unreasonable and that structure BI (SN bond distance 1.416 Å.) is the correct one.

If one assumes, as has been proposed,[12] that the bond order is linearly related to the inverse square of the bond distance for a given pair of atoms, *i.e.*, if

$$N = \frac{a}{R^2} + b$$

where N is the bond order, R is the bond distance and a and b are constants which depend only on the chosen pair of nuclei, then a and b may be evaluated from knowledge of single and double bonded covalent radii by use of the Schomaker–Stevenson rule as modified by Gordy to include double bonds. This was done using the single and double bonded covalent radii of nitrogen as given by Gordy[13] and the single and double bonded covalent radii of sulfur as given by Pauling.[14] The single and double bond distances were calculated and, using these distances, the constants a and b were evaluated. The constants a and b were used in turn to calculate the bond distances of bonds of order 1, 1.5 and 2.7.

$$R(1) = 1.74 \text{ Å.}$$
$$R(1.5) = 1.63 \text{ Å.}$$
$$R(2.7) = 1.42 \text{ Å.}$$

The first two are in reasonable agreement with the observed values for $SN_2O_5^{--}$ and S_4N_4. While the calculated value of the SN distance for a bond of order 2.7 is no doubt fortuitously close to the observed distance for structure B I of NSF_3, this calculation in addition to the observed values for known SN and SF distances leads to the conclusion that structure B I is the correct structure for NSF_3.

The Dipole Moment of NSF_3.—The dipole moment was obtained by measuring the displacement of the $M = \pm 1$ and $M = 0$ second order Stark lobes of the 2←1 transition as a function of the square of the applied Stark modulating voltage. The spectrometer was calibrated by measuring the displacement of the $M = \pm 1$ and $M = 0$ Stark lobes for the 2←1 transition of OCS. The dipole moment of OCS was taken to be 0.7124 Debye.[15] The data were fitted by least squares to give

$$\mu = 1.91 \pm 0.03 \text{ Debye}$$

The ^{14}N Quadrupole Coupling Constant of NSF_3.—Hyperfine structure due to the ^{14}N electric quadrupole was observed at low pressures for the 1←0 transition. Given in Table IV are the observed and calculated frequencies for the hyperfine structure. The calculated values are based on a coupling constant of $eqQ = +1.19 \pm 0.05$ mc. and $\nu_0 = 2B = 9{,}272.48$ mc. Since the three components were not completely resolved, it was difficult to obtain meaningful relative intensities, but semi-quantitatively, the calculated and observed intensities were in good agreement.

TABLE IV

CALCULATED AND OBSERVED QUADRUPOLE HYPERFINE STRUCTURE FOR THE 1←0 TRANSITION OF NSF_3

F_1	F_f	Obsd. frequency, mc.	Calcd. frequency, mc.
1	0	9271.90	9271.88
1	2	9272.42	9272.42
1	1	9272.79	9272.78

Discussion

The confirmed structure of NSF_3 may be considered naïvely as a derivative of SF_6 with three of the fluorine atoms replaced by a triply bonded nitrogen atom. The FSF angle has been increased by only four degrees and the SF distance has been diminished slightly. The SN distance agrees well with the expected value for a covalent nitrogen–sulfur triple bond. It should be mentioned that NSF_3 appears to be the first reported example of a molecule containing a nitrogen–sulfur triple bond. On the other hand, the triple bond in NSF_3 differs markedly from the triple bond in the cyanides with respect to the quadrupole coupling constant of the nitrogen atom since, in the cyanides, eQq ranges from -2.5 to -5 mc. Indeed, the only previously reported examples of a positive coupling constant have been in molecules where the nitrogen bonds are not cylindrically symmetrical or where the nitrogen atom has more than three bonds.[16] However, in all of the reported cases the nitrogen atom has been bonded exclusively to elements of the first row of the periodic table. Thus it appears that the 3s, 3p and 3d orbitals of the sulfur atom have a pronounced effect on the electronic distribution in the vicinity of the nitrogen nucleus.

Acknowledgments.—The authors wish to thank Dr. T. S. Piper for calling their attention to this compound and for supplying an early sample and Professor R. M. Badger for his helpful suggestions concerning the preparation.

(12) W. Gordy, *J. Chem. Phys.*, **15**, 305 (1947).

