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Proton Magnetic Resonance Studies of the Hydrogen-Bonding Properties of Several Hydrazines^{1a}

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RECEIVED FEBRUARY 29, 1964

Proton magnetic resonance solvent dilution studies are reported on the isomeric dimethylhydrazines and on trimethylhydrazine in cyclohexane. The results support the presence of a monomer-dimer equilibrium with the following association constants (mole fraction units): N,N-dimethylhydrazine, 1.8; N,N'-dimethylhydrazine, 1.0; trimethylhydrazine, 0.8. Evidence has also been obtained for the H-bond interaction between trimethylhydrazine and carbon tetrachloride; the association constant for a postulated 1:1 complex was determined to be $0.4X^{-1}$.

Introduction

Quantitative information concerning the hydrogen-bonding properties of several hydrazines has been obtained utilizing the proton magnetic resonance (p.m.r.) technique. The hydrazines studied in detail were N,N-dimethylhydrazine, $(\text{CH}_3)_2\text{NNH}_2$, N,N'-dimethylhydrazine, $\text{CH}_3\text{NHNHCH}_3$, and trimethylhydrazine, $(\text{CH}_3)_3\text{NNHCH}_3$. Less extensive studies were also performed on hydrazine itself, N_2H_4 , and upon monomethylhydrazine, CH_3NHNH_2 . Although certain modifications have been made, the basic techniques used in this investigation were developed previously in p.m.r. studies of the self-association properties of alcohols,²⁻⁴ phenols,^{2,3,5} and amines.⁶ This, however, is the first attempt to quantitatively assess the H-bonding properties of the hydrazines.

Experimentally, the chemical shift value of the N-H proton(s) of each of the hydrazines studied is determined as a function of its mole fraction in the "inert" solvent, C_6H_{12} . In these solutions, all of the nuclei of all of the hydrogens nominally bonded to nitrogen contribute to a single N-H peak as would be expected under conditions in which proton exchange among the various species present occurs rapidly.⁷ The single N-H resonance signal undergoes a shift to higher field as the hydrazine is successively diluted with C_6H_{12} (or CCl_4). The major portion of this solvent dilution shift can be attributed to changes in the H-bonding equilibria upon dilution. From these curves, the equilibrium quotients relating the various H-bonded species in solution can be obtained by methods outlined below.

A basic assumption in the interpretation of solvent dilution data from p.m.r. measurements is that the observed chemical shift at each concentration is simply the weighted average of the characteristic chemical shift values for all of the hydrogen nuclei contributing to the resonance peak. A characteristic chemical shift parameter (δ_1 , δ_2 , etc.) is assigned to each species (monomer,

dimer, etc.) which represents an average proton shift of all the N-bonded protons in that species, *whether or not they are directly involved in H bonding*. (The extent to which the characteristic chemical shift values, δ_n , vary with other changes in the nature of the medium will be considered below.) On this basis, the observed N-H chemical shift, δ_{obsd} , in a solution containing m hydrazine species is

$$\delta_{\text{obsd}} = \frac{\sum_{n=1}^m nx_1^n K_n \delta_n}{\sum_{n=1}^m nx_1^n K_n} \quad (1)$$

in which n is the number of monomeric units in a given species, x_1 is the mole fraction of monomer, K_n is the equilibrium quotient for the association $nA \rightleftharpoons A_n$, and δ_n is the chemical shift value associated with the N-H protons of the n -mer. In eq. 1, at a given concentration of solute, there are $m - 1$ values of K_n , m values of δ_n , and a value of x_1 to be determined ($2m - 1$ independent variables). A general solution or a solution for a system in which several values of K_n are important requires data of high precision which cover as large a concentration range as possible. At the present time, it does not appear feasible to obtain such solutions from p.m.r. measurements alone and some simplification must be sought. In particular, over a range of concentrations in which only two species, the monomer and an n -mer, are important, eq. 1 can be rearranged to give

$$\delta_{\text{obsd}} = -(x_1/X')\Delta_n + \delta_n \quad (2)$$

where $\Delta_n = \delta_n - \delta_1$ and $X' = (x_1 + nx_1^n K_n)$. X' is related to the stoichiometric mole fraction of the hydrazine, X , by the relation

$$X = \frac{X'}{1 + (n-1)x_n} \quad (3)$$

Equation 2 will be used in the analysis of the data obtained in the present study.

While the major portion of the solvent dilution shifts observed in this study are certainly due to H-bonding effects, the δ_n values are also subject to other factors which can be considered under the heading of medium effects. If eq. 2 is to be successfully applied to the experimental data, it is necessary that the δ_n values be constant within experimental error or that their variation as a function of medium composition be known.

(1) (a) Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964; (b) from the Ph.D. Thesis of Joseph R. Crook, Illinois Institute of Technology, 1963; (c) to whom requests for reprints should be sent.

(2) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(3) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(4) In particular, see M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958); E. D. Becker, U. Liddel, and J. N. Shoolery, *J. Mol. Spectry.*, **2**, 1 (1958); and J. C. Davis, Jr., K. S. Pitzer, and C. N. Rao, *J. Phys. Chem.*, **64**, 1744 (1960).

(5) C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *ibid.*, **60**, 1311 (1956).

