2,3-Epoxy-1,2,3,4,4a,8b-hexahydro-*endo*-1,4-methanobiphenylene (32) was obtained as colorless plates, mp 48–50 °C (from the methanobiphenylene **31**):[70] ^{1}H NMR (CDCl$_3$) δ 1.14 (1 H, d, J = 10.0 Hz, H$_{9an}$), 1.74 (1 H, d, J = 10.0 Hz, H$_{9sn}$), 2.60–2.78 (4 H, m, H$_1$–H$_4$), 3.66–3.82 (2 H, m, H$_{4a}$, H$_{8b}$), 7.0–7.26 (4 H, m, aromatic H). Exact mass calcd for C$_{13}$H$_{12}$O, 184.0888; found, 184.0900.

The residue from the reaction of the syn methyl ether **17e** with MCPA was treated with alcoholic KOH at reflux for 1 h. The solution was poured into water followed by extraction with ether. Evaporation of solvent led to the formation of a single solid product whose structure is tentatively assigned as **33** (R = H): IR (CCl$_4$) 3610 cm^{-1} (free OH); ^{1}H FT NMR (CDCl$_3$) δ 3.86 (1 H, HCO), 3.76 (2 H, HCO), 2.5–1.0 (13 H; br m). Exact mass calcd for C$_{12}$H$_{16}$O$_2$, 192.115; found, 192.115.

Kinetic Studies. All solvents were purified immediately prior to use. Dimethyl sulfoxide was distilled under reduced pressure from calcium hydride. Chloroform and dichloromethane were distilled from anhydrous potassium carbonate.

The *s*-tetrazine **2** was recrystallized from benzene. *m*-Chloroperbenzoic acid was obtained from Aldrich and used without further purification. However, the amount of peracid present in the material was determined by adding excess KI to a known weight of peracid and titrating the liberated iodine with thiosulfate solution.

Absolute rates of the reactions of compounds **17** with the *s*-tetrazine **2** in the appropriate solvent were determined spectrophotometrically by monitoring the decrease in the absorbance of **2** at 550 nm with time. Measurements were carried out on a Perkin-Elmer 124 instrument which was fitted with a constant-temperature cell compartment. The initial concentrations of the reactants were made equal, and the measurements were carried out over at least 3 half-lives. Second-order rate constants were determined by the method of integration.[71]

The general procedure for the determination of the relative rates of epoxidation by the competition method is as follows. To a magnetically stirred solution of the competing pair of olefins (0.5 mmol each) in CH$_2$Cl$_2$ (2 mL) at 22.8 °C was added rapidly *m*-chloroperbenzoic acid (0.5 mmol) in CH$_2$Cl$_2$ (2 mL) at the same temperature. The solution was stirred at 22.8 °C until a sample of it gave a negative starch–iodide test. The solution was then shaken with saturated NaHCO$_3$ (2 × 25 mL), dried (Na$_2$SO$_4$), evaporated, and analyzed by ^{1}H NMR spectroscopy (CDCl$_3$ solution).

Acknowledgment. This work was supported by the Australian Research Grants Committee (Grant C66/16344), to whom we express our gratitude. We thank H. Gotthard (NSWIT) and B. McQuillan (NSWIT) for help with the UV and GLC work, respectively, and G. Forster (NSWIT) for the NMR spectra. We are grateful to NSWIT computer center for a generous allocation of computer time. The drawings by P. Harrison (ANU) are greatly appreciated.

Registry No. 2, 1671-87-0; **16**, 28267-19-8; **17a**, 15914-93-9; **17b**, 28068-45-3; **17c**, 36204-31-6; **17d**, 36197-15-6; **17e**, 67401-91-6; **17f**, 67425-33-6; **18**, 33163-94-9; **19**, 36197-32-7; **20d**, 67401-94-9; **21e**, 71369-83-0; **22a**, 71369-84-1; **22b**, 71369-85-2; **22c**, 71369-86-3; **22f**, 71369-87-4; **23a**, 498-66-8; **23f**, 13041-10-6; **24a**, 35909-32-1; **24c**, 67401-96-1; **24f**, 67425-36-9; **25**, 71369-88-5; **29**, 40488-88-8; **30**, 36197-31-6; **31**, 27297-13-8; **32**, 40644-04-0; **33** (R = H), 71369-89-6; 5-norbornenone, 694-98-4; cyclopentadiene, 542-92-7.

