PMR Studies of Bromothiophenes[*]

By Kensuke TAKAHASHI, Tyo SONE, Yasuo MATSUKI and Genjiro HAZATO

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At the beginning of the study of thiophene derivatives by PMR, 2, 5- and 3, 4-dibromothiophenes were measured in order to estimate the chemical shift between α- and β-hydrogens in thiophene.[1,2] In this note we will present the experimental results for all bromothiophenes. Tables I and II list the results for the chemical shifts and the coupling constants in cyclohexane solutions at 60 Mc./sec. Chemical shifts for all protons of bromothiophenes occur at a higher applied magnetic field than do those of thiophene itself. Table I shows that the chemical shifts of β-hydrogens fall into the 5.26—5.43 p. p. m. range with reference to cyclohexane, whereas those of α-hydrogens fall at 5.54—5.72 p. p. m., so that the α- and β-hydrogens in bromothiophenes can readily be distinguished from each other by measuring the chemical shifs. The results obtained here are quite useful from the standpoint of the identification of bromothiophenes. The substitution effect of bromine has been discussed in benzene derivatives by many authors and summarized in Smith's paper.[3] Diehl expressed the effect of the X substituent as $S_{o,x}$ or $S_{m,x}$ and stated that the substitution effects in *p*- and *m*-disubstituted benzenes are additive.[4] The S_o, S_m and S_p values estimated by Diehl for bromine in some benzene derivatives are 0.22, −0.11 and −0.06 p. p. m. In thiophene, those effects must be expressed as $S(\mathrm{X})_{ab}$, where *a* and *b* are the positions of the substituent and of the hydrogen in question respectively. By comparing the chemical shifts of the monosubstituted thiophenes with those of the unsubstituted one, S_{23}, S_{24}, S_{25}, S_{32}, S_{34} and S_{35} for bromine are estimated as -0.07, -0.28, -0.13_5, -0.12_5, -0.09 and -0.11 p. p. m. respectively, in which the negative values of $S(\mathrm{Br})$ indicate the displacement toward a higher applied magnetic field. The most pronounced effect appears in 4-hydrogen of 2-bromothiophene as about a shift of −0.28 p. p. m. The additivity of the substitution effect is also roughly valid in the cases of 2, 4- and 2, 5-dibromothiophenes. In other cases of di- and tribromothiophenes, however, the additional effects on the chemical shift of the proton coming from the interaction between the substituents must be considered.

Now if we only consider the interaction between the *ortho*-positioned substituents, the so-called *ortho*-effect, this additional effect may be expressed as follows: $S(\mathrm{X}, \mathrm{Y})_{abc}$, where *a*, *b* and c are the positions of the substituents X and Y and the hydrogen in question. From the shifts of 2, 3- and 3, 4-dibromothiophenes, we can estimate S_{234}, S_{235} and S_{342} for the effects of two ortho-positioned bromines, which are 0.16, 0.13 and 0.18 p. p. m. respectively. Using this additional effect, we can estimate the chemical shifts of 2, 3, 4- and 2, 3, 5-tribromothiophenes by additivity in agreement with the experimental values as follows:

$$\delta_5(2,3,4\text{-Br}_3) = 5.73_5 + S_{25} + S_{35} + S_{32} + S_{235} + S_{345}$$
$$= 5.67_5 \quad (\delta_{\mathrm{exp}} = 5.72)$$
$$\delta_4(2,3,5\text{-Br}_3) = 5.54 + S_{24} + S_{34} + S_{23} + S_{234}$$
$$= 5.26 \quad (\delta_{\mathrm{exp}} = 5.32)$$

The observed coupling constants between the ring protons in bromothiophenes have the usual magnitude[1,5] and the values for 3, 4- and 2, 5-dibromothiophenes have been observed in the spectra of the ^{13}CH satellites in pure liquid.

Another fact of interest is the magnitude of $J(^{13}\mathrm{CH})$. $J(^{13}\mathrm{CH}_\alpha)$ is somewhat larger than $J(^{13}\mathrm{CH}_\beta)$ by about 15 c. p. s., as is shown in Table II. Many more experimental values are needed before we can discuss these results. However, it should be noted that this $J(^{13}\mathrm{CH})$ is concerned with the bond length and s-character of the C–H bond.[6] Therefore, it is assumed that the C–H_α bond has a somewhat larger s-character than the C–H_β bond, and also that the latter is somewhat longer than the former in thiophene and its derivatives. Some results for thiophene and its derivatives have been reported by Goldstein and Reddy, and discussed in connection with the magnetic

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2) S. Fujiwara, S. Hayashi, M. Katayama, H. Shimizu and S. Nishimura, This Bulletin, **32**, 201 (1959).

3) G. W. Smith, *J. Mol. Spectr.*, **12**, 146 (1964).

4) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).

5) K. Takahashi, Y. Matsuki, T. Mashiko and G. Hazato, This Bulletin, **32**, 156 (1959).

