Pure & Appl. Chem., Vol. 68, No. 2, pp. 267–274, 1996.
Printed in Great Britain.

Trimethylenemethanes extended with aromatic rings

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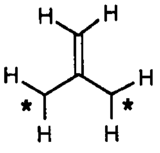
Abstract - Hexaaryl substituted trimethylenemethane dications and dianions extended with thiophenes or benzenes have been synthesized through regioselective lithiation and functionalization of the corresponding triarylmethanes. These molecules are featured by highly tetrapolar properties and long-wavelength absorption in near infrared region. While thiophene-extended dications and dianions are considerably stable, benzene-extended dications are very sensitive to acidity of media to exist in equiribrium with protonated trications.

INTRODUCTION

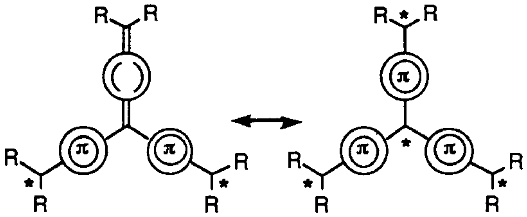
Trimethylenemethane (TMM **1**) and its ionic species $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$ have attracted much attention from theoretical, physicochemical and synthetic points of view. 1) Diradical **1** has been theoretically predicted and experimentally confirmed to be ground state triplet (1). 2) The molecule is, however, extremely unstable and was observed only at very low temperatures. 3) On the other hand, dianion $\mathbf{1}^{2-}$ was found to be unusually stable for such a simple hydrocarbon dianion. The notion of "Y-aromaticity" was once proposed for the stabilization (2), but later theoretical studies has ascribed the unusual stability to maximally distant localization of the π-electrons by virtue of the D_{3h} symmetry (3). 3) Dication $\mathbf{1}^{2+}$ itself remains unknown, though some derivatives have been reported (4). Efforts have been made for stabilization of these species by aid of proper substituents; however, improvements have been rather limited probably because the substituents introduced interact sterically each other to decrease thier conjugative effects (5).

We designed trimethylenemethane analogues, general structure **2**, where aromatic rings are inserted into each carbon-carbon bond of **1**. Simple Hückel MO calculation on a model compound (R = H and benzene ring insertion) shows similar situation with **1** having two degenerated nonbonding orbitals, but the orbitals are much denser with narrow LUMO-HOMO energy gap owing to extended conjugation. Our question on the properties of **2** are following: (a) do they show increased stability electronically or sterically by proper substituents and decreased steric repulsion between the terminal substituents ?, (b) are their diradicals ground state triplet too ?, and (c) do di-ionic species show enhanced charge separation owing to aromatic stabilization of the inserted rings, namely greater resonance contribution of **2 B** ?

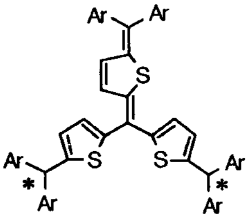
Among a good variety of such extended TMM conceivable, we have at first studied hexaaryl substituted thiophene- or benezene-extended TMM, **3** and **4**. We here describe the results so far obtained on these molecules.



1: * = •
1^{2+}: * = +
1^{2-}: * = -



2A 2B



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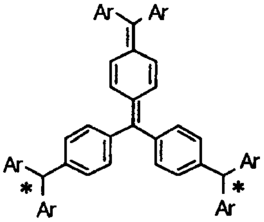

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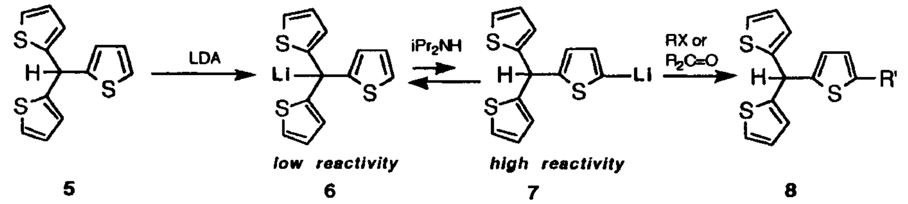
THIOPHENE EXTENDED TRIMETHYLENEMETHANE DICATIONS AND DIANIONS

