^{14}N NQR Study of Diphenylamine

Janez Seliger[a,b] and Veselko Žagar[a]

[a] "Jozef Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia
[b] University of Ljubljana, Faculty of Mathematics and Physics, Department of Physics,
Jadranska 19, 1000 Ljubljana, Slovenia

Reprint requests to J. S.; E-mail: janez.seliger@fmf.uni-lj.si

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The temperature dependence of the ^{14}N NQR frequencies has been measured in a polycrystalline sample of diphenylamine by nuclear quadrupole double resonance. Two non-equivalent diphenylamine molecules have been observed. The NQR parameters in diphenylamine were related to the NQR parameters obtained in other amines and to the molecular and crystal structure.

Key words: NQR; Nitrogen; Amines; Biphenyl.

1. Introduction

The structure and properties of bridged biphenyl molecules $(C_6H_5)_2X$ (X = O, S, CO, NH, ...) have attained a considerable interest. The attention is mainly focused on the orientation of the phenyl rings with respect to the C-X-C plane. It is believed that the properties of these molecules depend on the ring orientation. In diphenylamine (DPA) with the chemical formula $(C_6H_5)_2NH$ the orientation of the rings is determined by the competition between two effects: the steric repulsion of the rings and the desired conjugation of the electronic π systems on the rings mediated through a lone electron pair orbital on the nitrogen atom.

DPA has various applications. It is used as a stabilizer in single-based propellants, a rubber antioxidant fungicide etc.

There are only a few experimental data available on the structure of DPA [1, 2], which is not yet completely known.

Several theoretical studies on the structure of DPA have been performed. Ito et al. [3] performed an ab initio molecular orbital study of DPA and some DPA derivatives. As the most favourable molecular conformation they obtained a skewed conformation where the two phenyl rings are rotated with respect to the C-N-C plane by an equal angle, $\phi = \phi' = 26.2°$, and the C-N-C angle θ is 128.4°. These results are close to the experimental data [2], where $\phi = 23.0°$, $\phi' = 36.9°$, and $\theta = 124.5°$. Pankratov [4] obtained with a semi-empirical CNDO/2 method $\phi = 13.8°$, $\phi' = 34.1°$, and $\theta = 124.1°$. Boogaarts et al. [5] performed ab initio calculations at the Hartree-Fock level. They found that a DPA molecule in the ground state has a pyramidal structure with $\phi = 14.7°$, $\phi' = 44.5°$, and $\theta = 126.9°$. Boyle [6] used the AM1 semi-empirical method. He obtained the global minimum energy molecular conformation in case of a pyramidal amine group. In this case $\phi = 2.7°$, $\phi' = 52.0°$, and $\theta = 122.7°$. His results also showed that the hybridization state for the nitrogen atom is closer to a planar sp^2 configuration than to a pyramidal sp^3 configuration.

In order to contribute to the understanding of the molecular and crystal structure of DPA we performed a ^{14}N nuclear quadrupole resonance (NQR) study. ^{14}N NQR is a sensitive tool for the investigation of the electron distribution around the nitrogen nucleus. A comparison of the experimental NQR data, as presented in the present paper, and the NQR data obtained by the quantum chemical calculations can be used to differentiate between the proposed structures of the DPA molecule.

2. Experimental

A ^{14}N nucleus has a spin $I = 1$. It has in zero magnetic field three non-degenerated quadrupole energy levels and correspondingly three NQR frequencies labeled as ν_+, ν_-, and ν_0:

$$\begin{aligned} \nu_+ &= \frac{e^2qQ}{4h}(3+\eta),\ \nu_- = \frac{e^2qQ}{4h}(3-\eta), \\ \nu_0 &= \nu_+ - \nu_- = \frac{e^2qQ}{2h}\eta. \end{aligned} \tag{1}$$

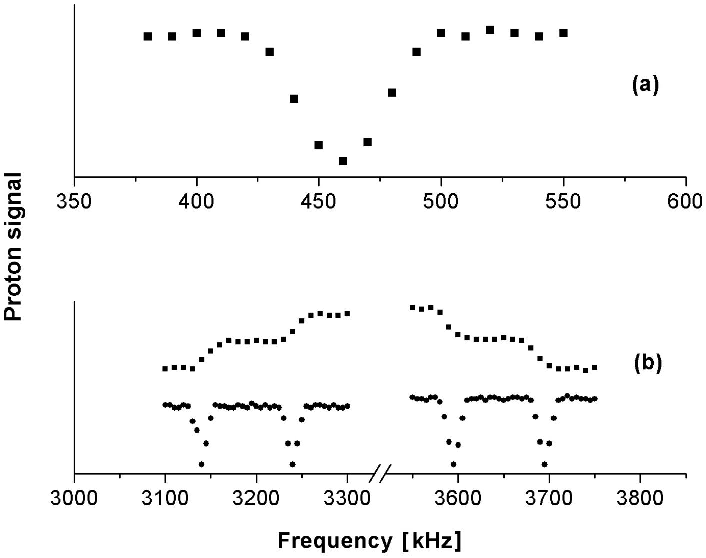

Fig. 1. Experimental determination of the ^{14}N NQR frequencies in diphenylamine at -110 °C by double resonance. (a) Determination of ν_0; (b) determination of ν_+ and ν_-. The experimental procedure is in details described in the text.

