

pected again to be near zero and the value selected for J_3^σ (see 4) is that estimated by Bothner-By, Naar-Colin, and Günther,¹¹ and J_4^π (see 4) is taken as the value of this coupling in 3,3-di-*tert*-butyl-1-propene.¹¹ The value of J_4^π and J_3^π at $\phi = 90^\circ$ (see 5) is taken to fit approximately the observed $|J_4|$ in 4-*tert*-butylcyclohexenone and its ethylene ketal derivative in which the allylic hydrogen is considered to occupy the quasi-axial conformation ($\phi \sim 80^\circ$). This value is in qualitative agreement with the value of 3.4 c.p.s. that is estimated from the equation $J_{3,4}^\pi = ka_{\text{H}a_{\text{H}}'} \sin^2 \phi$.³ Using the coupling parameters shown under 3 to 5 and the angular relationships discussed earlier, the following equations that relate J_3 and J_4 to ϕ may be written.

$$J_3^{\text{est}} \cong \begin{cases} 6.6 \cos^2 \phi + 2.6 \sin^2 \phi & (0^\circ \leq \phi \leq 90^\circ) \\ 11.6 \cos^2 \phi + 2.6 \sin^2 \phi & (180^\circ \geq \phi \geq 90^\circ) \end{cases}$$

$$J_4^{\text{est}} \cong \begin{cases} 1.3 \cos^2 \phi - 2.6 \sin^2 \phi & (0^\circ \leq \phi \leq 90^\circ) \\ -2.6 \sin^2 \phi & (180^\circ \geq \phi \geq 90^\circ) \end{cases}$$

Table I lists a series of alkenes for which J_3 and J_4 values have been reported or determined in connection with this work. Angles ϕ selected for the simple unsaturated hydrocarbons will be discussed,¹² and the angles selected for the remaining alkenes, unless indicated otherwise, were estimated from Dreiding models. Most angles and experimental coupling constants probably are reliable to $\pm 15^\circ$ and ± 0.3 c.p.s., respectively. When two or more angles ϕ are given, the observed couplings (J_3° and J_4°) are averages of the couplings representative of these angles, unless stated otherwise.

As a whole, the estimated and observed couplings in Table I appear to be in qualitative agreement. Several prominent discrepancies between the estimated and observed couplings are the J_3 values for the norbornenes, norbornadiene, and the J_4 values, in magnitude but not

in sign, for several of the cycloalkenes. As the assumed angles are only approximate and coupling constants in many instances were derived by first-order spectral analyses and, in addition, many variables other than dihedral angles appear to affect vicinal and probably long range proton couplings,¹³ it would not seem profitable at this time to undertake to pinpoint the origin of these discrepancies.

Several conclusions may be drawn, it is felt, from the data in Table I: (1) J_3^π and J_4^π are likely to be of opposite signs and J_3^σ and J_4^σ are likely to be of the same sign and positive as predicted by rudimentary theory.³ (2) Because of apparent positive σ -bond contributions for $0^\circ \leq \phi \leq 90^\circ$, J_4 appears to pass through zero with a concurrent change of sign at about $40^\circ > \phi > 20^\circ$. (3) J_4^σ for $180^\circ \geq \phi \geq 90^\circ$, if significant, is probably small (< 1 c.p.s.) and of a negative sign. For example, when $180^\circ \geq \phi \geq 90^\circ$, the frequently larger negative values of J_4^σ as compared with J_4^{est} suggest either that there may be negative σ -bond contributions to J_4 over these conformations or that the J^π contributions have been underestimated. (4) J_3 appears to be appreciable, > 1 c.p.s., for all angles ϕ . For $0^\circ \leq \phi \leq 90^\circ$, J_3 varies by about 4 c.p.s. with a maximum at about 6–7 c.p.s.; whereas, for $180^\circ \geq \phi \geq 90^\circ$, J_3 varies by about 9 c.p.s. with a maximum at about 11–12 c.p.s.

In conclusion, the small change in J_3 upon going from $\phi \sim 0^\circ$ to $\phi \sim 90^\circ$ permits, at best, only the crudest estimations of allylic proton conformations within these boundaries. Estimations of approximate allylic hydrogen conformations for all angles ϕ may be rendered most reliable if the mutual compatibility of J_3 and J_4 in magnitude and in sign is demonstrated.

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Nitrogen-15 Magnetic Resonance Spectroscopy. II. Coupling Constants^{1,2}

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Coupling constants have been measured between nitrogen-15 and directly bonded hydrogen or carbon-13, and between nitrogen-15 and hydrogen separated by two or more bonds. The data may generally be interpreted in terms of the Fermi contact coupling mechanism except for those cases where the electron distribution around the nitrogen atom is highly anisotropic. Empirical relationships have been developed which relate the observed J_{N^H} and J_{N^C} to the hybridization of the orbitals involved. These relationships fail for J_{N^H} in diphenylketimine and for J_{N^C} in benzaldehyde and acetonitrile, probably because of contributions to the nuclear spin-spin coupling from electron orbital motion. The data are consistent with the interpretation that nitrogen in ammonia forms nearly sp^3 bonds to hydrogen, rather than p bonds as suggested by Pauling.

The nature of the hybridization of atoms, such as nitrogen, oxygen, and fluorine, which carry unshared

electron pairs, has been a matter of controversy for many years. Pauling⁴ has maintained that these elements form predominantly p -type σ -bonds, while others⁵ have suggested that the nitrogen forms perturbed sp^3 -hybrid σ -bonds, or else^{5,6} that the hybridiza-

(1) For the first paper in this series, see J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Natl. Acad. Sci., U. S.*, **51**, 735 (1964).

