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EFFECTS OF FORMATION OF AN ADDUCT OF TRIALKYLPYRAZOLE WITH $CdBr_2$ IN ^{15}N NMR

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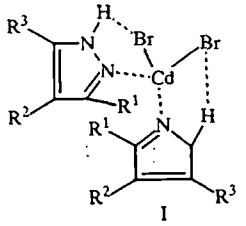
The ^{15}N NMR chemical shifts for the analogous diamagnetic adduct of 3,5-dipropyl-4-ethylpyrazole with cadmium dibromide were measured to obtain reference data for estimating the isotropic paramagnetic NMR shifts of nitrogen in paramagnetic adducts of alkylpyrazoles with transition metal salts. The ^{13}C and ^{1}H NMR spectra were obtained for the same adduct in conditions of frozen protometallotropic rearrangement of the hydrogen in the NH group and the temperature-dependent NMR spectra of isotopes of Cd were made.

Data on the chemical shifts of nitrogen in adduct (I) of cadmium dibromide with the homolog of 3,5-diethyl-4-methylpyrazole, 3,5-dipropyl-4-ethylpyrazole, were used previously for reading the isotropic paramagnetic NMR shift in adducts of 3,5-diethyl-4-methylpyrazole with nickel and cobalt dibromides [1].



I

$R^{1,3}$ = $\overset{\alpha}{CH_2}\overset{\beta}{CH_2}CH_3$

$R^2 = CH_2CH_3$

Similar data on the NMR of isotopes of nitrogen are of interest for evaluating the effect of the metal in diamagnetic complexes on the NMR of nitrogen, which has virtually not been studied for pyrazole ligands. They are also important for studying the effect of complexation on the protometallotropic rearrangements so characteristic of NH-pyrazoles.

The ^{15}N, ^{13}C, and ^{1}H NMR spectra for adduct I and the temperature-dependent NMR spectra of isotopes of Cd were recorded in the present study to obtain the reference data required in estimating the isotropic paramagnetic NMR shifts of nitrogen in paramagnetic adducts of alkylpyrazoles with transition metal salts. The ^{1}H and ^{13}C NMR studies were necessary for selecting the conditions in which metal–hydrogen "shuttling" is frozen. For some diamagnetic adducts of alkylpyrazole ligands, these conditions were partially investigated previously [2, 3], but the NMR of the nitrogen in the adducts was not investigated in the cited studies. The data obtained are illustrated in Figs. 1-3. It was found that due to a small difference in the chemical shifts, lines R^1 and R^3 can be observed in the ^{1}H NMR spectrum separately only at 218 K and below (Fig. 1); at 233 K and lower, separate observation of the ^{13}C lines, including $C_{(3)}$ and $C_{(5)}$, is possible (Fig. 2).

The following hypothetical assignments (in the δ_C scale) were made for the lines in the ^{13}C NMR spectrum: 14.08) forbidden lines of α-CH_2 in R^1 and R^3, 15.91) CH_3 in R^2; 16.00) α-CH_2 in R^2 (see extended part of the spectrum at 13.50-16.50 ppm); 22.53) CH_3 in R^3; 23.50) CH_3 in R^1; 26.05) β-CH_2 in R^3; at 28.12) β-CH_2 in R^1; approximately 77.00 ppm)

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solvent lines; 118.59, 142.98, and 152.32) $C_{(4)}$, $C_{(5)}$, and $C_{(3)}$ of the ring, respectively. These assignments are based on the empirical correlations in [2-5] and on the ratio of the intensities of the carbon lines determined with the values T_{1C} of the ^{13}C relaxation times. The qualitative estimation of T_{1C} is based on a comparison of the intensities of the lines with comparatively small lags between pulses (of the order of 1.5 sec). Since the motion (rotational diffusion) of the molecule is far from spherical in shape and is anisotropic, the correlation times of the dipole interaction of the ^{13}C and ^{1}H nuclei are different. The lines of the less mobile and thus more rapidly relaxing nuclei belonging to α-C are saturated to the least degree, like the lines of the $C_{(4)}$ atom for which the internuclear vectors $\bar{r}_{CH}$ are directed approximately parallel to the axis of the most stable rotation of the molecule of the adduct.