(13) W. Gordy, *ibid.*, **15**, 81 (1947).

(14) L. Pauling, "Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 224.

(15) S. A. Marshall and J. Weber, *Phys. Rev.*, **105**, 1502 (1950).

(16) For a list of many of the N-14 coupling constants which have been measured, see C. H. Townes an d A. L. Shawlow, ref. 9, pp. 613–642.

[CONTRIBUTION OF DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY, ATLANTA 22, GA.]

N.m.r. Studies of Pyrimidine, Imidazole and their Monomethyl Derivatives

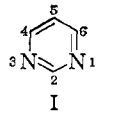
BY G. S. REDDY, R. T. HOBGOOD, JR., AND J. H. GOLDSTEIN

RECEIVED AUGUST 25, 1961

Pyrimidine, imidazole and their monomethyl derivatives have been studied by n.m.r. techniques. In all cases the spectra were simple patterns, easily analyzable by first-order theory. Additional information for pyrimidine itself was obtained from its C^{13}–H spectrum. The results are discussed in relation to the structures and bonding aspects of the ring systems.

Introduction

Various derivatives of pyrimidine (1) and imidazole (II) are of great importance in biological chemistry and have received considerable attention in recent years.[1] Among the newer techniques to be applied in this area, nuclear magnetic resonance (n.m.r.) spectroscopy gives promise of providing



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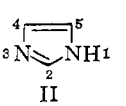

II

(1) See, for example, A. Albert, "Heterocyclic Chemistry," University of London, The Athlone Press, London, 1959.

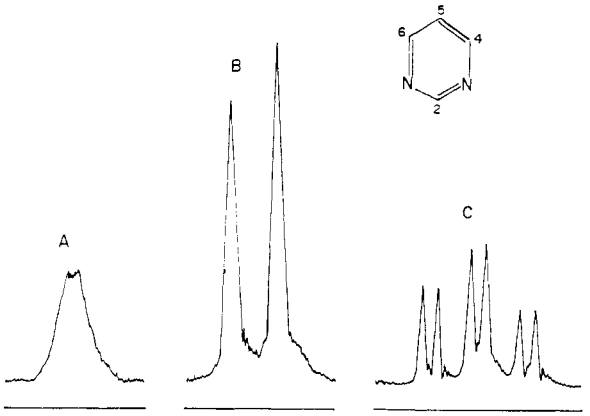

Fig. 1.—Proton magnetic resonance spectrum of pyrimidine at 40 Mc./sec. in *d*-chloroform: A, proton 2; B, protons 4 and 6; C, proton 5.

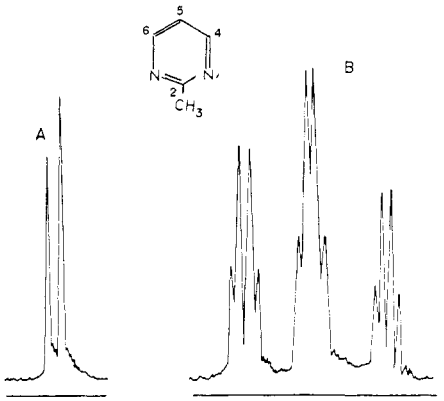

Fig. 2.—Proton magnetic resonance spectrum of 2-methylpyrimidine at 40 Mc./sec. in *d*-chloroform: A, protons 4 and 6; B, proton 5; A and B are not on the same scale.

more detailed information about these heterocyclic systems, of such a nature as to perhaps prove valuable in deciphering their role in vital processes. However, up to this time only a few n.m.r. studies of such molecules and their derivatives appear to have been reported, especially in the case of the simpler derivatives.[2-4]

For some time, now, we have been carrying out investigations of such properties as proton mobility and tautomerism in a series of uracils and related compounds by means of n.m.r. techniques.[5] The purpose of this communication is to report the results of an n.m.r. study of pyrimidine, imidazole and their monomethyl derivatives. The spectral pattern obtained for all these compounds proved to be easily analyzed by first-order methods, without necessitating extensive calculations. However, in order to obtain a complete set of n.m.r. parameters for pyrimidine it was necessary to study also the C^{13}–H spectra (in natural abundance) in the pure liquid. The results have been discussed in terms of the structure and electronic distribution of these molecules.