(2) Supported in part by the Public Health Service Research Grant 11072-01 from the Division of General Medical Sciences, the Office of Naval Research, and the National Science Foundation.

(3) (a) National Science Foundation Graduate Fellow, 1962–1965; (b) National Academy of Sciences–National Research Council Postdoctoral Fellow, 1963–1964.

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(5) For a discussion, see E. Cartmell and G. W. A. Fowles, "Valency and Molecular Structure," Butterworths, London, 1961, pp. 162 ff.

TABLE I
¹⁵N-H COUPLING CONSTANTS

No.		Solvent	Method	$ J_{\text{NH}} $, ^a c.p.s.	j_{NH} , \hbar^2/μ_0^2 sec.	S_N^k
1	(C ₆ H ₅) ₂ C=NH	Pentane	^d	51.2 ± 0.4	16.2	33.3
2	NH ₃ ^b	None	^d	61.2 ± 0.9	19.4	..
3	NH ₄ Cl	Water	^{d,e}	73.2	23.2	25.0
4	CH ₃ NH ₂ Cl	Water	^{d,e}	75.6	23.9	25.0
5	HO ₂ CCH ₂ NH ₂ Cl	Water	^{d,e}	77.0	24.4	25.0
6	H ₂ NCONHCONH ₂	DMSO	^g	88.4 ± 1.0	28.0	32.0
7	H ₂ NCONH ₂	DMSO	^{d,e}	89 ± 1	28.2	32.0
8	CH ₃ CONH ₂	Water	^{d,e}	89 ± 2	28.2	32.0
9	H ₂ NCN	DMSO	^g	89.4 ± 1.0	28.3	32.0
10	C ₆ H ₅ NHNHC ₆ H ₅	DMF	^{d,e}	90.5	28.6	..
11	Pyridinium ion	H ₂ SO ₄	^f	90.5 ± 1.0	28.6	33.3
12	C ₆ H ₅ NHCOCH ₃	Acetone	^{d,e,g}	90.9	28.8	..
13	C ₆ H ₅ NH(CS)NH/CH ₃	Ethanol	^{d,e}	91.2	28.9	..
14	1-Methylcytosine ⁱ	DMSO	^d	92.0	29.1	..
15	HCONH ₂ ^c	None	^d	92.0 ^h	29.1	..
				88.0 ⁱ	27.8	..
16	(C ₆ H ₅) ₂ C=NH ₂ Cl	SO ₂	^d	92.6 ± 0.4	29.3	33.3
17	Phthalimide	DMSO	^d	93.0 ± 0.8	29.4	..
18	CH ₃ CONHCH ₂ CO ₂ H	DMSO	^d	94.5	29.9	..

^a Unless otherwise indicated, the average deviation is about 0.2 c.p.s. ^b Ref. 10. ^c Ref. 12. ^d Obtained from the proton spectrum of the ¹⁵N compound. ^e From the nitrogen-15 spectrum. ^f By calculation from the ¹⁴N-H splitting in the proton n.m.r. spectrum. ^g From the ¹⁵N satellites of the proton spectrum of the unlabeled compound obtained by time averaging over about 50 runs. ^h Coupling to the proton *trans* to the carbonyl group. ⁱ Coupling to the proton *cis* to the carbonyl group. ^j H. T. Miles, R. B. Bradley, and E. D. Becker, *Science*, **142**, 1569 (1963). ^k These values are used for the plot in Fig. 2.

tion is primarily a function of the angles of the bonds to nitrogen. Recently a new experimental approach to the problem of hybridization has become available through the measurement of nuclear spin-spin coupling constants. A linear correlation between the per cent of s-character of carbon orbitals and ¹³C-H coupling constants has been established,⁷ not only yielding a direct method for the determination of hybridizations at carbon atoms, but also strongly supporting the theoretical postulate that the Fermi contact term is responsible for essentially the whole magnitude of the ¹³C-H coupling constants.⁸ These results have stimulated the extension of this approach to the hybridization problem of nitrogen. No extensive studies on coupling involving nitrogen have been reported, apparently because such coupling is obscured in most cases by the electric quadrupole interaction of nitrogen-14. This paper is therefore concerned with the determination of ¹⁵N-H and ¹⁵N-¹³C coupling constants, with the hope of trying to establish the type of hybrid bonds formed by nitrogen in its σ -bonds with hydrogen and carbon-13. The latter nucleus was included in order to study a larger range of hybridization at nitrogen than is possible with nitrogen bonded to hydrogen. It was also expected that by these data further insight might be gained into the mechanism of spin-spin coupling.

Results

Coupling of Nitrogen-15 with Directly Bonded Protons.—The ¹⁵N-H coupling constants have previously been measured in ammonia,^{9,10} ammonium ion,^{9,11} and formamide.¹² Table I contains the absolute

values of J_{NH} for these compounds as well as for those studied in this work. The last column lists the corresponding reduced coupling constants, j_{NH} ,¹³ which are obtained by dividing the coupling constant by the product of the gyromagnetic ratios of the nuclei involved. In general

$$j_{\nu\mu} = \frac{J_{\nu\mu}}{\gamma_{\nu}\gamma_{\mu}} \text{ (in multiples of } \hbar^2/\mu_0^2 \text{ sec.)}$$

The process of division removes the specific properties of the nuclei and generates a quantity which depends on the electronic structure of the molecule under consideration. This is a valid manipulation because all three terms which describe the coupling constant are directly proportional to the product of the gyromagnetic ratios.⁸

The measurement of the ¹⁵N-H coupling in diphenylketimine presented experimental difficulties because intermolecular exchange caused line broadening or complete collapse of the spin-spin splitting, depending on the solvent and the temperature. At 40°, the imine hydrogen resonance varied from a single sharp peak (in carbon disulfide and sulfur dioxide) or a broad singlet (in carbon tetrachloride or dimethyl sulfoxide) to no observable peak at all (in acetonitrile, deuteriochloroform, and pentane), depending upon the rate of exchange. The proton spectrum of the ketimine was examined in 2% solutions of the last three solvents¹⁴ down to -50°, at which temperature the solutions solidified. No change occurred in this temperature

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(14) The authors wish to thank Dr. D. L. Dreyer of the Fruit and Vegetable Chemical Laboratory, Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Pasadena, Calif., for the use of the A-60 which was equipped with a temperature probe.

