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A Proton Resonance Study of Bis-(acetylacetone)-ethylenediimine and Related Schiff Bases

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RECEIVED NOVEMBER 7, 1960

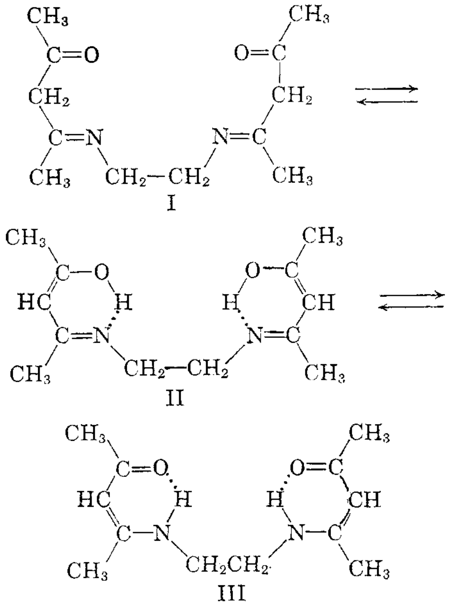
The tautomeric equilibria of bis-(acetylacetone)-ethylenediimine and related Schiff bases have been studied by proton magnetic resonance. The spectra of the compounds examined indicate that in common solvents except acetone they exist almost entirely as chelated hydrogen-bonded tautomers. A significant portion of these tautomers is present in the ketamine form. The solvent dependence of these equilibria is small. The effect of aromatic solvents on the proton spectrum is large. The aromatic diamagnetic shifts are, however, explicable in terms of the geometry of the system and an association between the carbonyl of the base and the protons of the aromatic. The use of these diamagnetic shifts for structural inferences in n.m.r. studies is briefly discussed.

Introduction

Condensation products of acetylacetone (2,4-pentanedione) and related β-diketones with mono- and diamines have been the subjects of a variety of physical studies in recent years. Martell and coworkers have examined the infrared[1,2] and ultraviolet[2,3] spectra and obtained dipole moments[4,5] of a number of these Schiff bases derived from diamines while Holtzclaw, *et al.*,[6] have studied the infrared spectra of several analogous bases obtained from monoamines. Studies of these compounds assume additional importance in view of the ability of the Schiff bases to coordinate divalent metal ions.[2,6,7]

Paramount in the consideration of these Schiff bases are the questions of the positions of the keto-enol or amine–imine equilibrium and the nature of the hydrogen bond in the six-membered chelate ring.

Selecting bis-(acetylacetone)-ethylenediimine as the prototype of the compounds to be considered in this work, the forms I–III may be present in tautomeric equilibrium as shown.


I

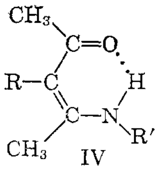
II

III

The distinction between II and III is not large as a slight displacement of the hydrogen nucleus would interconvert the two forms. Nevertheless, the two forms should be distinguishable entities provided the potential barrier separating the two sites adjacent to the oxygen and nitrogen is sufficiently great.

Clearly some of the same considerations apply when dealing with β-diketones, β-ketoesters and related dicarbonyl compounds. Of the physical methods applied to the study of the equilibria of these compounds, proton magnetic resonance has been conspicuous in its ability to assess keto–enol ratios and to reflect the electronic nature of the protons involved in the hydrogen bond of the enol-chelate.[8]

In an attempt to answer the foregoing questions we report here the results of an investigation of the proton resonance spectra of a number of bis-(acetylacetone)-diimines in a variety of solvents. It has been concluded from infrared evidence that these compounds are largely tautomerized into both II and III with appreciable amounts of each existing in the solid and solution.[1,2] Similar spectra have been obtained for acetylacetone-monoimines.[6] In addition Cromwell, *et al.*,[9] have inferred from an infrared study of the carbonyl region that the α,β-unsaturated-β-amino ketones examined by them have the chelated ketamine structure


IV

No previous proton resonance studies of Schiff bases appear to have been done except for the very recent work of Reeves, Allen and Strømme,[10] who report chemical shifts for protons in the hy-

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[1] K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955).