(2) C. D. Jardetsky, *J. Am. Chem. Soc.*, **82**, 229 (1960).

(3) S. Gronowitz and R. A. Hoffman, *Arkiv. Kemi*, **16**, 459 (1961).

(4) R. J. Gillespie, A. Grimson, J. H. Ridd and R. F. M. White, *J. Chem. Soc.*, 3228 (1959).

(5) J. P. Kokko, J. H. Goldstein and Leon Mandell, *J. Am. Chem. Soc.*, **83**, 2909 (1961), and further work being readied for submission.

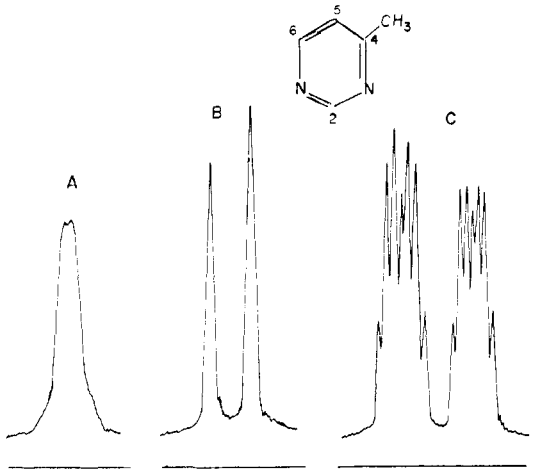

Fig. 3.—Proton magnetic resonance spectrum of 4-methylpyrimidine at 40 Mc./sec. in *d*-chloroform: A, proton 2; B, proton 6; C, proton 5; A, B and C are not on the same scale.

Experimental

All of the pyrimidines and imidazoles studied were kindly provided us by Southern Research Institute (Birmingham, Ala.) and in each case it was ascertained from their n.m.r. spectra that the purity was adequate for our purposes.

The spectra were taken with a Varian Associates model 4300-B n.m.r. spectrometer, equipped with a flux stabilizer and operating at 40 Mc./sec. Calibrations were performed by the usual side-band technique.[6] The peak frequencies were obtained by averaging measurements taken on several successive forward and reverse sweeps. The typical mean deviation was 0.1 c.p.s. or less. The solvent used was *d*-chloroform with a small amount of tetramethylsilane (TMS) added to serve as an internal reference. All the solutions were very dilute (2–3% by weight) and it was ascertained that none of the C–H peaks was appreciably affected by dilution in this range. This means that not only are the internal comparisons within the pyrimidine and imidazole series highly reliable, but also that comparisons can be safely made with other systems at high dilution in different solvents, provided that an internal TMS reference is uniformly employed.

The C^{13}–H spectra of pyrimidine were taken on the pure liquids, since these patterns were viewed in the isotopically unenriched compounds. These spectra were used only as a source of values of coupling constants, which are believed to be largely insensitive to the medium employed.

Results

The spectrum of pyrimidine is shown in Fig. 1 and those of 2-methyl- and 4-methylpyrimidine are shown in Figs. 2 and 3. Figures 5 and 6 contain the spectra of all the imidazoles studied.

All the spectra were simple first-order patterns which made it possible to compute all the chemical shifts and most of the coupling constants with sufficient accuracy by a first-order analysis. The coupling constant, J_{46}, in pyrimidine itself was obtained from the C^{13}–H_4 pattern (Fig. 4), since coupling between these two magnetically equivalent protons does not produce any splitting in the observed spectrum. The parameters for the pyrimidines are listed in Table I and those for the imidazoles are given in Table II. It should be mentioned that the mobile N–H proton in the imidazoles was not considered in the present study since traces of water so markedly affect its chemical

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

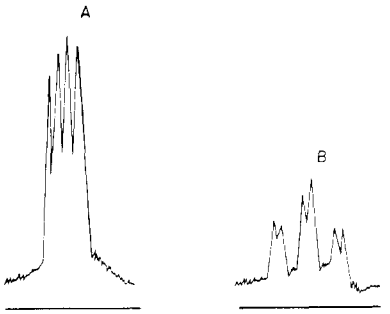

Fig. 4.—C^{13}–H spectra of pyrimidine; the two spectra were observed at different sweep rates: A, protons 4 and 6; B, proton 5. The C^{13}–H pattern of position 2 is a broad single peak and is not shown in the figure.