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TABLE II
 ^{15}N - ^{15}N AND ^{15}N - ^{13}C COUPLING CONSTANTS

No.	Compound	Solvent	$ J_{^{15}\text{N}^{15}\text{N}} $ c.p.s.	$ J_{^{15}\text{N}^{13}\text{C}} $ c.p.s.	J , $\text{h.}^2/\mu_0^2 \text{ sec.}$	S_C	S_N	$S_N S_C^a$
1	$\text{C}_6\text{H}_5^{15}\text{N}=\text{N}^+-\text{C}_6\text{H}_5$	Ether	13.7 ± 0.8		42.8
2	$\text{C}_6\text{H}_5\text{CH}=\text{N}^+-^{13}\text{CH}_3$	None		<3	<3.8	25.0	33.3	833
3	$^{13}\text{CH}_3-^{15}\text{NH}_2$	None		7 ± 1	8.8	25.0	20.0	500
4	$\text{C}_6\text{H}_5^{13}\text{CH}=\text{N}^+\text{CH}_3$	None		7.1 ± 0.3	8.9	33.3	33.3	1109
5	$^{13}\text{CH}_3^{15}\text{NH}_3\text{Cl}$	Water		<8	<10	25.0	25.0	625
6	$\text{C}_6\text{H}_5^{15}\text{NH}-^{13}\text{C}(=\text{O})-\text{CH}_3$	Methanol		13.0 ± 1.5	16.4	33.3	32.0	1066
7	$^{13}\text{CH}_3^{15}\text{N}=\text{C}(=\text{S})-\text{CH}_3$	None		13.4 ± 0.2	16.9	25.0	44.1 ^b	1103
8	$\text{C}_6\text{H}_5\text{NH}-\text{C}(=\text{S})-\text{NH}^{13}\text{CH}_3$	Ethanol		<15	<19	25.0	32.0	800
9	$\text{CH}_3-^{13}\text{C}(=\text{O})-\text{NH}_2$	Water		<15	<19	33.3	32.0	1066
10	$\text{CH}_3^{13}\text{C}\equiv\text{N}^c$	None		17.5 ± 0.2	22.0	50.0	50.0	2500

^a These values are used for the plot in Fig. 3. ^b Calculated from the CNC bond angle [C. I. Beard and B. P. Dailey, *J. Am. Chem. Soc.*, **71**, 929 (1949)] by eq. 2 (*vide supra*). ^c Chemical shift: 245 p.p.m. downfield from ammonia.

range for the acetonitrile and deuteriochloroform solutions. However, in pentane, a doublet appeared at about 0° , sharpened at -20° , and underwent no further change to -45° (Fig. 1a, b). That this was the doublet associated with the imine hydrogen coupled

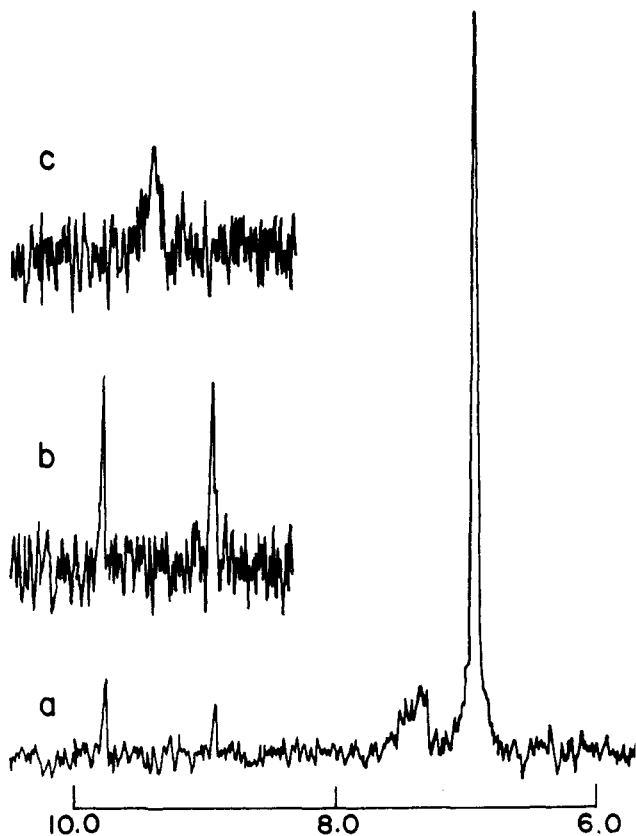


Fig. 1.—Proton spectrum of diphenylketimine- ^{15}N (a,b) and ^{14}N (c) at -20° in a 2% pentane solution.

with nitrogen-15 was substantiated by observing the spectrum of the nitrogen-14 compound under identical conditions. The single broad resonance which was observed (Fig. 1c) fell at a position which corresponded to the average of the two nitrogen-15 peaks. Integration showed that the sum of the areas of the ^{15}N -H peaks was precisely $1/10$ of the area of the phenyl peaks. The distance between the two peaks was measured from five runs to be 51.2 ± 0.4 c.p.s. The magnitude

of this coupling, which was expected to be much larger from considerations of hybridization correlations alone, will be discussed later in this paper. This study will be extended in the future to other imine systems and will include the quantitative measurement of the barrier to exchange.

