

since the dielectric constant of the mixture in which these studies were carried out (75/25 dioxane/water) is about 13, an interpretation involving ion pair formation is preferable. Earlier Raman studies on perchlorates in various alcohols³⁹ revealed that the actual positions of the Raman lines varied with the salt under study. Here also no report of any perchlorate complexes was made.

There are three factors which make it very difficult to *prove* that the extra lines found in some of these Raman spectra have their origin in a coordinate linkage between the perchlorate ion and a cation. The first of these is the extreme faintness of the extra lines in conjunction with the proximity of many of them to the exciting line. The second factor is the difficulty of completely eliminating the hydrolytic products as possible sources of the observed very weak Raman lines. This becomes an increasingly troublesome factor as the charge on the cation increases. The third factor is the possibility that these extra lines may be due to the water itself.

(39) J. Goubeau, *Z. Physik. Chem.*, **36B**, 45 (1937).

In summary, of the perchlorates examined, only those of Hg^{+2} , La^{+3} , Tl^{+} , Cd^{+2} , Mg^{+2} and Mn^{+2} show any irregularities in their Raman spectra. These irregularities were for the most part very faint and lead only to the inference that complexes *may* be present. This inference is most strongly supported in the case of the perchlorates of Tl^{+} , La^{+3} and Mn^{+2} using the intensities of the lines as a basis. Since one of the purposes of this study was to determine the validity of the procedure, generally used in studying complexes in aqueous solution, of starting with the non-complex perchlorates, it is necessary to ask how the results of this study bears on this question. From the intensities of the extra lines observed and the rarity of their occurrence, it may safely be said that the perchlorates will, in general, be far more satisfactory as examples of simple salts than salts of any other common anion.

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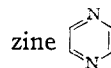
Protonation Effects on $n \rightarrow \pi^*$ Transitions in Pyrimidine¹

By V. G. KRISHNA AND LIONEL GOODMAN

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The T \rightarrow S luminescence spectra at 77° in several rigid glasses are reported for pyrimidine and pyrimidine hydrochloride. The emission is assigned ${}^3\text{B}_1(n, \pi^*) \rightarrow {}^1\text{A}_1$ from the mirror image relationship with the ${}^1\text{A} \rightarrow {}^1\text{B}_1(n, \pi^*)$ absorption spectrum in pyrimidine. The o,o band is observed at $28290 \pm 30 \text{ cm.}^{-1}$ yielding an experimental singlet-triplet interval of 2630 cm.^{-1} between o,o bands. Both the observed singlet-triplet interval and the observed principal vibrational progression (1080 cm.^{-1}) in the spectrum (corresponding to the 1066 cm.^{-1} angular ring distortion) suggest the σ orbitals of the nitrogen atoms are not in sp^2 hybridization in the excited state. The observed pyrimidine hydrochloride emission proves that the N...H hydrogen bond is broken or is very weak in the excited state. A similar conclusion is drawn from the pyrazine hydrochloride emission (also reported), thus placing the well known $n \rightarrow \pi^*$ absorption blue shift on a sound basis. A relationship between H-bond energy and the absorption blue shift is proposed and tested on the three diazines.

In a previous communication (I)² the effect of a hydrogen bonding solvent mixture (EPA) on the $n \rightarrow \pi^*$ absorption and emission spectra of pyra-



zine was reported. The present investigation

on the solvent effects on pyrimidine



throws light on another aspect of the problem—the hydrogen bonding in the excited state.

Experimental

Pyrimidine (Nutritional Biochemicals Corporation) was purified by vacuum distillation. Absorption measurements of $n \rightarrow \pi^*$ bands of pyrimidine in isopentane, isopentane-ethanol mixtures and of pyrimidine hydrochloride in ethanol were carried out on a Beckman model DU quartz spectrophotometer with a recording accessory of Warren Electronics Inc.

EPA (5, 5, 2 parts by volume of ether, isopentane and ethanol), methylcyclohexane-isopentane (1:4), 1-butanol-isopentane (3:7) and isopropyl alcohol-ethanol (1:1) glasses at 77°K. were used as solvents for emission. The T \rightarrow S

emission spectra were recorded on a Perkin-Elmer model 13 spectrophotometer using an f/1 quartz lens to focus the emission on the slits. The instrument is equipped with a fused silica prism and RCA IP28 photomultiplier tube. Samples of pyrimidine were excited at 77°K. using an unfiltered G.E. AH-6 lamp. A blade phosphoroscope, with chopping frequency in excess of 1,000 c.p.s., was used to eliminate the exciting beam. The high quantum yield of emission allowed the spectra to be recorded at slits of 0.02–0.05 mm.

