for either benzoic acid-*h* or acid-*d* (Table VI). If indeed there was an effect on the monomer–dimer ratio, it did not appear to be reflected in the rate data.

No firm evidence can be adduced for the dimer hypothesis from the activation parameters in the two solvents (Table VII). Nevertheless, it is noticeable that there is a significant difference in the balance of enthalpies and entropies of activation. The diminished entropy of activation in toluene would seem consistent with the view of a second acid molecule firmly bonded in the transition state for reaction of the dimer.

In conclusion, it may be claimed that the detailed mechanism of the DDM reaction 1 in hydroxylic solvents is now fairly well understood. For the reaction in toluene the situation is less satisfactory. The evidence from the products, kinetics, and hydrogen isotope effect suggest that there is no change in rate-determining step from the proton transfer established for the solvent ethanol. Furthermore, there is strong indication that the reactive acidic species in toluene is the dimer. On the other hand, the concentration dependence of the rate constant on acid and the associated trend in the hydrogen isotope effect are not understood or accounted for.

Experimental

Diphenyldiazomethane was prepared by a standard method. Its purification and the determination of the extinction coefficient of its absorption maximum (ϵ_{max} = 102 at 525 mμ) have been described previously.[7] So too have the details of kinetic measurements of its reaction with carboxylic acid, both in ethanol and toluene, been given. All kinetic runs were followed spectrophotometrically using a Beckman Model DK-2 automatic recording spectrophotometer.[7]

Toluene was purified by distillation from sodium and stored in a tightly stoppered bottle. The benzoic acid was of primary standard quality. Commercially available absolute ethanol was used without further purification. Ethanol-*d* (98% deuterium) was obtained from Volk Radiochemical Co.

Benzoic-*d* acid was prepared from benzoyl chloride (purified by distillation) by heating under reflux for 2 hr. with 99.8% D_2O in the absence of moisture. The acid was sublimed and stored in a desiccator. Samples were used within a few days of preparation. Before standard solutions were prepared, the deuterium content of the acid was determined from its infrared spectrum in carbon tetrachloride. The OH peak at 1425 cm.$^{-1}$ was used for analysis and its extinction coefficient determined from spectra of the undeuterated acid. The measurements were made with a Perkin-Elmer Model 21 recording spectrophotometer. The proportion of benzoic-*h* in the deuterio acid varied from 3–9%, and all rate constants had to be corrected for its presence. After correction, different samples of acids with different deuterium contents gave reproducible rate constants.

Determination of α, the Product Ratio of Combined Acid to Unreacted Acid.—In the reaction of DDM with acids, acid is consumed only in the reaction path leading to an ester, and the product ratio of ester to ether may be determined by direct kinetic measurement. Under second-order conditions, the kinetic form of the reaction is expressed by the equation

$$kt = \frac{1}{(a - \alpha b)} \ln \frac{b(a - \alpha x)}{a(b - x)} \qquad (3)$$

where a is the initial concentration of acid, b is the initial concentration of DDM, and x is the amount of DDM that has reacted after time t. Following a variation of the Guggenheim procedure, one obtains

$$e^{(a - b\alpha)kT} = \frac{(a - \alpha x')(b - x)}{(a - \alpha x)(b - x')} = \frac{(a - b\alpha)/(b - x') + \alpha}{(a - b\alpha)/(b - x) + \alpha}, \text{ and} \qquad (4)$$

$$\frac{1}{(b - x')} = \frac{e^{(a - b\alpha)kT}}{(b - x)} + \frac{\alpha(e^{(a - b\alpha)kT} - 1)}{(a - b\alpha)} \qquad (5)$$

where x' is the amount of DDM reacted after time t', and $t' - t = T$, a fixed interval that should be at least as great as one half-life. Plots of $1/(b - x')$ *vs.* $1/(b - x)$ yield a straight line. From its intercept i and slope m, both k and α may be determined.

$$\alpha = \frac{ai}{m - 1 + bi} \qquad k = \frac{2.303 \log m}{(a - b\alpha)T} \qquad (6)$$

Previous measurements of α have been made by reaction of a known quantity of DDM with acid and titration of the excess acid after the reaction was complete. However, the present method is readily applicable even with acids of low solubility or if only a small amount of solvent is available, as was the case for our measurements in deuterioethanol. Since the concentration of DDM is estimated spectrophotometrically, the magnitude of α is determined by the choice of its extinction coefficient. The accepted value for $\epsilon_{525\ m\mu}$ is 95[19]; measurements in this laboratory indicate that this is probably low, and we have corrected all product ratios recorded here by using the value ϵ = 102.[7] α-Values determined both kinetically and titrimetrically gave fair agreement. Typical data are given in Table VIII.

