phenylhydrazone is weaker.

In accord with XV is also the sharper change in the chemical shifts of butanone phenylhydrazone than in those of methyl *t*-butyl ketone as the phenylhydrazone concentration increases (Fig. 5). Increase in R_2 should weaken self-association and favor solvent competition for the NH.

We have considered several alternative structures to XV that might adequately accommodate the results. Of these, the most likely candidates are cyclic dimers and trimers. Conformation XVI predicts that in aliphatic solvents increase in the concentration of phenylhydrazone should lead to stronger shielding of *trans*-hydrogens rather than *cis*. Conformation XVII, failing to accommodate adequately the results of dilution studies in benzene and suffering from the same severe steric interactions as XI, must also be rejected. Cyclic trimers can be rejected from similar arguments.



XVI XVII

In closing we want to emphasize, as several investigators have done in the past, the advantage of n.m.r. over infrared in detecting weak hydrogen bonding (in the present case the infrared spectra show little if any hydrogen bonding), and to point out that extensive information can be elicited from the behavior of hydrogens other than those undergoing hydrogen bonding. In phenylhydrazones the NH signal is masked by the resonances of the aromatic hydrogens; it is broad whenever detectable and totally uninformative in the matters discussed.

Experimental

Preparation of Phenylhydrazones.—All phenylhydrazones were prepared according to well known procedures. Liquid phenylhydrazones were distilled under reduced pressure and solid phenylhydrazones were recrystallized twice from ethanol–water solutions. Their infrared spectra showed a single N–H stretch (unassociated) at 3.01–3.03 μ.

N.m.r. Spectra.—All n.m.r. spectra were determined at 60 Mc. on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.), at a temperature of about 36°. Undegassed solutions were used with tetramethylsilane as internal reference.

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