Some line broadening was also observed in acetamide. Changing the solvent, however, had no effect on the spectrum. Hence, in this case, restricted rotation about the amide bond is responsible for line broadening, as was the case for the series of N-mono- and disubstituted amides.¹⁵

Coupling of Nitrogen-15 with Directly Bonded Carbon-13 and Nitrogen-15.—Couplings of nitrogen-15 to directly bonded nuclei other than protons have been obtained from the nitrogen-15 spectra of compounds isotopically enriched at specific positions. The results are listed in Table II. Because of the low sensitivity of nitrogen-15 resonances,¹ the complications in the spectra from long-range coupling with neighboring protons, and the small absolute value of these coupling constants produced by the small gyromagnetic ratio of ^{15}N , the average deviations are relatively large, and in some cases only upper limits estimated from the half-widths of the peaks can be given.

Coupling of Nitrogen-15 with Protons Separated by Two and Three Bonds.—Long-range couplings have previously been observed between protons and nitrogen-14 in isonitriles¹⁶ and ammonium compounds.¹⁷⁻¹⁹ Table III lists such couplings, which have been determined by first-order analysis of the various proton spectra. Some other couplings are also included in the table.

Discussion

Nuclear spin-spin interactions *via* the electron cloud have been proposed to proceed by three different mechanisms,⁸ which arise, respectively, from: (1) the Fermi contact interaction, (2) the nuclear spin-electron orbital interaction, and (3) the electron-nuclear dipole-

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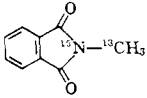
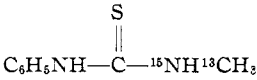
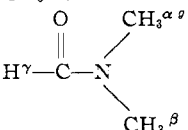
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TABLE III
 LONG-RANGE ^{15}N -PROTON COUPLING CONSTANTS^a

	$J_{^{15}\text{NCH}}$	$J_{^{15}\text{NCC}}$	$J_{^{13}\text{CH}}$	$J_{^{13}\text{CCH}}$	$J_{^{13}\text{CNH}}$	$J_{^{13}\text{CNC}}$	J_{HCNH}	J_{HCNC}
$^{13}\text{CH}_3^{15}\text{NH}_2$	1.0		133.2					
$^{13}\text{CH}_3^{15}\text{NH}_2\text{Cl}$	0.8		145.0		3.5		6.2	
$\text{C}_6\text{H}_5^{15}\text{N}(\text{CH}_2\text{CH}_3)_2$	0.0	0.7						
$\text{HCO}^{15}\text{NH}_2^b$	19.0							
$\text{CH}_3^{13}\text{CO}^{15}\text{NH}_2$		1.3		6.1				
$\text{C}_6\text{H}_5^{15}\text{NH}^{13}\text{COCH}_3$		0.7		6.4	2.5			
	1.4		141.5					
	0.9		140.3		2.7		3.8 ^e 4.4 ^f	
$\text{C}_6\text{H}_5\text{CH}^\alpha=^{15}\text{N}-^{13}\text{CH}_3^\beta$	3.9 ^c 0.6 ^d		134.2			13.2		1.7
$\text{C}_6\text{H}_5^{13}\text{CH}^\alpha=^{15}\text{N}-\text{CH}_3^\beta$	3.9 ^c 0.6 ^d		156.8			9.0		1.7
$^{13}\text{CH}_3-^{15}\text{N}=\text{C}=\text{S}$	3.3		145.3					
$\text{CH}_3^{13}\text{C}\equiv^{15}\text{N}$		1.7		10.0				
	15.6 ^h 1.2 ^c 1.1 ^d							

^a All constants are expressed in c.p.s. and are accurate to about ± 0.2 c.p.s. ^b Ref. 12. ^c Coupling to the α -proton. ^d Coupling to the β -proton. ^e Solution in CDCl_3 . ^f Solution in ethanol. ^g A. J. R. Bourn and E. W. Randall, *J. Mol. Spectry.*, **13**, 29 (1964). ^h Coupling to the γ -proton.

dipole interaction. In the molecular orbital treatment, these terms may be further divided into one- and two-electron contributions.²⁰ Since the original calculations of Ramsay,²¹ the second and third terms have commonly been neglected. Karplus and Grant,²² O'Reilly,²³ and others have corroborated and extended the earlier calculations, thus arriving at the conclusion that coupling of protons with other nuclei derives principally from the contact term. On this basis, the coupling constant between nuclei ν and μ should be proportional to the per cent of s-character, s_ν and s_μ , of the orbitals forming the bond, and inversely proportional to the mean triplet excitation energy, $^3\Delta E^{13}$

$$J_{\nu\mu} \propto s_\nu s_\mu / ^3\Delta E$$

Following this manner of interpretation, ^{13}C -H coupling constants have been widely used to calculate bond hybridizations,^{7,24} and fairly accurate empirical relationships have been derived among coupling constants between the group IV elements and hydrogen or fluorine.²⁵ Muller²⁶ in fact feels that $J_{^{13}\text{CH}}$ provides the best experimental method of determining the hybridization of a carbon atomic orbital. However, one must keep in mind the nature and extent of the assumptions utilized in these treatments.²⁷ In addition to the restraints

placed by the assumptions of the predominance of the contact term, the presence of perfect pairing, and (for some authors²⁷) the neglect of overlap, the validity of the calculations rests on the assumption of correctly representing all the various excited states by a mean excitation energy, which, furthermore, must remain constant throughout a given series.^{28,29}