For the synthesis of **3**, we chose tri(2-thienyl)methane **5** as the starting material based on the possible retrosynthesis. Nakayama *et al.* recently reported that compound **5** is regioselectively lithiated at the central methyne position (Cα) with n-BuLi or n-BuLi-TMEDA in THF (6). This selectivity is unfavorable for our purpose, because we need regioselective metalation and/or functionalization of **5** at 5-positions (C-5) of the thienyl groups. However, our recent findings on the regioselective metalation and functionalization of di(2-thienyl)methane either at Cα and C-5 (7) led us to use lithium diisopropylamide (LDA) as a promising base.

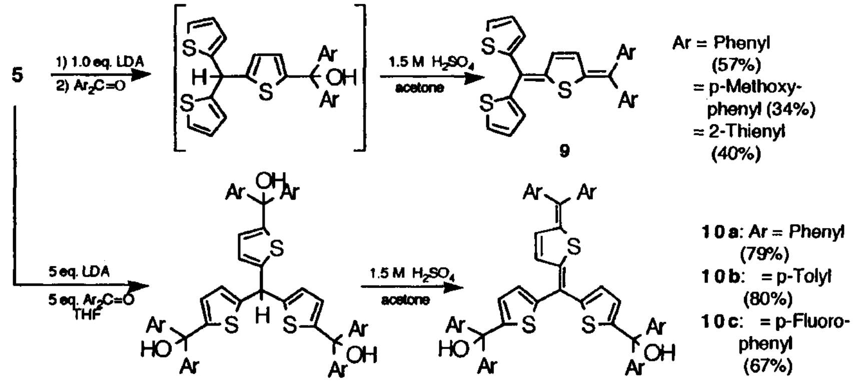
Treatment of **5** with LDA in THF followed by addtion of weak or bulky electrophiles at below to 0 °C was found to indeed furnish C-5 functionalized compounds **8** (Scheme 1) (8). Although LDA in fact forms thermo-dynamically more stable Cα-anion **6** much predominantly (^{1}H NMR), liberated diisopropylamine mediates slight but smooth equilibrium with C-5-anion **7**. On account of large reactivity difference between **6** and **7** featured by notably poor reactivity of **6** due to extensive delocalization and stronger steric hindrance, the equilibrium mixture tends to favor C-5-functionalization.

Scheme 1



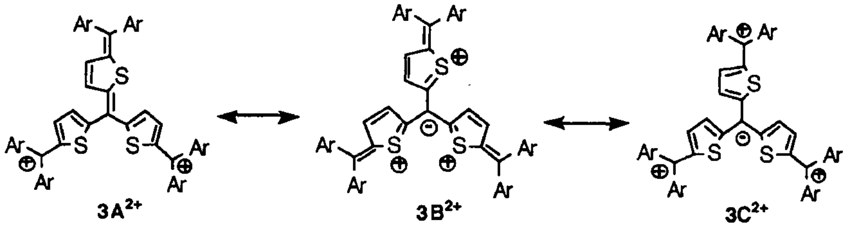
Thus, upon treatment with one equivalent of LDA and diaryl ketones followed by acid treatment (dil. H_2SO_4) of the crude alcohols gave dehydrated thienoquinoid compounds **9** in moderate yields, providing a new synthetic way for a vriety of thienoquinoid sompounds, in particular non-symmetric compounds (Scheme 2). The limited yields are due to some concurrent multi-functionalization. But tri-functionalization is free of the selectivity problem met with the mono-functionalization and proceeds in higher yields by use of excess LDA and diaryl ketone, leading to diols **10** that are suitable for the generation of dications **3**$^{2+}$. It should be noted that the triple functionalization does not proceed in one step through the trilithio compound but does in stepwise manner through the equilibrium.

