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^{13}C NMR SPECTRA OF 1,3-DITHIOLYLIUM TETRAFLUOROBORATE AND RELATED COMPOUNDS

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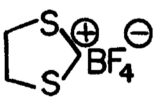
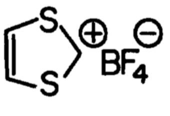
^{13}C NMR spectra of 1,3-dithiolylium tetrafluoroborate and related compounds are recorded. The ^{13}C spectra offer firm proof for the presence of aromatic character in the 1,3-dithiolylium ring, which was deduced from the ^{1}H NMR spectral data.

Tetrathiafulvalene (TTF) has been a focus of intense research for recent years since the finding1) of its formation of highly conducting charge-transfer complex with tetracyanoquinodimethane. The metallic like property of its salts is discussed on the basis of the ionization potential.2) The stabilities of the complexes may be related to the stability of radical cations derived from TTF to, at least, some extent.

A considerable number of literatures have appeared which report ^{1}H NMR data of resonance-stabilized 1,3-dithiolylium cations,3) key intermediates in TTF synthesis. The cations are considered to possess the partial structure of the TTF radical cation. However, to our knowledge, ^{13}C NMR spectra of the 1,3-dithiolylium cations have not been reported. Since the ^{13}C NMR spectrum should give direct insight into the electron densities of carbons, it is generally a more powerful tool than the ^{1}H NMR spectrum for studying the charge delocalization within systems.4) We wish to report the results of ^{13}C NMR study of 1,3-dithiolanyl (1), 1,3-dithiolylium (2), 2-methylthio-1,3-dithiolylium (3), 1,3-benzodithiolylium (4), and 1,3-naphtho[2,3-d]-dithiolylium (5) salts and to describe the effectiveness of these spectral data in discussing the charge delocalization in these compounds.


(1)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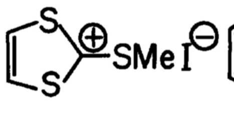
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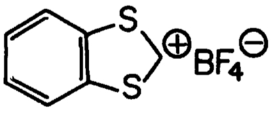
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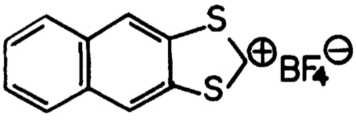

(5)

Known compounds (2,[5] 3,[5] and 4[6]) were prepared according to literatures, whereas new compounds (1 and 5) were prepared by treatment of 2-methylthio-1,3-dithiolane (8) and 2-isopentyloxy-1,3-naphtho[2,3-d]dithiole with tetrafluoroboric acid, respectively. ^{13}C FT NMR spectra were recorded at 27°C on a JEOL JNM-FX 60 spectrometer operating at 15.04 MHz, whereas ^{1}H NMR spectra at 34°C on a Hitachi R-20B spectrometer operating at 60 MHz. Spectra were taken as trifluoroacetic acid-O-d solutions in the cases of the salts, whereas as chloroform-d solutions for the non-ionic species. Assignment of the signals were performed according to the known rules of chemical shifts and intensities. The results are given in Table 1. Estimated errors for carbon-13 chemical shifts are 0.06 ppm for the cations and 0.05 ppm for the corresponding precursors, whereas those for the coupling constants are 0.1 Hz.

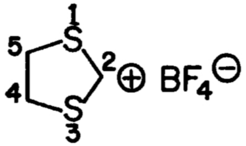
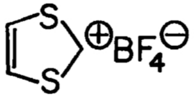
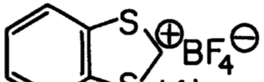
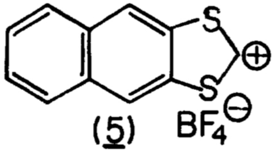
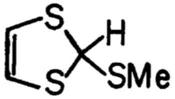
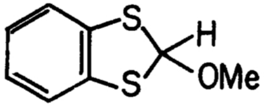
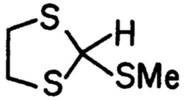
^{1}H NMR spectra of 2-substituted 4-phenyl-1,3-dithiolylium cations in trifluoroacetic acid were reported[3b] and the shift of 5-H signals toward high field was noticed when they carried an electron-donating substituent in 2-position. In accordance with this observation, the signal of vinyl protons of 3 moves to higher field by 0.73 ppm from that of 4,5-protons of 2. However, it must be noticed that the chemical shifts of C_2-H's are almost indifferent among the dithiolylium salts studied here, although the extent of charge-delocalization is expected to differ from compound to compound. The signal of C_2-H in 1 appears at a higher field than those of dithiolylium salts in spite of the fact that the positive charge is most localized in this compound. The anomaly must be attributed to the ring current effect of the aromatic ring.

