

NUCLEAR QUADRUPOLE RESONANCE OF ^{35}Cl IN HYDROGEN BONDED COMPLEXES*

BY J. PIETRZAK AND B. NOGAJ

Solid State Spectroscopy Laboratory, Institute of Physics, A. Mickiewicz University, Poznań

Z. DEGA-SZAFRAN AND M. SZAFRAN

Institute of Chemistry, A. Mickiewicz University, Poznań**

(Received March 21, 1977)

^{35}Cl NQR spectra from complexes of trichloroacetic acid (A—H) and bases (B) are studied at 77 K for pK_a ranging from -10 to $+11$. A characteristic dependence of $\Delta\bar{\nu}_Q$ vs ΔpK_a is obtained. The proton transfer problem is discussed, and good agreement with the dielectric and spectroscopic data of others is achieved.

2. Introduction

Nuclear quadrupole resonance permits the determination of the electric field gradient at the nucleus under investigation. When a complex is formed, the electron structure surrounding the resonating nucleus, and thus the field gradient, undergo a modification. From the latter, one can draw conclusions concerning the amount of charge transferred within the complex as well as the direction in which the transfer occurred. Numerous papers deal with "charge-transfer" complexes by the method of NQR [1-8].

Especially interesting are complexes involving hydrogen bonds. Lucas and Guibe [5] carried out an assessment of the charge transferred in complexes of chloroform and various bases. Chihara and Nakamura [6] studied complexes of pyridine and chloroacetic acids, and found them to exhibit proton transfer.

After Mulliken [9], a system of two molecules forming a complex can be described in terms of a wave function ψ_N , given by the superposition of functions describing the states of the complexes with normal and ionized hydrogen bond (ψ_0 and ψ_1 , respectively)

$$\psi_N = a\psi_0[(\text{A}-\text{H})(\text{B})] + b\psi_1[(\text{A})^-(\text{H}-\text{B})^+]. \quad (1)$$

* This work was financially supported by the Polish Academy of Sciences under program MR. I. 9. 4. 4. 3. and 03. 10. 6. 02. 05.

** Address: Instytut Chemii, Uniwersytet A. Mickiewicza, Grunwaldzka 6, 60-780 Poznań, Poland.

Once the preceding function is known, the electric field gradient at the point of the nucleus can be obtained from the formula [10]

$$q = \sum_i e_i \langle \psi_N | (3 \cos^2 \theta_i - 1) / r_i^3 | \psi_N \rangle + q_{\text{ex}}, \quad (2)$$

where summation extends over all electrons of the complex having the coordinates (r_i, Q_i) with respect to the central point of the system i.e. the point of the nucleus under consideration. q_{ex} denotes the gradient due to all the other molecules of the crystal. Calculations lead to the following formula for the NQR frequency of hydrogen bonded complexes

$$\nu_Q = \nu'_0 + b^2 \Delta \nu_{\text{pt}}, \quad (3)$$

where $\nu'_0 = \nu_0 + \nu_{\text{ex}}$ and $\Delta \nu_{\text{pt}} = \nu_{\text{pt}} - \nu_0$.

ν_0 is the frequency for the complex with normal hydrogen bond and ν_{pt} that for the complex with proton completely transferred. The problem of proton transfer within the hydrogen bond of the complex and that of the degree of transfer as a function of the nature of the acid and base, appeared to us to be of much interest. Accordingly, so as to omit no aspect of the problem, we proceeded to a study of the complexes of trichloroacetic acid and a variety of bases, ranging from the weakest to very strong ones.

2. Experimental

Complexes were obtained in the form of crystals by dissolving the base in a small volume of chloroform and adding trichloroacetic acid (TCA) in a small volume of carbon tetrachloride. The complexes were recrystallized from chloroform-carbon tetrachloride mixture (3 : 1). Correct analyses were obtained. The melting points were: TCA · 4-methylpyridine N-oxide, 56°C; TCA · 3-bromopyridine, 56°C; TCA · 4-methylquinoline, 98–99°C; TCA · 4-methylpyridine, 83–84°C; TCA · 2,4-dimethylpyridine, 68–69°C; TCA · 2,6-dimethylpyridine, 78°C; TCA · 2,4,6-trimethylpyridine, 63–64°C.

