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Nuclear Quadrupole Resonance of Nitrogen-14 in the Naphthalene-Tetracyanoethylene Complex

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Tetracyanoethylene (TCNE) is known to be a strong electron acceptor capable of forming various stable molecular complexes,[1] of which naphthalene-TCNE is an example. The present investigation has been undertaken on the nuclear quadrupole resonance of ^{14}N in the complex in order to compare the spectra with those of TCNE previously reported[2] and to discuss the nature of intermolecular interaction between naphthalene and TCNE.

The 1 : 1 molecular complex of naphthalene and TCNE was prepared by a method described by Merrifield and Phillips.[3] Red-brown needle crystals deposited on mixing equimolar warm concentrated solutions of the components in ethyl acetate followed by cooling. Although the crystals gradually turned wine red on cooling to liquid nitrogen temperature, the appearance of the crystals showed no changes indicative of the first-order phase transition taking place in the temperature range investigated. The nuclear quadrupole resonance of ^{14}N was observed by means of a modified Pound-Watkins type spectrometer already described.[4] Frequency modulation was used for the determination of resonance frequencies, while Zeeman modulation was employed for the assignment of resonance signals to $\nu^{\rm I}$ and $\nu^{\rm II}$. Resonance frequencies were measured by use of a Model VP-43A frequency counter from Matsushita Communication Industry Co., Ltd.

Since ^{14}N has a nuclear spin equal to unity, one can usually observe two resonance frequencies, $\nu^{\rm I}=eQq\cdot(3+\eta)/4$ and $\nu^{\rm II}=eQq(3-\eta)/4$, for resonant nuclei having a nonvanishing asymmetry parameter, η. Naphthalene-TCNE yielded two sets of $\nu^{\rm I}$ and $\nu^{\rm II}$ frequencies at liquid nitrogen temperature ($\nu^{\rm I}=3278.2\pm0.1$ and 3246.2 ± 0.1 kHz and $\nu^{\rm II}=3145.2\pm0.3$ and 3082.3 ± 0.1 kHz). The appearance of the two sets indicates that there are two kinds of crystallographically nonequivalent nitrogen atoms in crystals. Williams and Wallwork[5] have carried out X-ray analysis of this complex, and found that it forms monoclinic crystals belonging to the space group C2/m with two units of the complex in a unit cell. Naphthalene and TCNE molecules are stacked alternately in infinite columns aligned parallel to the c axis. Centrosymmetric TCNE molecules are located at inversion centers, and C=C bonds are directed along twofold axes. Therefore, all cyano groups are equivalent in a crystal in contradiction to the results of the present study. However, the X-ray analysis carried out at room temperature showed that the thermal vibration of a naphthalene molecule about an axis perpendicular to the molecular plane is abnormally large and that the geometry of naphthalene molecules could hardly be determined exactly. Therefore, the disagreement may be attributable to a slight change in crystal structure possibly taking place between room and liquid nitrogen temperatures. Although sharp and fairly intense signals were observed at liquid nitrogen temperature

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except for a very weak line of the second lowest frequency, no resonance could be detected at dry ice and room temperatures. This suggests that an order-disorder phase transition involving naphthalene molecules takes place between dry ice and liquid nitrogen temperatures.

Because two ν^{I} frequencies as well as two ν^{II} frequencies observed for naphthalene-TCNE are close to each other, one-to-one correspondence is infeasible between ν^{I} and ν^{II}. Therefore, averages were taken for the calculation of the quadurpole coupling constant and the asymmetry parameter. The results are shown in Table 1 along with those of some related compounds.

TABLE 1. QUADRUPOLE COUPLING CONSTANTS, eQq, AND ASYMMETRY PARAMETERS, η, OF ^{14}N IN NAPHTHALENE-TCNE AND RELATED COMPOUNDS AT LIQUID NITROGEN TEMPERATURE

Compound	eQq (kHz)	η (%)	Reference
Naphthalene-TCNE	4251	7.0	
TCNE	4221[a]	4.4	2)
Acrylonitrile	3800	4.77	6)
Methacrylonitrile	3831	4.46	6)

a) eQq=4331 kHz in Table 1 of Reference 2 should read 4221 kHz.

As has been reported in a previous paper,[7] the quadrupole coupling constant and the asymmetry parameter of nitrogen in a cyano group having unequal π-electron populations, $1+i_{\pi\perp}$ and $1+i_{\pi//}$, can be expressed by

$$eQq = \left| s+i_\sigma-si_\sigma-\frac{1}{2}(i_{\pi\perp}+i_{\pi\parallel}) \right| \frac{eQq_{\mathrm{p}}}{1+i\varepsilon} \tag{1}$$

$$\eta eQq = \frac{3}{2}\left| i_{\pi\perp}-i_{\pi\parallel} \right| \frac{eQq_{\mathrm{p}}}{1+i\varepsilon} \tag{2}$$

Here it is assumed that the sp-hybridized σ-bond orbital and the lone pair orbital of nitrogen accommodate $1+i_\sigma$ and 2 electrons, respectively. The symbols, s, eQq_{p}, i, and ε denote the extent of s-character of the σ-orbital, the absolute value of the quadrupole coupling constant of an electron in a 2p-orbital of ^{14}N, the total ionicity of nitrogen, and the screening constant introduced by Townes and Schawlow,[8] respectively.

According to Eq. (2), relatively small asymmetry parameters observed for naphthalene-TCNE and TCNE indicate that the difference, $i_{\pi\perp}-i_{\pi//}$, in π-electron population is fairly small. This means that the π-electron systems of cyano groups in a TCNE molecule are not conjugated with the ethylenic double bond to a great extent. The same conclusion can be derived for acrylonitrile and methacrylonitrile. The quadrupole coupling constants of the complex and TCNE are considerably higher than those of acrylonitrile and its derivatives. This is rather difficult to interpret quantitatively because the theoretical equations involve several unknown parameters. However, Eq. (1) clearly shows that the quadrupole coupling constant decreases with increasing polarization of π-electrons in a cyano group. Accordingly, it is concluded that the π-bonds of cyano groups are less polarized in TCNE molecules than in acrylonitrile and its derivatives.

Since naphthalene-TCNE is a charge transfer complex, electron transfer is expected to take place from naphthalene to TCNE. In view of the stacking structure of the complex, such a transfer would result in an increase in the electronic population of π-orbitals directed at right angles to the molecular plane of TCNE. This leads to an increase in the asymmetry parameter and a decrease in the quadrupole coupling constant of nitrogen atoms in a TCNE molecule. In fact the observed asymmetry parameter of the complex is larger than that of TCNE. However, the difference between the observed asymmetry parameters of the two compounds is so small that it can be explained in terms of the effect of crystal field as well. Furthermore, the quadrupole coupling constant of the complex is slightly larger than that of TCNE in contradiction to the expectation. These facts suggest that the extent of charge transfer is fairly small and that the electronic state of nitrogen atoms in TCNE molecules remains essentially unaffected on forming a charge transfer complex with naphthalene.

Quite recently, Murgich and Pissanetzky[9] studied the nuclear quadrupole resonance of ^{14}N in potassium tetracyanoquinodimethanide, and found a small quadrupole coupling constant, 3.4 MHz (average), and a large asymmetry parameter, 52% (average). These results support the adequacy of the foregoing theoretical prediction.

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