[2] A. E. Martell, R. L. Belford and M. Calvin, *J. Inorg. Nuclear Chem.*, **5**, 170 (1958).

[3] K. Ueno and A. E. Martell, *J. Phys. Chem.*, **61**, 257 (1957).

[4] P. J. McCarthy and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 264 (1956).

[5] R. J. Hovey and A. E. Martell, *ibid.*, **82**, 364 (1960).

[6] H. F. Holtzclaw, Jr., J. P. Collman and R. M. Alire, *ibid.*, **80**, 1100 (1958).

[7] P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, *ibid.*, **77**, 5820 (1955).

[8] For a summary and references to work in this area up to 1958, see J. A. Pople, W. G. Schneider, H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 433–441.

[9] N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, *J. Am. Chem. Soc.*, **71**, 3337 (1949).

[10] L. W. Reeves, E. A. Allen and K. O. Strømme, *Can. J. Chem.*, **38**, 1249 (1960).

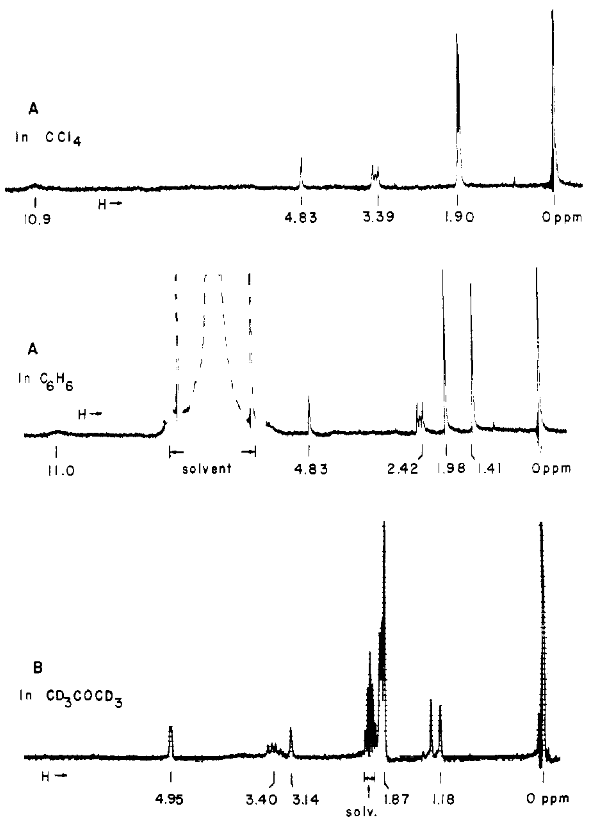

Fig. 1.—Proton spectra (at 60.000 Mc.) of: A, bis-(acetylacetone)-ethylenediimine and B bis-(acetylacetone)-propylenediimine (in B, the low field signal at 10.8 p.p.m. is omitted).

drogen bonded rings of several bis-(salicylaldehyde)-diimines.

Experimental

Preparation of Compounds.[11] The condensation products of acetylacetone and amines were synthesized according to previously published methods from freshly distilled acetylacetone and the corresponding diamine.

Base	Ref.	M.p., °C. This work	M.p., °C. Lit.
Bis-(acetylacetone)-ethylenediimine-(A_2en)[a]	7	111	111–111.5
Bis-(acetylacetone)-propylenediimine	7	89–90	91
Bis-(acetylacetone)-trimethylenediimine[b]	2	61	51
Bis-(acetylacetone)-tetramethylenediimine	12	103–104	105.5–106.5
Bis-(benzoylacetone)-ethylenediimine	7	181	180.5
Acetylacetone anil-(4-anilino-3-pentene 2-one)	13	47–48	48
Diethyl-(ethylene-β-aminocrotonate)[c]	2	. . .	. .