Here the quadrupole coupling constant e^2qQ/h is calculated from the sum $(\nu_+ + \nu_-)$, and then the asymmetry parameter η is calculated from ν_0. The quadrupole coupling constant is in fact the largest principal value $V_{ZZ} = eq$ of the electric field gradient (EFG) tensor at the position of the nitrogen nucleus multiplied by the electric quadrupole moment eQ of the nitrogen nucleus and divided by Planck's constant h. The EFG tensor is a traceless second rank tensor composed of the second derivatives of the electrostatic potential with respect to the coordinates. It has three principal values, labeled as V_{XX}, V_{YY} and V_{ZZ} ($|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$). The asymmetry parameter η is defined as $\eta = (V_{XX} - V_{YY})/V_{ZZ}$. The quantities eQV_{YY}/h and eQV_{ZZ}/h are calculated as $eQV_{YY}/h = (e^2qQ/h)(1+\eta)/2$ and $eQV_{XX}/h = (e^2qQ/h)\,(1-\eta)/2$.

The ^{14}N NQR frequencies are typically below 5 MHz, and in addition, the nitrogen magnetic moment is low. The detection of the ^{14}N NQR frequencies by the conventional NQR techniques is thus demanding or sometimes even impossible. We therefore applied two highly sensitive nuclear quadrupole double resonance (NQDR) techniques based on magnetic field cycling [7, 8]. The main advantage of these techniques is a simultaneous measurement of the three ^{14}N NQR frequencies from a given nitrogen position in the crystal, which clarifies complex ^{14}N NQR spectra.

The basic details of the experimental procedure are as follows. We used a purified sample purchased from Sigma-Aldrich Co. The mass of the polycrystalline sample was approximately 0.5 g. The proton spin system was polarized in a magnetic field $B \approx 0.75$ T, where the proton Larmor frequency is $\nu_L = 32$ MHz. The polarization time of the proton spin system in this field depends on the proton spin-lattice relaxation time, and was typically several minutes. The sample was pneumatically transferred into the second magnet and then back into the first magnet within approximately 0.1 s for each way. In the low magnetic field the sample was kept for 0.3 s – 0.8 s, depending on the proton spin-lattice relaxation time. The amplitude of the rf magnetic field was in the range between 3 mT and 5 mT in cases when a strong rf magnetic field was needed. The range of the NQR frequencies was scanned in steps of 5 kHz, 10 kHz or 20 kHz, depending on the NQDR technique applied. Signal averaging was used to improve the NQDR signals.

3. Results and Discussion

The measurement of the ^{14}N NQR frequencies by the present techniques is a three-step process. The measurements performed at -110 °C are illustrated in Figure 1.

In the first step (Fig. 1a) multiple frequency sweeps of the rf magnetic field are used to detect the lowest ^{14}N NQR frequency ν_0. The sweep frequency limits ν_U and ν_L are chosen so that the sweeps cover both ν_+ and ν_-: $\nu_U > \nu_+ > \nu_- > \nu_L$. The low-frequency region is scanned by varying in steps ΔB the value of the low magnetic field B in the magnetic field cycle. The step ΔB between repetitive magnetic field cycles corresponds to the step $\Delta\nu_\mathrm{H}$ in the proton Larmor frequency ν_H, $\nu_\mathrm{H} = \gamma_\mathrm{H} B/2\pi$, equal to 10 kHz. When in resonance, $\nu_\mathrm{H} = \nu_0$, an additional relaxation of the proton spin system occurs which results in a lower proton NMR signal at the end of the magnetic field cycle. In DPA we observe the resonance $\nu_\mathrm{H} = \nu_0$ at $\nu_\mathrm{H} = 460$ kHz.