(6) J. Feeney and L. H. Sutcliffe, *J. Chem. Soc.*, 1123 (1962).

(7) H. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1683 (1953).

Known medium effects have been considered in detail⁸⁻¹³ and include p.m.r. effects due to the bulk magnetic susceptibility of the medium, dispersion, solvent magnetic anisotropy, van der Waals effects, and a polar effect. While it is not currently possible to assess quantitatively most of these effects upon observed chemical shift values, their influence in many cases can be minimized. In the present work, it is felt that the use of an internal reference contained within the molecules under study (*i.e.*, the methyl protons of the hydrazines) and the use of the isotropic solvents C_6H_{12} and CCl_4 removes from consideration all known medium effects except the polar effect.^{8,12} Detailed calculation have been made of the polar effect in the systems studied here.¹⁴ The results indicate this effect to be small (see below).

Experimental

Preparation and Purification of Materials. Hydrazine.— N_2H_4 (anhydrous, 95+%, Matheson Coleman and Bell, Inc.) was purified by double distillation from crushed BaO.¹⁵ The sample to be purified was refluxed *in vacuo* with five times its weight of BaO at 70° and distilled. The process was repeated with one-half the original amount of BaO. The material so obtained analyzed as 100 wt. % N_2H_4 by oxidimetric titration with standard KIO_3 in the presence of excess HCl using wool red 40F internal indicator.^{16,17}

Monomethylhydrazine.— CH_3NHNH_2 (>97% purity from the Aldrich Chemical Co., Inc.) was purified by fractional distillation from CaH_2 after refluxing for 3 hr. under 1 atm. of N_2 . The distillate was collected over the range 88.0–88.1°. The p.m.r. spectrum of the material so obtained indicated that the maximum concentration of proton-containing impurity was 0.005 mole fraction.¹⁸

N,N-Dimethylhydrazine.— $(CH_3)_2NNH_2$ (anhydrous, 98–99%, from Matheson Coleman and Bell, Inc.), which had been refluxed *in vacuo* at 50–60° for 1 hr. with five times its weight of crushed BaO and then distilled, analyzed as 100 wt. % $(CH_3)_2NNH_2$ both by a pH titration of its acid salt and by oxidation with standard KIO_3 .^{16,17}

N,N'-Dimethylhydrazine.— $CH_3NHNHCH_3 \cdot 2HCl$ (Aldrich Chemical Co., Inc.) was treated with crushed reagent grade NaOH pellets *in vacuo* to obtain free $CH_3NHNHCH_3$. The material so obtained was dried over NaOH pellets and distilled three times. Finally, CaH_2 was added to remove the last traces of moisture, and the material was fractionated. Distillate was collected over the range 81.0–81.1°. Based on the p.m.r. spectrum, the maximum concentration of proton containing impurity was less than 0.01 mole fraction.¹⁸

Trimethylhydrazine.— $(CH_3)_2NNHCH_3$ was prepared from $(CH_3)_2NNH_2$ by a modification of a procedure given by Class, Aston, and Oakwood.¹⁹ $(CH_3)_2NN=CH_2$, methylenedimethylhydrazine, prepared as described, was reduced to $(CH_3)_2NNHCH_3$ using $LiAlH_4$ followed by hydrolysis under basic conditions using a method described by Gaylord.²⁰ The material obtained

(boiling range 64–66°) was dried over 10 g. of NaOH pellets and distilled. It was then fractionated on an 80 theoretical plate, spinning band column. A 10-ml. cut containing no impurities, as judged by its vapor phase chromatogram, was taken for the p.m.r. work. The p.m.r. spectrum of the $(CH_3)_2NNHCH_3$ indicated the maximum mole fraction of proton containing impurity to be less than 0.01.

Cyclohexane and Carbon Tetrachloride.—Analytical reagent grade C_6H_{12} and CCl_4 were stored over Na ribbon and distilled immediately before use.

Preparation of Samples for Proton Magnetic Resonance Measurements.—The hydrazines are very hygroscopic, and great care must be taken in the preparation of samples for p.m.r. measurements to avoid contamination of the samples with water. For example, a mole fraction of water of 2.7×10^{-3} in a sample of N,N-dimethylhydrazine is sufficient to shift the position of the N–H resonance signal of the hydrazine by 0.01 p.p.m. For this reason, the p.m.r. samples were prepared using a high vacuum system. A sample of purified hydrazine or solvent from a storage vessel was admitted as a vapor to a bulb(s) of known volume and the pressure measured. The gas was then transferred, using a liquid nitrogen bath, to a p.m.r. tube sealed directly to the vacuum system. When both the hydrazine and the solvent had been transferred, the tube was sealed from the system. Using the perfect gas relationship, the approximate concentrations of the hydrazines in each sample could be computed. The determination of the actual concentrations is described below.

It was found that $(CH_3)_2NNH_2$, $CH_3NHNHCH_3$, and $(CH_3)_2NNHCH_3$ were miscible in all proportions with C_6H_{12} and CCl_4 . However, the mutual solubilities of N_2H_4 and CH_3NHNH_2 with these solvents is very limited near 25°, thus precluding the possibility of solvent dilution H-bonding studies in these systems. Some data were, however, obtained at compositions near the limiting values for comparison with the other hydrazines.