[a] Deuterated form was prepared by re-crystallization from D_2O. [b] % N calcd., 11.75; found, 11.46. [c] Deuterated form was prepared by dissolving 0.5 g. in the minimum volume of hot dioxane and then adding D_2O slowly until the solution became cloudy. The solution then was cooled and filtered. The procedure was repeated once and this sample used in the spectral work.

Spectra of 4-amino-3-pentene-2-one and 4-amino-4-(β-pyridyl)-3-butene-2-one were obtained from E. Hand of this department.[14]

Solvents and Solutions.—Common solvents were commercial reagent grade. Chloroform was treated with Woelm alumina to remove alcohol. Spectra in benzene dried with phosphorus pentoxide were identical with those using the undried solvent.

Hexadeuterioacetone was New England Nuclear Co. material of 99% isotopic purity.

Tetramethylsilane (Anderson Chemical Co.) was purified by distillation from concentrated sulfuric acid.

Pyrrole was distilled and used immediately to prepare the necessary solutions. The required solution was prepared and a sample sealed *in vacuo* in an n.m.r. tube and stored in liquid nitrogen until used.

With the exception of studies involving hexadeuterioacetone as the solvent, the solutions were made up to a concentration of 200 mg. of base (~0.2 *M*) in 5.00 ml. of a solvent which contained 0.15 ml. (3% v./v.) of tetramethylsilane as an internal standard. In all cases the concentration of the solute was only slightly less than its solubility limit in carbon tetrachloride. To assist in sidebanding these dilute solutions, the concentration of the internal standard was slightly larger than usual.

When hexadeuterioacetone was used as the solvent the solutions were prepared on a weight basis in the sample tube. Concentrations were ~0.4 *M* so that the methyl signals of the base were clearly defined relative to the residual protium in the solvent.

All samples were degassed, sealed, and stored in liquid nitrogen until used.

Spectra.—Spectra were obtained on a Varian V-4300 spectrometer operating at 60.000 Mc. The line positions were determined by the sideband method with the audio oscillator being monitored by a frequency counter. The line positions, with reference to tetramethylsilane as the internal standard,[15] are accurate to ± 0.2 c.p.s. or 0.003 p.p.m. except where the band width precluded such accuracy. The chemical shifts δ (in p.p.m.) are defined as $\mu - \mu_r/\mu_0$ where μ_r and μ_0 are the resonant reference frequency and the fixed radio frequency, respectively.

Results and Discussion

Because the spectrum of acetylacetone in carbon tetrachloride solution with tetramethylsilane as an internal reference is useful for comparison purposes, it was measured and the results are listed in Table II. The agreement with previous investigators is good.[8] However, in this solvent the compound is primarily in the enolic form so that at the concentrations necessary for equivalence to the much less soluble diimines, the signals from the small amount of keto form (~5%) were not discernible.

The spectrum of bis-(acetylacetone)-ethylenediimine(A_2en) in carbon tetrachloride solution is pictured in Fig. 1 and the exact band positions are listed in Table I. The two bands near 1.88 p.p.m. are due to the slightly non-equivalent methyl groups in the acetylacetone moiety. The group at 3.46 p.p.m. is the ethylene bridge; its peculiar shape will be discussed later. The signal at 4.81 p.p.m. corresponds to the vinylic hydrogen (at 5.39 p.p.m. in acetylacetone) and, coupled with the very broad absorption (~30 c.p.s. wide) at 10.9 p.p.m. ascribable only to a hydrogen-bonded proton, indicates that in this solvent the diimine is primarily in the hydrogen-bonded chelate form II or III. The absence of a methylene band near 3.07 p.p.m. (see following discussion of the spectrum in acetone) is further confirmation of the tautomerized chelate character of the base.

The other diimines studied which differ only in the nature of the bridge joining the nitrogens have the anticipated spectra (*cf.* Fig. 1 and Table

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(11) Throughout this paper the compounds studied will be referred to as diimines; however, this terminology is not intended to imply structure.

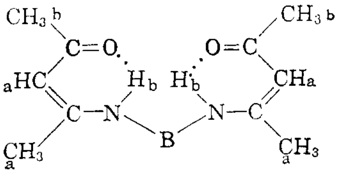
(12) R. J. Hovey, J. J. O'Connell and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 3189 (1959).