Acknowledgment.—We wish to thank Professor Chapman and his co-workers for an interesting discussion and for a preprint of their paper.[6] The experimental data in our paper and in theirs are complementary. Although there is essential agreement on the rate-determining step of the DDM reaction, the views on the partitioning steps differ.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINN., AND THE UNIVERSITY OF CHICAGO, CHICAGO, ILL.]

Conformations. VI. Vinyl–Allylic Proton Spin Couplings

BY EDGAR W. GARBISCH, JR.[1]

RECEIVED AUGUST 12, 1964

Three- (J_3) and four-bond (J_4) vinyl–allylic proton spin couplings have been estimated for a series of olefinic substrates by considering σ- and π-bond contributions to both couplings as a function of allylic proton conformations. The qualitative agreement between observed and estimated couplings suggests that π-bond contributions to J_3 and σ-bond contributions to J_4 are important and should not be neglected in approximating allylic proton conformations.

The assumption has been made often[2] that the magnitudes of both the three- and four-bond vinyl–allylic proton couplings will follow a $\cos^2 \phi$ and $\sin^2 \phi$ relationship, respectively, where ϕ is the dihedral angle be-

(1) Address correspondence to University of Minnesota.

(2) (a) E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4249 (1962); (b) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016 (1963); (c) L. D. Hall, *J. Org. Chem.*, **29**, 297 (1964); (d) R. M. Carman and R. D. Ward, *Australian J. Chem.*, **15**, 807 (1962); (e) ref. 4.

TABLE I[a]

ESTIMATED AND OBSERVED VINYL–ALLYLIC PROTON SPIN COUPLINGS

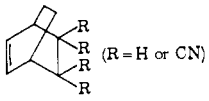
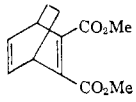
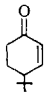
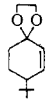
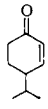
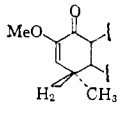
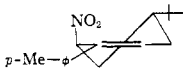
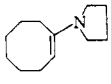
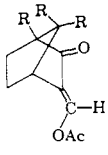
Structure	ϕ (deg.)	J_3^{est}	J_4^{est}	J_3^{o}	J_4^{o}
 (R = H or CN)	0	6.6	1.3	6.6	1.3
	0	6.6	1.3	6.1	1.6
Norbornenes	20	6.1	0.8	2.8–3.0[b]	0.55–0.7[b]
Norbornadiene	20	6.1	0.8	2.7[b,c]	0.95[b,c]
Cyclopentenone	60	3.6	−1.6	2.8	±2.2
4-Bromocyclopent-2-enone	60	3.6	−1.6	3.0	±1.3
	40 and 80	3.9	−1.4	2.1	±1.8
Cyclopentene	40 and 80[d]	3.9	−1.4	2.1[e] (3.7)[b]	−1.4[e]
Cyclohexenone	40 and 80	3.9	−1.4	3.7	±1.5
	40 and 80	3.9	−1.4	2.6	±1.3
	40 and 80	3.9	−1.4	3.5	±1.8
Cyclohexene	40 and 80[d]	3.9	−1.4	3.1[e] (3.6)[b] (3.6–4.1)[f]	−1.4[e]
	80	...	−2.4	[g]	±2.3
	80	...	−2.4	[g]	±2.1
	80	...	−2.4	[g]	±2.1[h]
	80	2.8	...	1.8–2.5[i]	...
	80	2.8 ($J_{2,3a}$)	...	2.5[j]	...
	40	5.0 ($J_{2,3e}$)	−0.3 ($J_{2,6e}$)	5.0[j]	None obsd.[k] (<1 c.p.s.)
Cycloheptene	15 and 135[d]	6.7	−0.2	5.7[e] (5.6)[l]	−1.0[e]
1-*tert*-Butylcycloheptene	15 and 135	6.7	−0.2	6.8	≲0.6 (W_H = 1.2)[m]
cis-Cyclooctene	25 and 145[d]	7.3	−0.1	7.8[e] (7.8)[l]	−0.7[e]
1-Methylcyclooctene	25 and 145	7.3	...	7.8	...
	25 and 145	7.3	−0.1	7.9	≲0.7 (W_H = 1.4)[m]
cis-Cyclononene	35 and 155[d]	7.7	−0.2	8.2[e]	−0.8[e]
cis-Cyclodecene	60 and 180[d,n] 0 and 120[d,n]	6.7	−0.6	6.8[e]	−0.8[e]
	160	...	−0.3	...	±0.8 (R = H) ±0 7 (R = Me)
Propene	60, 60, and 180°	6.3	−1.1	6.4[p]	−1.3[p]
3-Iodo-1-propene	60 and 180[q]	7.6	−0.8	7.7[q]	−0.4[q]
1,1-Dimethyl-3,3-di-*tert* butyl-1-propene	180[p]	11.6	...	11.4[p]	...
3,3-Di-*tert*-butyl-1-propene	180[p]	11.6	0.0	10.6[p]	−0.1[p]