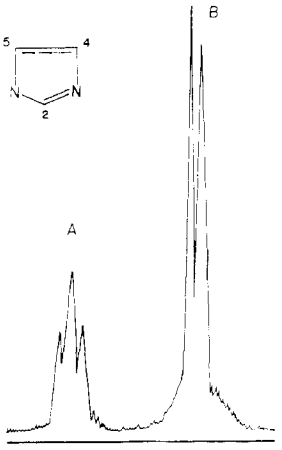

Fig. 5.—Proton magnetic resonance spectrum of imidazole at 40 Mc./sec. in *d*-chloroform: A, proton 2; B, protons 4 and 5; A and B are on the same scale.

shift that special precautions will be required to obtain meaningful data. (The properties of this proton will be made the subject of a separate investigation.)

TABLE I

N.M.R. SPECTRAL PARAMETERS FOR PYRIMIDINE AND MONOMETHYLPYRIMIDINES[a]

Parameter	Substituent: None	2-Methyl	4-Methyl	5-Methyl
ω_2	−370.4	....	−363.5	−361.8
ω_4	−351.0	−346.0	....	−342.9
ω_5	−294.4	−284.8	−288.3	...
ω_6	−351.0	−346.0	−343.7	−342.9
J_{24}	~0	0[c]	0[c]	~0
J_{25}	1.5	0.6[c]	1.4	0.6 or 0.8[d]
J_{26}	~0	0[c]	~0	~0
J_{45}	5.0	4.9	0.5[c]	0.8 or 0.6[d]
J_{46}	2.5[b]	....	0[c]	.....
J_{56}	5.0	4.9	5.1	0.8 or 0.6[d]
$J(C_2{}^{13}H)$	206.0	....	....	.....
$J(C_4{}^{13}H)$	181.8	....	....	.....
$J(C_5{}^{13}H)$	168.0	....	....	.....

[a] All values are in c.p.s. at 40 Mc./sec. fromTMS (internal) in *d*-chloroform solution, except for values obtained from C^{13}–H spectra in which case the pure liquid was used. [b] From C^{13}–H spectrum. [c] CH_3–H coupling. [d] CH_3–H coupling. The couplings J_{25} and J_{45} (J_{56}) are either 0.6 and 0.8 or 0.8 and 0.6 c.p.s., respectively. Precise assignments cannot be made.

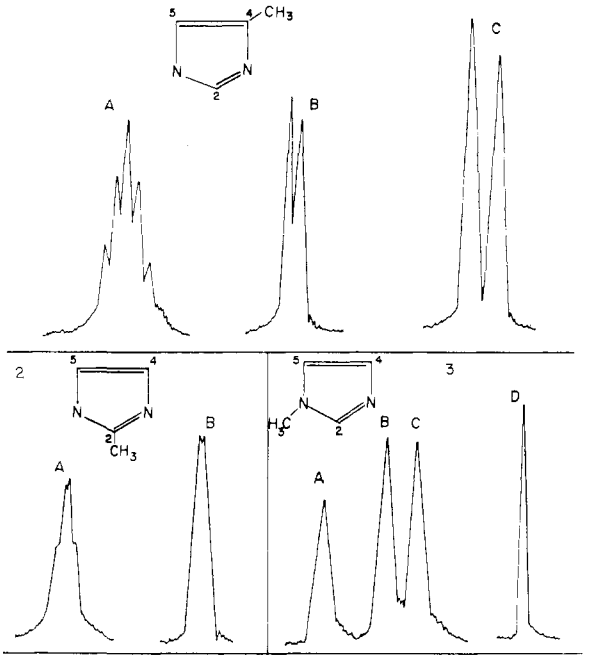

Fig. 6.—Proton magnetic resonance spectra of monomethylimidazoles at 40 Mc./sec. in *d*-chloroform. 1, 4-methylimidazole: A, proton 5; B, proton 2; C, methyl group; A, B and C are not on the same scale. 2, 2-methylimidazole: A, protons 4 and 5; B, methyl group; A and B are not on the same scale. 3, N-methylimidazole: A, proton 2; B, proton 4; C, proton 5; D, methyl group; A B and C are on the same scale.