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(70) M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, 81, 5409 (1959).

(71) K. J. Laidler, "Chemical Kinetics", 2nd ed., McGraw-Hill, New York, 1965, p 5.

Substituent Effects on the Rotational Barrier in Protonated 2,2′-Bithienyl and the Relation to Charge Development in Protodetritiation

David A. Forsyth* and Dennis E. Vogel

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

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Protonation of 2,2′-bithienyl in superacid media occurs at the 5-position to give the stable arenium ion, 2-(2′-thienyl)-5-thiophenium ion (1). The energy barrier to rotation about the bond connecting the two rings was determined to be $\Delta G^{\ddagger}$ = 11.4 kcal mol^{-1} by dynamic NMR methods. Substituent effects on the rate of rotation are correlated by σ_p^+ constants with a ρ value of 4.8. The relation between substituent effects on the rotational barrier and on the rate of protodetritiation is discussed in terms of charge development in the transition state for protodetritiation.

Despite extensive NMR studies of the structure and rearrangements of stable carbocations,[1,2] relatively little attention has been paid to conformational equilibria and dynamics in these ions. The dynamic NMR (DNMR) study of conformational changes in carbocations is a potentially rich source of information about electronic interactions that may differ considerably from those in neutral systems. In this paper, we report a study of the electronic character of an arenium ion by application of DNMR methods. Specifically, we examine substituent effects on the rotational barrier in stable, protonated 2,2′-bithienyl. By comparison with substituent effects on the kinetics of protodetritiation of 2,2′-bithienyl, we gain insight into the extent of charge development in the arenium ionlike transition state for protodetritiation.

The formation of stable arenium ions by protonation of arenes in superacid media is well established.[3] The stable 2-thiophenium ion is formed by the protonation of thiophene at the 2-position.[4,5] Similarly, we find that

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(1) G. A. Olah, "Carbocations and Electrophilic Reactions", Wiley, New York, 1974.

(2) For reviews of the methods and types of ions, see "Carbonium Ions", Vol. I–V, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York.

(3) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions", Vol II, G. A. Olah and P. v. R. Schleyer, Ed., New York, 1970.

(4) H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, 85, 1072 (1966).

Table I. ^{1}H and ^{13}C NMR Chemical Shift Data for 1 at -75 °C[a]

atom positions[b]	δ_H, ppm[c]	δ_C, ppm[c]
2		204.0, 205.1
3	8.09, 8.28	135.9, 136.7
4	8.66	169.4, 170.6
5	5.20 (2 H)	54.6
2′		136.4, 137.5
3′	8.64, 8.84	143.9
4′	7.84, 7.87	133.3, 134.7
5′	8.97, 9.01	151.2

[a] Chemical shifts are given for both conformers. Specific assignments for cis or trans conformers were not attempted. Assignments were made on the basis of deuterium labeling experiments and by comparison to spectra of a series of 2-thienylcarbenium ions (D. A. Forsyth and G. A. Olah, *J. Am. Chem. Soc.*, in press) and a series of protonated thiophenes (G. A. Olah and D. A. Forsyth, unpublished data). Where two chemical shifts are listed for a position, an averaged signal was observed at -20 °C. [b] Numbering as illustrated for 1 in the text. [c] Relative to Me_4Si, referenced to tetramethylammonium tetrafluoroborate (δ 3.20, ref 4).