TABLE I (*Continued*)

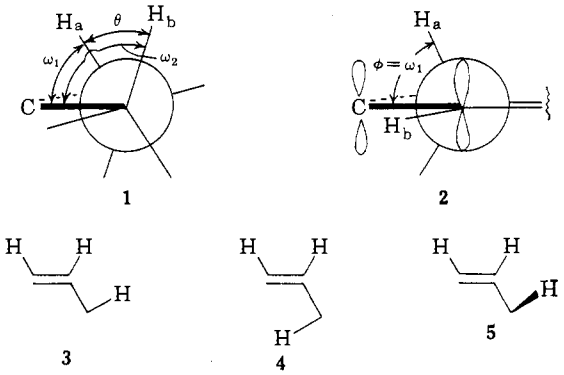
[a] Details of the analyses of the n.m.r. spectra previously unreported will be given in a forthcoming paper. For a brief discussion see ref. 10b. [b] P. Laszlo and P. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964). [c] F. S. Mortimer, *J. Mol. Spectry.*, **3**, 528 (1959). [d] This selection of angles will be discussed; see ref. 12. [e] Ref. 1b. [f] Range of couplings for over twelve substituted cyclohexene derivatives; see E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4243 (1962). [g] Undeterminable because of the likely existence of virtual coupling to a single homoallylic hydrogen. [h] Ref. 4. [i] Five structures were investigated giving an average coupling of 2.1 c.p.s.; see ref. 1d. [j] See ref. 1a. Upon re-examination of the spectrum of this alkene, the coupling parameters were found to be several tenths of a cycle larger than reported previously. [k] Based upon the full width at half-height (*ca.* 1 c.p.s.) of each component of the resonance of the vinyl proton (doublet of doublets). [l] Estimated by first-order analysis of the ^{13}C satellite pattern. [m] Full width at half-height of each component of the vinyl proton triplet resonance. [n] The four allylic hydrogens are taken to occupy four unique conformations. [o] These angles are based upon the known threefold torsional potential function for propene that exhibits a potential minimum at the conformation indicated with $\Delta E_t = 2$ kcal. mole^{-1}; see D. R. Lide and E. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957), and D. R. Herschback and L. C. Krisher, *ibid.*, **28**, 728 (1958). [p] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); see also ref. 11. [q] A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, **34**, 127 (1962).

