

on themselves are not entirely conclusive: they clearly decide between monoprotation at N(1) or at N(3), as well as with respect to the possibility of a 50 % protonation of both N atoms; the same is not true about the hypothesis of diprotonation, for the effect of N(3)—H⁺ on J₂₅, J₂₆ and J₅₆ is small.

The conclusion is also in accordance with the chemical shifts for the phenyl protons. Protonation at N(1) is expected to affect the *ortho* and *para* protons in the phenyl ring to a similar extent, whereas protonation at N(3), as in 2-phenyl-pyrimidine, is known to increase τ_2' ($=\tau_6'$) by 0.12 and decrease $\tau_3'=\tau_5'\simeq\tau_4'$ by about 0.34, this difference being explained in terms of an increase in the average dihedral angle of the two rings (1). Now, for 4-phenyl-pyrimidine, the effects of protonation on τ_2' ($=\tau_6'$) is -0.26 and that on $\tau_3'=\tau_5'\simeq\tau_4'$ is about -0.28 thus suggesting protonation essentially at N(1).

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SUBSTITUENT EFFECTS ON NUCLEAR SPIN COUPLING CONSTANTS

I — The effect of electron lone pairs on ¹³CH coupling constants

1 — COUPLING BETWEEN DIRECTLY BONDED NUCLEI

Most work on the interpretation of substituent effects upon the coupling constant (¹J_{CH}) between directly bonded ¹³C and ¹H nuclei has been partially based on an apparent proportionality between ¹J_{CH} values for simple hydrocarbons and the *s* character (ρ_{CH}) of the carbon hybrid orbital directed to the proton

$$^1J_{CH} \simeq 500\rho_{CH} \quad (1)$$

the type of hybridization considered being *sp*³, *sp*² and *sp*, respectively for saturated ($\rho = 1/4$), olefinic ($\rho = 1/3$) and acetylenic ($\rho = 1/2$) C atoms (1,2).

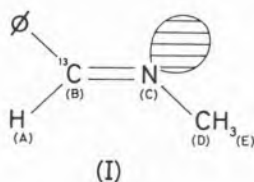
For substituted hydrocarbons, ¹J_{CH} usually increases as the electronegativity of the other atoms bonded to C increases, and this has then been ascribed chiefly to a rehybridization of the carbon atom, with an increase of the *s* character for the bond in question with respect to the parent hydrocarbon (3,4). Another important effect is due to changes in the effective nuclear charge of the C atom (2,5).

The rationalization of eq. (1) assumes several approximations, the most important one being a localized bond approach (1,4). It has recently been shown that this approach is not valid (as far as CH coupling constants are concerned) and that eq. (1) is purely accidental (6, 7, 8). The application of this equation to substituted hydrocarbons has also been criticized on the grounds of an underlying misunderstanding regarding the concept of orbital hybridization.

A new approach based on the Pople-Santry molecular orbital theory of nuclear spin coupling (9) and taking into account σ -electron delocalization has

been proposed (7). The total effect of a substituent group is divided into various contributions arising from: changes in Coulomb integrals (closed associated with electronegativity), changes in resonance integrals (taken proportional to overlap integrals), and presence of additional orbitals. The latter contribution is particularly important in the case of lone pair orbitals, and can be physically ascribed to partial delocalization of the lone pair electrons into the CH bonds.

The lone pair effect is highly stereospecific. For example, for the $\text{H}_2\text{C}=\text{X}$ system a sp^2 lone pair on X should increase J between the ^{13}C spin and the proton *cis* to the lone pair, and decrease J_{CH} for the *trans* situation. The effect may be of such magnitude as to overcome the one usually associated with the X electronegativity. This means that for a *trans* arrangement of the CH bond and the nonbonding orbital, an electronegative X substituent may lead to an abnormally low J_{CH} . In order to confirm this prediction we have obtained the spectrum (Figure) of the *syn* conformation of N-benzylidenemethylamine (naturally substituted ^{13}C molecules). The observed $J_{\text{C(B)H(A)}}$ value is 153.9 ± 0.5 Hz for the pure liquid and 153.5 ± 0.5 Hz for a 1:3 V/V



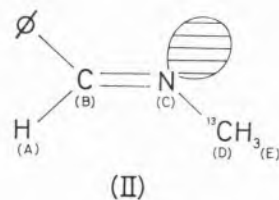
solution in CCl_4 . If the electronegativity factor was the most important one in determining changes in J_{CH} upon substitution, then an increase of J_{CH} by about 20 Hz with respect to ethylene would be expected, by analogy with the values for pyridines (10) (the effect of the phenyl group is negligible); however, the observed value is even smaller than that for ethylene [156.4 Hz (11)].

A similar but not so striking situation occurs in the case of the *syn* and *anti* forms of acetaldoxime. $J_{\text{CH}}^{\text{syn}} = 163 \pm 1$ and $J_{\text{CH}}^{\text{anti}} = 177 \pm 1$ Hz (12), although due account must also be taken of the hydroxyl group effect, and in N-methylaziridine for which J_{CH} values of 161 ± 1 and 171 ± 1 Hz have been reported (12).

