

Pure Quadrupole Spectra of Bromine Compounds. (II)

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Received September 8, 1954

Pure quadrupole resonance spectra have been studied on several solid bromobenzene compounds for the purpose of comparison between the effects of the various substituents. These spectra are due to bromine nuclei (Br^{79} and Br^{81}) and have been found in the frequency range of 210 Mc/s to 280 Mc/s. Dean and Pound¹⁾ reported about the nuclear quadrupole resonance spectra of the solid chlorobenzene compounds in the frequency range of 30 Mc/s to 40 Mc/s. The spectrometer used in the present investigation is the same as that mentioned in the preceeding report²⁾.

The resonane frequencies are listed in the table. There were measured both at room and dry ice temperatures, in order to examine the temperature dependence of the resonance frequencies. For $p\text{-Br}\phi\text{NH}_2\cdot\text{HCl}$, the authors' values can be compared with the one which Bray obtained at liquid nitrogen temperature³⁾. The temperature dependence of the frequencies reported in the table agrees qualitatively with the theory of Bayer⁴⁾.

The resonance frequency increases in the molecule formed by replacing H at the para-position in the bromobenzene by any of OH, NH_2 and NO_2 . These effects

Compound	Frequency (Mc/s)	Temperature
$p\text{-Br}^{79}\phi\text{OH}$	264.97 ± 0.05	Room
	267.10 "	Dry ice
$p\text{-Br}^{81}\phi\text{OH}$	221.37 "	Room
	223.12 "	Dry ice
$p\text{-Br}^{79}\phi\text{NH}_2\cdot\text{HCl}$	273.75 "	Room
	275.85 "	Dry ice
$p\text{-Br}^{81}\phi\text{NH}_2\cdot\text{HCl}$	228.75 "	Room
	230.48 "	Dry ice
$p\text{-Br}^{79}\phi\text{NO}_2$	275.10 "	Room
	276.99 "	Dry ice
$p\text{-Br}^{81}\phi\text{NO}_2$	229.93 "	Room
	231.43 "	Dry ice

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NOTES

are chiefly due to the changes of the bond character of the bromine atom which result from the replacement of H, especially those relating to the π -electrons. However, it is difficult to explain more quantitatively, from these changes of the resonance frequencies, the changes of the bond character caused by the substitutions. It is because the resonance frequencies are also affected by the effects of the environment of the molecule in the crystal, and the magnitudes of these solid state effects cannot easily be estimated, though they are presumable small for the molecular crystals. Moreover, even when the solid state effects are neglected, it is difficult to carry out the exact calculation about the amount of the change in the resonance frequency caused by the substitution mentioned above. Meal⁵⁾ has reported that the linear relations approximately hold between Hammett's constants σ 's and the changes of the resonance frequencies for the chlorobenzene compounds. It seems probable that the same relations hold for the bromobenzene compounds, but in order to verify if these relations hold or not, further data are necessary about the bromobenzene compounds other than those reported above.

The authors would like to thank Prof. R. Nozu, Prof. R. Goto and Prof. S. Kunichika for their continued interest in these researches and taking trouble to prepare the samples.

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