tween the vinyl and allylic carbon–hydrogen bonds. It would appear that this assumption is valid approximately, providing π-bond contributions to the three-bond and σ-bond contributions to the four-bond couplings (J_3 and J_4, respectively) are negligible. Stereospecific π-bond contributions to J_3, in fact, are expected[3] and many examples of proton couplings over four σ-bonds[4] suggest that σ-bond contributions to J_4 may be expected also and that these contributions too may be stereospecific. For practical purposes of qualitatively estimating conformations of allylic hydrogens in unsaturated molecules, it would appear important to consider both σ- and π-bond contributions to the vinyl–allylic proton couplings, since the couplings observed represent the algebraic sum of the two contributions $[J^\circ = (\pm J^\sigma) + (\pm J^\pi)]$. Neglecting π-bond contributions to J_3 and σ-bond contributions to J_4 could lead to erroneous and mutually inconsistent conclusions regarding allylic hydrogen conformations—even at a qualitative level, since, depending upon the relative signs of the two contributions, these couplings may not pass through minima that approach zero as ϕ changes from 0 to 180°, or the couplings may approach zero at angles ϕ that differ markedly from those required by simple $\cos^2$ and $\sin^2$ relationships.

Molecular orbital[5] and valence bond[3] theory predict that J_3^π and J_4^π be given by the relationship $J_{3,4}^\pi = ka_H a'_H \sin^2 \phi$ where a_H and a_H' are the hyperfine couplings in the triplet state fragments H–$\dot{C}$ and H–C–$\dot{C}$, respectively. The signs of a_H and a_H' are known experimentally to be negative and positive, respectively,[3,6] and J_4^π, therefore, would be negative (proton spins parallel). In the three-bond couplings, both protons are coupled with opposite signs to the same π-electron and consequently the proton spins are antiparallel, giving a positive sign to J_3^π; J_3^π and J_4^π are expected, then, to be of opposite sign but of equal magnitude. Since J_3^σ appears to be positive consistently,[7] J_3^π is expected to augment J_3^σ, and when $\phi = 90$ and 270°, J_3^σ will be near zero but J_3^π will be at a maximum.

In accordance with theory[8] and experiment,[7] J_3^σ is expected to be positive and to be an approximate function of $\cos^2 \phi$. The theory of σ-bond dominated couplings over four bonds (H_a–C–C–C–H_b) is not understood[8a]; however, these couplings are known to be highly stereospecific and appear to be more sensitive to angles ω than to angles θ in **1** (propane fragment).[4,9] For example, in cyclohexane and bicyclo[2.2.1]heptane derivatives, 1,3-diequatorial and 2,6-diexo protons are found to couple by about 1–2 c.p.s. ($\omega \sim 0°$ and $\theta \sim 0°$); whereas, for 1,3-diaxial and 2,6-diendo protons, no detectable couplings are observed ($\omega \sim 120°$ and $\theta \sim 0°$).[4,9] For the olefinic systems **2** considered in this paper, one angle (ω_2) is kept constant at 0° while the second angle (ω_1) is varied. As a trial, J_4^σ is taken to be a function of $\cos^2 \phi$ ($= \cos^2 \omega_1$).

In order to derive a set of empirical equations that would qualitatively relate J_3 and J_4 to ϕ in structures bearing vinyl–allylic proton stereorelationships ranging from those shown in **3** to **4**, coupling parameters for $\phi \cong 0$, 180, and 90° have been estimated. For $\phi \cong 0°$, J_3^π and J^π are expected to be near zero.[3] The J_3 and J_4 values for bicyclo[2.2.2]octene ($\phi \cong 0°$) are expected, then, to be dominated by σ-bond contributions, and



$\phi = 0°$	$\phi = 180°$	$\phi = 90°$
$J_4^\sigma = +1.3$	$J_4^\sigma = 0.0$	$J_4^\sigma = 0.0$
$J_3^\sigma = +6.6$	$J_3^\sigma = +11.6$	$J_3^\sigma = 0.0$
$J_{3,4}^\pi = 0.0$	$J_{3,4}^\pi = 0.0$	$J_4^\pi = -2.6$
		$J_3^\pi = +2.6$

the observed values (see **3**) are taken as J_3^σ and J_4^σ, respectively.[10] For $\phi = 180°$, J_3^π and J_4^π are ex-

(3) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(4) For an excellent review of the subject of long range proton spin couplings, see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(5) H. M. McConnell, *J. Mol. Spectry.*, **1**, 11 (1957); and M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2704 (1963).

(6) M. C. R. Symons, "Advances in Physical Organic Chemistry," V. Gold, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 284 ff.