The NQR spectrum of ^{35}Cl isotope in the complexes was observed by means of a spectrometer with synchronized superreactive detector [11] and modulated frequency similar to the setup of Tong [12]. We applied a system of automatic frequency calibration, marking the recorder tape. The accuracy of the position of the frequency marks was assessed as ± 1 kHz. The measurements were performed at 77 K immersing the sample and spectrometer generator coil directly in liquid nitrogen in the Dewar flask.

3. Results and discussion

Table I gives the NQR line frequencies, measured for the complexes, in the order of increasing strengths of the base (pK_a). The data of Chihara and Nakamura [6, 13], as well as the latest results of Poleshchuk et al. [14] for other complexes of TCA, are included in the present analysis.

All the complexes exhibit a shift in NQR spectrum towards lower frequencies as compared with TCA. This proves that, on formation of a hydrogen bond, the electron

TABLE I

Frequencies of the NQR line of ^{35}Cl isotope in hydrogen bonded complexes of the type $\text{CCl}_3\text{COOH} \cdot \text{B}$ at 77 K, mean values of spectral frequencies $\bar{\nu}_Q$ variations of the mean frequency $\Delta\bar{\nu}_Q$ and pK_a -values of the bases

Complex	ν_Q [MHz]	$\bar{\nu}_Q$ [MHz]	$\Delta\bar{\nu}_Q$ [MHz]	pK_a base B ^b
CCl_3COOH (\equiv TCA)	39.969 ^a 40.162 40.242	40.124	0	
TCA · 4-methylpyridine N-oxide	38.413 ^a 38.877 39.011	38.767	-1.357	1.29
TCA · 3-bromopyridine	38.430 38.476 38.476 38.697 38.811 38.908	38.633	-1.491	2.84
TCA · 4-methylquinoline	38.124 38.376 38.451 38.494	38.361	-1.763	5.67
TCA · 4-methylpyridine	37.868 ^a 38.037 39.003	38.303	-1.821	6.02
TCA · 2,4-dimethylpyridine	37.877 38.194 38.539	38.203	-1.921	6.63
TCA · 2,6-dimethylpyridine	37.456 37.840 38.669	37.988	-2.136	6.75
TCA · 2, 4, 6-trimethyl- pyridine	37.600 38.125 38.306	38.010	-2.114	7.44

^a Ref. [15] ^b Ref. [16]

structure in the vicinity of the chlorine nucleus is modified: the ionicity of the C—Cl bond increases [17] and the electric field gradient decreases accordingly.

By having recourse to mean values of the NQR line frequencies it was possible to avoid taking into consideration the crystal effect related with the inequivalency of the

positions of the three chlorine nuclei in TCA and thus to concentrate entirely on the change in electron structure due to the formation of intermolecular hydrogen bonds.

Figure 1 shows $\Delta\bar{\nu}_Q$ as a function of $\Delta pK_a = pK_a(\text{base}) - pK_a(\text{acid})$. The dependence $\Delta\bar{\nu}_Q = f(\Delta pK_a)$ in the range of negative ΔpK_a -values (lower left hand portion of figure 1) defines the NQR frequency for a complex with normal hydrogen bond. In accordance with the notation of Eq. (3), this is the frequency ν_0 (39.994 MHz). However, the largest