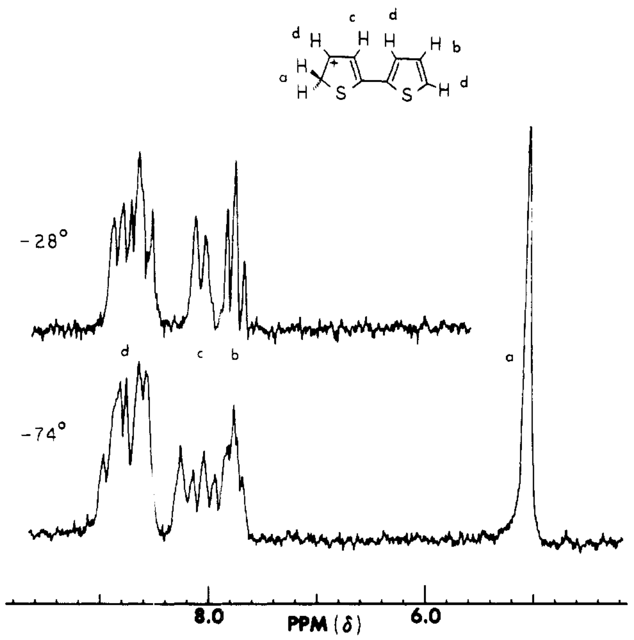
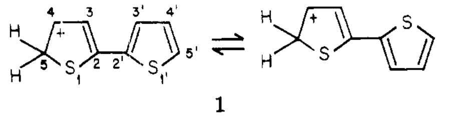


Figure 1. 60 MHz ^{1}H NMR spectra of protonated 2,2′-bithienyl (1).

2,2′-bithienyl protonates at the 5-position to give the arenium ion, 2-(2′-thienyl)-5-thiophenium ion (1). This ion undergoes rotation about the bond connecting the two rings at rates accessible to standard DNMR techniques of line shape analysis.



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Results

^{1}H and ^{13}C chemical shifts for protonated 2,2′-bithienyl, 1, formed in the addition of 2,2′-bithienyl to 1:1 FSO_3H-SbF_5 in SO_2ClF at -78 °C, are listed in Table I. The ^{1}H NMR spectrum (Figure 1) of protonated bithienyl displays two doublets of equal size for H_3 (H_c in Figure 1) at -74 °C, indicating equal populations for two different conformers. At -28 °C, exchange is fast on the NMR time scale, and the two doublets have collapsed to a single doublet. The process is entirely reversible, and the spectra at intermediate temperatures show the broadening and coalescence of the two doublets.

Table II. Rotational Barriers for 5-Protonated 5′-Substituted 2,2′-Bithienyls

substituent	$\Delta G^{\neq}$, kcal/mol	temp, °C	$\log k_X/k_0$ (-23 °C)
I	11.1 ± 0.2	−40	0.22
Br	11.2 ± 0.3	−46	0.25
H	11.4 ± 0.3	−50	0.00[a]
Cl	11.7 ± 0.2	−41	−0.34
F	12.3 ± 0.3	−23	−0.79
CH_3	13.5 ± 0.3	−3	−2.11

[a] At -23 °C, $k_0 = 5.25 \times 10^2$ s^{-1}.

Spectra of 1 taken at six temperatures in the range of intermediate rates of exchange were matched to theoretical spectra generated by DNMR3[6a] simulation for different exchange rates to determine rate constants for the conformational change. The spectra were simulated for H_3, H_4, and H_5, which form a spin system not coupled to $H_{3'}$, $H_{4'}$, or $H_{5'}$.[6b] From the rate data, the energy barrier for conformational interconversion in protonated 2,2′-bithienyl was determined to be $\Delta G^{\ddagger} = 11.4 \pm 0.3$ kcal mol^{-1} at -49 °C.

However, before this energy of activation is used to represent the energy barrier for simple rotation, other possible mechanisms must be considered. Any rapid process which gives an intermediate having less π bond character between the thiophene rings will lower the barrier to rotation. In addition to simple rotation, three other mechanisms can be envisioned for conformational interconversion. One possible mechanism is deprotonation–rotation–protonation. This is a possibility since the rotational barrier for bithienyl is lower than that for protonated bithienyl, and rapid proton exchange between arenium ions and solvent is known.[7] The deprotonation–rotation–protonation sequence has been reported for conjugate acids of benzaldehydes.[8] A second competitive mechanism could be protonation–rotation–deprotonation, where the first step would be protonation of the second thiophene ring to give a dication. A similar mechanism is observed with the conjugate acid of *p*-methoxybenzaldehyde.[9] A third alternative mechanism is 1,2-hydride shift–rotation–2,1-hydride shift.