In the spectra of the pyrimidines, peaks due to proton H_2 (between N_1 and N_3) are quite broad and appreciable, though smaller broadening is also discernible in peaks arising from H_4 and H_6, each of which is adjacent to a single N atom. Al-

TABLE II

N.M.R. SPECTRAL PARAMETERS FOR IMIDAZOLE AND MONOMETHYLIMIDAZOLES[a]

Parameter	Substituent: None	2-Methyl	4-Methyl	N-Methyl[c]
ω_2	−308.1	.....	−302.3	−296.5
ω_4	−285.1	−277.7	.....	−274.3
ω_5	−285.1	−277.7	−270.0	−282.0
$\omega(CH_3)$	.....	− 96.6	− 90.8	−146.8
J_{24}	1.0	.....		
J_{25}	1.0	.....	1.1	
J_{45}	.....	.....	1.0[b]	

[a] All values in c.p.s. at 40 Mc/sec. in *d*-chloroform (2.3%) relative to TMS (internal). [b] CH_3–H coupling. [c] Calibrated by superposition; values reliable to ±0.5 c.p.s.

though it is reasonable to attribute the broadening to the effect of the N atoms, the width of the unresolved lines places a limit on the reliability of J_{24}. In the absence of observable splitting, this is listed as ~0 in Table I but, in any case, it is probably no greater than a few tenths of a cycle.

Discussion

A. Pyrimidines.—The general appearance of the spectrum and the chemical shifts in pyrimidine are in accord with expectations, inasmuch as $\omega_2 < \omega_4 = \omega_6 < \omega_5$ and the magnetic equivalence of H_4

and H_6 was predicted from the symmetry of the molecule. The values of J_{45}, 5 c.p.s., and J_{25}, 1.5 c.p.s., are reasonable for *ortho* and *para* couplings by comparison with aromatic systems.[7] Of the two *meta* couplings, J_{46} = 2.5 c.p.s. falls in the normal aromatic range, but J_{24} is zero (or a very small value). It is noteworthy that in both the 2-methyl- and 5-methylpyrimidines the value of the *para* H–CH_3 coupling (0.6–0.8 c.p.s.) is appreciable, even though the coupled protons are separated by six bonds, while the *meta* CH_3–H couplings are not discernible.

The absolute magnitudes of the shifts in pyrimidine are not easy to interpret, although it should be remarked that ω_5 is reasonably near the value for benzene (*ca.* 290 c.p.s. in TMS). One factor that makes reliable comparisons difficult to achieve is lack of knowledge of the ring current anisotropy effect in pyrimidine. However, it recently has been found that this problem sometimes can be eliminated by reliance on C^{13}–H coupling constants. As has been shown by Muller and Pritchard,[8] C^{13}–H coupling constants depend in a linear fashion upon the density of s-electrons on the C atom involved. It has been found that in some cases where anisotropy effects are small, the $J(C^{13}–H)$ values correlate well with chemical shifts,[9] and it has been possible to proceed from this point to show that anisotropies can in certain cases be calculated satisfactorily by appropriate use of $J(C^{13}–H)$ values.[10] It appears justifiable, therefore, to propose the use of C^{13}–H couplings as a more reliable index of the s-charge density and orbital character (C–H) in the pyrimidine ring than can be provided by the chemical shift values.

In pyrimidine, the values of ω_2, ω_4, and ω_5 parallel the corresponding C^{13}–H couplings reasonably well, but the relationship is not precisely linear, possibly because of the previously mentioned anisotropy effects. However, a plot of the methyl shifts in the three methylpyrimidines *versus* the C^{13}–H couplings at the corresponding positions of substitution gives a quite satisfactory straight line (see Fig. 7). Although only three points are available, this result is cited primarily to substantiate the use made here of the C^{13}–H coupling values. Thus, the downfield trend in the methyl shifts is interpreted as reflecting increasing s-character in the sequence $C_5 < C_4 < C_2$, and a corresponding order of inductive withdrawal of charge from the methyl group. (Any anisotropy effects in pyrimidine should be somewhat smaller at the methyl protons.)