In the second step the frequencies ν_+ and ν_- are located by varying the frequency limits ν_U and ν_L. The experimental results are shown in the upper part of Figure 1b. The low magnetic field is fixed at the resonance $\nu_\mathrm{H} = \nu_0$. One of the frequency limits, say ν_U, is kept constant above ν_+, whereas the other limit (ν_L in this case) is varied in steps of 10 kHz between repetitive cycles. When ν_L passes ν_- we observe a larger proton NMR signal at the end of the magnetic field cycle. In the present case we observe two steps in the proton NMR signal, one at $\nu_\mathrm{L} = 3140$ kHz and the other at $\nu_\mathrm{L} = 3240$ kHz. Thus there are two non-equivalent nitrogen positions in the sample with $\nu_-(1) \approx 3140$ kHz and $\nu_-(2) \approx 3240$ kHz. By keeping ν_L constant at a frequency below $\nu_-(1)$ and varying ν_U we observe two steps in the ν_U dependence of the proton NMR signal at $\nu_\mathrm{U} = 3595$ kHz and $\nu_\mathrm{U} = 3695$ kHz. Thus $\nu_+(1) \approx 3595$ kHz and $\nu_+(2) \approx 3695$ kHz. The reason that we observe a single line in the first step of the experiment is a small difference $\nu_0(1) - \nu_0(2)$ as compared to the proton NMR line width.

An improvement of the resolution as obtained by the two-frequency irradiation technique is illustrated in the lower part of Figure 1b. Here the low magnetic field in a magnetic field cycle is fixed in resonance at $\nu_\mathrm{H} = \nu_0$. The rf magnetic field is during the stay in the low magnetic field B applied in pulses with the frequencies ν_1, ν_2, ν_1, ν_2 … The width of a pulse is in the present case equal to 1 ms. When $\nu_1 = \nu_+$ and $\nu_2 = \nu_-$, or vice versa, the two-frequency irradiation causes an increase of the proton relaxation and correspondingly a lower proton NMR signal at the end of the magnetic field cycle. Since the ^{14}N NQR frequencies ν_+ and ν_- are approximately determined by the previous technique, it is easy to apply this technique. First ν_1 is fixed at $\nu_1 \approx \nu_+$ and the region around ν_- is scanned by ν_2. The lowest proton NMR signal is observed when $\nu_2 = \nu_-$. Then ν_2 is fixed at $\nu_2 = \nu_-$ and the region around ν_+ is scanned by ν_1. The lowest proton NMR signal is observed when $\nu_1 = \nu_+$. By this technique we obtain the following ^{14}N NQR frequencies in DPA at −110 °C: $\nu_+(1) = 3596$ kHz, $\nu_-(1) = 3139$ kHz, $\nu_0(1) = 457$ kHz, $\nu_+(2) = 3695$ kHz, $\nu_-(2) = 3240$ kHz, and $\nu_0(2) = 455$ kHz.

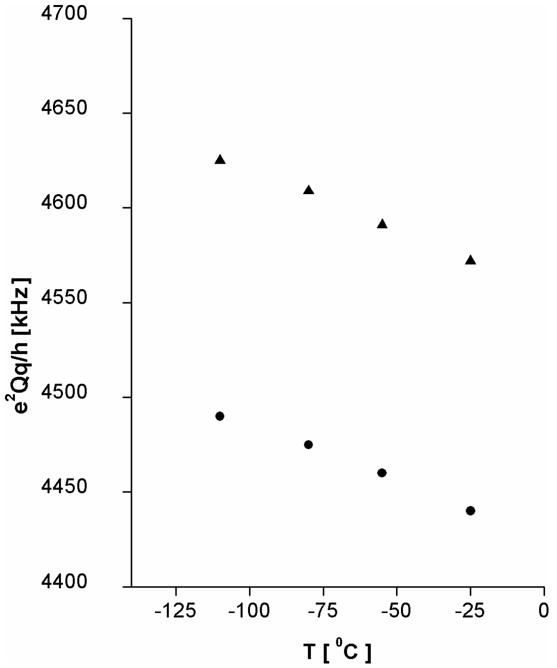

Fig. 2. Temperature dependence of the ^{14}N quadrupole coupling constants e^2qQ/h in diphenylamine. ●, N(1); ▲, N(2).

The measurements were performed between −110 °C and −25 °C. At higher temperatures the proton spin-lattice relaxation time in the low magnetic field shortens which makes the double resonance measurements with the present experimental setup impossible. In the whole temperature range we observe two non-equivalent nitrogen positions in the crystal. The reason that they are not observed by X-ray crystallography is presumably the very small difference between the two diphenylamine molecules. ^{14}N NQR is namely very sensitive to even small structural changes which are hard to be observed by other techniques.