Assuming by analogy with ^{13}C -H coupling that the magnitude of the coupling between nitrogen-15 and directly bonded hydrogen is determined by the contact interaction, the amount of s-character of the nitrogen bond orbital should be linearly related to the ^{15}N -H coupling constant as in eq. 1,³⁰ which was derived from the couplings in an sp^3 system (NH_4^+ , $s = 25\%$, $J = 73.2$ c.p.s.) and an sp^2 system [$(\text{C}_6\text{H}_5)_2\text{C}=\text{NH}_2^+$, $s = 33.3\%$, $J = 92.6$ c.p.s.]; pyridinium ion could have served as well for the sp^2 standard, but the coupling constant was known with less accuracy].

$$s = 0.43J_{^{15}\text{NH}} - 6 \quad (1)$$

This relationship is illustrated in Fig. 2. Those compounds for which s -values can reasonably be assigned (Table I) are included on the plot. Equation 1 predicts an s -value of 19.9 ± 0.4 for ammonia.

Having suggested a quantitative correlation between s -character and $J_{^{15}\text{NH}}$, we are now in a position to compare our results with values of s calculated in different manners. Pauling⁴ prefers to describe the nitrogen atom in ammonia as remaining almost completely p -hybridized. Deviations in the bond angles from 90° are taken as perturbations on this system. The lone

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(30) This is analogous to the relation,²⁴ $s = 0.20J_{^{13}\text{CH}}$, for the s -character of the carbon orbital in a ^{13}C -H bond.

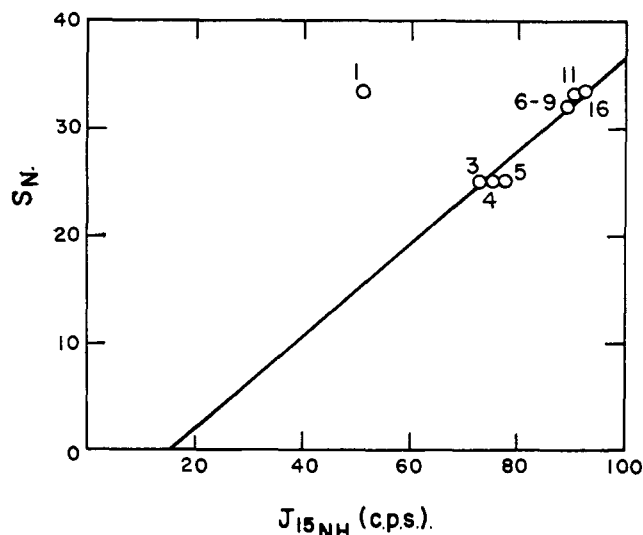


Fig. 2.—Plot of per cent s-character of the nitrogen orbital directed toward hydrogen vs. the ^{15}N -H coupling constant, based on compounds 3 and 16, but including others for which the hybridization is reasonably well known. The significant deviation of compound 1 is discussed in the text.

pair must therefore have an s-character of nearly 100% and be symmetrically distributed around the nucleus. From the s-p promotion energy and the N-H bond energy, Pauling⁴ calculates an s-character of about 4.8% for the nitrogen orbitals to hydrogen in ammonia, which accords with his hypothesis of nearly pure p-hybridization.

However, using arguments based on normalization and orthogonality conditions,⁶ it has also been suggested that the s-character depends only on the bond angles (or, more precisely,²⁶ the interorbital angles). If the bonds in question are equivalent and are separated by an angle θ , the following relationship holds

$$s = 100 \cos \theta / (\cos \theta - 1) \quad (2)$$

From this equation, the s-value for ammonia ($\theta = 107.3^\circ$ ^{4,5}) is calculated to be 22.9%. Thus the hybridization predicted from the ^{15}N -H coupling constant is in much better agreement with the theory that hybridization is a function of bond angle than with the theory of p-bonding. Furthermore, the Pauling theory fails to predict the bond angle accurately (92.7° predicted) and cannot account for the large difference in dipole moment between NH_3 and NF_3 ,³¹ for which a directed lone pair must be invoked. Provided that the contact term is dominant, nearly pure p-hybridization would also require a zero or almost zero coupling constant. Although the orthogonality relationships predict a value in good agreement with that calculated from eq. 1, this model is still not necessarily the best. Methylene chloride, for instance, appears to take exception to the orthogonality rules in that both the HCH and CICC1 bond angles are near 112° .

The coupling constants of other ammonium compounds (3-5) in Table I are also consistent with approximately sp^3 hybridization as computed from eq. 1. The J -values of compounds 6-18 fall in a relatively narrow range between 88 and 94 c.p.s., corresponding to s-characters of 31-34%. All these substances have as a common feature the involvement of the nitrogen atom

in a conjugated system. As a consequence, the nitrogen orbital involved in the π -system tends to assume a high degree of p-character, thus allowing the other orbitals to approach sp^2 hybridization.

Application of the above relationship to diphenylketimine gives a rather unreasonably low value of 15.6% for the s-character of the ^{15}N -H bond. Thus the expected value of about 33% falls far off the plot in Fig. 2. In this case, at least one other factor must be operative which makes a contribution of opposite sign to the coupling constant. The situation here is hardly expected to be as simple as with ^{13}C -H bonds³² because of the presence of a lone pair and of cross-conjugation. The fact that diphenylketimine has a very large downfield nitrogen-15 chemical shift (308 p.p.m. relative to anhydrous ammonia) suggests that the nuclear spin-electron orbital interaction may become important in this molecule. Pople^{8,34} has found that orbital contributions are large if the screening constant for either of the nuclei is highly anisotropic. This anisotropy, which determines the paramagnetic term in the shielding expression, appears to be the dominant factor responsible for nitrogen-15 chemical shifts.¹ The anisotropy may intuitively be associated with a low-lying excited state by consideration of the fact that diphenylketimine, which exhibits the anomalous spectral properties, is the only compound other than ammonia for which one cannot write a canonical structure with positive charge on nitrogen, which would indicate partial or complete bonding of the lone pair.