(13) E. Roberts and E. E. Turner, *J. Chem. Soc.*, 1832 (1927).

(14) For further details see E. Hand, Thesis, Harvard Univ., 1961.

(15) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

TABLE I



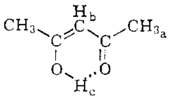
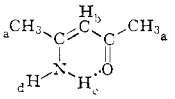
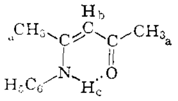
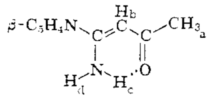
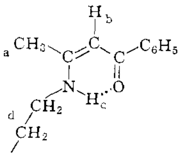
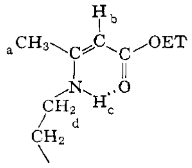
PROTON RESONANCE DATA FOR BIS-(ACETYLACETONE) SCHIFF BASES IN P.P.M. RELATIVE TO TETRAMETHYLSILANE

Compound	Solvent	Methyls a	Methyls b	Hydrogens a	Hydrogens b^a	B 1^b	B 2	B 3	Comments
Bis-(acetylacetone)-ethylenediimine	CCl_4	1.85	1.90	4.83	10.9	3.39, 3.49			
	C_6H_6	1.41	1.98	4.83	11.0	2.42, 2.53			
B = $-CH_2-CH_2-$ 1	$CHCl_3$	1.91	2.00	4.99	10.9	3.37, 3.48			B collapsed to single broad signal, new band at 3.07 (acetone)
	CD_3COCD_3	1.87	1.91	4.95	10.8	3.50			
	CS_2	1.82		4.81	10.9	3.29, 3.39			
	Pyridine	1.80	2.03	5.02	11.2	3.18, 3.28			Me's only slightly split (CS_2)
	Pyrrole	1.39	1.83	4.81	10.7	2.38, 2.48			
	$C_6H_5NO_2$	1.91	1.97	4.95	11.1	3.37, 3.48			
	C_6H_5Br	1.58	1.94	4.82	10.9	2.79, 2.89			
Bis-(acetylacetone)-propylene diimine	CCl_4	1.89	1.84	4.79	11.1	3.37 M	Unresolved	1.24, 1.35	
	C_6H_6	1.47, 1.51	1.97	4.81	11.1	2.53 M	Unresolved	0.59, 0.70	
1 B = $-CH-CH_2{}^2$ $\vert$ CH_3 3	CD_3COCD_3	1.93	1.87	4.95	10.9	3.40 M		1.18, 1.29	New band at 3.14
Bis-(acetylacetone)-trimethylenediimine	CCl_4	1.90		4.83	10.9	3.33, 3.43	Under methyl		1 is a quartet, Me's only (<1 c.p.s.) slightly split (CCl_4)
B = $-CH_2CH_2CH_2-$ 1 2	C_6H_6	1.42	2.02	4.86	11.1	2.68, 2.59	1.05 M		
Bis-(acetylacetone)-tetramethylenediimine	CCl_4	1.87		4.82	10.9	3.32, 3.25	1.71 M		Me's only slightly split (<1 c.p.s.)
B = $CH_2CH_2CH_2CH_2-$ 1 2	C_6H_6	1.42	2.04	4.88	11.1	2.56, 2.46	1.01 M		

[a] Positions ±0.05 p.p.m. [b] M = Multiplet.