The samples showed no changes in their p.m.r. spectra after standing several weeks at room temperature when C_6H_{12} was used as the solvent. Consequently, these samples were stored at room temperature until their spectra could be taken. Carbon tetrachloride was used as a solvent only with $(CH_3)_2NNHCH_3$. There is evidence²¹ that even freshly distilled CCl_4 reacts with amines to give the amine hydrochloride. In the present work, it was found that if a $(CH_3)_2NNHCH_3$ - CCl_4 solution was allowed to stand at room temperature for several days, the chemical shift of the N–H proton moved to lower field by several tenths of a p.p.m. and the originally broad N–H signal sharpened dramatically. This is consistent with the presence of small amounts of the hydrazinium ion in solution which undergoes rapid exchange with the N–H protons of the free base. As a consequence of this observation, the $(CH_3)_2NNHCH_3$ - CCl_4 solutions were stored in liquid nitrogen until their spectra could be taken. By doing so, it is felt that no appreciable reaction between the hydrazine and the solvent occurred before the spectra were recorded.

In the $(CH_3)_2NNH_2$ - C_6H_{12} and $(CH_3)_2NNHCH_3$ - CCl_4 systems, a known amount of water (0.1 to 1 part of water per thousand parts of hydrazine) was added intentionally to samples which were quite dilute in hydrazine. The addition of traces of water to these dilute solutions sharpens the N–H signals and thus allows measurements of signal positions to be made at considerably lower concentrations of hydrazine than would otherwise be possible. In all cases in which water was added to the p.m.r. samples, correction of the observed N–H resonance position for the effect of the water was made.

The Spectra.—All spectra were taken with a Varian Model A-60 analytical n.m.r. spectrometer. Due to rapid proton exchange, only one signal could be found in the spectra of N_2H_4 , CH_3NHNH_2 , $(CH_3)_2NNH_2$, $CH_3NHNHCH_3$, and $(CH_3)_2NNHCH_3$ which could be identified with the N–H protons. Neither the N–H protons nor the CH_3 protons exhibited any spin-spin splitting. Chemical shift values were determined using the side-band technique developed by Arnold and Packard²² and are accurate to ± 0.1 c.p.s. at 60 Mc./sec. (0.002 p.p.m.).

Results

In Table I, the chemical shift values of the methyl and amino protons of the hydrazines studied (relative to C_6H_{12}) are given for solutions 0.99 mole fraction in the

(8) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

(9) R. J. Abraham, *Mol. Phys.*, **4**, 369 (1961).

(10) R. J. Abraham, *J. Chem. Phys.*, **34**, 1062 (1961).

(11) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *ibid.*, **34**, 1064 (1961).

(12) P. Diehl and R. Freeman, *Mol. Phys.*, **4**, 39 (1961).

(13) B. B. Howard, B. Lüder, and M. T. Emersou, *J. Chem. Phys.*, **36**, 485 (1962).

(14) Copies of this calculation have been deposited with the American Documentation Institute. Photocopies or microfilms are available (Serial No. 8057) for \$1.25 each from ADI, Library of Congress, Washington, D. C. 20525.

(15) C. G. Hale and F. F. Shetterly, *J. Am. Chem. Soc.*, **35**, 1071 (1911).

(16) W. R. McBride, R. A. Henry, and S. Skolnik, *Anal. Chem.*, **25**, 1042 (1953).

(17) R. A. Penneman and L. F. Audrieth, *ibid.*, **20**, 1058 (1948).

(18) In computing the maximum mole fraction of impurity, it was assumed that any p.m.r. signal, not due to the hydrazine, represented an impurity containing a single proton.

(19) J. B. Class, J. G. Aston, and T. S. Oakwood, *J. Am. Chem. Soc.*, **75**, 2937 (1953).

(20) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 1011.

(21) R. F. Collius, *Chem. Ind. (London)*, 704 (1957).

(22) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

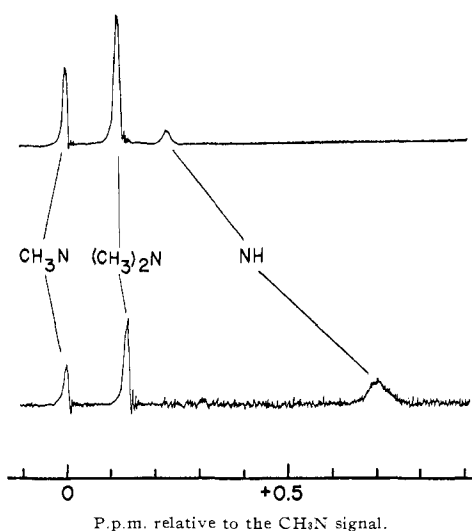


Fig. 1.—Typical p.m.r. spectra from the trimethylhydrazine- CCl_4 study: upper curve, mole fraction of hydrazine = 1.0; lower curve (at higher instrument gain), mole fraction of hydrazine = 0.14.

hydrazines. The N-H signals of all of these hydrazines are naturally broad. The width at half-height of the N-H signals of pure $(\text{CH}_3)_2\text{NNH}_2$, $\text{CH}_3\text{NHNHCH}_3$, and $(\text{CH}_3)_2\text{NNHCH}_3$ are 1.4, 1.0, and 1.0 c.p.s. at 60 Mc./sec., respectively. The corresponding widths for the methyl signals are all less than 1.0 c.p.s. The broadness of the N-H signals is presumably due to interaction with the nitrogen quadrupole. As these hydrazines are diluted with solvent, the CH_3 signal widths do not vary, but the N-H signals become progressively broader reaching values near 10 c.p.s. at mole fraction 0.05. It is suggested that in the more concentrated solutions, rapid proton exchange between N-H protons modifies the broadening effect of the nitrogen.