The similarity of $J_{15\text{NH}}$ for the protonated form of diphenylketimine (the hydrochloride) with those of all other conjugated, nearly sp^2 systems indicates that π -contributions are probably small with respect to those arising from the asymmetric environment at the nitrogen atom caused in this particular system by the lone pair. If the orbital term does provide a contribution of opposite sign to the coupling constant in the unprotonated case, then the protonated species, which appears to have no significant orbital contribution, should have a correspondingly less anisotropic screening constant. On this basis, a large upfield shift with protonation was predicted for the nitrogen resonance.^{1,35} In agreement with this, it was found that the ^{15}N resonance of the protonated imine occurs 168 p.p.m. downfield from ammonia, near the amide resonances, a shift of 140 p.p.m. to higher field with respect to the imine itself.

The observations in the ^{13}C - ^{15}N series of coupling constants (Table II) are consistent with the proposed interpretation of the ^{15}N -H coupling data. Again assuming for the moment the dominance of the Fermi contact term, one would expect a direct proportionality between $J_{15\text{N}^{13}\text{C}}$ and the product of the s-characters of the carbon and nitrogen orbitals forming the σ -bond. Reasonable values for the hybridization parameters at

(32) Actually, even the ^{13}C -H couplings are not altogether simple since Juan and Gutowsky²⁴ report that $J_{13\text{CH}}$ calculated for substituted ethylenes from additivity relationships is systematically about 7 c.p.s. below the observed values. They suggest a negative π -contribution to the coupling constant. Coupling in π -systems offers still greater irregularities with $J_{13\text{C}^{13}\text{C}}$.^{27,33}

(33) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. (London)*, **A269**, 385 (1962).

(34) J. A. Pople, *Mol. Phys.*, **1**, 216 (1958).

(35) The normal shift with protonation, as in ammonia and amines, is downfield because of reduction in the shielding from the lone pair. An upfield shift in the protonation of *trans*-azobenzene was attributed to a decrease in the paramagnetic term arising from an increased mean electronic excitation energy.¹

(31) L. Burnelle and C. A. Coulson, *Trans. Faraday Soc.*, **53**, 403 (1957).

the two centers are included in Table II and their product is plotted *vs.* $J_{15N^{13}C}$ in Fig. 3. Whereas $J_{15N^{13}C}$ in compounds 3, 5-9 can be correlated roughly by the relation

$$S_N S_C = 80 J_{15N^{13}C} \quad (3)$$

the points corresponding to the substances 2, 4, and 10 clearly fall far off the straight line. Their coupling constants are considerably smaller than predicted from the contact term alone. These same compounds happen to be the ones which have large downfield nitrogen-15 chemical shifts,¹ again suggesting that these deviations are associated with low-lying excited states and are probably due to contributions from orbital terms. However, the data are still too few to draw any definite conclusions. π -Electron contributions have not been totally excluded from playing an important role.

Experimental

Coupling constants involving protons were measured on the Varian A-60 spectrometer and checked against the nitrogen-15 spectra where applicable. The data obtained in Table I have been obtained by three different methods. For the most part, isotopically labeled materials were synthesized, permitting direct observation of the coupling by proton or nitrogen-15 magnetic resonance spectroscopy. Dimethyl sulfoxide (DMSO) was a particularly useful solvent since it reduces intermolecular proton exchange by forming strong, nonexchanging hydrogen bonds with the solute protons under observation. For certain cases, such as acetanilide, biuret, and cyanamide, computer averaging of low intensity signals permitted observation of the ^{15}N satellites. The 400 channel Mnemotron "CAT" was triggered reproducibly to 0.1 c.p.s. by an audiofrequency sideband of tetramethylsilane at the beginning of each sweep. This point and the end of the sweep were calibrated with respect to the ^{14}N -H center band. Fifty to eighty sweeps were usually sufficient to define the ^{15}N satellite accurately (S/N about 3/1). Finally, J_{15NH} could be measured from J_{14NH} provided that the N-H resonance consisted of three peaks (pyridinium ion); usually only a single peak would be present because of quadrupole relaxation (Fig. 1c).

The ^{15}N - ^{15}N and ^{15}N - ^{13}C couplings were determined from the nitrogen-15 spectra¹ obtained with a Varian Model V-4300 spectrometer operated at 6.08 Mc.p.s. and 14,100 gauss. Details of the measurements have been previously reported.¹ All of the spectra could be readily analyzed by first-order procedures.

Most of the following compounds were prepared on 0.5- to 2.0-g. scales.

Phthalimide- ^{15}N was obtained by acidifying an aqueous solution of potassium phthalimide- ^{15}N (96.0% ^{15}N ; Merck Sharp and Dohme of Canada).

N-Methyl- ^{13}C -phthalimide- ^{15}N was prepared by prolonged heating of potassium phthalimide- ^{15}N in an atmosphere of methyl- ^{13}C iodide (62.4% ^{13}C ; Volk Radiochemical Co.) according to the procedure of Cox and Warne.³⁶

Methyl- ^{13}C -amine- ^{15}N Hydrochloride was obtained from the phthalimide by treatment with hot 50% potassium hydroxide solution, followed by distillation of the liberated amine, necessarily with some water, into a dilute aqueous solution of hydrochloric acid.

