SHORT COMMUNICATIONS

Nuclear Magnetic Resonance Spectra of Dibromothiophene

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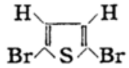
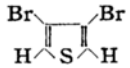
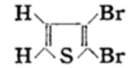
An extensive investigation of nuclear magnetic resonance of substituted thiophenes was carried out recently by Hazato et al.¹⁾, and the results of the measurements of the chemical shifts and of the indirect spin-spin coupling constants J for these molecules were reported. The observed values of the chemical shifts were found in good accord with the values expected from the electronic structures of the substituents, but the chemical shifts due to the difference in the substituent positions were not fully elucidated, since their measurements were not made of 2, 3- or 3, 4-disubstituted thiophene. We, thus, report here the results of the measurements of these compounds.

The apparatus used is the one constructed in this laboratory of the type of high resolution slow-sweep setup which is composed of oscillator, null-T bridge, pre-amplifier, Collins 51J4 receiver, Sanborn recorder, oscillograph, magnet and saw-tooth generator. The magnet has the same structure as the one previously described by Gutowsky²⁾. The field strength of the magnet is about 6200 gauss in 4.8 cm. gap with 12.5 cm. pole face diameter.

The resonance was observed at 27.030 Mc. The disubstituted thiophene and cyclohexane were mixed equally in volume, and sealed in a capillary of about 1 mm. diameter. The shifts were measured as the separations between the spectra of the sample and of cyclohexane. The results are shown in Table I. As the two protons of 2, 3-dibromothiophene are not chemically equivalent, multiple resonance lines should be observed. It was, however, unsuccessfull probably owing to the lack of the intensity.

TABLE 1

CHEMICAL SHIFTS OF DIBROMOTHIOPHENE

substance	shift from cyclohexane
 2, 5-dibromothiophene	140 cps
 3, 4-dibromothiophene	150
 2, 3-dibromothiophene	145

We see in Table I that the diamagnetic shieldings for the 3, 4-protons in 2, 5-dibromothiophene are larger than those for the 2, 5-protons in 3, 4-dibromothiophene. The shift of 2, 3-dibromothiophene falls in the middle of the former two molecules. Our results presented here may be taken as the supplementary data for those of Hazato et al., and all the results will be used for the interpretations of the electronic nature of substituted thiophene.

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1) K. Takahashi, Y. Matsuki, T. Mashiko and G. Hazato. Lectured at the Annual Meeting of Chemical Society of Japan, Tokyo, April, 1958.

2) H. S. Gutowsky, L. H. Meyer and R. E. McClure: *Rev. Sci. Inst.*, **24**, 644 (1953).