CHEMISTRY LETTERS, pp. 825-828, 1979. Published by the Chemical Society of Japan

IODINE NUCLEAR QUADRUPOLE RESONANCE OF SEVERAL MOLECULAR COMPLEXES OF IODOHYDROCARBONS

Tsutomu OKUDA, Hideta ISHIHARA, Koji YAMADA, and Hisao NEGITA
Department of Chemistry, Faculty of Science, Hiroshima University,
Hiroshima 730

The ^{127}I NQR was observed for the five molecular complexes of iodohydrocarbons such as CHI_3, C_2I_4, and C_2I_2. The assignments of the resonance lines are made from the temperatures of the disappearance and the temperature coefficients of the relevant lines. It is suggested for CHI_3-1,4-dithiane that the atomic orbitals of the iodine atoms are sp^3d hybridized to form the charge transfer bonds.

It has been known from the NQR study that the atomic orbitals of iodine atoms are sp^3d hybridized in the complexes of I_2, IBr, and ICl with some nitrogen-containing donors.[1)] This hybridization is also probable in the complexes of iodohydrocarbons with n-type donors consisting of endless chains of alternating donor and acceptor molecules.[2-5)] Therefore, the NQR study of these iodohydrocarbon complexes was purposed to clarify the charge transfer bond.

The five complexes were prepared according to Ref. 2-5. The melting points of these complexes were as follows: 71 °C for CHI_3-1,4-dithiane, 101 °C for $2CHI_3$-1,4-diselenane, 126 °C for C_2I_4-1,4-diazine, 96 °C for C_2I_2-1,4-diselenane, and 78 °C for C_2I_2-1,4-dithiane. These complexes except C_2I_2-1,4-dithiane decomposed during melting. The NQR line was observed on an oscilloscope using a push pull oscillator consisting of the tubes 6AF4A with transmission line tuning circuit. The observed frequency range was between 200 MHz and 380 MHz.

The NQR frequencies observed are listed in Table 1. The resonance lines of the component iodohydrocarbons could be observed only for C_2I_2. These resonance lines were assigned to $\pm 1/2 \leftrightarrow \pm 3/2$ transition or ν_1 line, in reference to the resonance frequencies of other relevant compounds. For these complexes studied, the resonance frequencies decreased monotonously with increasing temperature. The average temperature coefficients of the resonance frequencies were calculated by the following equation:

$$\langle \alpha \rangle = 2(\nu_{273} - \nu_{77})/[(273-77)(\nu_{273} + \nu_{77})] , \qquad (1)$$

where ν_{273} and ν_{77} are the frequencies at 273 K and 77 K, respectively. The temperature coefficients thus obtained are listed in Table 1.

For CHI_3-1,4-dithiane, two resonance lines were observed. According to the X-ray analysis,2) the intensity ratio of two resonance lines is expected to be 1 to 2. In other words, one iodine atom is free from the charge transfer but two iodine atoms form the charge transfer bonds in the crystal of CHI_3-1,4-dithiane. The higher frequency line having a stronger intensity disappeared at 50 °C, whereas the lower at 36 °C. Therefore, the higher line is assigned to the iodine atoms which form the S-I bond and is expected to be less affected by the thermal vibration.

Table 1. The frequencies and the temperature coefficients of five molecular complexes and the relevant compounds

Compound	ν_{77}/MHz	ν_{273}/MHz	$\langle \alpha \rangle$ /deg^{-1}
CHI_3-1,4-dithiane	309.96	306.44	-5.82×10^{-5}
	299.23	295.51	-6.37×10^{-5}
$2CHI_3$-1,4-diselenane	307.34	303.72	-6.04×10^{-5}
	304.19	301.12	-5.15×10^{-5}
	297.44	294.92	-4.34×10^{-5}
CHI_3-$3S_8$ a)	307.11	303.96	-5.25×10^{-5}
C_2I_4-1,4-diazine	316.70	314.65	-3.30×10^{-5}
	308.49	307.30	-1.96×10^{-5}
C_2I_2-1,4-diselenane	343.48	339.17	-6.45×10^{-5}
C_2I_2-1,4-dithiane	348.06	341.83	-9.22×10^{-5}
	346.35	340.47	-8.73×10^{-5}
C_2I_2	349.07	339.49	-14.19×10^{-5}
	348.38	339.66	-12.92×10^{-5}

a) Ref. 6.