TABLE I

CHEMICAL SHIFT VALUES OF THE N-H AND CH_3 PROTONS OF SEVERAL HYDRAZINES RELATIVE TO C_6H_{12} ^a

Hydrazine	Chemical shift values, p.p.m.		
	$\delta_{\text{NH}} - \delta_{\text{C}_6\text{H}_{12}}$	$\delta_{\text{CH}_3} - \delta_{\text{C}_6\text{H}_{12}}$	$\delta_{(\text{CH}_2)_2} - \delta_{\text{C}_6\text{H}_{12}}$
N_2H_4	-2.217
CH_3NHNH_2	-2.132	-1.085	...
$(\text{CH}_3)_2\text{NNH}_2$	-1.778	...	-0.913
$\text{CH}_3\text{NHNHCH}_3$	-1.948	-1.042	...
$(\text{CH}_3)_2\text{NNHCH}_3$	-0.785	-1.016	-0.897

^a Mole fraction of C_6H_{12} = 0.01; temp. $28.5 \pm 1^\circ$.

The p.m.r. spectra were used in the determination of sample concentrations in the following way. The area under a signal of one of the groups of the hydrazine (the dimethyl group for $(\text{CH}_3)_2\text{NNHCH}_3$ and the methyl group(s) for the other hydrazines) was compared with the area under the signal due to a standard. For the systems in which C_6H_{12} was used as the solvent, the area of the signal from its protons provided the standard for comparison. The relative areas corrected statistically to the area per proton were used to compute the mole fraction of hydrazine present. For the $(\text{CH}_3)_2\text{NNHCH}_3\text{-CCl}_4$ system, the area of the dimethyl group for a given sample was taken and compared with the area of the signal from the same group in the pure $(\text{CH}_3)_2\text{NNHCH}_3$; concentrations in molarities result from such area comparisons.

The validity of the above method for concentration determination was checked by showing that at the radio-

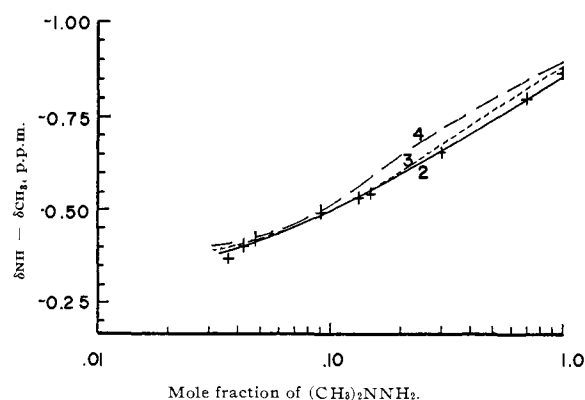


Fig. 2.—Experimental points (+) and calculated curves based on monomer-dimer (2), monomer-trimer (3), and monomer-tetramer (4) models for the system $(\text{CH}_3)_2\text{NNH}_2\text{-C}_6\text{H}_{12}$.

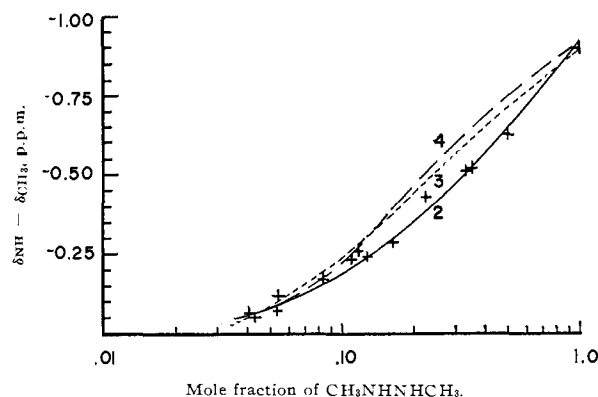


Fig. 3.—Experimental points (+) and calculated curves based on monomer-dimer (2), monomer-trimer (3), and monomer-tetramer (4) models for the system $\text{CH}_3\text{NHNHCH}_3\text{-C}_6\text{H}_{12}$.

frequency intensity corresponding to maximum signal area, the statistically corrected relative areas of the hydrazine and cyclohexane signals corresponded to the value expected on the basis of the number of protons in the group giving rise to the signals. It is assumed that these results apply to all solutions although they were only obtained for the pure materials.

In the case of the $(\text{CH}_3)_2\text{NNHCH}_3\text{-CCl}_4$ system in which concentrations in molarities were obtained, these molarities have been converted to mole fraction units by assuming that there is no volume of mixing in the preparation of solutions. This assumption is not entirely justifiable; however, the data from this system are used only to demonstrate the existence of an interaction between $(\text{CH}_3)_2\text{NNHCH}_3$ and CCl_4 , and it is not necessary for this purpose that the concentrations be known with high precision.