2—COUPLING BETWEEN NON-BONDED NUCLEI

Electron lone pairs are also known to influence geminal CH coupling ($^2J_{\text{CH}}$) in systems of the type $\text{H}-\text{CX}-^{13}\text{C}$, the effect being similar to that for $^2J_{\text{HH}}$ (13).

Less is known about the influence of nonbonding electrons on vicinal CH ($^3J_{\text{CH}}$) coupling constants. Some predictions on this subject can be made by considering the effect of substituents on vicinal HH coupling and assuming a similar behavior for $^3J_{\text{CH}}$. This assumption is supported by the experimental evidence on geminal coupling constants (13) as well as on vicinal and long range couplings in hydrocarbons (14, 15). Since $^3J_{\text{HH}}$ in systems like $-\text{HC}=\text{CH}-\text{X}$ usually decreases upon increasing electronegativity of X (16, 17), the same will be expected for $^3J_{\text{CH}}$ in $-\text{HC}=\text{C}(^{13}\text{C})-\text{X}$. Some examples are found in the literature that substantiate this conclusion (18). Physically the changes in $^3J_{\text{HH}}$ (or $^3J_{\text{CH}}$) correspond to an electron transfer from the CH (or CH and CC) bonding molecular orbitals into the CX antibonding molecular orbital. For the case $-\text{HC}=\text{N}-^{13}\text{C}$ provided by N-benzylidenemethylamine



electron transfer occurs in the opposite direction, from the nitrogen nonbonding orbital into the antibonding CH and NC molecular orbitals.

Therefore, providing this is the dominant factor, a large (as compared to a corresponding unsubstituted hydrocarbon) $^3J_{\text{CH}}$ value is to be expected. In addition to the lone pair effect we have the electronegativity of N but this is not likely to influence $^3J_{\text{CH}}$ appreciably. This is supported by the fact that vicinal coupling constants in $-\text{HC}=\text{NH}^+-$ systems are almost the same as the corresponding ones through carbon atoms (19, 20).

Contrary to $^1J_{\text{CH}}$ (molecule I), $^3J_{\text{CH}}$ (molecule II) is not easily observed in the spectrum of N-benzylidenemethylamine having ^{13}C in natural abun-

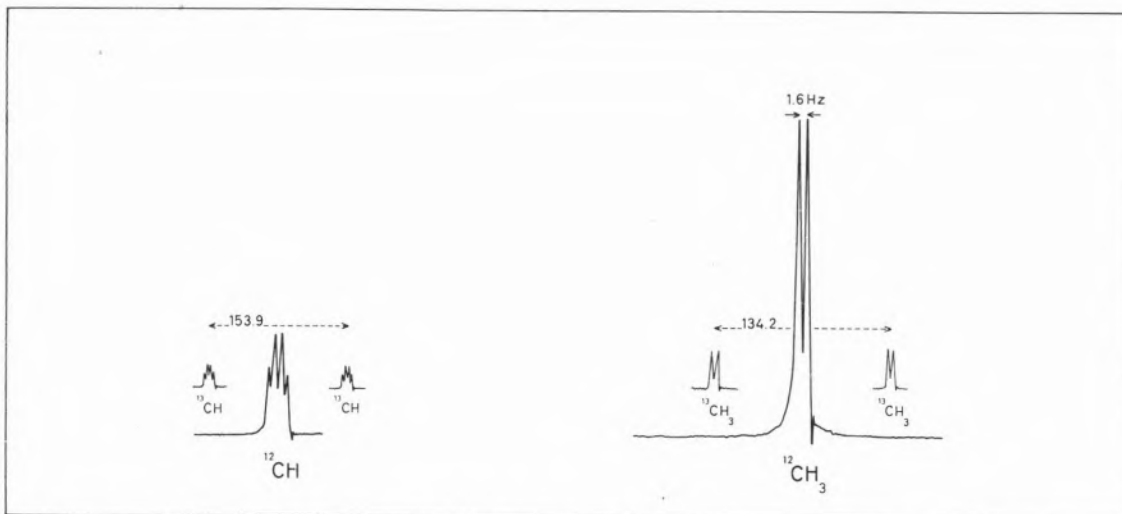


Fig. 1 — Proton spectrum of ^{12}C and ^{13}C molecules of syn-N-benzylidenemethylamine (the phenyl signal is not included).

dance, because the olefinic proton signals of (II) are now buried under the corresponding signal arising from the ^{12}C containing molecules. Their position was determined by spin-decoupling experiments, i.e. observing the CH_3 doublets (Figure) while irradiating with a variable frequency (close to the ^{21}CH signal) until the $\text{H}-\text{C}-\text{N}-\text{C}-\text{H}$ coupling (1.6 Hz) was eliminated with a minimum power. The value found is $+12.0 \pm 0.6$ Hz for the pure liquid and $+11.8 \pm 0.6$ Hz for a 1:3 V/V CCl_4 solution. This is quite large for a *cis* CH coupling constant. In fact, the value expected for a *cis* coupling — $\text{HC}=\text{C}^{13}\text{C}$ — is around $+5$ Hz (15, 21), in any case certainly less than $+7.4$ Hz which is the *trans* $^3J_{\text{CH}}$ in benzene (15).

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