The magnitude and distribution of the substituent effect on the chemical shifts in pyrimidine is of some interest, since previous studies here have indicated that such observations in heterocyclic compounds can be correlated with the aromatic character of these compounds, and can provide detailed information concerning the effects of substituents upon the charge distribution.[11] In furan, pyrrole and thiophene it was found that the total effect on all ring C–H shifts produced by a single methyl substituent was *ca.* 30 c.p.s. However, the replacement of =CH— in the ring by =N—, as in thiazole, reduced the total effect to *ca.* 20–25 c.p.s., depending on the position of the methyl substituent. Presumably, this reflects the absorption of some charge by the =N— atom, which does not then appear in any of the shifts. It also was found that the total methyl effect in toluene was *ca.* 30 c.p.s., *i.e.*, an average of 6 c.p.s. for the five ring protons. This value, 30 c.p.s., has accordingly been interpreted as a measure of the charge transferred from a methyl group to an unsaturated system beyond the point of attachment of the methyl group, presumably by hyperconjugation or an equivalent long-range process.

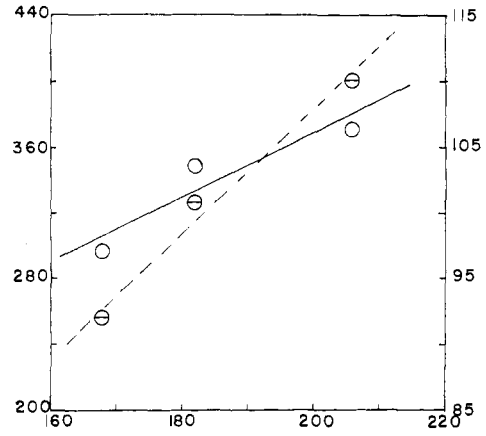

Fig. 7.—Plot of C^{13}–H coupling constants against chemical shifts: —O—O—, Jc^{13}–H *vs.* ring proton chemical shifts; - -O- -O- -, Jc^{13}–H *vs.* methyl group chemical shifts at the corresponding position in the ring.

Turning now to the methylpyrimidines, we see from Table III that the observed total methyl substituent effect ranges from *ca.* 20 to 25 c.p.s., significantly below the values of 30–33 c.p.s. observed in benzene, thiophene, pyrrole and furan. However, as in the case of thiazole, these results are interpreted as indicating that some of the charge transferred from CH_3 to the pyrimidine ring is localized on the nitrogen atoms (which, of course, have no attached protons to be observed) in the order 2-methyl > 4-methyl > 5-methyl.

The interpretation of the detailed substituent effect, shown in Table III, is complicated somewhat by the necessity for simultaneously considering the inductive effects of the nitrogen atoms and the resonance forms of the ring system, as well as by the lack of a more precise measure of the charge absorbed by the nitrogen atoms. In 2-methylpyrimidine, the *para* effect is clearly larger than the meta effect, which indicates that resonance is the predominant factor here. In 4-methylpyrimidine the effect is, practically speaking, uniform. The fact that in this case the *meta* and *ortho* effects

(7) J. A. Pople, W. G. Schneider and J. H. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 193.

(8) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

(9) E. B. Whipple, W. E. Stewart, G. S. Reddy and J. H. Goldstein, *ibid.*, **34**, 2136 (1961).

(10) J. H. Goldstein, paper delivered at the Symposium on Molecular Spectroscopy and Structure, Ohio State University, June 12–16 1961.

(11) G. S. Reddy and J. H. Goldstein, *J. Am. Chem. Soc.*, to be published.

are comparable may reflect, in part, the inductive effect of the nitrogen atoms as well as a decreased resonance effect due to the fact that those structures which place negative charge at positions *ortho* to the substituent are now no longer equivalent. In the 5-methyl compound, the effect is again essentially uniform, but here there is no *meta* value for comparison.

TABLE III

METHYL SUBSTITUENT EFFECTS IN PYRIMIDINE[a]

	Position				
Substituent	2	4	5	6	Sum
2-Methyl	..	5	9.6	5	19.6
4-Methyl	6.9	..	6.1	7.3	20.3
5-Methyl	8.6	8.1	..	8.1	24.8

[a] All values are the displacements of the proton shifts in c.p.s. at 40 Mc./sec. relative to the same position in the unsubstituted ring.