In Fig. 1, typical spectra for high and low concentrations are shown. These spectra demonstrate quite clearly the large solvent dilution shift and the broadening of the NH signal on dilution.

In Fig. 2-3, the chemical shift values of the N-H protons of $(\text{CH}_3)_2\text{NNH}_2$, $\text{CH}_3\text{NHNHCH}_3$, and $(\text{CH}_3)_2\text{NNHCH}_3$ relative to their methyl groups are plotted against the logarithm of the stoichiometric mole fraction of the hydrazine in the solution. The uncertainties in chemical shift values are dictated by the magnitude of the polar effect.^{8,12} Calculations of this effect indicate that the relative influence of the reaction field upon the N-H and reference protons necessitates that a correction of 0.02-0.03 p.p.m. be applied to the observed solvent dilution shifts. The calculated correc-

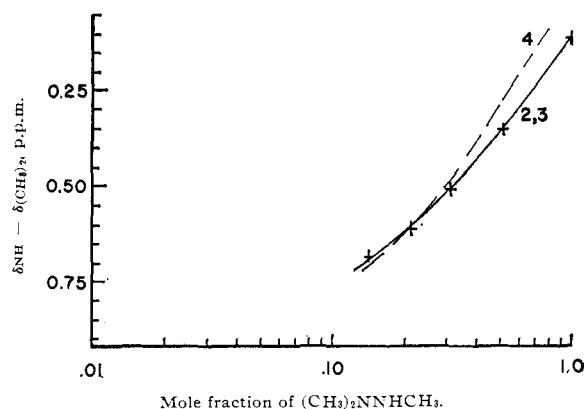


Fig. 4.—Experimental points (+) and calculated curves based on monomer-dimer (2), monomer-trimer (3), and monomer-tetramer (4) models for the system $(CH_3)_2NNHCH_3-C_6H_{12}$.

tions are only approximate due to uncertainties in the parameters used in the calculation; an uncertainty of ± 0.02 p.p.m. has been placed on all chemical shift values in lieu of attempting to make individual corrections. The concentration uncertainties in the solvent dilution curves ($\pm 5\%$) are based on day-to-day reproducibilities of peak areas. Figures 2–5 also show solvent dilution curves calculated using eq. 2.

Self-Association in Cyclohexane Solutions.—The experimental data from the solvent dilution studies have been used to calculate values of K_n , δ_1 , and δ_n with the aid of eq. 2. It should be recalled that the derivation of eq. 2 involves the assumptions (a) that the association behavior can be described by a single monomer- n -mer equilibrium and (b) that the parameters K_n , δ_1 , and δ_n do not vary with the composition of the solution. It can be seen that, if eq. 2 is applicable, a proper choice of n and K_n will lead to a linear plot of δ_{obsd} vs. $-(x_1/X')$ with slope Δ_n and intercept δ_n . The procedure employed in the present study consists of a trial-and-error selection of n and K_n values to obtain the best fit with eq. 2. The parameters obtained are then used to calculate solvent dilution curves for

TABLE II
ASSOCIATION PARAMETERS FOR DIMER FORMATION FOR THE METHYL-SUBSTITUTED HYDRAZINES IN CYCLOHEXANE AT $28.5 \pm 1^\circ$

Compound	K_2^a (X^{-1})	Δ_2^b p.p.m.	δ_2^b p.p.m.	δ_1^b p.p.m.
$(CH_3)_2NNH_2$	1.8	-0.83	-1.14	-0.31
$CH_3NHNHCH_3$	1.0	-1.81	-1.74	+0.07
$(CH_3)_2NNHCH_3$	0.8	-1.75	-0.62	+1.13

^a The uncertainty placed upon the K_2 values is $\pm 10\%$. With these limits, all experimental points are included in the calculated curve. ^b $\Delta_2 = \delta_2 - \delta_1$; δ_2 (or δ_1) = $\delta_{NH} - \delta_{C_6H_{12}}$. For $(CH_3)_2NNHCH_3$, the $(CH_3)_2N$ group was used as the reference. The uncertainty in the Δ_2 and δ_2 values is ± 0.02 p.p.m.

comparison with the experimental results. Such calculations were carried out for the systems $(CH_3)_2NNH_2-C_6H_{12}$, $CH_3NHNHCH_3-C_6H_{12}$, and $(CH_3)_2NNHCH_3-C_6H_{12}$ using $n = 2, 3$, and 4. The solvent dilution curves calculated from the parameters obtained are shown in Fig. 2–4. It can be seen from these curves that the experimental points in each case agree very satisfactorily with a monomer-dimer model ($n = 2$). The values of K_2 , Δ_2 , and δ_2 used in constructing these curves are given in Table II. For the $(CH_3)_2NNH_2$ and $CH_3NHNHCH_3$ systems, the monomer-trimer and monomer-tetramer