Methyl- ^{13}C -amine- ^{15}N was generated from the parent hydrochloride with concentrated potassium hydroxide solution and swept into a trap cooled with Dry Ice-acetone by a slow stream of nitrogen. The trap was then connected to a vacuum line, and the amine condensed in a flask containing potassium hydroxide pellets and, when dry, distilled into the n.m.r. tube.

Benzaldehyde- ^{13}C -amine- ^{15}N .—The doubly labeled methylamine was condensed into an equimolar quantity of freshly distilled benzaldehyde. The solution was allowed to stand overnight; then ether was added, the layers were separated, and the benzaldehyde was isolated in 94% yield by reduced-pressure distillation.

Methyl- ^{13}C isothiocyanate- ^{15}N was prepared from methyl- ^{13}C -amine- ^{15}N according to the method described by Moor and Croseley.³⁷

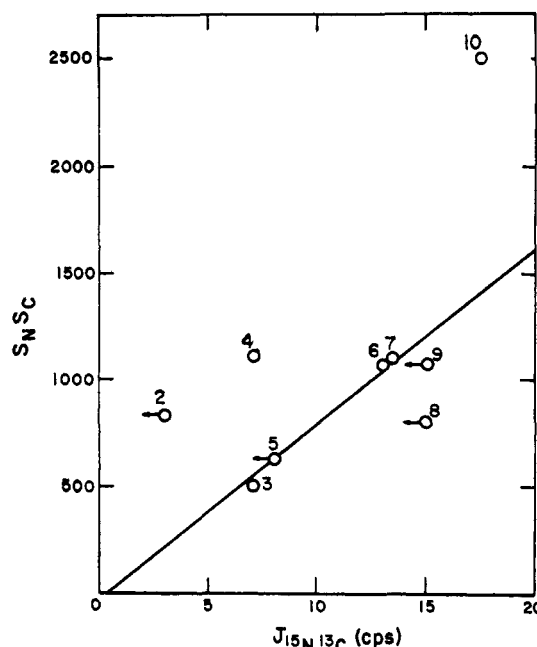


Fig. 3.—Plot of the product of the per cent s-character of carbon and nitrogen *vs.* the ^{15}N - ^{13}C coupling constant. The deviations of points 2, 4, and 10 are discussed in the text. Those circles associated with an arrow signify upper limits of the coupling constants only.

^{15}N -Methyl- ^{13}C -N'-phenylthiourea was obtained as colorless crystals of m.p. 111–114° (lit.³⁸ m.p. 113°) by allowing an equimolar mixture of aniline and methyl- ^{13}C isothiocyanate- ^{15}N in ether to stand at room temperature for 8 hr. followed by removal of the solvent.

Acet-1- ^{13}C -amide- ^{15}N .—Sodium acetate-1- ^{13}C (56.3% ^{13}C ; Merck Sharp and Dohme of Canada) was treated with an excess of benzoyl chloride to yield acetyl-1- ^{13}C chloride (92% yield). The reaction of the product with 2 moles of liquid ammonia- ^{15}N , liberated from ammonium- ^{15}N chloride (97.0% ^{15}N ; Merck Sharp and Dohme of Canada), in ether gave 91% of doubly labeled acetamide and 96% of ammonium- ^{15}N chloride, which were separated by extraction with chloroform.

Aceto-1- ^{13}C -nitrile- ^{15}N was prepared by distillation of acet-1- ^{13}C -amide- ^{15}N over phosphorus pentoxide in 51% yield.

Acet-1- ^{13}C -anilide- ^{15}N was prepared by reaction of equimolar quantities of aniline- ^{15}N (*vide infra*), acetyl-1- ^{13}C chloride, and triethylamine in ether solution.

Nitrobenzene- ^{15}N was prepared from benzene and 38% nitric- ^{15}N acid (Volk Radiochemical Laboratories; 97% ^{15}N) in the presence of sulfuric acid at 55°. The mixture was extracted with ether, the organic portion was washed with water and base, and the nitrobenzene was purified by distillation.

Aniline- ^{15}N was obtained by the reduction of nitrobenzene- ^{15}N with granulated tin and hydrochloric acid at 80°. The mixture was steam distilled and the aniline isolated by extraction of the aqueous distillate with ether, followed by distillation.

Benzal- α - ^{13}C -methylamine- ^{15}N .—Benzoic- α - ^{13}C acid was made from barium carbonate- ^{13}C (58.5% ^{13}C ; Merck Sharp and Dohme of Canada) and phenylmagnesium bromide according to the method of Dauben, Reid, and Yankwich.³⁹ It was reduced with lithium aluminum hydride to benzyl- α - ^{13}C alcohol by standard procedures and converted to benzyl- α - ^{13}C chloride by reaction with thionyl chloride in an over-all yield of 66%. A Sommelet reaction of the chloride in 50% acetic acid gave 72% of benzaldehyde- α - ^{13}C which with methylamine- ^{15}N generated from methylammonium- ^{15}N chloride (*vide supra*) yielded benzal- α - ^{13}C -methylamine- ^{15}N .

Diethylaniline- ^{15}N .—Aniline- ^{15}N and triethyl phosphate were heated under reflux for 2 hr. An aqueous solution of sodium hydroxide was added, followed by an additional hour of refluxing.

(37) M. L. Moor and F. S. Croseley, "Organic Syntheses," Coll. Vol. 111, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 599.

(38) W. Gebhardt, *Ber.*, **17**, 3033 (1884).

(39) W. G. Dauben, J. C. Reid, and P. E. Yankwich, *Anal. Chem.*, **19**, 828 (1947).

(36) J. D. Cox and R. J. Warne, *J. Chem. Soc.*, 1896 (1951).