The alternative mechanisms can be ruled out simply from the observation that the methylene peak in the ^{1}H NMR spectrum of 1 shows no exchange broadening, indicating that these protons do not exchange rapidly with the FSO_3H protons after initial protonation and that there is no rapid exchange with protons at other positions. To prove that these mechanisms do not compete even at slower rates, the ^{1}H NMR spectra of species 2 and 3 were obtained from 5,5′-dideuterio-2,2′-bithienyl in 1:1 FSO_3H-SbF_5 and SO_2ClF and 2,2′-bithienyl in 1:1 FSO_3D-SbF_5 and SO_2ClF, respectively. After several hours at -20 °C, there was no scrambling due to 1,2-hydride shifts, no loss

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(5) H. Hogeveen, R. M. Kellogg, and K. A. Kuindersma, *Tetrahedron Lett.*, 3929 (1973).

(6) (a) D. A. Kleier and G. Binsch, *J. Magn. Reson.*, **3**, 146 (1970); QCPE Program No. 165, Indiana University. (b) Simulated using $J_{3,4} = 5.5$ Hz, $J_{3,5} = 1.0$, and $J_{4,5} = 1.7$. Coupling to the two H_5 nuclei is evident in the broadened H_5 peak and was well resolved in spectra of some of the substituted compounds.

(7) C. MacLean and E. L. Mackor, *Discuss. Faraday Soc.*, **34**, 165 (1962).

(8) J. Sommer, T. Drakenberg, and S. Forsen, *J. Chem. Soc., Perkin Trans. 2*, 520 (1974).

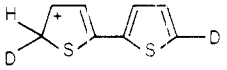
(9) J. Sommer, P. Rimmelin, and T. Drakenberg, *J. Am. Chem. Soc.*, **98**, 2671 (1976).

Table III. Time-Averaged ^1H Chemical Shifts[a] for 5′-Substituted 2-(2′-Thienyl)-5-thiophenium Ions

substituent	H_3	H_4	H_5	H_3'	H_4'	other
I	7.92	8.48	4.97	8.14	7.87	
Br	7.93	8.46	5.06	8.33	7.68	
H	8.19	8.66	5.20	8.74	7.84	8.99 H_5'
Cl	7.77	8.31	4.94	8.24	7.34	
F	8.12	8.59	5.29	8.59	7.39	
CH_3	7.74	8.19	5.01	8.28	7.33	3.94 CH_3

[a] δ scale, $Me_4Si = 0$. Parent compound was referenced to tetramethylammonium tetrafluoroborate (δ 3.20, ref 4). Others were referenced to the methyl signal of the external sample of methanol.

of deuterium from species **2**, and no further incorporation of deuterium in species **3**. Also, no dependence of the rotation rate on superacid strength was observed in spectra of **1** obtained by protonation with FSO_3H, HF/SbF_5, or $FSOH/SbF_5$. This last result suggests that ion pairing plays no role in determining the rotation rate, since the rate is the same in the presence of different counterions.



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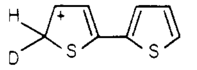

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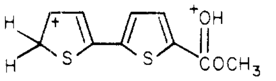
Rotational barriers were also determined for 5-protonated 2,2′-bithienyl substituted by halogens or methyl in the 5′-position. In Table II are listed the values of $\Delta G^{\ddagger}$ determined from rates found by DNMR3 line shape analysis of ^1H NMR spectra obtained at 5 to 12 temperatures in the intermediate exchange region. In each case, the cation was formed by protonation with FSO_3H in SO_2ClF. Also listed in Table II are logarithms of the relative rate constants ($\log k_X/k_0$) at −23 °C, determined from rates extrapolated from the Arrhenius equation. The time-averaged ^1H chemical shifts for the substituted 2-(2′-thienyl)-5-thiophenium ions are given in Table III.

We attempted to obtain data for a broader range of substituents but failed for a variety of reasons. The 5′-trimethylsilyl group is cleaved immediately in FSO_3H, resulting simply in the formation of **1**. Another problem is that most common electron-withdrawing groups protonate in superacid media, thereby changing their electronic character. For instance, we found that 5′-carbomethoxy-2,2′-bithienyl protonated on both the ring and side chain to give the dication **4**. With the very strong electron-withdrawing group formed by protonation of the carbonyl oxygen, the barrier for ring–ring rotation becomes so low that we were not able to obtain the "frozen out" spectra of the two conformers. On the other hand, the strongly electron-donating 5′-methoxy substituent increased the barrier to the point that the protonated species underwent decomposition, at about 20 °C, before the spectra began to coalesce.



