NMR IN PARAMAGNETIC RADICAL COMPLEXES WITH ORGANIC LIGANDS

III. PARAMAGNETIC SHIFTS OF C^{13} NUCLEI

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The paramagnetic shifts of C^{13} nuclei were measured for some organic ligands in donor-acceptor complexes with a stable amine oxide radical. The magnitudes and signs of the hyperfine interaction constants were determined for these nuclei and complexes. Paramagnetic shifts were identified and the hyperfine interactions of C^{13} nuclei were determined in the complexes of contact and collision type. It appears that spin density transfer in such complexes takes place during the van der Waals interactions.

Stable organic radicals in solution form short-lived complexes with many organic molecules. In these complexes there occurs a delocalization of the unpaired electron of the radical to the molecular orbitals of the ligand which, in turn, leads to the paramagnetic shifts of its nuclei in the NMR spectra. The magnitude as well as the sign of the shift are related to the magnitude and the sign of the hyperfine interaction constant for these nuclei by the relationship

$$\Delta\omega = ap_{L}\frac{\gamma_e^2}{\gamma_p}\frac{\omega_0}{4kT}, \qquad (2)$$

where $\Delta\omega$ is the paramagnetic shift, γ_e and γ_p are the gyromagnetic ratios of the electron and of the nucleus, respectively, $p_L = \tau_L/\tau_S$ is the mole fraction of the complexes, and τ_L and τ_S are the lifetimes of the complex and of the free solvent molecule, respectively.

The equilibrium of the radical complex formation has the form

$$S + \dot{R} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} L. \qquad (2)$$

Then $p_L = K[R_\Sigma]/1 + K[S]$, where [S] is the concentration of free solvent molecules, $[R_\Sigma]$ is the overall radical concentration, and $K = K_1/K_2$. By combining (1) and (2) we obtain

$$\frac{\Delta\omega}{\omega_0} = \delta = -\alpha\frac{K[R_\Sigma]}{1 + K[S]}a, \qquad (3)$$

where α is equal to $7.5 \cdot 10^{-5}$ for the protons and $2.9 \cdot 10^{-4}$ for the C^{13} nuclei, respectively, at $T = 298°K$.

The proton resonance in paramagnetic radical complexes was investigated in the studies [1-3]. In the present paper we report the results of studies of the paramagnetic shifts of C^{13} nuclei in some organic ligands.

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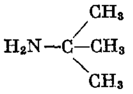
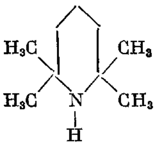
TABLE 1. Hyperfine Interaction Constants in Hydrogen-Bonded Complexes

Ligand	Hyperfine interaction consts. for C^{13}, Oe			
	$-\overset{\mid}{\underset{\mid}{C}}-$	γ-CH_3	γ-CH_2	δ-CH_2
	$-0{,}017$	$+0{,}02$		
	$-0{,}035$	$+0{,}045$	$+0{,}025$	$+0{,}03$

EXPERIMENTAL

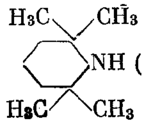
For the purpose of determining the C^{13} NMR spectra we prepared solutions of the stable 2,2,6,6-tetramethylpiperidine-N-oxide free radical in the following organic materials: tert-butyl amine, 2,2,6,6-tetramethylpiperidine, chloroform, carbon tetrachloride, and acetone (the free radical concentration was from 10^{-2} to 0.4 mole per 1 mole of the solvent).

The chemical shift changes of the organic ligands were determined at 15.1 MHz using a universal spectrometer operated in the time sharing mode [6]. The spectra were determined either by the double resonance absorption method, or by the semi-adiabatic transmission method (chloroform, carbon tetrachloride).

It should be pointed out that the line intensities in NMDR spectra of C^{13} are relatively insensitive to the presence of the free radical. Thus, at a concentration of $1 \cdot 10^{-2}$ mole of free radical per mole of tert-butyl amine, the nuclear Overhauser effect remains partially preserved, whereas at the radical concentration of $1 \cdot 10^{-1}$ mole per mole of the solvent the C^{13} nuclei line broadening is substantially absent, even though the Overhauser effect is not observed.