The ^{15}N NMR spectra were made in selective proton irradiation (INEPT) at the temperature of 233 K in deuterochloroform or at 203 K in deuteroacetone. In the last case, a good result was obtained for the line of the $N_{(1)}$ atom (J_{NH} ~ 94 Hz, Fig. 3a). The difference between the chemical shifts of the nitrogen atom found in these experiments was 4.3 ppm, and the NMR line of this atom in acetone solution was shifted to the weaker field. The chemical shifts of the $N_{(2)}$ atom can be estimated with the data from the corresponding experiment on $\{3CH_2\}-N_{(2)}$ ($^3J_{NH}$ ~ 2 Hz, ^{15}N signal at the noise level), confirmed by the results of taking the ^{14}N NMR spectrum (Fig. 3b).

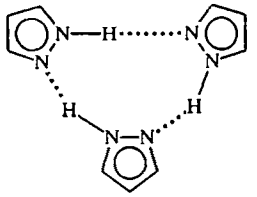
NMR of $^{111,113}Cd$ isotopes did not provide any important information (chemical shifts from an aqueous solution of $CdCl_2$ of 280-290 ppm in the temperature range of 233-293 K, line width $\Delta\nu$ = 10-15 Hz). No indications of the presence of SSCC of the nuclei of cadmium isotopes with ligand protons or carbons could be found.

The application of NMR to the study of metal coordination compounds is based on the presence of complexation effects on the parameters of the NMR spectra — the chemical shifts and SSCC. With respect to the chemical shifts δ_i, the complexation increments $\Delta^k\delta_i$ were determined in the linear approximation by comparing the chemical shifts of the nucleus j in the "free" ligand $\delta^L{}_j$ and in the complex $\delta^K{}_j$ according to the equation:

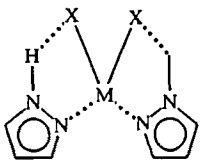
$$\Delta^k\delta_i = \delta^K{}_i - \delta^L{}_i.$$

Hence, the importance of the data on the chemical shifts in the ligand and the importance of understanding that the concept of a "free" ligand is inaccessible in the idealization experiment. Special difficulties in determination of reference chemical shifts arise in attempting to describe the effects of complexation in the NMR of pyrazoles, since there are almost no published data on the chemical shifts of nitrogen in frozen "shuttling" due to the complexity of obtaining the conditions necessary for this. According to the data in [2], it is evident that adduct (I) investigated has the structure reported above.

The pyrazole molecule or its derivative is characterized by the presence of neighboring nitrogen atoms of so-called pyrrole (−NH−) and pyridine (=N−) types in the ring. The formation of oligomers and prototropic exchange is the unavoidable fate of any pyrazole derivative if a hydrogen atom which participates in intermolecular and, as the results of studying some adducts of pyrazole with metal salts, intramolecular (in the adducts) hydrogen bonds is the substituent in position 1 at the pyrrole nitrogen.



II



III

The method of ^{13}C NMR was successfully used in [4] for solid derivatives of pyrazole, but it was found that for 3,5-dimethylpyrazole at room temperature, prototropic rearrangement neutralizes the chemical shifts of the substituents even in the crystal! This stimulated the same group of investigators to synthesize 3,5-dimethylpyrazole isotopically enriched with ^{15}N and to study it in the solid phase and on cooling (to −50°C). It was found in [15] that a ring-shaped trimer of 3,5-dimethylpyrazole is formed in the solid phase (structure of type II with three hydrogen bonds of the $N_{i(1)}-H...N_{j(2)}$ type, where subscripts i, j belong to different molecules of 3,5-dimethylpyrazole), and the mechanism of prototropic rearrangement includes "jumping" of protons simultaneously for all hydrogen bonds. This hydrogen-bond structure has an important characteristic common to the structure of the complex of pyrazole NH with a metal salt (for example, $MX_2\cdot$(III)) — the formation of an additional hydrogen bond by the NH hydrogen. Transfer of alkylpyrazole bases to the solid phase or the formation of adducts with metal