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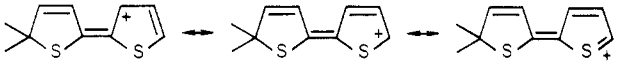
Discussion

The temperature-dependent NMR spectra of protonated 2,2′-bithienyl clearly indicate a rotational equilibrium between s-cis and s-trans conformers, which are equally stable. The energy barrier of ~11 kcal mol^{-1} measured for the interconversion corresponds to rotation through a conformation where the two rings are perpendicular. This barrier is more than twice as large as the rotational barrier of ~5 kcal mol^{-1} estimated for neutral 2,2′-bithienyl.[10] The evidence discussed below suggests that the increased barrier is due to the increased π-electron interaction between the two rings associated with charge delocalization from the protonated ring into the second ring as shown in **5–7**. Because of the π interaction, the s-trans and s-cis conformers are probably planar or nearly so and should be considerably more stable than the perpendicular form where charge delocalization via the π system is not possible. A similar effect of electron delocalization is seen in the radical anion of 2,2-bithienyl, in which there is a substantial barrier to interconversion of conformers.[11]



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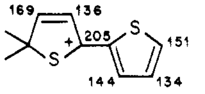
^{13}C NMR chemical shifts in protonated bithienyl provide evidence for charge delocalization into the second ring. Particularly noteworthy is the δ_C 151 ppm for C_5' in the thienyl ring of **1**,[12] which is substantially deshielded relative to δ_C 124 for the corresponding position in neutral thiophene **8**. Also, the carbons in the thiophenium of **1** are less deshielded at each position than those in the thiophenium ion **9** itself. Although due caution must be observed when interpreting ^{13}C shifts in terms of electronic charge, these results are obviously consistent with resonance delocalization of charge from the thiophenium ring into the thienyl ring. Further, the ^{13}C shifts at each position for the two conformers of **1** are very similar (Table I), suggesting approximately equal π overlap between the two rings in the two conformations.



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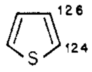

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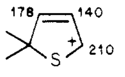

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Other evidence for π charge delocalization is provided by the observed substituent effects (Table II). The log k/k_0 correlate better with σ_p^+ constants ($\rho = 4.81$, $i = 0.47$, corr coef = 0.93) than with σ_p constants ($\rho = 4.66$, $i = -0.87$, corr coef = 0.76). The correlation with σ_p^+ constants indicates the importance of resonance donation of electrons by the substituents to stabilize the positive charge delocalized into the thienyl ring. In fact, the balance of polar and resonance effects is perhaps weighted more heavily toward resonance than is represented by the σ_p^+ constants, since both fluoro and chloro decrease the rate of rotation relative to the unsubstituted system. However, the number and type of substituents are not sufficient to justify treatment by a dual substituent parameter equation to rigorously examine this question.[13]

The value of ρ of 4.8 is also informative. Since the value of ρ is positive, it is clear that there is greater interaction with the positive charge in the ground state (planar or near-planar geometry) than in the transition state (geometry with rings perpendicular). Also the magnitude of ρ is relatively high, indicating a substantial change in charge development at the site of substituent attachment during the reaction. Obviously, the total charge in the ion does not change during the rotation, but the positive charge which is delocalized through both rings in the

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(10) P. Bucci, M. Longeri, C. A. Veracini, and L. Lunazzi, *J. Am. Chem. Soc.*, **96**, 1305 (1974).

(11) P. Cavalieri d'Oro, A. Mangini, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Tetrahedron Lett.*, 4179 (1969).

(12) Time-averaged shifts are shown in the illustration.