Scheme 2



Diols **10** are expected to be direct precursors for dications **3**$^{2+}$. Dissolution of **10** in trifluoroacetic acid cleanly yielded the corresponding dications in geen solutions [e.g. **3a**$^{2+}$; λ_{max} 423 (logε 4.51), 779 nm (4.74)]. Diperchlorate salts were isolated by treatment of **10** with perchloric acid in acetic anhydride ^{1}H NMR spectra of **3**$^{2+}$ show some broadening of the signals around room temperature. It is the signals of terminal aryl groups that show the broadening, and the signals of thiophene protons are observed as a sharp AB quartet (Figure 1), indicating restricted bond rotation of the diarylmethylene group. Variable temperature NMR measurements (10-50 °C) on **3b**$^{2+}$ gave the following kinetic parameters: $\Delta H^{\neq} = 15.4$ kcal/mol, $\Delta S^{\neq} = 1.6$ eu. ^{13}C NMR spectra of **3**$^{2+}$ also show the temperature dependence due to the dynamic process. The most notable feature of the molecule is a large chemical shift difference between the central methyne carbon Cα (e.g. **3a**$^{2+}$; δ 115.8 ppm) and the diphenylmethylene carbon Cβ (δ 175.9) (Figure 2). The chemical shift of Cα is even higher than that of precursor diol **10a** (δ 116.9). Since Cα protons were difficult to observe, in particular for dianions, ^{13}C-enriched samples at Cα were also prepared starting from ^{13}C-enriched ethyl formate to make sure the assignments. The large chemical shift differences suggest highly tetrapolar property of dications **3**$^{2+}$, namely importance of the resonance structures **3B**$^{2+}$ and/or **3C**$^{2+}$, and the restricted bond rotation indicates appreciable importance of the thiafulvene sttructure **3B**$^{2+}$ (Scheme 3). Attempts to protonate at Cα in stronger acid such as conc. H_2SO_4 and CF_3SO_3H were, however, not successful enough resulting in decomposition.

Scheme 3



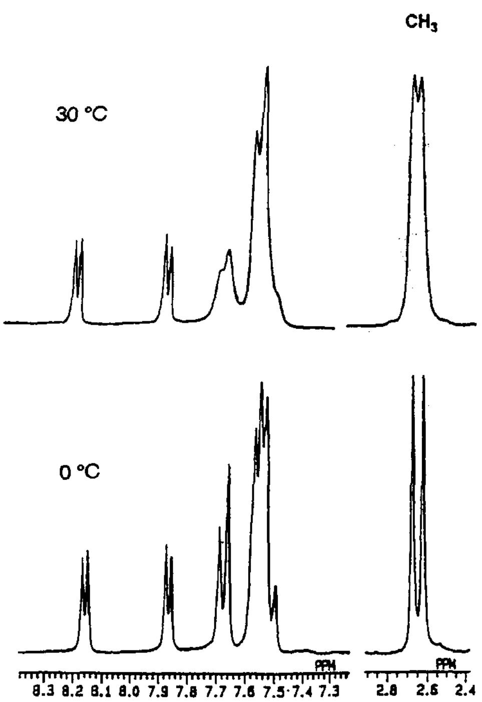


Figure 1. ^{1}H NMR spectra of **10b** in CF_3COOH (270 MHz). The upper spectrum is at 30 °C and the lower at 0 °C.