The organic portion was extracted with ether and treated with acetic anhydride overnight. Concentrated hydrochloric acid was added, and the solution was extracted with ether to remove any undesired organic material. The amine was liberated from the aqueous solution with sodium hydroxide, separated by extraction with ether, and isolated by distillation.

trans-Azobenzene-¹⁵N was prepared by the reduction of nitrobenzene-¹⁵N with zinc in a basic methanol-water solution.

trans-Azoxybenzene-¹⁵N was prepared by treatment of *trans*-azobenzene-¹⁵N with acetic acid and 30% hydrogen peroxide at 55° for 24 hr. After 8 hr. and after 20 hr., additional hydrogen peroxide was added. Water was added and the product was isolated by extraction with 60–70° petroleum ether and evaporation of the solvent.

Hydrazobenzene-¹⁵N.—*trans*-Azoxybenzene-¹⁵N was heated with zinc in a basic ethanol-water solution at 100° for 1 hr. The mixture was filtered hot and the filtrate then placed in the refrigerator. The resulting solid was washed with 50% ethanol containing sodium bisulfite until white (m.p. 121.5–125°). The alcoholic solutions yielded *trans*-azobenzene after removal of most of the ethanol by distillation.

Benzamide-¹⁵N.—Benzoyl chloride in ether solution was cooled in a Dry Ice-acetone bath and treated over a 1.5-hr. period with ammonia-¹⁵N generated from ammonium-¹⁵N chloride and base. After 12 hr. at room temperature, the solution was filtered and the ammonium-¹⁵N chloride (collected quantitatively) was

washed with acetone. The filtrate was evaporated to incipient crystallization, treated with benzene, heated to boiling, and filtered hot. Benzamide was obtained in several crops from the benzene solution (89% yield).

Benzonitrile-¹⁵N was prepared from benzamide-¹⁵N by treatment with sodium aluminum chloride and distillation with a free flame.

Diphenylketimine-¹⁵N.—Phenylmagnesium bromide in ether was heated under reflux with benzonitrile-¹⁵N for 7 hr.; the complexes were destroyed with methanol, the slurry filtered, and the ketimine isolated by distillation.⁴⁰

Diphenylketimine-¹⁵N hydrochloride was prepared by bubbling dried hydrogen chloride gas through an ether solution of the parent ketimine in a nitrogen atmosphere; the solid was removed by filtration and dried under reduced pressure.

Glycine-¹⁵N (96% ¹⁵N) was obtained from Bio-Rad Laboratories.

Acetylglycine-¹⁵N was prepared from glycine-¹⁵N and acetic anhydride according to the procedure of Herbst and Shemin.⁴¹

Urea-¹⁵N₂ was prepared from ammonia-¹⁵N (*vide supra*) and diphenyl carbonate according to the procedure of Leitch and Davidson.⁴²

(40) P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).

(41) R. M. Herbst and D. Shemin, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 11.

(42) L. C. Leitch and W. M. Davidson, *Sci. Agr.*, **29**, 189 (1949).

[CONTRIBUTION FROM THE CONVERSE LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASS. 02138]

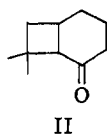
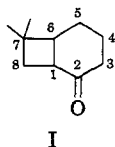
A Study of the Photochemical Reactions of 2-Cyclohexenones with Substituted Olefins¹

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The photochemical reactions of 2-cyclohexenone and other conjugated enones with a variety of unsaturated substances have been investigated to determine the scope, orientation, and stereochemistry of cycloaddition. The occurrence of marked orientational specificity is confirmed as is the frequent formation of *trans*-fused ring systems. The susceptibility of a number of olefinic substrates to attack by excited 2-cyclohexenone has been measured by competition experiments which establish the series: 1,1-dimethoxyethylene > methoxyethylene > cyclopentene > isobutylene > allene >> acrylonitrile. An hypothesis is advanced to explain (1) the observed orientational specificity, (2) the stereochemistry of photoaddition, and (3) the relative reactivity of different olefins with excited 2-cyclohexenone. Because orientational specificity and high olefin reactivity have been found to coincide and to appear with those olefins which are good π -donors, these factors are linked in the theory; for good π -donors an oriented π -complex is considered as an intermediate. The generation of a cyclobutane unit by cycloaddition seems to occur in two distinct stages with *sequential* formation of the two new carbon-carbon bonds, *i.e.*, via a 1,4-diradical system, at least in certain instances.

During the recent program of research in these laboratories on the total synthesis of caryophyllene,² an investigation was made of possible synthetic routes to the bicyclic ketone I and it was discovered that the photochemical cycloaddition of isobutylene and 2-cyclohexenone was an efficient and practical one-step procedure. This reaction which was effected by ultra-



violet excitation of 2-cyclohexenone in the presence of a high concentration of isobutylene (nonabsorbing at the ultraviolet wave lengths used) is formally analogous to a number of other cycloaddition processes which have been described in recent years.³ In general, these in-

volve the addition of a photoactivated double bond to an unactivated multiple bond which is not in the absorbing chromophore. Apart from being of great utility, the photoaddition of 2-cyclohexenone to isobutylene was of exceptional interest for other reasons. First, the major product I was formed in much larger amount than the alternative cycloaddition product II; in fact, in our early experiments the isomer II escaped detection. Second, both *cis* and *trans* forms of I were obtained with the latter predominating by a considerable margin even though it is a relatively strained system. At the time of our initial studies of this reaction there were no indications that photoaddition processes would involve such orientational and stereochemical effects. We have, therefore, investigated several

(1) This work was supported by the National Science Foundation (GP 221) and the National Institutes of Health (GM 7484).

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