BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1575—1576 (1973)

The NQR Spectrum and Structure of Hexachloropentafulvene[1]

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(Received July 10, 1972)

Pure nuclear quadrupole resonance (NQR) studies on molecular crystals have been applied to the determination of distribution of molecular electrons.[3–6] Recently, West and his co-workers have successfully applied NQR spectroscopy to the study of the perchlorocarbon series.[7–9] The validity of this method depends on correct assignments of the wealth of resonance (obtained experimentally) to the different chlorine atoms present in the molecule under study. We wish to report the ^{35}Cl NQR spectra of hexachloropentafulvene (I)[10,11] and 3,4-bis(dichloromethylene)-1,2-dichlorocyclobutene (II)[12] and their analyses in

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[1] Fulvenes and Thermochromic Ethylenes. Part 76.

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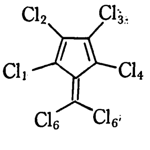
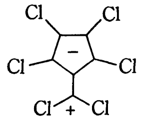
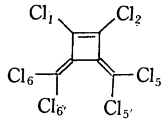
terms of the dipolar and spatial structures of these nonbenzenoid cyclic conjugated chlorocarbons.[13,14)]



I



Ia



II

The spectrum of I consists of the following six frequencies: 36.783, 37.163, 37.805, 38.086, 38.179, and 38.303 MHz. They fall into two groups, A and B, centered at 37.0 MHz (2 lines) and 38.1 MHz (4 lines), respectively. The large frequency separation between the two groups of lines ($>$1 MHz) indicates the presence of at least two types of chlorine atoms. The splitting within each group may still be attributed to solid-state intermolecular forces.[5,6,15)] In order to draw any conclusions from the NQR spectrum pertaining to the dipolar character or to the spatial structure of I, a correct assignment of the resonances of the NQR spectrum is necessary. Out of the various possible alternatives, one point emerges clearly: the frequencies of Cl_2 and Cl_3 are represented by group A and not by Group B. This assignment is based on the analysis of the NQR spectra of a series of 1,2,3,4-tetrachlorofulvenes and related substances, which indicate that the ^{35}Cl resonance of Cl_2 and Cl_3 appears consistently in the 36.5 MHz region, and is not affected by the substituents at the exocyclic (6,6′) positions.[16)] Thus group B should be assigned to Cl_1, Cl_4, Cl_6, and $Cl_{6'}$. The alternative assignment suggested by Hashimoto and Mano[17)] which attributed group A to Cl_6 and $Cl_{6'}$ and group B to Cl_1, Cl_2, Cl_3, and Cl_4 does not seem to be justified. They claimed that their assignment was supported by the contribution of the dipolar, "aromatic" structure Ia to the ground state of I. The experimental dipole moment of I in (cyclohexane) solution (1.00D),[18)] *does not* indicate any substantial contribution of Ia in the ground state. In any event, the extent of such a contribution cannot account for a decrease in the resonance frequencies of Cl_6 and $Cl_{6'}$. Moreover, such a contribution should cause not only a decrease in the electron density of the p_π orbitals of Cl_6 and $Cl_{6'}$, but also an increase in the respective electron densities of Cl_1, Cl_2, Cl_3, and Cl_4. As shown above, there is no evidence of a shift to higher frequencies of Cl_2 and Cl_3 which should have accompanied such an increase. We conclude that the NQR spectrum of I does not reveal the presence of a contribution of Ia.

The most striking feature in the NQR spectrum of I is the shift to higher frequencies (38.1 MHz region) of the two chlorine atoms "*ortho*" to the "fulvenic" double bond, Cl_1 and Cl_4. The shift is even greater than the one observed in the ^{35}Cl NQR spectrum of octachloropentafulvalene (37.7 MHz region) and interpreted as due to noncovalent intramolecular interactions of the bucking C–Cl groups.[19)] This shift (in I) could be explained in terms of the strong perturbations of the electrons of Cl_1 and in the C_1–Cl_1 bond produced by the C_6–Cl_6 dipole.[20)] The spatial relationship between Cl_1 and Cl_6 resembles somewhat the *peri*-relationship of the chlorine atoms in positions 1 and 8 in the naphthalene nucleus. Accordingly, an analogy may be drawn from the ^{35}Cl NQR spectrum of 1,2,3,6,7,8-hexachloronaphthalene, in which the resonance representing Cl_1 and Cl_8 appears at *ca.* 38.2 MHz (77 K).[21)]

In contrast to I, the ^{35}Cl NQR spectrum of its pseudoalternant isomer II (3 lines at 36.358, 37.835, and 37.971 MHz) was not irregular. For II, Hashimoto and Mano reported six lines falling into two groups centered at *ca.* 36.4 MHz (two lines) and 38.0 MHz (four lines).[17)] In particular, the 36.4 MHz resonance due to the chlorine atoms attached directly to the cyclobutene ring (Cl_1 and Cl_2) appears in the normal region for such chlorine atoms. The absorption is thus not shifted to higher frequencies by the electrostatic field of the C_6–Cl_6 and C_5–Cl_5 dipoles. The absence of such an effect (relative to the respective effect observed in I) may be explained by the different geometry of the molecule imposed by the cyclobutene ring. Consequently, the distances between the C_6–Cl_6 dipole and Cl_1 (and the C_1–Cl_1 bond) are larger and their relative orientation is different from that in I.

On the basis of the NQR spectrum of I we predict a small distance between Cl_1 and Cl_6.

We are greatly indebted to Dr. K. Mano of the Research Institute for Atomic Energy, Osaka City University, Sumiyoshiku, Osaka, Japan, for conveying to us his results prior to publication.

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