The temperature dependence of the two quadrupole coupling constants is presented in Figure 2. They are both rather high, approximately 4.5 MHz and 4.6 MHz. Both quadrupole coupling constants weakly increase with decreasing temperature, what may be the consequence of thermal motions. The difference of the two

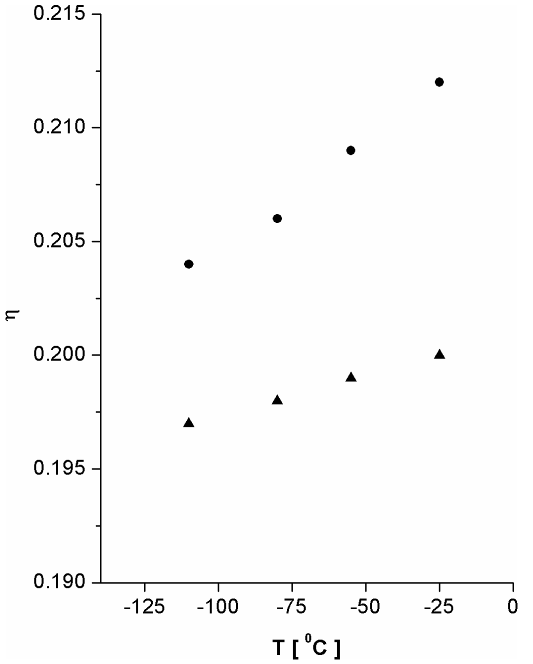

Fig. 3. Temperature dependence of the asymmetry parameters η of the EFG tensor in diphenylamine. ●, N(1); ▲, N(2).

quadrupole coupling constants is nearly temperature-independent.

The temperature dependence of the asymmetry parameter η is presented in Figure 3. It is in both cases close to 0.2. The difference of the two asymmetry parameters is small, but the temperature dependence definitely shows a different dynamics of the two molecules.

We may compare the results of the present study to the results of the ^{14}N NQR study of 4-*N*-cytosine derivatives [9]. At the amine –NHR position (R = H, CH_2CH_2SH, CH_2CH_2Ph, CH_2Ph and naphthyl), the quadrupole coupling constant is for R = H, CH_2CH_2SH and CH_2CH_2Ph below 3 MHz, whereas it is for R = CH_2Ph and naphthyl approximately equal to 3.4 MHz and 3.6 MHz respectively. In that study it was concluded that the amine group, which acts as a π electron acceptor in the majority of molecular systems, becomes an electron donor in phenylcytosine and naphthalenecytosine. This effect seems to be even more pronounced in DPA. On the other hand we observed in a recent study of several amides forming strong N-H$\cdots$O hydrogen bonds a ^{14}N quadrupole coupling constant of about 2.6 MHz [10]. This low value of e^2qQ/h is associated with the nearly planar structure of the amide groups and an increased population of the lone electron pair orbital on the nitrogen atom. It seems that in DPA steric repulsion of the rings increases the C-N-C angle θ and lowers the population of the lone electron pair orbital on the nitrogen atom. As a result, the ^{14}N quadrupole coupling constant increases.

Rather large quadrupole coupling constants as observed in DPA are thus presumably the effect of the deviation of the molecular structure from the planar structure, caused by the steric repulsion of the phenyl rings.

The two ^{14}N EFG tensors in DPA differ in the principal values at -110 °C in the following way: $\Delta eQV_{ZZ}/h = \pm 135$ kHz, $\Delta eQV_{YY}/h = \mp 65$ kHz and $\Delta eQV_{XX}/h = \mp 70$ kHz. The differences are small. We therefore assume that the orientation of the principal axes of the EFG tensor with respect to the molecule in the two molecules differs negligibly. The difference of the two EFG tensors is under this assumption a nearly axially symmetric tensor with the symmetry axis along the principal *Z*-axis. If we further assume that the two nitrogen positions differ in the population of the lone electron pair orbital we may conclude, that the *Z*-axis of the EFG tensor points approximately in the direction of the lone electron pair orbital.

4. Conclusions

The ^{14}N NQR measurements in a polycrystalline sample of DPA show the presence of two non-equivalent molecules. In one molecule we observe, at -110 °C, $e^2qQ/h = 4623$ kHz and $\eta = 0.197$, whereas in the other molecule, at the same temperature, $e^2qQ/h = 4490$ kHz and $\eta = 0.204$. The difference of the two quadrupole copupling constants is small and nearly temperature-independent. There are two crystallographically non-equivalent DPA molecules in the unit cell. Rather large quadrupole coupling constants suggest that the amine group, which acts as a π electron acceptor in the majority of molecular systems, becomes in DPA an electron donor, what may be associated with the steric repulsion of the phenyl rings, which causes the deviation of the molecular structure from the planar form and decreases the conjugation of the electronic π systems on the rings mediated through a lone electron pair orbital on the nitrogen atom. A comparison of the two EFG tensors suggests that the principal *Z*-axis of the EFG tensor points in the direction of the lone electron pair orbital.

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