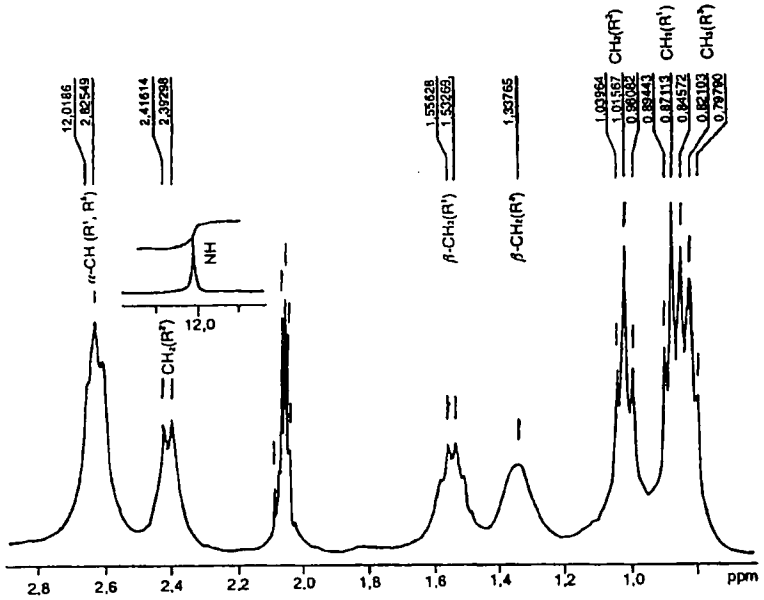


Fig. 1. Proton magnetic resonance spectrum of a solution of adduct I in deuteroacetone at 218 K. δ_H Scale (ppm).

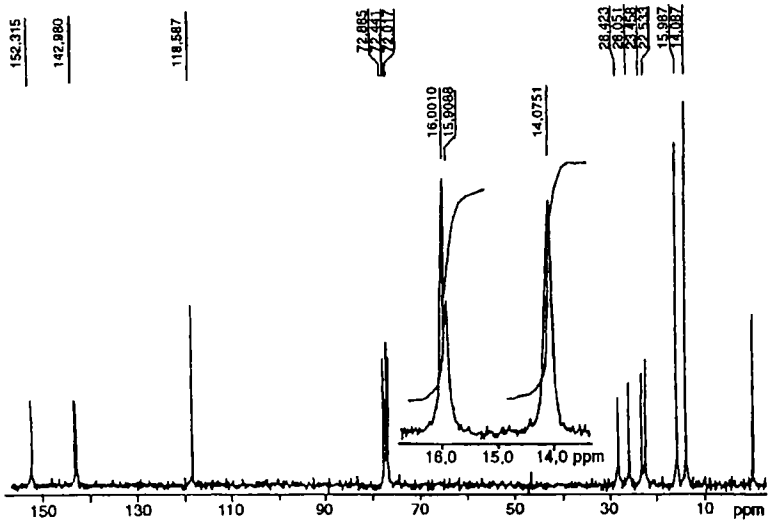


Fig. 2. ^{13}C NMR spectrum of a solution of adduct I in deuterochloroform at 233 K. δ_C Scale (ppm). See text for hypothetical assignments.

salts thus results in effects of "freezing" of prototropic rearrangement of a similar nature, which is in agreement with the mechanisms (similar for solid and adduct) of formation of intermolecular associates in the first case and intramolecular bonds by hydrogen bridges in the second case.

The chemical shifts of nitrogen at 233 K on conversion to the standard scale were obtained in [5] by the method of cross polarization on rotation by the magic angle for 3,5-dimethylpyrazole 95% enriched with ^{15}N isotope: δ_N of 279 ppm for the pyridine $N_{(2)}$ atom and 205 ppm for the pyrrole $N_{(1)}$ atom bound with hydrogen. The values of δ_N for the pyrazole ring nitrogen in the complex of 3,5-diethyl-4-methylpyrazole with cadmium dibromide were obtained in deuteroacetone in the present study and were equal to 244 ppm for $N_{(2)}$ and 195.5 ppm for $N_{(1)}$. We consider it valid to compare these values with those reported in [5] since according to the data in [6], the increments of the alkyl substituents at the carbon atoms of the pyrazole ring in the chemical shifts of pyrazole nitrogen atoms are small (2-5 ppm), and the difference in the corresponding shifts in solution and solid are scarcely higher in order of magnitude than for the ^{13}C nuclei (according to the data in [4], under 2 ppm). The effect of the temperature and solvent on the nitrogen shifts is of the same order (see above).