TABLE II

PROTON RESONANCE DATA FOR ADDITIONAL SCHIFF BASES AND ACETYLACETONE IN P.P.M. RELATIVE TO TETRAMETHYLSILANE

Compound	Solvent	a	b	c	d
	CCl_4 C_6H_6	1.99 1.61	5.39 4.96	15.3 16.2	
	$CDCl_3$	1.88, 1.98	5.16	9.78	6.75
	CCl_4	1.98	5.04	12.6	
	$CDCl_3$	2.05	5.35	9.50	6.75
 Bis-(benzoylacetone)-ethylenediimine	$CHCl_3$	2.04	5.71	11.6	3.50 3.60
 Diethyl-(ethylenebis-β-aminocrotonate)	$CHCl_3$	1.91	4.48	8.72	3.41 3.30

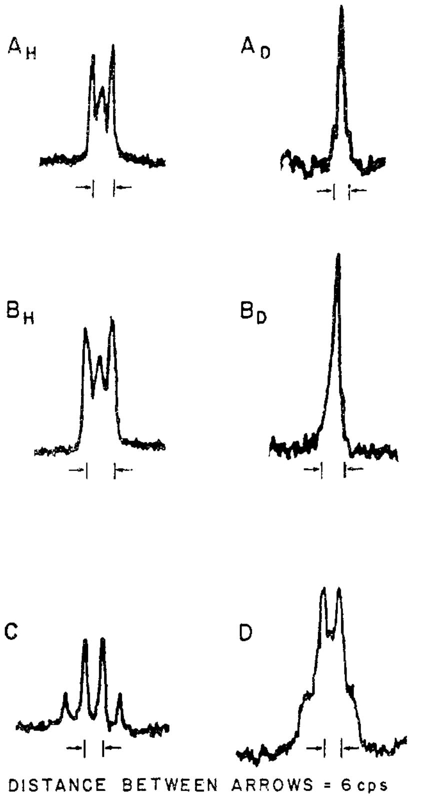


Fig. 2.—The methylene bridge signals (near 3.4 p.p.m.) of the diimines: A_H, bis-(acetylacetone)-ethylenediimine, A_D, the same compound monodeuterated; B_H, diethyl-(ethylenebis-β-aminocrotonate), B_D, the same compound monodeuterated; C, bis-(acetylacetone)-trimethylenediimine; D, bis-(acetylacetone)-tetramethylenediimine.

I) and tend to confirm the signal assignments in the A_2en spectrum. It is further evident that tautomeric character of the base does not depend significantly on the nature of the bridge.

The spectra in various solvents of the prototype, A_2en, are set out in Table I. Except for solvent shifts, most marked in the case of aromatic solvents, the spectra are similar to that in carbon tetrachloride. Only in acetone does a new signal appear, this at 3.07 p.p.m., and may be assigned to the methylene group of tautomer I. From a ratio of the intensities of the methylene to the vinyl signals, the compound is about 22% in the ketimine form I. It may, therefore, be safely concluded that in the other solvents the contribution of form I to the equilibrium concentrations is less than ~5%. It is further observed that alteration of the polar character of the solvent does not noticeably affect the tautomeric equilibrium whereas the equilibrium concentrations of the keto and enol tautomers of acetylacetone[16] and ethyl acetoacetate[17] are clearly susceptible to solvent and dilution through bulk dielectric effects and, where possible, preferential hydrogen bonding to one tautomer. Because of the rather low solubilities of the bases studied here, meaningful dilution studies could not be made.

The small sensitivity of the A_2en equilibrium to solvent effects and the similarity of the spectra in Tables I and II suggest that in these bases the acidic proton may be bonded primarily to the nitrogen in the ketamine form III. The equilibrium is not measurably disturbed by $CHCl_3$, a hydrogen-bonding solvent of weak to moderate strength,[18] or by pyrrole, which is very effective in producing sizable amounts of acetylacetone and ethylacetoacetate keto forms, presumably by hydrogen bonding with the carbonyl oxygen.[16,17] With the very weak hydrogen bonding solvent benzene the acidic proton resonance in acetylacetone is lowered by 1 p.p.m. (Table II) whereas the analogous resonances in the bases of Table I are affected by 0.2 p.p.m. at the most. Further, the hydrogen bonded proton signals in the bases of both Tables I and II are much broader than that of the corresponding acetylacetone proton, an effect which may be due primarily to N^{14} quadrupole relaxation. However, broadening by intramolecular proton exchange of intermediate rate[19] cannot be entirely discounted.