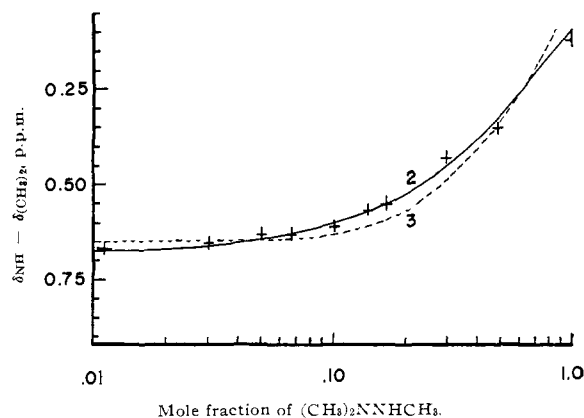


Fig. 5.—Experimental points (+) and calculated curves based on monomer-dimer (2) and monomer-trimer (3) models for the system $(CH_3)_2NNHCH_3-CCl_4$; the curves have been corrected for the solvent-solute interaction.

curves are clearly not adequate over most of the concentration ranges studied.²³ This of course does not rule out the possibility of the presence of trimers, tetramers, or higher polymers in these solutions, but it strongly argues against any of these species being a predominant constituent. In Fig. 4, it is seen that the monomer-dimer and the monomer-trimer curves calculated for the $(CH_3)_2NNHCH_3-C_6H_{12}$ system both fit the experimental data well and are indistinguishable from one another. This apparent equivalence of the monomer-dimer and monomer-trimer models is due to the fact that an insufficient portion of the dilution range was studied in this case (the N-H proton signal of this hydrazine could not be distinguished at concentrations below $X = 0.14$ due to the merging of its signal and that of the solvent, C_6H_{12}). This can be verified by inspection of the monomer-trimer curves in Fig. 2 and 3. If the data below $X = 0.14$ are neglected, it would be an easy matter to fit the remaining portion of the curve with a calculated monomer-trimer curve.

A further indication of the inadequacy of the monomer-trimer model is given by studies on $(CH_3)_2NNHCH_3$ using CCl_4 as a solvent. In Fig. 5, the solvent dilution curve for the $(CH_3)_2NNHCH_3-CCl_4$ system is shown. Figure 6 compares this curve with that of the $(CH_3)_2NNHCH_3-C_6H_{12}$ system. Although it is not expected that the K_n and δ_n values from the C_6H_{12} study would be exactly the same in the CCl_4 study, it would be surprising if they differed by more than a few per cent. It is obvious from the two curves in Fig. 6 that large differences apparently exist between the two systems. The reason for these differences is most likely the existence of an interaction between the hydrazine and CCl_4 . It is suggested that CCl_4 is acting as an acceptor molecule in H-bond formation with $(CH_3)_2NNHCH_3$.

(23) The parameters used in calculating the monomer-trimer and monomer-tetramer curves of Fig. 2–4 are as follows.

	Monomer-trimer curves			
	K_3	Δ_3	δ_3	δ_1
$(CH_3)_2NNH_2$	$9.0X^{-2}$	-0.612	-1.002	-0.390
$CH_3NHNHCH_3$	$19X^{-2}$	-1.075	-1.045	+0.030
$(CH_3)_2NNHCH_3$	$2.6X^{-2}$	-1.027	-0.067	+0.959
	Monomer-tetramer curves			
	K_4	Δ_4	δ_4	δ_1
$(CH_3)_2NNH_2$	$110X^{-3}$	-0.547	-0.947	-0.400
$CH_3NHNHCH_3$	$115X^{-3}$	-0.982	-1.012	-0.030
$(CH_3)_2NNHCH_3$	$7X^{-3}$	-0.990	-0.083	+0.907

This type of interaction for CCl_4 is not unknown; for example, Emerson and Howard,²⁴ making use of a method of analysis similar to that used in the present work, determined the self-association constant of CHCl_3 and the association constant for the $\text{CHCl}_3\text{-CCl}_4$ interaction to both be about $0.1\text{-}0.2X^{-1}$.

In order to calculate the magnitude of the $(\text{CH}_3)_2\text{NNHCH}_3\text{-CCl}_4$ interaction, it is necessary to know the equilibrium quotients for the self-association of the hydrazine in this solvent. It was assumed that the K_n and δ_n values from the C_6H_{12} study applied, and theoretical curves were calculated assuming a 1:1 interaction between the hydrazine and CCl_4 . The curves for the monomer-dimer and monomer-trimer models for self-association are shown in Fig. 5. It is seen that within the limits dictated by the assumptions made in obtaining these curves, the monomer-trimer model is clearly inadequate. However, the monomer-dimer model, coupled with the $(\text{CH}_3)_2\text{NNHCH}_3\text{-CCl}_4$ interaction does fit the experimental results well. Again, it cannot be stated that there are no trimers or higher polymers in solutions of $(\text{CH}_3)_2\text{NNHCH}_3$ in C_6H_{12} or CCl_4 , but the data strongly suggest that monomer-dimer association equilibria predominate. The value of K_c , the equilibrium quotient for formation of a 1:1 complex, and the value of δ_c , the chemical shift value of the N-H proton in the complex, are $K_c = 0.38X^{-1}$ and $\delta_c = +0.050$ p.p.m.