(13) R. T. C. Brownlee, S. Ehrenson, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1 (1973).

ground state is shifted to the thiophenium ring in the transition state, leaving the thienyl ring essentially neutral. In comparison, the magnitude of ρ is smaller for the protodetritiation of 5′-X-5-tritio-2,2′-bithienyl in trifluoroacetic acid–acetic acid at 25 °C ($\rho = -1.7$).[14]

The rate-determining process in protodetritiation is that of formation of the arenium ion from the neutral arene. The transition state leading to the arenium ion would have only a partially developed bond between the ring and the proton and thus there would not be full charge development in the protodetritiation transition state. A rough estimate of charge development is that $\sim^1/_3$ (35%) of the charge in the fully formed ion is present in the transition state for protodetritiation. This estimate is obtained by comparing the relative magnitudes of ρ for protodetritiation of 2,2′-bithienyl and ρ for the rotational process in protonated bithienyl ($\rho/\rho = 1.7/4.8$), while making the assumption that the magnitude of ρ is a measure of charge development.[15] The comparison is reasonable because for either process, the substituents exert their influence through the thienyl ring which is involved in π delocalization of a positive charge in one state and is essentially uncharged in the other state.[16] Of course, the estimate is only a rough approximation, and no corrections are made for solvent or temperature effects.

The estimate of $\sim^1/_3$ charge development in the transition state for protodetritiation is in agreement with an estimate which can be made on the basis of molecular orbital calculations. Streitwieser et al.[17] calculated substituent effects on the proton affinity of benzene, using the ab initio STO-3G method,[18] and obtained a value of ρ of -17 at 25 °C. The value of -17 is derived from MO calculations in which the benzenium ions are fully formed and thus carry the full positive charge in the π system. The experimental data of Eaborn and Taylor[19] for the protodetritiation of p-X-$C_6H_4{}^3H$ in CF_3CO_2H–H_2O–H_2SO_4 at 25 °C yield a value of ρ of -6.5. Comparison of the experimental and theoretical values of ρ leads to the conclusion that there is 38% or again $\sim^1/_3$ charge development in the transition state for protodetritiation.

Experimental Section

Materials. The superacids FSO_3H, 1:1 FSO_3H-SbF_5, 1:1 FSO_3D-SbF_5, and 1:1 HF-SbF_5 and SO_2ClF were obtained from Cationics, Inc., and were used without further purification. 2,2′-Bithienyl (**10**) was prepared by a known method[20] and was also obtained commercially (Pfalz and Bauer). All other bithienyls, except 5-bromo-2,2′-bithienyl, were prepared from **10** by first forming 5-lithio-2,2′-bithienyl (**11**), followed by quenching with the appropriate reagent. Lithiation of **10** in ether with n-butyllithium in hexane to form **11** followed a procedure used for lithiation of benzothiophene.[21] A sample of each substituted 2,2′-bithienyl compound was obtained in >96% purity, as indicated by GC, NMR, IR, and MS analysis, by using column chromatography on silica gel. All compounds were previously known except 5-fluoro-2,2′-bithienyl.

5-Chloro-2,2′-bithienyl (12). Chlorine gas was bubbled through a solution of **11** (0.012 mol) at 0 °C until the solution turned dark and opaque. After the solution had been stirred overnight, it was washed (H_2O) and dried ($MgSO_4$), and the solvents were evaporated. The residue was separated by elution with hexane from a column of silica gel into **8** and 0.57 g (24%) of **12**. IR data were consistent with literature data.[22]

5-Fluoro-2,2′-bithienyl (13). Perchloryl fluoride was reacted with **11** (0.02 mol) following the procedure used by Scheutz[23] for 2-fluorothiophene. Following workup, chromatography on silica gel with hexane gave 0.56 g (15%) of **13**: NMR ($CDCl_3$) δ 6.30 (dd, J = 4 Hz, J_{HF} = 2 Hz, 1 H, H-4), 6.65 (t, J = 4 Hz, J_{HF} = 4 Hz, 1H, H-3), 6.82–7.15 (m, 3 H, H-3′,4′,5′);[24] IR (film) 1185 (C-F), 835 (5′-unsubstituted bithienyl), 780 (2,5-disubstituted thiophene), and 685 cm^{-1} (5′-unsubstituted bithienyl); mass m/e 184 $[M]^+$. MS indicated contamination by 5,5′-difluoro-2,2′-bithienyl (m/e 202, ~1% of intensity of m/e 184) and possible contamination by a maximum of ~2% of **10**.