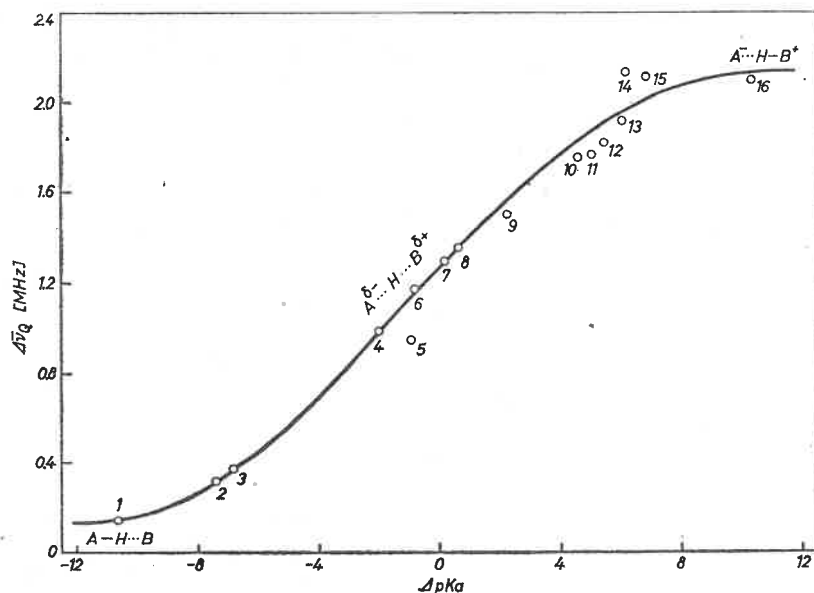


Fig. 1. Shift in mean NQR frequency of the TCA·B complexes versus ΔpK_a . The complexes are labelled according to their base as follows: 1 — acetonitril [14], 2 — cyclohexanone [14], 3 — acetophenone [14], 4 — acetamide [14], 5 — α -pyrolidone [14], 6 — N, N-dimethylacetamide [14], 7 — pyridine N-oxide [13], 8 — 4-methylpyridine N-oxide, 9 — 3-bromopyridine, 10 — pyridine [6], 11 — 4-methylquinoline, 12 — 4-methylpyridine, 13 — 2,4-dimethylpyridine, 14 — 2,6-dimethylpyridine, 15 — 2, 4,6-trimethylpyridine, 16 — triethylamine [14]

shift in NQR (upper right hand part of figure 1) is due to complete transfer of the proton in the hydrogen bond. Thus, for $\Delta\nu_{pt}$, we obtain a value of about 2 MHz. On insertion of the values thus determined into Eq. (3) and on the assumption of $\nu_{ex} \approx 0$, we obtained the value of the coefficient "b" for each complex. Next, by having recourse to the normalization condition for the function $\psi_N(a^2 + 2abS + b^2 = 1)$ and the value $S = 0.20$ [18] characteristic for this type of complexes, we determined the coefficients "a". Their value for the complexes are given in figure 2.

For comparison, the coefficient P , providing a direct measure of the degree of transfer of the proton in the hydrogen bond and obtained from the simple relation [6]

$$\nu_Q = P\nu_{pt} + (1 - P)\nu_0 \quad (4)$$

is also plotted vs. ΔpK_a .

A dependence similar to that of Fig. 1 has been obtained for the function $\Delta\vec{\mu} = f(\Delta pK_a)$, with $\Delta\vec{\mu}$ — the electric dipole moment of the hydrogen bond, in cases of complexes of phenols and carboxylic acids with pyridine, triethylamine and aniline [19–24].

It results from IR [24, 25] and NQR studies that, in complexes of strong bases ($pK_a \gg 0$), an ion pair with hydrogen bond appears ($A^- \cdots H-B^+$), whereas in cases of

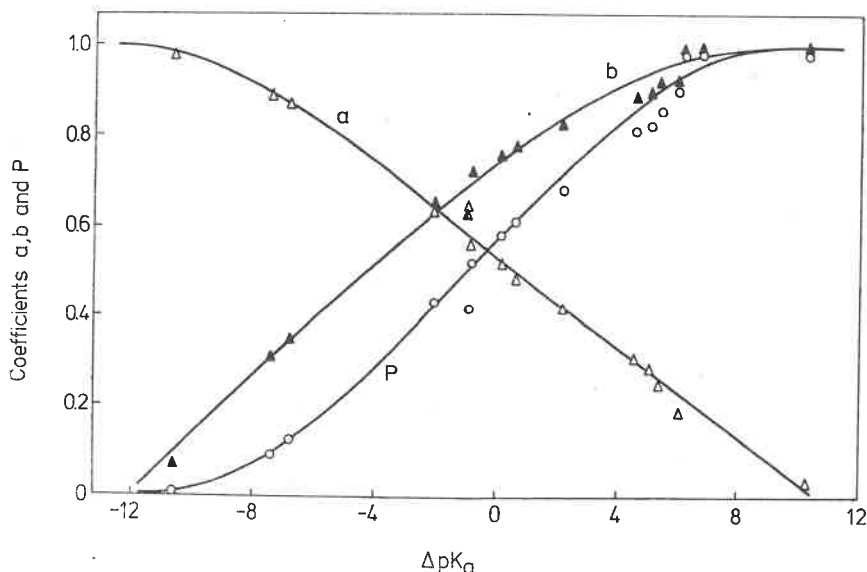
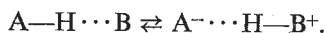


Fig. 2. The coefficients a , b and P as function of ΔpK_a , for the TCA · B complexes studied

weak bases ($pK_a \ll 0$) one has a complex involving a normal hydrogen bond ($A-H \cdots B$). Complete transfer of the proton from the acid to the base causes a change in NQR frequency by $\Delta\bar{\nu}_Q \approx 2\text{MHz}$.