As an extension of the work on pyrazine (I) the emission spectra of both pyrazine hydrochloride and pyrimidine hydrochloride in EPA and in isopropyl alcohol-ethanol glasses were recorded. The hydrochlorides were prepared by condensing the vapor of the base with HCl gas. Pyrimidine hydrochloride (white solid) showed a quite different absorption spectrum from that of free base (*cf. H* in Fig. 3).

The results are reproduced in Figs. 1, 2, 3 and 4.

Assignment of the Transition.—The band shape of the observed T \rightarrow S emission (Fig. 1) is similar to the $n \rightarrow \pi^*$ absorption spectrum in the vicinity of $34,000 \text{ cm.}^{-1}$ (Fig. 2). The $34,000 \text{ cm.}^{-1}$ S \rightarrow S¹ transition has been assigned on the basis of rather crude theoretical reasons³ as ${}^1\text{B}_1(n, \pi^*) \leftarrow {}^1\text{A}_1$ involving an excited π^* MO derived from the benzene MO with (n, π^*) electron population (A).

(3) (a) S. F. Mason, *J. Chem. Soc.*, 1240 (1959). (b) L. Goodman and R. W. Harrell, *J. Chem. Phys.*, **30**, 1131 (1959).

(1) Presented at the Symposium on Molecular Structure and Spectroscopy, June 13–17, 1960, Columbus, Ohio. This work is supported by the Office of Naval Research.

(2) V. G. Krishna and L. Goodman, *J. Chem. Phys.*, **33**, 381 (1960).

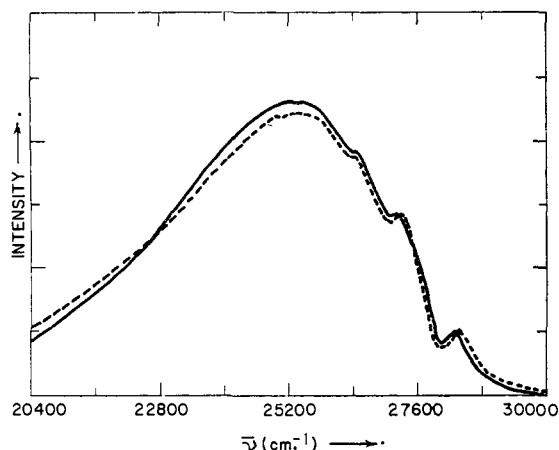
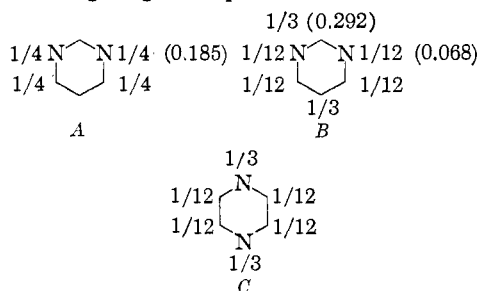


Fig. 1.—T \rightarrow S emission spectrum of pyrimidine at 77°K. in various glasses: —, in hydrocarbon glass; ---, in EPA, *n*-butanol-isopentane, isopropyl alcohol-ethanol glasses. The spectrum of pyrimidine hydrochloride in EPA is also given by the broken line.

Another $n \rightarrow \pi^*$ transition of the same symmetry involving an excited π^* MO, which correlates with the benzene MO (B), is predicted from the same treatment at higher energies.³ The observed o,o bands at $28,290 \pm 20 \text{ cm.}^{-1}$ for the ${}^3B_1(n, \pi^*) \rightarrow {}^1A$, emission and $30,930 \pm 10 \text{ cm.}^{-1}$ for the ${}^1B_1(n, \pi^*) \rightarrow {}^1A$, absorption in the same solvent provide a method of confirmation of the above assignment. The resulting singlet-triplet interval of 2630 cm.^{-1}



π^* populations for benzene orbitals; values in parentheses include nitrogen perturbations.