More definite evidence for the location of the low field proton may be adduced from infrared data and the structure of the bridging group proton resonance signal. The infrared spectra of a large majority of condensation products of β-dicarbonyl compounds and mono- and diamines have three strong bands in the 1700–1490 cm.$^{-1}$ range.[1,2,6,9] The highest energy band, which in most instances falls in the 1620–1590 cm.$^{-1}$ region when chelated hydrogen bonding is possible, has been assigned as a perturbed carbonyl stretch with the frequency lowering from a free carbonyl ascribed to conjugation and hydrogen bonding. However, in several instances with the same general type of compound this band has been found at significantly higher energies, strongly implying an appreciable amount of a ketamine structure with weakened hydrogen bonding. Witkop[20] found a band at 1667 cm.$^{-1}$ in ethyl β-aminocrotonate and two sharp bands at 3509 and 3344 cm.$^{-1}$, assigned as N–H stretches. In the ethylene bridged analog, diethyl-(ethylene-*bis*-β-aminocrotonate), Martell, Calvin and Belford[2] report a strong carbonyl band at 1645 cm.$^{-1}$ and a sharp N–H stretch at 3260 cm.$^{-1}$. We have confirmed these spectra and have examined the proton resonance spectra (*cf.* Table II) of the latter crotonate base, assuming that in this case the independent infrared evidence most strongly favors an appreciable portion of the ketamine form. Of all the bases examined the low field proton is most shielded in this compound, reflecting a weaker hydrogen bond in accord with infrared evidence and is broadened (~20 c.p.s.).

Comparison within Fig. 2 shows quite clearly that the signals of the ethylene bridge in the crotonate base and A_2en, in which the location of the proton may be assumed less certain, are identical "triplets." A singlet is anticipated but a doublet could arise through spin-spin coupling of the methylene group with the proton on the nitrogen. Studies of pyrrole,[21] N-methylformamide[22] and

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[16] L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

[17] M. Geissner-Prettre, *Compt. rend.*, **250**, 2547 (1960).

[18] G. C. Pimentel and A. D. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp. 197–199.

[19] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

[20] B. Witkop, *J. Am. Chem. Soc.*, **78**, 2873 (1956).

N-methylacetamide[23] demonstrate that in certain instances a proton on a nitrogen can effect spin–spin splittings of protons on an adjacent carbon. The spectra of bridging portions of bis-(acetylacetone)-trimethylene- and tetramethylenediimine are also shown in Fig. 2. In the trimethylene compound the low field signal from the hydrocarbon bridge is split into a quartet whereas the maximum spin-spin splitting expected in the tautomer of type II is a triplet from the central methylene group. Additionally, in the tetramethylene case the methylenes adjacent to the nitrogen are split into a slightly broadened quartet.

In the ethylene bridged compounds monodeuteration causes the low field proton signal to disappear and the bridge signal to collapse into a singlet, thus proving that the satellites result from coupling with the proton on the nitrogen with $J = 6$ c.p.s. The central band could be the result of slightly different coupling constants in conformers produced by rotation about the C–N bond. Alternatively, this signal, which persists on deuteration and is intensified, might be indicative of the presence of tautomer II in which a single bridge resonance is anticipated. However, the ratio of intensities of the triplet components is insensitive to solvent changes and, significantly, to the electronic nature of the group (CH_3, C_2H_5, EtO) appended to the oxygen-bonded carbon. Future temperature studies and double irradiation spectra may be useful in clarifying the assignment of the bridge portion of the spectrum.

From the above evidence it is concluded that at least with A_2en a detectable amount ($\geq 5\%$) of the ketimine form I exists only in acetone solution, and that in other solutions the bridged Schiff bases are present in appreciable amounts (at least $\sim 80\%$) in the ketamine form III. Definite proof of the existence of any of the enol-imine form II must await further experiments.