The chemical shifts were measured relative to the external CS_2 standard. In some cases an internal standard (cyclohexane) was also used.

RESULTS AND DISCUSSION

1. Amines and Cyclohexane. Since the paramagnetic shifts are related to the magnitude and the sign of hyperfine interactions of the ligand nuclei, they may be used for the study of the relationships involving the delocalization of the unpaired electron in various molecules. Of particular interest is the study of the spin density distribution in saturated systems. Since tert-butyl amine (I) and the amine  (II) form hydrogen bonded complexes with the radical, and since in these complexes the nitrogen atoms acquire a positive spin density [3], they were selected as model compounds for defining the relationships governing the spin density delocalization through the quaternary carbon atom in systems of this type.

Let us analyze the change in the shifts of the C^{13} nuclei in solutions of I in cyclohexane relative to the lines of carbon disulfide external standard resulting from the addition of radical to the system. In these solutions, cyclohexane was used as the internal standard since the molecules of this compound do not undergo complex formation with the radical and whose shift relative to the external standard should depend only on the change of the volume susceptibility os the solution in the presence of the radical. It is known that the line shifts in the NMR spectra (ΔH) caused by the change of the volume susceptibility of solutions obey the following relationship on addition of paramagnetic materials to their solutions:

$$\Delta H = \left(\alpha - \frac{4\pi}{3}\right) M, \qquad (4)$$

where M is the magnetization generated by the paramagnetic compound, and the quantity depends on the sample shape, and in the case of cylindrically shaped samples (as in our case) is equal to 2π. It follows from this relationship that the NMR line shift due to the effect of the paramagnetic material on the volume susceptibility of the solution must be positive. However, only the lines of the C^{13} cyclohexane nuclei are shifted toward low field, while the NMR proton lines of this compound are shifted toward high field. This is apparently due to the fact that the molecules of cyclohexane form weakly bonded complexes with the radical and in these complexes a delocalization of the unpaired electron takes place to the carbon atom orbitals. For this reason, its lines undergo a paramagnetic shift toward low field which overlaps a shift toward high field due to the change of volume susceptibility. The magnitude of the shift leads to the conclusion that these are complexes of the contact or of the collision type whose fraction is $p_L = b[R_\Sigma]$. This may be easily demonstrated by examining the rate of formation and of the decay of contact pairs. It follows from this examination that $b = (k/\nu_{\text{trans}})$, where k is the bimolecular rate constant of the

TABLE 2. Hyperfine Interaction Constants for C^{13} Nuclei in Contact Complexes, Oe

Atomic grouping(1)	C_6H_{12}	$H_2N-C(CH_3)_3$
CH_2	+0,05	—
CH_3	—	+0,06
$-\overset{\vert}{\underset{\vert}{C}}-$	—	+0,03

encounters (10^9-10^{10} liter/mole • sec), $\nu_{\text{trans}} \approx 10^{11}$ $\sec^{-1}$. Hence b ≈ 10^{-1}-10^{-2}. Then the paramagnetic shift in contact-type complexes may be expressed in accordance with Eq. (3) by the relationship

$$\delta_C = -ab[R_\Sigma]a_C. \tag{5}$$

For this reason, the total shift of the C^{13} nuclei of cyclohexane may be determined relative to the carbon disulfide external standard as follows:

$$\delta' = \delta_C' + \delta_a = -ab[R_\Sigma]a_C' + C[R_\Sigma], \tag{6}$$

where $\delta_{C'}$ is the paramagnetic shift in contact complexes, and $C[R_\Sigma]$ is the shift due to the change of the volume susceptibility, where C is the constant for a given solution. Molecules of tert-butyl amine must also form complexes with the radical. Then the paramagnetic shift of the C^{13} nuclei of this amine must be determined relative to the carbon disulfide lines by the following expression:

$$\delta'' = \delta_e + \delta_C'' + \delta_a = -\alpha\frac{K[R_\Sigma]}{1+K[S]}a_e - ab[R_\Sigma]a_C'' + C[R_\Sigma], \tag{7}$$

where δ_e is the paramagnetic shift in hydrogen-bonded complexes, determined by Eq. (3), and δ_C'' is the paramagnetic shift in contact complexes (equation 5). By combining (6) and (7) we obtain an expression for the C^{13} nuclei shift of the amine relative to the C^{13} nuclei shift of cyclohexane:

$$\delta = -\alpha\frac{[R_\Sigma]K}{1+K[S]}a_e + ab[R_\Sigma](a_C' - a_C''). \tag{8}$$