is approximately half that observed (4050 cm.^{-1}) for the $n \rightarrow \pi^*$ transitions in pyrazine, for which there is no doubt that the excited π^* population correlates with the benzene π^* -MO with electron population (C).⁴ Goodman and Harrell^{5b} have proposed that the singlet-triplet interval in nitrogen heterocyclic $n \rightarrow \pi^*$ transitions should be equal to the atomic nitrogen valence state interval weighted by the $2p_z$ (nitrogen) electron density in the π^* orbital. If we assume identical nitrogen valence states in pyrimidine and pyrazine the atomic S-T interval is constant and only the $2p_z$ population is variable. The "memory" of the benzene orbitals largely, but not completely, determines these populations^{5b} and yields predicted ratios of the singlet-triplet intervals for pyrazine relative to the singlet-triplet interval in pyrimidine of: 4.0 for (B) and 1.3 for (A), with an observed ratio of 1.54. Refinement of the nitrogen populations (values in parentheses) by assuming a realistic value^{5b} of the nitrogen π -orbital

(4) L. Goodman and M. Kasha, *J. Mol. Spec.*, **2**, 58 (1958).

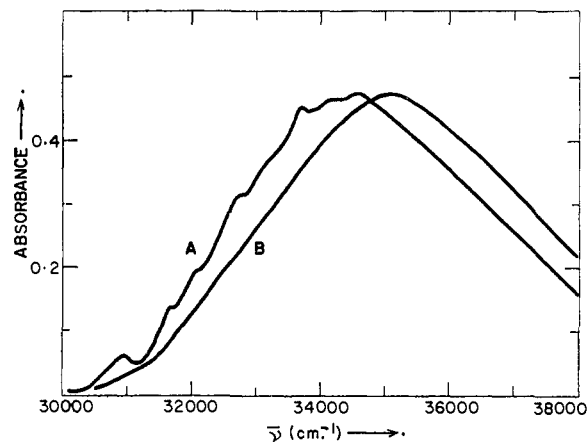


Fig. 2.—Absorption spectrum of pyrimidine ($34,000 \text{ cm.}^{-1}$ band) in rigid glasses at 77°K.: (A) in hydrocarbon glass; (B) in EPA glass.

coulomb integral yields predicted ratios of: 4.3 for (B) and 1.6 for (A). The observed singlet-triplet interval thus confirms the assignment to orbital (A). Of course this can only be an approximate description of the transition inasmuch as configuration interaction between the B_1 configurations will introduce some (B) character. The similar appearance of the S \rightarrow S¹ absorption and T \rightarrow S emission bands is strong evidence for *only one electronic transition in the $34,000 \text{ cm.}^{-1}$ absorption band* inasmuch as only the lowest triplet may emit. Therefore the transition corresponding to orbital (B) may be assumed to be buried under the $\pi \rightarrow \pi^*$ transitions.

The vibrational structure of the emission encompasses a sequence of bands of approximately 1080 cm.^{-1} spacing. In benzene there are two frequencies involving ring vibrations of approximately 1000 cm.^{-1} in frequency corresponding to an a_1 vibration in pyrimidine: $\nu_1'' = 991 \text{ cm.}^{-1}$ (a_{1g} ring stretch) and $\nu_{12}'' = 1010 \text{ cm.}^{-1}$ (b_{1u} angular ring distortion). In pyrimidine⁵ the corresponding frequencies are 991 and 1066 cm.^{-1} respectively. Our observation of $1,080 \text{ cm.}^{-1}$ made at 77°K. undoubtedly corresponds to the $1,066 \text{ cm.}^{-1}$ ring distortion ground state vibration in pyrimidine. The appearance of this ring distortion vibration is not surprising in light of the appearance of the analogous angular distortion vibration (609 cm.^{-1}) as the principal sequence in the pyrazine $n \rightarrow \pi^*$ emission.⁴ Such a conclusion requires rehybridization of the n orbital upon $n \rightarrow \pi^*$ excitation.

Protonation Effects. Emission Spectra.—Figure 1 shows the T \rightarrow S emission spectra of pyrimidine in various glasses. All the spectra except those in the hydrocarbon glass are identical within the experimental error. There is a small shift between the emissions in hydrocarbon and in hydrogen bonding solvents, amounting to approximately 120 cm.^{-1} to the blue for the o,o band. The absorption spectra of pyrimidine in EPA and hydrocarbon glasses (Fig. 2) do not show any marked change compared to the room temperature spectra and therefore, unlike in pyrazine, the rigid glass correction is small.