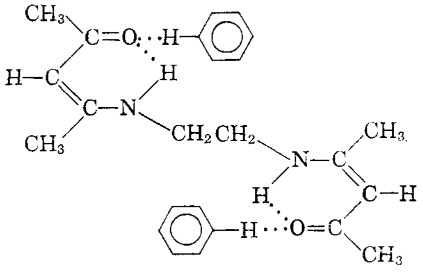
Aromatic Solvents.—The methyl and vinyl signals of a dilute solution of acetylacetone in benzene are shifted to higher fields with reference to the internal standard whereas the enolic hydrogen is moved to lower fields by 0.9 p.p.m. The first effect is usual for an aliphatic solute in benzene.[24] The decreased shielding of the enolic proton may be due to hydrogen bonding of the carbonyl group by the solvent, rendering the proton more acidic by virtue of competition with aromatic protons for the electrons on the oxygen. This type of hydrogen bonded interaction is similar to that proposed by Schaefer and Schneider for certain *p*-disubstituted aromatics in acetone.[25]

When A_2en and the other diimines of Table I are dissolved in benzene, they exhibit quite a different spectral behavior. The methyl signals are now separated by 0.5–0.6 p.p.m. and the hydrocarbon bridges are moved to more shielded positions by ~0.7–1.0 p.p.m. The vinyl and acidic proton signals are altered only slightly in comparison. Because one methyl peak moves only a few cycles compared to the standard whereas the other may move over 30 cycles, the separation between methyls provides an internal measure of the aromatic diamagnetic shift. In Table III the effect of altering the aromatic solvent on the methyl signals of A_2en is listed.

TABLE III

Solvent	ΔCH_3, p.p.m.
CCl_4	0.05
$C_6H_5NO_2$	.06
C_6H_5Br	.36
$C_6H_5OCH_3$	.42
$C_6H_5CH_3$	.51
C_6H_6	.57
Pyrrole	.44

The enhanced splitting of the methyl signals in aromatic solvents and the attendant high field shift of the bridging group is understandable using a model similar to that of Schaefer and Schneider[25] involving hydrogen bonded interactions of aromatic protons with the carbonyl groups of the base as is shown in V.



V

In a low dielectric solvent the molecule is most likely in an extended configuration with the polar carbonyls opposed. The aromatic complexed to the carbonyl would be at approximate right angles to the bridge moiety and at a distance from it. The methyl near the carbonyl would then experience little effect from the aromatic diamagnetic ring current of the associated molecule. However, models indicate that the other methyl and the hydrocarbon bridge between the nitrogens would experience the full effect of the ring current from the aromatic and hence be shifted up field.[26]

When the propylene compound is dissolved in benzene, the methyl signal which moves upfield is slightly split. The presence of a methyl group on the hydrocarbon bridge renders the two methyl groups slightly inequivalent by virtue of differing steric interactions of the bridge with the hydrogen bonded aromatic. This suggests that in conformity with the explanation above the methyl groups shifted upfield are adjacent to the hydrocarbon bridge. The assignments of the methyl resonance in Table I have been made on this basis.

The superiority of benzene to other aromatics in producing the greatest solvents shifts may be in

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(21) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959).

(22) V. J. Kowaleski and D. G. deKowaleski, *J. Chem. Phys.*, **32**, 1272 (1960).

(23) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

(24) Ref. 8, pp. 425–431.

(25) T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218 (1960).

(26) Models indicate that a π complex involving the acidic proton in A_2en and benzene would give rise to a diamagnetic shift opposite to that observed. A π complex of this type has been proposed (I. Suzuki, M. Tsuboi and T. Shimanouchi, *J. Chem. Phys.*, **32**, 1263 (1960)) to account for the small variation in the N–H stretching frequencies of N-methylacetamide in aromatic solvents.