Discussion

Implicit in the above treatment is the assumption that the activity coefficient component of the expression for the thermodynamic equilibrium constant does not change over the experimental concentration range. To test this hypothesis, it would be desirable to have access to the results of careful studies on equilibria involving polar molecules in nonpolar media which are relatively free of other sources of nonideal behavior. Although it appears that no truly appropriate systems have been studied, Moelwyn-Hughes²⁵ has discussed two equilibria^{25a} which show rather small medium effects over the entire concentration range from pure solute to pure solvent: (a) $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ in chloroform at 0° and (b) the acetic acid-ethyl alcohol esterification in binary mixtures. On the other hand, the variation with solvent of the N_2O_4 equilibrium and the acetic acid dimerization suggests somewhat larger variations of the equilibrium quotient with medium.^{25b} An important factor which is difficult to evaluate is the extent to which the deviations of the *individual* activity coefficients may cancel in the equilibrium expression. It would also be dangerous to argue that the ability to fit the present data with a single constant provides strong support for the validity of the assumptions involved.

With the reservations expressed above, it is felt that no species other than monomers and dimers need be considered in order to interpret the experimental data. The association constants for monomer-dimer association of these systems are of a reasonable magnitude when compared with the values from other systems. Becker, Liddel, and Shooley⁴ reported dimeric associa-

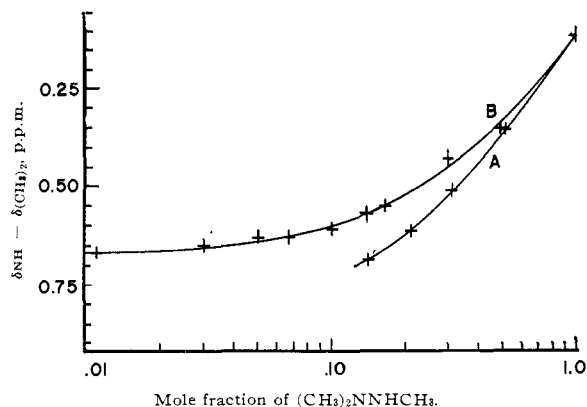


Fig. 6.—Comparison of solvent dilution curves for $(\text{CH}_3)_2\text{NNHCH}_3$ in cyclohexane (A) and carbon tetrachloride (B).

tion constants for $\text{C}_2\text{H}_5\text{OH}$ as $6.5X^{-1}$ for a (favored) cyclic dimer and $13X^{-1}$ for an open dimer. These constants are approximately a factor of five to ten larger than those obtained in this work. The self-association constant of CHCl_3 , mentioned above,²⁴ was found to be $0.19X^{-1}$. These values suggest that the strength of H-bond formation of dimers in the hydrazine systems lies between those of the ethanol and chloroform systems. This is entirely reasonable on the basis of the expected acceptor characteristics of the oxygen, nitrogen, and chlorine atoms. To demonstrate more clearly the extent of association in the methylhydrazine-cyclohexane systems, some calculations have been made using the equilibrium quotients in Table II. These show that the fraction of total hydrazine present in the form of dimers increases from about 15% at a stoichiometric mole fraction of 0.1 to about 50% at mole fraction unity.

It is not possible to compare the hydrazine K_2 values with the equilibrium quotients obtained by Feeney and Sutcliffe⁶ in their p.m.r. studies of the self-association of $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_2\text{H}_5\text{NH}_2$ for two reasons. First, the amine constants reported are for (cyclic) tetramer formation. Second, the authors used CCl_4 as a solvent but apparently did not consider H-bonding interactions between CCl_4 and these amines which surely exist. It is suggested on the basis of present results that self-association of these amines to give cyclic trimers is a reasonable alternative to tetramer formation.

The absence of appreciable amounts of trimers and higher polymers in the C_6H_{12} solutions of $(\text{CH}_3)_2\text{NNH}_2$, $\text{CH}_3\text{NHNHCH}_3$, and $(\text{CH}_3)_2\text{NNHCH}_3$ suggests that these dimers are cyclic in nature. It is hard to see why an open dimer would not polymerize further, whereas the formation of cyclic dimers could preclude the formation of higher aggregates. These cyclic dimers are pictured as being six-membered rings (counting the H-bonded protons). The H bonds in such rings must be considerably bent from the ideal linear configuration. However, it has been pointed out²⁶ that if the stability gained by the formation of two or more weak (bent) H bonds is greater than the stability gained from the formation of one strong (linear) H bond, the species with two weak bonds is expected to predominate. Examples of this are found in the cases of $\text{C}_2\text{H}_5\text{OH}$ ⁴ and CH_3OH ²⁶ in which cyclic dimers are postulated from infrared measurements.

(24) M. T. Emerson and B. B. Howard, *J. Chem. Phys.*, **35**, 1911 (1961).

(25) (a) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd Revised Ed., 1961, Pergamon Press, New York, N. Y., pp. 1021-1023; (b) pp. 1026, 1038-1041.

(26) M. Van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.*, **27**, 95 (1957).

Acknowledgments.—J. R. C. wishes to acknowledge gratefully support from National Science Foundation Cooperative Fellowships and from an I.I.T. Research Institute Fellowship during the course of this work.

The authors further wish to express thanks to the Chemistry Division of the Argonne National Laboratory for the use of their n.m.r. spectrometer during the initial phases of this study.