(5) R. C. Lord, A. L. Marston and F. A. Miller, *Spectrochim. Acta*, **9**, 113 (1957).

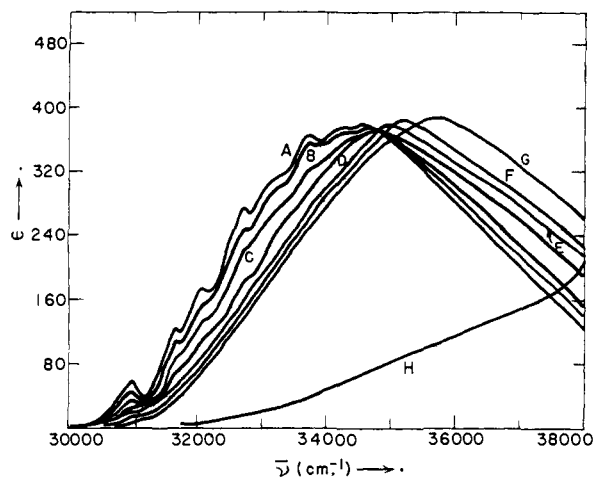


Fig. 3.—Absorption spectrum of pyrimidine ($34,000 \text{ cm}^{-1}$ band) in isopentane-ethanol mixture at 298°K .: (A) 0.0 (B) 2.0 (C) 5.0 (D) 10.0 (E) 25.0 (F) 50.0 (G) 100.0 per cent. ethanol concentration; (H) pyrimidine hydrochloride in EPA glass.

The outstanding characteristic of these spectra is that the emission spectra of pyrimidine hydrochloride dissolved either in EPA or in isopropyl alcohol-ethanol glasses is identical with that of free pyrimidine.

The emission spectrum should have a mirror-image relation with the absorption spectrum, and in fact does for pyrimidine, in methylcyclohexane-isopentane glass (Figs. 1 and 2). If there is identical hydrogen bonding in the ground and excited states in any of the hydroxylic solvents a mirror-image relation with the absorption spectra in the same solvent will be shown. (That the Franck-Condon destabilization effects are small is inherent in the argument.) But the emission spectra in the hydroxylic glasses do not show such a relation with the absorption spectra in hydroxylic solvents but instead with the absorption spectra of pyrimidine in hydrocarbon solvent. Therefore the solute-solvent interaction in the excited state corresponds to that present in isopentane solution. Thus the hydrogen bonding interaction is proved to be very weak in the excited state. In the case of pyrimidine hydrochloride, there can be little doubt regarding a strong hydrogen bond formation in the ground state. The absorption spectrum (H in Fig. 3) clearly bears this out. But the emission spectrum of pyrimidine hydrochloride resembles the absorption spectrum of pyrimidine in isopentane and not that of the pyrimidine hydrochloride, which has a very different spectral structure than pyrimidine. This conclusively proves that a hydrogen bond does not exist or is very weak in the (n, π^*) triplet excited state either for pyrimidine or for pyrimidine hydrochloride.

Absorption Spectra.—In Fig. 3 the absorption spectra of pyrimidine in isopentane, ethanol and isopentane-ethanol mixtures are recorded. The spectrum of pyrimidine hydrochloride in ethanol is also included. The spectra follow the same pattern observed in pyridazine.⁶ As the concentration of ethanol increases, more intensity is grouped into the blue side of the spectrum, while the individual

(6) G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

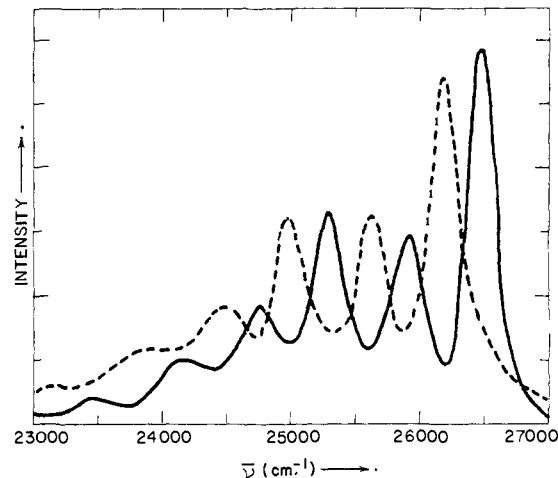


Fig. 4.— $T \rightarrow S$ emission spectrum of pyrazine hydrochloride and pyrazine at 77°K .: —, pyrazine in hydrocarbon glass; ---, pyrazine hydrochloride in EPA glass.

