^{13}C-NMR SPECTRA OF 3-METHYLSYDNONE AND 3-METHYLSYDNONEIMINE HYDROCHLORIDE

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The $\delta(C^{13})$ values of the ring carbon atoms for the C^{13}-NMR spectra of 3-methylsydnone and 3-methylsydnoneimine, described for the first time, are compared with the values calculated by the Karplus−Pople method. The interrelationship between the $\delta(C^{13})$ values of conjugated carbocycles, heterocycles, alkenes, and a number of carbonyl-containing compounds and the effective charges of the corresponding carbon atoms calculated by the complete neglect of differential overlap (CNDO/2) method is analyzed thoroughly.

In a continuation of our study of the interrelationship between the electronic structure and physicochemical properties of sydnones and sydnoneimines [1] we have for the first time obtained the C^{13}-NMR spectra of aqueous solutions of 3-methylsydnone (I) and 3-methylsydnoneimine hydrochloride (II). The C^{13}-NMR spectra of I and II under proton-decoupling conditions consist of a set of three signals, the assignment of which to the corresponding carbon atoms is unambiguous (Table 1).
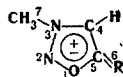
I R=O; II R=NH$_2^+$Cl$^-$

The diamagnetic (σ_d) and paramagnetic (σ_p) components of the chemical shifts of I and II calculated by the Karplus−Pople method [2, 3] from the formulas presented in [4], in which $\Delta E_{av} = 10$ eV and the $P_{\mu\nu}$ values were obtained for the 3-methylsydnone and 3-methylsydnoneimine cation by the CNDO/2 (complete neglect of differential overlap) method [5], are presented in Table 1.* The calculations, in agreement with the experimental results, indicate a shift to weak field of the $\delta(C^{13})$ signal of the C_4 atom of the sydnoneimine cation with respect to the signal of the C_4 atom of sydnone. The calculated chemical shifts of the signals of the C_4 atoms with respect to C_5 for I and II (65 and 61 ppm) are also in agreement with the experimental values within the limits of the standard deviation ($\Delta\delta$ 15 ppm) usually obtained for correlations calculated by semiempirical methods and the experimental $\Delta\delta(C^{13})$ values [4, 7, 8].

The chemical shifts of the C^{13} nuclei of a large group of organic compounds (including five- and six-membered carbo- and heterocycles, their ionized forms, substituted benzenes, ethylene, allene, and a number of carbonyl-containing compounds) are compared with the effective charges (Δq_{eff}) of the corresponding carbon atoms calculated by the CNDO/2 method in Fig. 1. The experimental and calculated values were taken from [4, 7-15] or were calculated by the CNDO/2 method. For compounds that do not contain carbonyl groups the signal as a whole is shifted to low field as the positive value of Δq_{eff} increases. The C_4 atoms in derivatives I and II, which have the highest negative effective charges of all of the examined heterocycles, are characterized by the greatest shifts of the $\delta(C^{13})$ signals to strong field. In contrast to the points for the C_4 atoms, the points for the C_5 atoms of I and II deviate somewhat from the correlation

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*The geometry of 3-methylsydnone was estimated from the data in [6], and the C_5-N_6 bond length in II was increased to 1.39 Å.
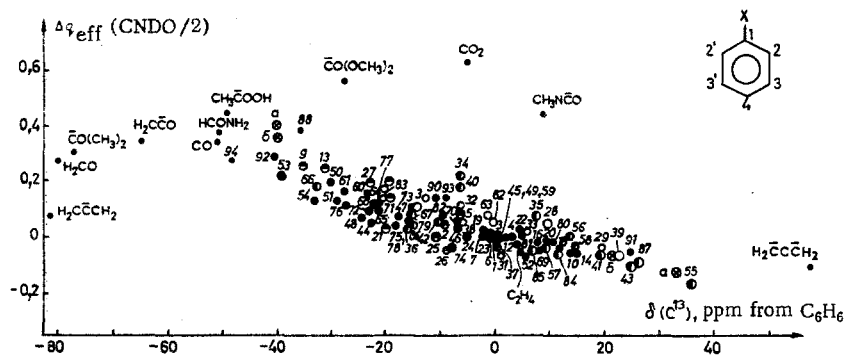
Fig. 1. Dependence of the $\delta(C^{13})$ values of six-membered (●) and five-membered (O) conjugated carbo- and heterocycles, their ionized forms (◐), a number of carbonyl-containing compounds, ethylene, and allene on the effective charges of the corresponding carbon atoms calculated by the CNDO/2 method. The data for the carbon atoms adjacent to the substituents in substituted benzenes are denoted by (◖), and the data for I and II are denoted by (⊕), The assignments, are as follows (the generally accepted number of the corresponding atoms of the examined systems are presented in parentheses): 1) benzene; 2) toluene (1); 3) toluene (3); 4) toluene (4); 5) chlorobenzene (1); 6) chlorobenzene (2); 7) chlorobenzene (3); 8) chlorobenzene (4); 9) fluorobenzene (1); 10) fluorobenzene (2); 11) fluorobenzene (3); 12) fluorobenzene (4); 13) anisole (1); 14) anisole (2); 15) anisole (3); 16) anisole (4); 17) aniline (1); 18) aniline (2); 19) aniline (3); 20) aniline (4); 21) nitrobenzene (1); 22) nitrobenzene (2); 23) nitrobenzene (3); 24) nitrobenzene (4); 25) benzonitrile (1); 26) trifluoromethylbenzene (1); 27) phenol (1); 28) pyrrole (2); 29) pyrrole (3); 30) furan (2); 31) furan (3); 32) imidazole (2); 33) imidazole (4,5); 34) imidazole cation (2); 35) imidazole cation (4, 5); 36) imidazole anion (2); 37) imidazole anion (4, 5); 38) pyrazole (3); 39) pyrazole (4); 40) pyrazole cation (3, 5); 41) pyrazole cation (4); 42) pyrazole anion (3, 5); 43) pyrazole anion (4); 44) pyridine (2); 45) pyridine (3); 46) pyridine (4); 47) pyrazine (2, 3, 5, 6); 48) pyridazine (3, 6); 49) pyridazine (4, 5); 50) pyrimidine (2); 51) pyrimidine (4, 6); 52) pyrimidine (5); 53) triazine; 54) tetrazine; 55) indenyl anion (1, 3); 56) indenyl anion (2); 57) indenyl anion (4); 58) indenyl anion (5); 59) indenyl anion (8); 60) purine (2); 61) purine (4); 62) purine (5); 63) purine (6); 64) purine (8); 65) purine anion (2); 66) purine anion (4); 67) purine anion (6); 68) quinoline (2); 69) quinoline (3); 70 quinoline (4); 71) quinoline (9, 10); 72) isoquinoline (1); 73) isoquinoline (3); 74) isoquinoline (4); 75) quinazoline (2); 76) quinazoline (4); 77) quinazoline (9); 78) quinoxaline (2, 3); 79) quinoxaline (9, 10); 80) benzimidazole (4, 7); 81) benzimidazole (5, 6); 82) benzimidazole (8, 9); 83) benzimidazole anion (2); 84) benzimidazole anion (4, 7); 85) benzimidazole anion (5, 6); 86) benzimidazole anion (8, 9); 87) cyclopentadienyl anion; 88) 2-pyridone (2); 89) 2-pyridone (3); 90) 2-pyridone (4); 91) 2-pyridone (5); 92) 1-methyl-3-pyridone (3); 93) 4-pyridone (2); 95) 4-pyridone (4);