[CONTRIBUTION FROM DEPARTAMENTO DE QUÍMICA ORGÁNICA, PATRONATO "JUAN DE LA CIERVA," UNIVERSITY OF BARCELONA, SPAIN, AND CHEMISTRY RESEARCH LABORATORY, ARL, WRIGHT-PATERSON AIR FORCE BASE, OHIO]

New Linear Law and Effects Relating the Ultraviolet Spectra of Substituted Benzenes and the Migration (Spectroscopic) Moment¹

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RECEIVED MARCH 23, 1964

Ultraviolet absorption spectra in the region of 40,000 cm.⁻¹ (250 m μ) were obtained with high reproducibility (better than 5% precision in molar absorptivity) for more than 100 benzene derivatives. These compounds, ranging from mono- to persubstitution, contained methyl, fluoro, chloro, bromo, iodo, methoxy, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, perchloroethyl, chlorocarbonyl, perchlorovinyl, and/or perchlorostilbyl substituents alone or in combination. The molar absorptivities observed, ranging from 100 to 3000, correlate much better with a here-proposed linear function of the moment obtained by vectorial addition of substituent contributions (of the Sklar "migration moment" type or the Platt "spectroscopic moment" type) rather than the currently accepted "square law." The effect of *ortho* substituents is successfully accounted for in terms of ring distortion and resonance inhibition and leads to the concept of a "constellation migration moment."

Introduction

The near-ultraviolet absorption spectrum of a simple benzene derivative consists of two band systems: the secondary band, centered in the unsubstituted benzene at about 40,000 cm.⁻¹ (250 m μ), and the primary bands, at higher wave numbers.⁴ The former is by far the better known and the most studied. It is due to the ¹A_{1g} → ¹B_{2u} or ¹L_b transition.⁵ In the vibrationless, undistorted benzene this transition is forbidden.

Sklar has shown⁶ that there are two separable contributions to the intensity of absorption in the secondary band: the *migrational* absorption, due to the electronic perturbation caused by the substituents, and the *vibrational* absorption, due to the symmetry-breaking atomic motions. The former is obtained simply by subtracting the latter from the total absorption.

The relevant migrational transition moment of a polysubstituted benzene is supposed to be an additive property of the substituents. Consequently, to every substituent a *migration moment* (Sklar) (or, equivalently, *spectroscopic moment* in the Platt⁸ nomenclature) is assigned.

The migration moment of a substituent is a vector in the plane of the benzene ring and perpendicular to

the bond axis. Its direction is reversed when the substituent is shifted to the next benzene carbon atom. The modulus (or intensity) of the migration moment vector can be calculated from the integrated absorptivity of the secondary band by means of expression I,

$$\left(\sum_{i=1}^6 \mathbf{m}_i\right)^2 = k \int (\epsilon - \epsilon_v) d\nu \quad (I)$$

where ϵ and ϵ_v are the observed maximum and the vibrational absorptivities, respectively, at frequency ν , k is a factor which can be considered constant, and \mathbf{m}_i is the migration moment of the i -substituent. The summation indicated is vectorial addition.

If one assumes that the half-width and shape of the "smoothed" secondary band¹⁰ are constant, then the integrated absorptivity is proportional to ϵ_{\max} and, hence, expression I can be replaced by the simpler and more convenient expression II¹¹

$$\left(\sum_{i=1}^6 \mathbf{m}_i\right)^2 = k'(\epsilon_{\max} - \epsilon_v) \quad (II)$$

where ϵ_{\max} represents the observed maximum absorptivity of the smoothed curve, and k' is a proportionality constant.

The migration moments of different substituents may vary not only in magnitude but also in sign (or direction). Their sign and value indicate, respectively, the direction and value of the resonance effect of the substituent. The migration moment of hydrogen is zero. The inductive effect seems to be relatively unimportant.¹²

(10) The secondary band usually has a vibrational structure with maxima and shoulders. The "smoothed" curve is obtained by averaging them out so that the over-all shape and integrated absorptivity are preserved. This can usually be reproduced within acceptable limits.

(11) The validity of such substitution has been checked for over 70 carefully selected benzene derivatives. The data fit the expression

$$\int \epsilon d\nu = 3240 \epsilon_{\max}$$

where ϵ is the molar absorptivity at frequency ν . The deviations from this expression are within 10%.

(12) Petruska, by comparison of the intensity with the frequency shifts, has concluded that the migration moment arises principally from the inductive effect.⁹ The low value of the moment for NH₂⁺,¹² the parallelism with

(1) Part of this work has been presented before the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 11-15, 1962. This paper includes portions of the thesis submitted by J. Riera in partial fulfillment of the requirements for the degree of Doctor in Sciences (University of Barcelona). One of the authors (M. B.) spent 1 year as Visiting Research Associate at ARL, 1961-1962.

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(4) L. Doub and J. M. Vanderbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(5) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 246, 299.

(6) A. L. Sklar, *Rev. Mod. Phys.*, **14**, 232 (1942). See also ref. 7-9.

(7) (a) H. Conrad-Billroth, *Z. Physik. Chem.*, **B26**, 135 (1934); (b) A. L. Sklar, *J. Chem. Phys.*, **10**, 135 (1942); (c) Th. Förster, *Z. Naturforsch.*, **2a**, 149 (1947).

(8) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

(9) J. Petruska, *ibid.*, **34**, 1111, 1120 (1961).