vibrational bands get blurred. The behavior was attributed by Brealey and Kasha⁶ in the case of pyridazine to an increase in the hydrogen bonded species with an increase of ethanol concentration and consequent decrease of the non-hydrogen bonded compound. At any given concentration of ethanol the two species are in equilibrium. The spectra of pyrimidine show an isosbestic point, within the limited range of 0–10% of ethanol concentration, favoring this view. No definite isosbestic point is found above ethanol concentrations of 10%.

The observation that the hydrogen bond is broken in the (long lived) triplet state raises a question concerning whether the hydrogen bond is broken upon $n \rightarrow \pi^*$ excitation to the singlet state. Inasmuch as hydrogen bonding is present in the ground state, it is reasonable to postulate that the transition takes place to a repulsive Franck-Condon state in terms of the N—H—O interaction energy. The repulsive Franck-Condon state will be destroyed within the time of a molecular vibration, not allowing time for vibrational quantization to take place and generating the free base in the excited state. The blurring of vibrational structure noted above is consistent with an excited state not having enough time for vibrational quantization to take place.⁷

Conclusion

The extreme weakness of the hydrogen bond in the excited state is very likely a general phenomenon for $n \rightarrow \pi^*$ transitions in the N-heterocyclics. The emission spectrum of pyrazine hydrochloride is shown along with that of pyrazine for comparison in Fig. 4. Applying the rigid glass correction found in I, the mirror image relation of the emission spectrum with the non-hydrogen bonded species becomes apparent.⁸ Repetition in dif-

(7) A vibrational lifetime ($\sim 10^{-13}$ sec.) corresponds to a Heisenberg blurring of $\sim 10^2 \text{ cm}^{-1}$. Other sources of blurring could be: different degrees of clustering of protonic solvent molecules and unequal hydrogen-bonding of the two nitrogen atoms.

(8) In I, because of the large rigid glass correction for pyrazine in EPA and because of the rather well resolved absorption spectrum of

ferent hydrogen-bonding glasses also yields emission spectra consistent with the absence of the hydrogen bond in the triplet state. Thus the hydrogen bond is found to be very weak in the excited state for two cases of different pK_a (pyrazine 0.6 and pyrimidine 1.30).⁹

The discussion in I, which was entirely in terms of Franck-Condon destabilization effects, now needs modification. Consistent with the view that the hydrogen bond breaks or becomes very weak on excitation to the singlet state (*i.e.*, $W_1 = 0$), eq. 1 of I becomes (see Fig. 7 of I)

$$\Delta\nu_a = W_0 + \omega_1 \quad (1)$$

Inasmuch as the emission spectra results show that the hydrogen bond is very weak in both the initial and final state (*i.e.*, $W_1, W_0 = 0$), eq. 2 of I becomes

$$\Delta\nu_e = -\omega_0 \quad (2)$$

where ω_0 and ω_1 are the analogs of the same quantities in I but now for a repulsive potential. From eq. 1 we conclude that the $n \rightarrow \pi^*$ absorption blue shift should be greater than the energy of the N—H—O hydrogen bond. For the N-heterocyclics where protonation effects have been studied in detail^{2,3a,7} the observed absorption blue shifts [are 2285 (pyrazine), 3340 (pyrimidine) and 3890 cm.⁻¹

pyrazine both in EPA and hydrocarbon solvents, the mirror image relation of the emission spectrum with the non-hydrogen bonded species was not apparent.