A similar situation is met with when analyzing the differences in mean NQR frequencies between mono- and bi-chloroacetic acid and their ammonia salts, which are of the completely ionized type [6]. The $\Delta\bar{\nu}_Q$ -values of these salts amounting to 2.0 and 1.9 MHz, respectively, are in good agreement with the value $\Delta\bar{\nu}_Q \approx 2\text{MHz}$, attributed to the complexes with total proton transfer ($A^- \cdots H-B^+$). It should be noted that the preceding comparison concerns studies on one, two and three chlorine nuclei of the various chloroacetic acids, and that the conformity of the results obtained is supplementary evidence in favour of the method of NQR frequency averaging adopted at the outset.

The results obtained show that the transfer of the proton from the acid to the base proceeds continuously in the complexes studied. The point of inflection (figure 1) corresponds to $\Delta pK_a \approx 0$, and is shifted by about 3–5 pK_a units downwards compared with the data from dielectric studies of solutions. In dielectric studies, the point of inflection corresponds to the equimolar tautomeric equilibrium



In the present work, performed in solid phase, tautomeric equilibrium is hardly conceivable. We presume the proton transfer in the solid phase to occur by way of proton delocalization ($A \cdots H \cdots B$).

We performed an evaluation of the shift in mean NQR frequency to be expected from the emergence of a dipole moment on the hydrogen bond of the complex. We selected the complex of TCA and triethylamine, for which the proton transfer has to be complete and the dipole moment the largest, as confirmed by the work of Sobczyk and Pawełka [22, 26].

Bloembergen [27] calculated the changes in quadrupole interaction energies within covalence bonds induced by an external electric field. His predictions were confirmed by numerous experimental papers [28–30]. In the case of an axially symmetric field gradient, for which the asymmetry parameter is initially zero, the electrically induced shift in frequency is of the following simple form:

$$\Delta\nu_Q^e = \frac{eQ}{2h} R_{zzz} E_z, \quad (5)$$

where R_{zzz} is a constant, and E_z the z -component of the external electric field.

In molecular crystals with a C—Cl bond, the most frequent value of R_{zzz} encountered (from $6 \times 10^{11} \text{ m}^{-1}$ to $7.5 \times 10^{11} \text{ m}^{-1}$) [29] is sufficient evidence that the electrons participating in the C—Cl bond are chiefly responsible for the value of the electric shift. In this case intermolecular interactions are less important, and the local field corrections are more or less identical for all substances having this type of bond. However, with regard to molecular crystals with hydrogen bonds as well as complexed compounds, it is not possible to neglect the strongly differing intermolecular interactions. Consequently, as done in reference [31], we took into account the influence of the electric field, originating essentially in the dipole of the hydrogen bond, on the polarization of the covalent C—Cl bond. The field in question can be expressed as follows:

$$E_z = \frac{\mu}{4\pi\epsilon_0\epsilon r^3} \cos\theta \sqrt{3 \cos^2\varphi + 1}, \quad (6)$$

where φ is the angle between the direction of the dipole and the radius vector connecting the centre of the dipole and the chlorine nucleus considered, θ is the angle between the radius vector and the direction of the C—Cl bond. From structural data [32], we calculated the distances r between the dipole and ^{35}Cl nuclei, as well as the angles φ and θ as: Cl_1 (4.00 Å, 5°, 63°); Cl_2 (4.35 Å, 30°, 45°); Cl_3 (4.35 Å, 30°, 45°). Hence, and assuming $\mu = 6.72 \text{ D}$ [26] and $R_{zzz} = 7.25 \times 10^{11} \text{ m}^{-1}$, we obtained $\Delta\bar{\nu}_Q = 2.095 \text{ MHz}$, in good agreement with the $\Delta\bar{\nu}_Q$ value measured [14].

Thus, the frequency shifts of the NQR spectrum of the successive complexes as compared with pure trichloroacetic acid are due to changes in the action of the electric field originating essentially in the polar group of the hydrogen bridge leading to a change in polarization of the covalent C—Cl bond which consists in a displacement of the shared electron pair towards the more strongly electronegative atom Cl.