B. Imidazole.—The spectrum of imidazole which consists of a triplet and a doublet of twice the triplet intensity is clearly that of an A_2B system, that is, H_4 and H_5 are a magnetically equivalent set despite the apparent difference of the N_1 and N_3 atoms. This equivalence has its origin in the fact that the N_1 proton is very mobile and undergoes rapid exchange either with water present or with other imidazole molecules, the various structures present being stabilized by resonance. A similar line of reasoning accounts for the fact that the 4-methyl and 5-methyl derivatives are indistinguishable.

The chemical shifts shown in Table II are in accord with expectations based on the structure of imidazole, and the coupling constants are all relatively small (*meta* values). The values of the methyl shifts are reasonable in view of the inductive situation at the various positions.

The methyl substituent effects in imidazole have been summarized in Table IV. The situation is qualitatively similar to that in pyrimidine, in that the 4-methyl group produces a greater total effect than the 2-methyl substituent, and both totals are well below the previously observed value of 30–33 c.p.s. It thus appears that here again charge has been transferred to the nitrogen atoms in the order 2-methyl > 4-methyl. Incidentally, these observations parallel the order in which the basicities increase: imidazole < 4-methylimidazole < 2-methylimidazole.[12] The N-methyl derivative presents a somewhat different situation, since there is no mobile proton present and the original symmetry is now destroyed. It is not too surprising, therefore, that its basicity is not as great as that of the other two methyl derivatives

TABLE IV

METHYL SUBSTITUENT EFFECTS IN IMIDAZOLE[a]

	Position			
Substituent	2	4	5	Total
2-Methyl	..	7.4	7.4	14.8
4-Methyl	5.8	..	15.1	20.9
N-Methyl	11.6	3.1	10.8	25.5

[a] All values are the displacements of the proton shifts in c.p.s. at 40 Mc./sec. relative to the same position in the unsubstituted ring.

The relatively large total methyl effect in N-methylimidazole is interesting in that it may in part reflect the general extent to which conjugated heteroatoms in the ring absorb the charge transferred by a long-range mechanism from the substituent.

Acknowledgments.—The authors are indebted to the National Institutes of Health and to the Army Chemical Center for their support of various phases of this work; and to the Southern Research Institute, Birmingham, Ala., for supplying all the compounds used in this study.

(12) Reference 1, p. 344–345.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH, PENNSYLVANIA AND THE BELL TELEPHONE LABORATORIES, INCORPORATED, MURRAY HILL, NEW JERSEY[1c]]

Hückel Molecular Orbital Computations to Describe the Benzidine Rearrangement[1a]

BY LAWRENCE C. SNYDER[1b]

RECEIVED JULY 31, 1961

Major qualitative features of the product distribution in the acid catalyzed benzidine rearrangement have been explained by Dewar in terms of a postulated monoprotonated pi complex. In this study, a molecular orbital model is employed to describe a pi complex and its subsequent unfolding to sigma complexes corresponding to possible products. Computations have been made in the Hückel approximation to describe the rearrangement of hydrazobenzene, 2,2′-hydrazonaphthalene, 1,1′-hydrazonaphthalene, 9′,9-hydrazoanthracene, hydrazotoluenes and hydrazoanilines. It is found that under assumption of either of two extreme pi complex wave functions, a covalent or a charge transfer structure, the product distributions predicted by the model are in qualitative agreement with experiment. The results support the model of a monoprotonated pi complex as an intermediate but fail to elucidate its wave function. Observed ionization potentials for benzyl radical and aniline suggest that the states corresponding to the extreme structures would be almost degenerate for an isolated monoprotonated pi complex. If one adds to the model a hypothetical description of the effect of solvation on the product distribution, then the usual minor role of *ortho*-benzidine as a product and the solvent effect on the diphenylene to *para*-benzidine ratio can be explained, and Dewar's generalization on the selective formation of diphenylenes can be interpreted to favor the covalent structure as predominant in the pi complex.

Introduction

The growing body of experimental knowledge of the product distribution and kinetics of the benzidine rearrangement makes the explanation of its mechanism more difficult and interesting. Many

(1) (a) Presented in part at the 138th meeting of the American Chemical Society, New York, September, 1960. Taken in part from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Carnegie Institute of Technology, 1959. (b) National Science Foundation predoctoral fellow 1953–1954, 1956–1958.