(9) In two recent papers (*Spectrochim. Acta*, **17**, 14, 30 (1961)) Shimada reports that the pyrazine ($10^{-3} M$) phosphorescence at 77°K. disappears in $10^{-2} N$ HCl (glass unspecified). Our experiments on pyrazine emission were repeated using high concentrations of acid up to 1.0 *N* in ether-ethanol (1:2) glass without an appreciable reduction in the pyrazine phosphorescence intensity. Shimada proposes solvent effects as a means of differentiating $n \leftarrow \pi^*$ from $\pi \leftarrow \pi^*$ emissions and suggests the persistence of pyrimidine emission in acidic media as an indication for a $\pi \leftarrow \pi^*$ emission. The work on pyrazine and pyrimidine reported here shows that the basicity for these molecules in the triplet states is very low and hence $n \leftarrow \pi^*$ emissions cannot be differentiated from $\pi \leftarrow \pi^*$ emissions by solvent effects.

(pyridazine)]. Inasmuch as the N—H (water) bond energy for the strongest base, pyridazine (as determined by McGowan equation), is only 5.24 kcal.¹⁰ (1880 cm.⁻¹)—a value less than the smallest blue shift—the absorption blue shifts are in full agreement with the above prediction. The blue shifts are in addition related linearly to H-bond energies as determined by McGowan equation¹⁰ (4.38, 4.84 and 5.24 for pyrazine, pyrimidine and pyridazine, respectively).¹¹

From eq. 2 it follows that $n \rightarrow \pi^*$ emissions (fluorescence or phosphorescence) should not undergo the large blue shifts inherent in absorption but should undergo small red shifts corresponding to the quantity ω_0 . For pyrazine $\Delta\nu_1 = -60 \text{ cm.}^{-1} \pm 30 \text{ cm.}^{-1}$ for pyrimidine $\Delta\nu_e = -100 \pm 30 \text{ cm.}^{-1}$.

These conclusions are in agreement, in the main, with Kasha's original suggestion¹² that the absorption blue shift of $n \rightarrow \pi^*$ transitions on protonation can be attributed to the hydrogen bonding of the solvent with the solute. For hydrogen bonding solvents (including direct protonation) both formation of a hydrogen bonding species in the ground state, and the Franck-Condon destabilization, as discussed in I, are seen to be operative in the absorption solvent shift but only the latter effect in the emission shift.

Acknowledgment.—The authors thank Professor Norman C. Deno for helpful suggestions and criticism of the manuscript.

(10) N. C. Deno, private communication; see *J. Chem. Eng. Data*, **5**, 1 (1960) for the method of determining hydrogen bond energies. E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958), has shown that the $n \rightarrow \pi^*$ blue shift is greater than the hydrogen bonding energy in the case of carbonyl compounds.

(11) Attention is called to A. Weller's work (*Z. Physik. Chem. N. F.*, **18**, 163 (1958), on pK_a values for both excited and ground states. In addition Kosower's correlation of spectroscopic absorption shifts with Z values (ref. 10) has indicated for several classes of compounds an empirical linearity of transition energy with hydrogen bond energy.

(12) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

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Methyl Group Substituent Effects on Chemical Shifts in the Nuclear Magnetic Resonance Spectra of Ethylenic Systems

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It has been found that in a series of ten ethylenic derivatives of the form $H_2C=CHX$, with $X = CN, Cl, Br$ and CH_3 , the effect of methyl substitution upon the chemical shifts of the ethylenic protons is approximately constant for each proton position relative to the methyl group. These substituent effects vary somewhat with the nature of X , but for each X this variation is nearly the same for all protons. Hence the effect of methyl substitution on the internal shifts can be rather reliably predicted. In the butenes it is found that the methyl group effects also appear to be additive. Examples are given to illustrate the utility of these generalizations in assigning and analyzing n.m.r. spectra.

Introduction

The accumulation of the data of nuclear magnetic resonance spectroscopy has now reached such a point as to permit the establishment of a number of reasonably reliable correlations and generalizations with at least a semi-theoretical justification. These results can be important for two reasons. In the first place, they are useful in the prediction and interpretation of n.m.r. spectra as related to conventional chemical structures, and, in the second place, they may ultimately provide new routes to

the understanding and evaluation of some of the working concepts of valence theory, *e.g.*, hyperconjugation.

In this investigation we have attempted to arrive at some new generalizations concerning the effect of methyl substitution on chemical shifts in n.m.r. spectra of various ethylenic systems, of the general structure $H_2C=CHX$, where $X = CH_3, Cl, Br, CN$, etc., and with the CH_3 group replacing one of the protons.

In certain cases the data employed were obtained