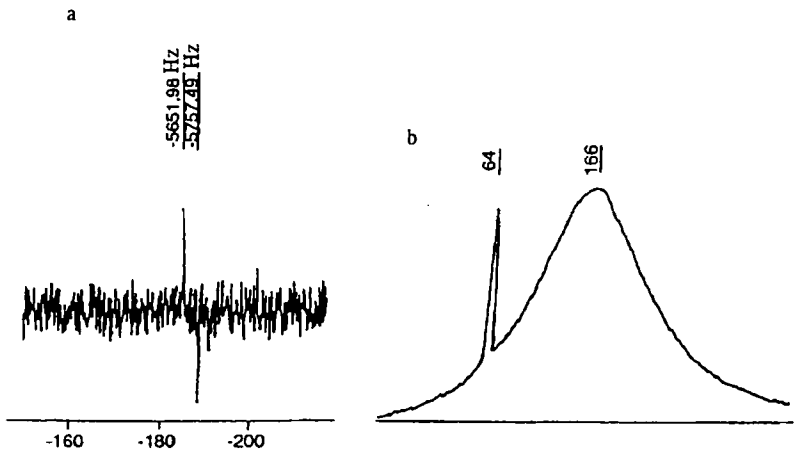


Fig. 3. NMR spectra of isotopes of nitrogen in adduct I: a) doublet signal of the ^{15}N atom in the NH group of a solution of adduct I in deuteroacetone at 203 K in the INEPT $^{15}N-\{1H\}$ mode. Scale in ppm of ^{15}N-nitromethane external standard; b) ^{14}N NMR line of a solution of adduct I in deuterochloroform at a frequency of 21 MHz at room temperature (the line of gaseous nitrogen dissolved in chloroform was used as the only reference. The shifts (ppm) to the strong field relative to NO_3^- are indicated).

The reported chemical shifts for the nitrogen atoms of 3,5-dimethylpyrazole of the 3,5-diethyl-4-methylpyrazole homolog can be set as the starting shifts with an accuracy of up to $\pm$5-6 ppm, although they were obtained not for the "free" but for the hydrogen-bound ligand and in solid DMP. It follows from this that in Levy's book [7] (Table 3.26), the chemical shift of the nitrogen atoms in the NH group in pyrazole is erroneously indicated as δ_N 245.5 in $CDCl_3$ and 199.4 ppm in methanol. It is obvious (see also [7], Table 3.28) that the average values of the shifts of $N_{(1)}$ and $N_{(2)}$ are reported in [7] (Table 3.26).

The increments of complexation with cadmium dibromide are 30-40 ppm for the $N_{(2)}$ atom according to our estimations (in reading from the free ligand, the increment would most likely have the same sign, that is, it could correspond to a more important (!) shift to the strong field) and approximately 10 ppm for NH. For complexes of this kind with the salts of paramagnetics [1], the values of the isotropic paramagnetic shift at 300 K are higher than the values of the increments in the chemical shifts of complexation with diamagnetic metals, by 10^3 times for $N_{(2)}$ and by 10^2 times for $N_{(1)}$.

We will now attempt to compare the effects of the different factors on prototropic rearrangements. This concerned measuring and interpreting the chemical shifts and other NMR parameters of the nitrogen atom only for adduct I. In this example, we see that not only (as demonstrated in [4, 5]) "freezing" or precipitation, i.e., transition to the crystalline form of the substance, but also to a slightly smaller degree, formation of adducts at a temperature 20 K lower (as demonstrated previously in [2, 3] and in the present study), correspond to freezing of prototropic rearrangements. What is common to these two processes? We found that association of the molecules with the formation (fixation) of hydrogen bonds is common to them. This involves self-association in the solid and association with a molecule of the salt in the adduct.

EXPERIMENTAL

The NMR spectra were made on a Bruker AC-200 spectrometer in deuterochloroform (above 233 K) or in deuteroacetone (at 233 K and lower to 203 K). The lower (by 30 K) melting point and lower viscosity (by 1.75 times at room temperature) are an advantage of acetone. The ^{14}N NMR spectra were made on a Bruker MSL-300 spectrometer in conditions of averaging the $N_{(1)}$ and $N_{(2)}$ shifts.

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