Upon formation of a complex, the charge from the donor is transferred to the antibonding σ orbital or the sp^3d hybrid orbital of the iodine atom.[1)] In the former case, the NQR frequency of the iodine atom is lowered as generally observed. In the latter case, the frequency can be expected to shift to the higher as stated below.

The sp^3d hybrid orbitals of a iodine atom have the following forms:[1)]

$$\begin{aligned}\varphi_1&=(s-d_{z^2}+2p_x)/\sqrt{6}\\ \varphi_2&=(s-d_{z^2}-p_x+\sqrt{3}p_y)/\sqrt{6}\\ \varphi_3&=(s-d_{z^2}-p_x-\sqrt{3}p_y)/\sqrt{6}\\ \varphi_4&=(s+d_{z^2}+\sqrt{2}p_z)/2\\ \varphi_5&=(s+d_{z^2}-\sqrt{2}p_z)/2\end{aligned} \qquad (1)$$

The orbitals φ_1, φ_2, and φ_3 are occupied by unshared pairs of electrons and direct trigonally in an plane. The orbital φ_4 forms the covalent C-I bond and directs oppositely to the orbital φ_5 which acts as the acceptor orbital. The occupation numbers of φ_4 and φ_5 orbitals are denoted by N_b and N_a, respectively. Then the quadrupole coupling constant of the iodine atom, e^2Qq/h, is given by:

$$\left|e^2Qq/e^2Qq_{atom}\right| = \left|2-(N_a+N_b)/2\right| , \qquad (3)$$

where e^2Qq_{atom}/h is the value for the free iodine atom. On the other hand, the quadrupole coupling constant of the iodine atom which is free from the charge transfer is given by the following equation neglecting s hybridization:

$$\left|e^2Qq/e^2Qq_{atom}\right| = \left|2-N_b'\right| , \qquad (4)$$

where N_b' is the occupation number of the iodine orbital forming the C-I bond. Therefore, assuming that N_b' is greater than $(N_a+N_b)/2$, the quadrupole coupling constant of the iodine atom which forms the charge transfer bond becomes larger than that of the iodine atom which is free from the charge transfer.

For CHI_3-1,4-dithiane, the iodine atom forming the S-I bond is expected to be in the above-mentioned state. Since the C-I-S bond gives a nearly straight line, the asymmetry parameter for the iodine atom is approximately zero. Therefore, the frequency of ν_1 line due to this iodine atom is higher than that of the iodine atom which is free from the charge transfer. For the other four complexes, the NQR frequencies of the iodine atoms shift to the lower when the charge transfer bonds are formed. Therefore, it is considered that either the charge from the donor is transferred to the antibonding σ orbital or to the sp^3d hybrid orbital in which $(N_a+N_b)/2$ becomes greater than N_b'.

For $2CHI_3$-1,4-diselenane, the three resonance lines were observed as expected from the result of the X-ray analysis.[3)] The two lower lines disappeared at 90 °C but the highest line at 68 °C. Therefore, two lower lines are assigned to the two iodine atoms forming the Se-I bonds and the highest line to the iodine atom free from the charge transfer.

For C_2I_4-1,4-diazine, two resonance lines with same intensity were observed. This is consistent with the result of the X-ray analysis.[4)] The lower frequency line is assigned to the iodine atom forming the N-I bond, since the absolute value of the temperature coefficient for the lower line is smaller than that for the higher line.

One resonance line was observed for C_2I_2-1,4-diselenane and two for C_2I_2-1,4-dithiane. This is consistent with the results of the X-ray analysis.[5)] For these two complexes, the NQR frequencies at 77 K are lower and the absolute values of the temperature coefficients are smaller than those for C_2I_2. Therefore, the iodine atoms in these two complexes form the charge transfer bonds.

References

1) G. K. Semin, T. A. Babushkina, and G. G. Yakobson, "Nuclear Quadrupole Resonance in Chemistry," Halsted Press, New York (1975). Chap. 7.

2) T. Bjorvatten and O. Hassel, Acta Chem. Scand., 15, 1429 (1961).

3) T. Bjorvatten, Acta Chem. Scand., 17, 2292 (1963).

4) T. Dahl and O. Hassel, Acta Chem. Scand., 22, 2851 (1968).

5) O. Holmesland and C. Rømming, Acta Chem. Scand., 20, 2601 (1966).

6) H. Robinson, H. G. Dehmelt, and W. Gordy, J. Chem. Phys., 22, 511 (1954).

(Received February 22, 1979)