In contrast, ^{13}C NMR spectra may be regarded to reflect charge density directly because carbon atoms of these compounds comprise the aromatic skeleton. The feature of ^{13}C NMR spectral data of the salts is that, while C_2 of 1 gives a signal at 221.2 ppm down field from the internal TMS, C_2's of others give signals at higher fields by 34 ppm or more. Among the high chemical shifts of C_2's, the highest of 3 may be attributed to the delocalization of the charge over the methylthio group. The results suggest that the positive charge is more delocalized in the dithiolylium cation than in the dithiolanyl cation.

The signals of C_4's of the dithiolylium salts are at the lower field by ca. 100 ppm relative to that of C_4 of the dithiolanyl salt 1. The chemical shift of C_4 in the dithiolylium salt 2 from TMS is larger than that of C_4 in the corresponding dithiole (6) by 30.8 ppm. Since the difference in chemical shfits of C_4's of 1 and 8 is only 7.8 ppm, the large difference between C_4's of 6 and 2 must be taken as an indication of charge-delocalization over this carbon atom. The same trend is also observed in ^{13}C NMR spectral data of C_4 in 3, although the difference between those in 3 and 6 becomes smaller due to delocalization of the positive charge over the methylthio group.

It deserves mention that benzo- and naphtho-annelated derivatives (4 and 5) of the dithiolylium cation show signals due to C_2, the cationic center, at lower fields than the mother compound by 3.3 and 7.6 ppm respectively. The results are reasonable in a sense that the positive charge is delocalized in these compounds at the expense of resonance energy of the aromatic system: the delocalization occurs to

Table 1. ^{1}H and ^{13}C NMR Data of 1,3-Dithiolylium Tetrafluoroborate and Related Compounds[a)]

Compound		^{13}C NMR Data[b)]				^{1}H NMR Data[b)]			
		2-C	4-C	Other Aromatic C's	Other C's	2-H	4-H	Aromatic H's	Other H's
	(1)	221.2	46.4			11.36[c)]	4.50[c)]		
	(2)	179.5	146.2			11.40 (J=1.9)	9.39		
	(3)	166.4	139.7		24.5		8.66		3.24
	(4)	182.4	146.0	128.1 133.5		11.49		8.17[d)] 8.78[d)]	
	(5)	187.1	139.6 (or 135.4)	128.8 129.9 132.7 135.4 (or 139.6)		11.60		7.99[d)] 8.28[d)] 9.29	
	(6)	61.2	115.4		11.8	6.13	6.07		2.20
	(7)	90.9	136.1	121.8 125.3		6.77		7.23[e)]	
	(8)	59.3	38.6		16.7	5.58	3.32		2.22

a) For conditions of the measurement, see the text.
b) Chemical shifts are shown in ppm downfield from the internal TMS.
c) These signals are broad due to long range coupling.
d) These signals are of AA'BB' type.
e) Center of multiplet due to closely located AA'BB' protons.

a lesser extent if the double bond in the 4,5-position is a part of the aromatic system. This idea is also consistent with a well known concept, that is, double bond character of the 2,3-bond in naphthalene is the less: it should cause still less delocalization of the charge. The observed chemical shifts of carbons in 4 are roughly correlated to the electron densities calculated by Koutecký et al.[7] with a simpler MO model neglecting contribution of d-orbitals. A relatively small shift (10.1 ppm) in chemical shifts of C_4's by going from 2-methoxybenzo-1,3-dithiole (7) to 4, compared with that (30.8 ppm) from 6 to 2, may be taken as a phenomenon in a same line: the effect of the methoxy and methylthio groups on the chemical shift of C_4 of the non-ionic compounds may be taken equal as a first approximation.

The results presented here suggest that the aromatic character is present in the 1,3-dithiolylium ring. The stability of the ring seems to be lessened by benzo-annelation. Search for chemical evidence for the order of the stability is under way.

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Note Added in Proof: After submission of this report, a report on NMR spectra of 3, 4 and related compounds in sulfur dioxide is noticed (G. A. Olah and J. L. Grant J. Org. Chem., 42, 2237 (1977)). The results are generally in agreement with ours.

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