From the analysis of the paramagnetic shifts of the amine proton according to Eq. (3), we obtained the value K = 1.5 liter/mole. For the solutions studied by us, where [S] = 8.7, 6.5, and 4.5 M, K[S] >> 1. Then

$$\frac{\delta}{[R_\Sigma]} = -\alpha\frac{a_e}{(S)} + ab(a_C' - a_C'') \tag{9}$$

By examining the dependence of δ on $[R_\Sigma]$ and [S], it is possible to arrive at the a_e values for the C^{13} nuclei of tert-butyl amine listed in Table 1. In an analogous way we obtained the hyperfine interaction constants in the hydrogen-bonded complexes involving the amine (II) which are likewise shown in Table 1. In this case it was assumed that the shifts in contact complexes involving the C^{13} nuclei of CH_2 groups in II are the same as those in cyclohexane, whereas the shifts in these complexes corresponding to carbon atoms of the CH_3 groups and in quaternary carbon atoms are the same as those in I.

The table indicates that in I, $a_{C^{13}_{\text{quat}}}/a_{C^{13}_\gamma} = -0.85$, whereas in II, $a_{C^{13}_{\text{quat}}}/a_{C^{13}_{\text{quat}}} = -0.8$. In case of the di-tert-butyl amine oxide radical where only the absolute values of these constants are known, $|a_{C^{13}_{\text{quat}}}/a_{C^{13}_\gamma}| \simeq 1$ [5]. Apparently, the relationships governing the distribution of spin density in I and di-tert-butyl amine oxide are similar. However, for a definite conclusion to be reached, it is necessary to know the hyperfine interaction constant for the γ-CH_3 groups of the amine. Let us also point out that the relationships determining the spin density delocalization in the σ systems of amines are the same for open-chain amines (I) as well as for cyclic amines (II).

If the value of C [Eq. (6)] obtained from the paramagnetic shifts of cyclohexane protons relative to the external standard is used, then it is possible to obtain the hyperfine interaction constants in the contact complexes from (6) and (8). These values are listed in Table 2.

2. Chloroform and Carbon Tetrachloride. Paramagnetic shifts of the C^{13} nuclei were also identified in chloroform and in CCl_4. It is apparent that the radical undergoes π-complex formation with the carbon tetrachloride molecules with the use of the p orbitals of the unshared electron pairs of the chlorine atoms. The $a_{C^{13}}$ value for CCl_4 obtained from paramagnetic shifts was equal to + 1.3 Oe. This indicates that positive spin density is transferred from the chlorine atoms to carbon.

The transfer of the unpaired electron from the radical to chloroform may take place in two ways: 1) By complex formation involving hydrogen bonding (K = 6 • 10^{-1} liter/mole [3]) and by π-complex formation involving chlorine atom participation (K = 5 • 10^{-2} liter/mole [3]).

The large difference between the equilibrium constants for these complexes leads to the conclusion that the main contribution to the observed paramagnetic shift in chloroform is due to the hydrogen-bonded complexes, where a_{C}^{13} = 1.9 Oe, which is in agreement with the molecular models of these complexes [3].

Taking into account the shifts in contact complexes, we obtained from the paramagnetic shifts of the C^{13} nuclei values of the hyperfine interaction constants for the carbonyl carbon atoms as well as for the methyl carbon atoms equal to 0.04 and 0.25 Oe, respectively. It may be assumed that the spin density is transferred to acetone molecules mainly through the methyl groups and not through the double bond. The negative value of the hyperfine interaction constant for the protons in these groups (−0.015 Oe) leads to the assumption that they form hydrogen-bonded complexes with the radical.

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