Hence, although atoms with a quadrupolar nucleus do not often occur in the immediate vicinity of changes taking place within molecular systems of the crystal lattice, they nonetheless are sensitive and true indicators of these changes. The shift in NQR spectrum suggests itself as the basis of a method for the determination of the dipole moments of hydrogen bonds. Much important information concerning intermolecular interactions in crystals can thus be gained from spectroscopic studies of nuclear quadrupole resonance.

REFERENCES

- [1] D. Biedenkapp, A. Weiss, *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.* **70**, 788 (1966).
- [2] R. A. Bennet, H. O. Hooper, *J. Chem. Phys.* **47**, 4855 (1967).
- [3] D. F. R. Gilson, C. T. O'Konski, *J. Chem. Phys.* **48**, 2767 (1968).
- [4] Y. K. Maksyutin, E. N. Guryanova, G. K. Semin, *Zh. Strukt. Khim.* **9**, 701 (1968).
- [5] J. P. Lucas, L. Guibe, *Mol. Phys.* **19**, 85 (1970).
- [6] H. Chihara, N. Nakamura, *Bull. Chem. Soc. Jap.* **44**, 1980 (1971).
- [7] S. Ardjomande, E. A. C. Lucken, *Helv. Chim. Acta* **54**, 176 (1971).
- [8] S. Ardjomande, E. A. C. Lucken, *J. Chem. Soc. Perkin II* 453 (1975).
- [9] R. S. Mulliken, *J. Am. Chem. Soc.* **64**, 811 (1952).
- [10] H. Chihara, N. Nakamura, *Bull. Chem. Soc. Jap.* **44**, 2676 (1971).
- [11] M. Ostafin, J. Pietrzak, Proceedings of the V Polish National Seminar on NMR and Its Applications, Kraków 1972, Report No 819/PL, 1973, p. 118.
- [12] D. A. Tong, *J. Sci. Instr.* **1**, 1153 (1968).
- [13] H. Chihara, N. Nakamura, *J. Phys. Soc. Jap.* **37**, 156 (1974).
- [14] O. H. Poleshchuk, Y. K. Maksyutin, O. F. Sychev, K. K. Koshelev, Y. G. Orlov, *Izv. Akad. Nauk SSSR* **6**, 1431 (1975).
- [15] J. Pietrzak, B. Nogaj, Z. Dega-Szafran, M. Szafran, Proceedings of the VI Polish National Seminar on NMR and Its Applications, Kraków 1973, p. 164.
- [16] *Physical Methods in Heterocyclic Chemistry*, ed. A. R. Katritzky, vol. 1, Academic Press 1962.
- [17] C. H. Townes, B. P. Dailey, *J. Chem. Phys.* **17**, 782 (1949).
- [18] H. Ratajczak, *J. Phys. Chem.* **76**, 3000 (1972).
- [19] J. Małecki, *J. Chem. Phys.* **36**, 2144 (1962).
- [20] J. Jadźym, J. Małecki, *Acta Phys. Pol.* **A41**, 599 (1972).
- [21] H. Ratajczak, L. Sobczyk, *Zh. Strukt. Khim.* **6**, 262 (1965).
- [22] L. Sobczyk, Z. Pawełka, *J. Chem. Soc. Faraday I*, **70**, 832 (1974).
- [23] P. Huyskens, G. Hernandez, *Ind. Chim. Belg.* **38**, 1237 (1973).
- [24] S. L. Johnson, U. A. Rumon, *J. Phys. Chem.* **69**, 74 (1965).
- [25] Z. Dega-Szafran, M. Z. Naskręt-Barciszewska, M. Szafran, *J. Chem. Soc. Perkin I*, 763 (1974).
- [26] L. Sobczyk, Z. Pawełka, *Roczniki Chemii* **47**, 1523 (1973).
- [27] N. Bloembergen, Proc. XIth Colloque Ampere, Eindhoven 1963, p. 39.
- [28] J. Duchesne, M. Read, P. Cornil, *J. Phys. Chem. Solids* **24**, 1333 (1963).
- [29] R. W. Dixon, N. Bloembergen, *J. Chem. Phys.* **41**, 1720 (1964).
- [30] J. L. Colot, *J. Molec. Struct.* **13**, 129 (1972).
- [31] J. Pietrzak, *Fizyka Dielektryków i Radiospektroskopii*, PTPN, Poznań **5**, 143 (1969), in Polish.
- [32] P. G. Jönsson, W. C. Hamilton, *J. Chem. Phys.* **56**, 4433 (1972).