(7) C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962).

(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Phys. Chem.*, **64**, 1793 (1960).

(8a) NOTE ADDED IN PROOF.—Dr. Michael Barfield (private communication) has treated theoretically the problem of vinyl–allylic proton couplings (J_4) transmitted through four bonds (indirect coupling) using a semi-empirical valence-bond approach (*J. Phys. Chem.*, in press). Close agreement in J_4 is found between Dr. Barfield's approach and the empirical approach described in this paper for $0° \leqslant \phi \leqslant 90°$; however, as $\phi \rightarrow 180°$, significant positive couplings (*ca.* 1 c.p.s.) are predicted by valence-bond theory, whereas near-zero or small negative couplings appear at this time to be compatible with experiment (see later, and also Table I). The author wishes to thank Dr. Barfield for a preprint of his paper prior to publication.

(9) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, 233 (1964); F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); J. I. Musher, *Mol. Phys.*, **6**, 93 (1963); and L. D. Hall and L. Hough, *Proc. Chem. Soc.*, 382 (1962).

(10) (a) $J_{1,4}$ in bicyclo[2.2.2]octene is <0.4 c.p.s. and substantiates the conclusion that the observed positive J_4 ($J_{1,3}$) is dominated by σ-contributions; see E. W. Garbisch, forthcoming publication; (b) E. W. Garbisch, Jr., *Chem. Ind.* (London), **41**, 1715 (1964).

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^σ (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 $\phi = 90°$ (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 ($\phi \sim 80°$). This value is in qualitative agreement with the value of 3.4 c.p.s. that is estimated from the equation $J_{3,4}^\pi = ka_H a_H' \sin^2 \phi$.[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.

$$J_3^{\text{est}} \cong \begin{cases} 6.6 \cos^2 \phi + 2.6 \sin^2 \phi \ (0° \leqslant \phi \leqslant 90°) \\ 11.6 \cos^2 \phi + 2.6 \sin^2 \phi \ (180° \geqslant \phi \geqslant 90°) \end{cases}$$

$$J_4^{\text{est}} \cong \begin{cases} 1.3 \cos^2 \phi - 2.6 \sin^2 \phi \ (0° \leqslant \phi \leqslant 90°) \\ -2.6 \sin^2 \phi \ (180° \geqslant \phi \geqslant 90°) \end{cases}$$

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 $\pm 15°$ 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^π and J_3^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 $0° \leqslant \phi \leqslant 90°$, J_4 appears to pass through zero with a concurrent change of sign at about $40° > \phi > 20°$. (3) J_4^σ for $180° \geqslant \phi \geqslant 90°$, if significant, is probably small (<1 c.p.s.) and of a negative sign. For example, when $180° \geqslant \phi \geqslant 90°$, the frequently larger negative values of J_4° 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 $0° \leqslant \phi \leqslant 90°$, J_3 varies by about 4 c.p.s. with a maximum at about 6–7 c.p.s.; whereas, for $180° \geqslant \phi \geqslant 90°$, 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 $\phi \sim 0°$ to $\phi \sim 90°$ 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.

Acknowledgment.—The author is grateful for support from the Petroleum Research Fund (Grant No. 1536) of the American Chemical Society and for a criticism of the manuscript by Dr. Aksel Bothner-By.

(11) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(12) E. W. Garbisch, Jr., *ibid.*, to be published.

(13) M. Karplus, *ibid.*, **85**, 2870 (1963).

[CONTRIBUTION NO. 3099 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA]

Nitrogen-15 Magnetic Resonance Spectroscopy. II. Coupling Constants[1,2]

BY GERHARD BINSCH, JOSEPH B. LAMBERT,[3a] BRYAN W. ROBERTS,[3b] AND JOHN D. ROBERTS

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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 $J_{^{15}NH}$ and $J_{^{15}N^{13}C}$ to the hybridization of the orbitals involved. These relationships fail for $J_{^{15}NH}$ in diphenylketimine and for $J_{^{15}N^{13}C}$ in benzalmethylamine 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. Pauling[4] has maintained that these elements form predominantly p-type σ-bonds, while others[5] 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).

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(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, pp. 120 ff.

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