5-Methyl-2,2′-bithienyl (14). Dimethyl sulfate (2.5 g, 0.02 mol) and a solution of **11** (0.02 mol) in ether were stirred at room temperature for 2 days. The solution was washed with a 10% solution of $NaHCO_3$ and with water and dried ($MgSO_4$), and the solvents were removed by evaporation. GC indicated the residue contained 67% **14**, 29% **10**, and 4% 5,5′-dimethyl-2,2′-bithienyl. Chromatography on silica gel with hexane gave a pure sample of **14**: IR data in agreement with literature.[25]

5-Iodo-2,2′-bithienyl (15). A solution of **11** (0.01 mol) was added to a solution of 12.5 g (0.05 mol) of I_2 in ether. After the mixture had been stirred for 15 h, it was washed with saturated sodium thiosulfate in water, washed with dilute HCl followed by water, and dried ($MgSO_4$). Removal of the solvents by evaporation gave a mixture of **15** (40%) and **10** (60%). Chromatography with hexane on silica gel gave pure **15**: IR data in agreement with literature.[22]

5,5′-Dideuterio-2,2′-bithienyl (16). A solution of **11** (0.01 mol) was quenched with excess (1 mL) D_2O to give partially deuterated **10**. The lithiation procedure was repeated to obtain partially deuterated **11** which was quenched again with D_2O. After isolation, NMR and MS analysis indicated that the 2,2′-bithienyl was 70% deuterated at the 5,5′-positions.

5-Bromo-2,2′-bithienyl (17). A solution of 6.64 g (0.04 mol) of Br_2 in 40 mL of $CHCl_3$ was added to a solution of 3.32 g (0.02 mol) of **10** in 180 mL of $CHCl_3$ at 35 °C over 45 min, followed by stirring at 35 °C for 1 h. The solvent was removed to give a mixture of **10** (85%) and **17** (15%). Chromatography with hexane on silica gel gave a pure sample of **17**: IR data in agreement with literature.[22]

Preparation of Ions. Solutions of the 2-(2′-thienyl)-5-thiophenium ions were prepared by the stepwise addition of the bithienyl precursor to a solution of FSO_3H and SO_2ClF (about 1:2 v/v) at -78 °C (dry ice–acetone bath). After addition of each portion, the mixture was alternately cooled and stirred vigorously with a vortex stirrer until all of the bithienyl compound had dissolved. The acid was used in about tenfold molar excess relative to the bithienyl compound. Similar procedures were used for preparation of ions with other superacids.

Nuclear Magnetic Resonance Spectroscopy. ^1H NMR spectra were obtained on a Varian A-60A spectrometer equipped with a V6040 temperature controller. The ^{13}C spectrum was obtained on a Bruker WP-90 spectrometer. Temperatures were determined by monitoring the peak separation in a methanol sample and are expected to be accurate to about ±1 °C. Spectra were not measured until the methanol sample indicated that the

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[14] Determined from the effect of the 5-CH_3 substituent only: A. R. Butler and C. Eaborn, *J. Chem. Soc. B*, 370 (1968).

[15] For evidence that ρ values can be used as a measure of charge, see (a) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, p 177; (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, p 360; (c) C. Eaborn, R. Eastmond, and D. R. M. Walton, *J. Chem. Soc. B*, 752 (1970); (d) D. A. Forsyth and D. S. Noyce, *Tetrahedron Lett.*, 3893 (1972); (e) H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, 1977; and (f) D. J. McLennon, *Tetrahedron*, **34**, 2331 (1978).

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probe temperature was constant, 10 min were allowed for temperature equilibration of the ion samples, and the temperature was rechecked following recording of the sample spectrum.

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Registry No. **1**, 71486-34-5; **8**, 110-02-1; **10**, 492-97-7; **11**, 71486-35-6; **12**, 3339-85-3; **13**, 71486-36-7; **14**, 18494-74-1; **15**, 3339-79-5; **16**, 18592-88-6; **17**, 3480-11-3; 5,5′-dimethyl-2,2′-bithienyl, 16303-58-5; 5′-iodo-2-(2′-thienyl)-5-thiophenium ion, 71486-37-8; 5′-bromo-2-(2′-thienyl)-5-thiophenium ion, 71486-38-9; 5′-chloro-2-(2′-thienyl)-5-thiophenium ion, 71486-39-0; 5′-fluoro-2-(2′-thienyl)-5-thiophenium ion, 71486-40-3; 5′-methyl-2-(2′-thienyl)-5-thiophenium ion, 71486-41-4.