6) N. Muller and D. E. Prichard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

TABLE I. CHEMICAL SHIFTS OF THE RING PROTONS IN BROMOTHIOPHENES, REFERRED TO CYCLOHEXANE IN p. p. m. AT 60 Mc./sec.

Substituent	Concn. in C_6H_{12} mol. %	Assignment 2-H	3-H	4-H	5-H
—*	0	5.73_5	5.54	5.54	5.73_5
2-Br*	5	—	5.47	5.26	5.60
3-Br*	14.5	5.61	—	5.45	5.62_5
2,3-Br_2	7.9	—	—	5.33	5.62
2,4-Br_2	7.4	—	5.43	—	5.54
2,5-Br_2	7.9	—	5.26	5.26	—
3,4-Br_2	10.7	5.68	—	—	5.68
2,3,4-Br_3	4.4	—	—	—	5.72
2,3,5-Br_3	3.2	—	—	5.32	—

* K. Takahashi, Unpublished result.

TABLE II. COUPLING CONSTANTS IN BROMOTHIOPHENES IN c. p. s. AT 60 Mc./sec.*1

Subsequent	J_{23}	J_{34}	J_{25}	J_{24}	$J_{^{13}CH_\alpha}$*2	$J_{^{13}CH_\beta}$*2
2-Br*3	5.3	3.6	—	1.4_5		
3-Br*3	4.9_5	—	3.2	1.2_5		
2,3-Br_2	5.7_5	—	—	—	$190._5$	$176._5$
2,4-Br_2	—	—	—	1.6_5	195	$178._5$
2,5-Br_2	—	3.7*2	—	—	—	$174._5$
3,4-Br_2	—	—	3.4_5*2	—	194	—
2,3,4-Br_3	—	—	—	—	$195._5$	—
2,3,5-Br_3	—	—	—	—	—	181

*1 The measured solutions are the same given in Table I.
*2 The measurement was made in pure liquid.
*3 K. Takahashi, Unpublished result.

anisotropy of the compounds.[7] The difference of about 15 c.p.s. measured in bromothiophenes corresponds to the difference in bond length of about 0.006 Å. The microwave analysis of thiophene suggests about the sameorder of difference in bond length between C-H_α and C-H_β.[8]

The solvent effects on the chemical shifts for ring protons were also observed. Three typical solvents were used. The measured samples are pure liquid containing 10 wt. % cyclohexane, a 10 wt. % solution in carbon tetrachloride containing 0.5 wt. % cyclohexane, and a 14 wt. % solution in acetone containing 14 wt. % cyclohexane. The results are summarized in Table III. The value in cyclohexane shown in Table I was used as a reference for each compound. The displacements of the chemical shifts in acetone are large and can be divided into two groups. One is that of β-hydrogen, which falls into the 0.27—0.40 p.p.m. range, while, the other is that of α-hydrogen, which falls into the 0.55—0.67 p.p.m. range; the latter shows larger displacement than the former. However, the displacements in carbon tetrachloride and in pure liquid are rather small and can not so clearly be divided into groups. These results are similar to those obtained in methylthiophenesulfonylchlorides.[9] The displacement of the chemical shift in acetone is practically dependent on the position of the hydrogen rather than on that of the substituent. It seems that

TABLE III. DISPLACEMENTS OF THE RING PROTON RESONANCES WHEN THE SAMPLES ARE DILUTED WITH CYCLOHEXANE, CARBON TETRACHLORIDE AND ACETONE, IN p. p. m., REFERRED TO THE VALUES DILUTED WITH CYCLOHEXANE, MINUS SIGN SHOWING THE DISPLACEMENT TOWARD HIGHER FIELD

Compound	Solvent Pure	CCl_4	Acetone
2,3-Br_2, 4-H	−0.03	0.11	0.27
5-H	−0.09	0.16	0.56
2,4-Br_2, 3-H	−0.03	0.09_5	0.27
5-H	0.00_5	0.12_5	0.54_5
2,5-Br_2	−0.01	0.11	0.33
3,4-Br_2	0.05	0.13	0.55
2,3,4-Br_3		0.15_5	0.66_5
2,3,5-Br_3	0.04_5	0.13	0.40

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[7] J. H. Goldstein and G. S. Reddy, *J. Chem. Phys.*, **36**, 2644 (1962).

[8] B. Bak, D. Christensen, L. H-Nygaard and J. R. Andersen, *J. Mol. Spectr.*, **7**, 58 (1961).

[9] K. Takahashi, Y. Matsuki, Y. Miyake and G. Hazato, This Bulletin, **34**, 1599 (1961).

the interaction between thiophenes and acetone occurs usually near the position of the sulfur atom in thiophene. The origin of the displacement of the chemical shifts of these compounds in the polar solvents has not yet been made clear; however, the experimental results concerning the solvent effect, especially in an acetone solution, can be used as criteria for estimating the position of the hydrogen in an unknown thiophene derivative which is α or β.

The Chemical Research Institute of
Non-Aqueous Solutions
Tohoku University
Katahira-cho, Sendai