of the calculated and experimental $\Delta\delta(C^{13})$ values found in [4]. In the latter case the disregard of overlap of the AO in the calculations of the $\Delta\delta$ values may be a possible reason for the deviation [11]. However, the realization of a joint correlation of $\delta(C^{13})$ and Δq_{eff} (C) for the carbon atoms adjacent to H or X (in C_6H_5X) and also of the carbon atoms of the C = R groups in I and II and of the C = O groups in the pyridones is not obligatory, inasmuch as the change in the local charges of the carbon atoms of the carbonyl groups does not determine the chemical shifts of the nuclei of these atoms, in contrast to the Δq_{eff} (C) changes in the indicated cyclic conjugated systems. This follows from the fact that in acyclic carbonyl-containing

TABLE 1. Calculated and Experimental Characteristics of the C^{13}-NMR Spectra of 3-Metylsydnone (I) and 3-Methylsydnoneimine Hydrochloride (II)

	Atom	σ_d	σ_p	$\sigma_d+\sigma_p$	δ (C^{13}), ppm (from TMS)
I	C_4	58.93	−247.68	−188.75	97.3
	C_5	54.65	−308.46	−253.81	170.4
	C_7				40.1
II	C_4	58.41	−254.16	−195.75	104.5
	C_5	55.00	−312.17	−257.17	170.1
	C_7				40.8

molecules the shift of the signal to weak field increases as the positive Δq_{eff} values decrease, whereas, for example, the values that characterize the carbon atoms of ethylene, allene, and the CH_2 group of ketene [δ(C^{13}) 126 ppm from C_6H_6 [13] and Δq_{eff} − 0.28 au] in coordinates of δ(C^{13}) and Δq_{eff} lie on a separate correlation line, the slope of which corresponds to the shift of the δ(C^{13}) signals to strong field as the electron density on the atom increases.

Our observed analogy in the C^{13}−NMR spectra of 3-methylsydnone and 3-methylsydnoneimine hydrochloride is yet another indication of the validity of the existing concepts [16] regarding the structure of the cation in sydnoneimine salts. The proposed structure of the cation is also confirmed by the presence in the PMR spectrum of a freshly prepared solution of II in D_2O of a broadened (due to H−D exchange) signal [δ^H 7.9 ppm from tetramethylsilane (TMS)] corresponding to the NH_2^+ group. Signals of this sort were previously identified [17] for betaine 3-hydroxysydnoneimines (δ^H 7.1-7.8 ppm).

EXPERIMENTAL METHOD

The measurements were made with XI-100 (with an operating frequency of 25.2 MHz) and PFT-100 (25.15 MHz) spectrometers under Fourier transformation conditions with suppression of the spin−spin coupling of the C^{13} nuclei and the protons at 40°. The concentrations of I and II in H_2O and D_2O were ~30%. Ampuls with outer diameters of 5 and 8 mm were used to record the spectra. The chemical shifts measured with respect to the internal standard (dioxane) were converted with respect to TMS or benzene. The width of the pulses was 9 μsec, and the interval between the pulses was 20 sec at 100-fold accumulation.

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