Aromatic Nucleophilic Substitution. 12.[1] Electronic Structures of 1,1-Disubstituted 2-X-4-Y-Naphthalene Meisenheimer Complexes

Shizen Sekiguchi,* Tetsuo Hirose, Kinzo Tsutsumi, Toshiaki Aizawa, and Haruo Shizuka

Department of Synthetic Chemistry, Gunma University, Tenjincho, Kiryu, Gunma 376, Japan

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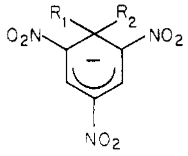
The electronic structures of 1,1-disubstituted 2-X-4-Y-naphthalene Meisenheimer complexes (**2b**⁻, X = NO_2, Y = CN; **2c**⁻, X = CN, Y = NO_2; **2d**⁻, X = Y = CN) were studied by UV–visible and IR spectrophotometry and compared with the results calculated by a semiempirical SCF–MO–CI method. The electronic transitions in the complexes were assigned to those of π–π^*. Calculated transition energies and intensities agree well with the observed values. Calculations showed that ca. 48–78% of one negative charge donated by a nucleophile ($^-OCH_3$) in the formation of the complex is distributed on the X and Y groups in the S_0 state, while ca. 67–86% is distributed on them in the S_1 state. The more the one negative charge is distributed on the X and Y groups, the more stable an anionic σ complex is.

A number of Meisenheimer complexes (hereafter referred to as anionic σ complexes) such as 1⁻ (hereafter the minus sign represents an anionic σ complex; R_1 and R_2 are alkoxyl, hydroxyl, amino, cyano, and halogeno groups, etc.) have been prepared by nucleophilic attack on polynitroaromatic compounds.[2] Since such anionic σ complexes were found as intermediates in some aromatic nucleophilic substitution reactions, much attention has been paid to them from mechanistic and theoretical points of view. The electronic structure of anionic σ complexes such as 1⁻ was already reported by several workers.[3-5] However, no MO treatment has been performed for naphthalene anionic σ complexes except for our work[5] on **2a**⁻. As a preliminary stage preceding a kinetic study on the formation and decomposition of **2a**⁻, **2b**⁻, **2c**⁻, and **2d**⁻, we have attempted the MO treatment of **2b**⁻, **2c**⁻, and **2d**⁻.



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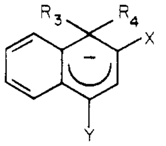
This paper reports the electronic structures of **2b**⁻, **2c**⁻, and **2d**⁻ and the comparison of the observed spectral results with those of the MO treatment.



2a⁻, X = Y = NO_2
b⁻, X = NO_2; Y = CN
c⁻, X = CN; Y = NO_2
d⁻, X = Y = CN
R_3 = OCH_3; R_4 = piperidyl

Method of Calculation

Calculation was carried out on the basis of a semiempirical SCF–MO–CI method according to the procedure described in a previous work.[6]

The geometry of complex 2⁻ was assumed as follows (see Figure 1). The C–C bond lengths and all bond angles were assumed to be 1.39 Å and 120°, respectively. The C–N, C≡N, and N–O bond lengths were assumed to be 1.486, 1.160, and 1.210 Å, respectively. The computation was carried out with a HITAC 8800/8700 located at the Computer Center of the University of Tokyo.

Experimental Section

Melting points are uncorrected. Elemental analyses were performed at the Microanalytical Center of Gunma University. Visible absorption spectra were measured with a Hitachi-124 UV spectrophotometer. All reagents were purified by repeated recrystallizations or by distillations.

1-Chloro-2-nitro-4-cyanonaphthalene (3b). 4-Hydroxy-1-naphthaldehyde (**4**) was prepared from α-naphthalenol according to the method of Gattermann and Horlacher;[7] mp 171–175 °C (lit.[7] mp 180 °C). 4-Hydroxy-1-naphthonitrile (**5**) was prepared

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