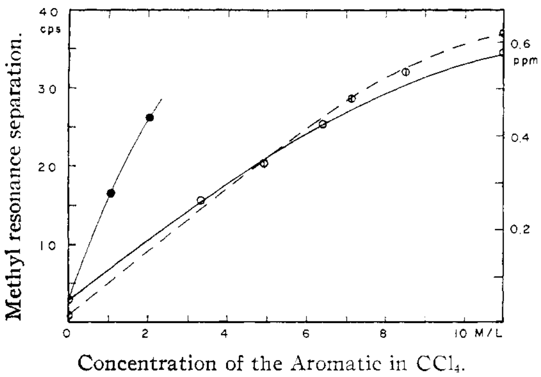


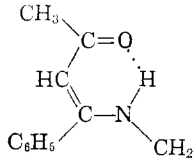
Fig. 3.—The dependence of ΔCH_3 (*cf.* Table III) on concentration of the aromatic solvent. Solid lines refer to bis-(acetylacetone)-ethylenediimine and dotted lines to bis-(acetylacetone)-tetramethylenediimine: ●, naphthalene in CCl_4; O and ⦶, benzene in CCl_4 (zero *M* is pure CCl_4, 11 *M* is pure benzene).

part ascribable to slightly differing steric requirements with attendant substantial changes in the shielding of the bridge and adjacent methyls since the secondary magnetic field of the aromatic falls off inversely with the cube of the distance of separation.[27] From Fig. 3 naphthalene exceeds even benzene in effecting shifts of the methyl signal in solutions in carbon tetrachloride. The solubility of naphthalene limited the concentration range studied.[28]

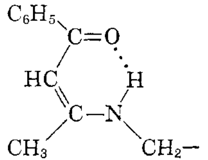
The concentration dependence of the association (Fig. 3) indicates that the complex formed is weak and that its strength is slightly greater as the hydrocarbon bridge is lengthened. The significant increase (0.77 D.) in dipole moment from the ethylene to the tetramethylene[4,5] compound in benzene indicates a greater randomness in the orientation of the chelate ring dipole allowed by the increased flexibility of the bridge. However, the average configuration of the tetramethylene compound must be such that the methyl group adjacent to the bridge experiences the same environment as in the ethylene case.

Recently Slomp and MacKellar[29] reported on the use of pyridine as differentiating solvent in proton resonance studies involving steroids. The difference in appearance of signals in pyridine *versus* chloroform solution was attributed to preferential association of pyridine with certain groups on the steroid and the attendant large proton shifts due to ring current effects. Here we find with the Schiff bases a simple example of the combined solvent effect of pyridine. With A_2en in pyridine solution, the solvent very likely associates with the chelated proton and the weakly acidic vinyl proton shifting these signals downfield by 0.3 and 0.2 p.p.m., respectively. Pyridine also associates with the carbonyl, albeit weakly, to produce a methyl splitting of 0.23 p.p.m.

The association of aromatic molecules with the carbonyl group of Schiff bases can in certain instances provide structural information. Consider the 2:1 condensation product of benzoylacetone and ethylenediamine which has either structure VI or VII.



VI



VII

McCarthy and Martell[4] previously had concluded from dipole moment data that the compound has structure VI. If the methyl signal is not strongly shifted upfield then on the basis of the preceding model, the compound has structure VI. The low solubility of the base precluded observation of spectra in carbon tetrachloride or benzene. The following results, relative to Me_4Si, were obtained in other solvents.

Solvent	Methyl resonance (p.p.m.)
$CHCl_3$	2.04
Pyridine	1.99
5.7 *M* benzene in $CHCl_3$	1.76
1.8 *M* naphthalene in $CHCl_3$	1.70

The signal of the methyl group of A_2en not directly affected by the associated aromatic is shifted slightly downfield in chloroform (*cf.* Table I) relative to carbon tetrachloride solution. In this case the methyl signal is shifted appreciably upfield which in aromatic media seems to be characteristic of methyls adjacent to the hydrocarbon bridge.

Acknowledgment.—Financial support by National Science Foundation Research Grant NSF-G12312 is gratefully acknowledged. We are indebted to Dr. E. Hand for making available data for two of the compounds listed in Table II.

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(27) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

(28) In view of the results of Schaefer and Schneider, it would be of considerable interest to observe the effect of the proposed interaction on the aromatic proton resonance. However, the large concentration of aromatic and the weakness of the complex even in the most favorable case, naphthalene, precludes such an observation.

(29) G. Slomp and F. MacKellar, *J. Am. Chem. Soc.*, **82**, 999 (1960).