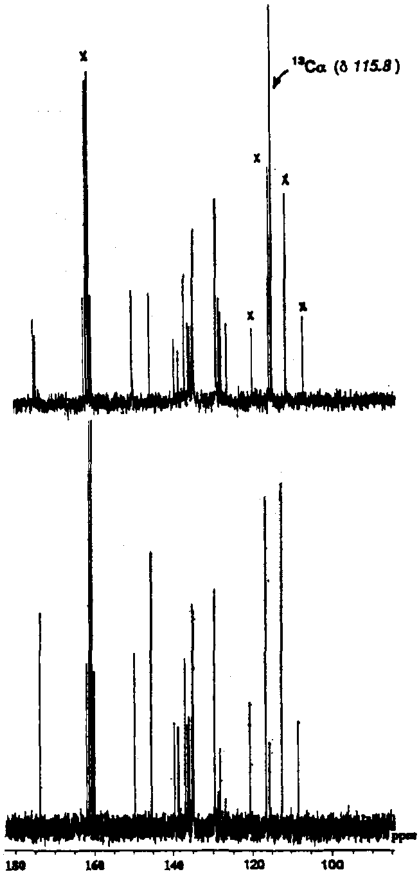
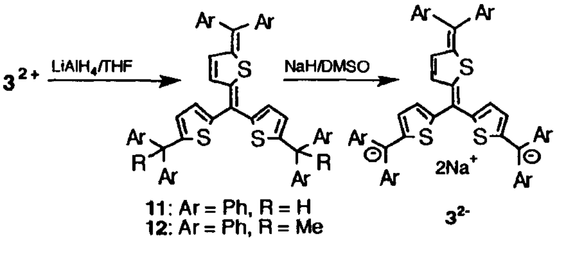


Fig. 2 ^{13}C NMR spectra of **10a** in CF_3COOH. The upper spectrum is of ^{13}C-enriched at Cα and the lower of natural abundance.

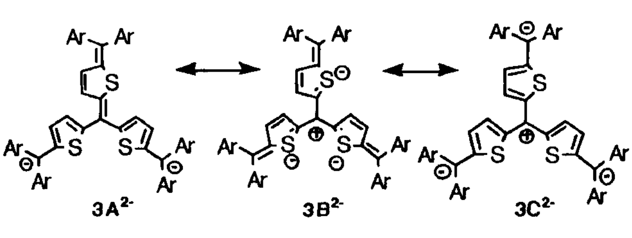
Reduction of dication salt $\mathbf{3a}^{2+}$ with $LiAlH_4$ gave dihydrocompound **1 1** (mp 163 °C, 90%). Treatment of **1 1** with dimsyl anion (NaH/DMSO) in turn cleanly afforded dianion $\mathbf{3a}^{2-}$ in deep red solution which produced dimethyl compound **1 2** (mp 79 °C, 90%) upon treatment with methyl iodide (Scheme 4). Dianion $\mathbf{3a}^{2-}$ exhibits a strong absorption at 918 nm (in DMSO) where is out of visible region.

^{1}H NMR spectrum of $\mathbf{3b}^{2-}$ in DMSO-d_6 [δ 7.02 (d, J=8.0 Hz, 12H), 6.90 (d, J=8.0 Hz, 12H), 6.74 (d, J=4.8 Hz, 3H), 5.76 (d, J=4.8 Hz, 3H), 2.19 (s, 18H)] does not show any sign of dynamic process around room temperarue. The large chemical shift difference between the two kind of thiophene protons (δ 6.74 and 5.76) is also suggestive of considerable charge separation. Its Cα was hardly observable, but the ^{13}C-enriched sample clearly showed Cα at δ 124.0, while Cβ was observed at δ 101 ppm. Notable here is the down field shift of Cα of $\mathbf{3b}^{2-}$ relative to Cα of a precursor diol **10b** (Δδ = 6.7 ppm) in spite of di-ionic nature of the molecule.

Figure 3 illustrates the change of chemical shifts of Cα, Cβ, and methyl carbon of *p*-tolyl series **10b**, $\mathbf{3b}^{2+}$, and $\mathbf{3b}^{2-}$, featuring large changes for Cβ and small changes for Cα. Here again significance of tetrapolar structure in dianions $\mathbf{3}^{2-}$ is suggested (Scheme 5). Easier bond rotation in dianions than in dications points to less importance of $\mathbf{3B}^{2-}$ than $\mathbf{3C}^{2-}$ in accordance with the higher stabilizing ability of 2-thienyl group on carbocation than on carbanion.



Scheme 4



Scheme 5

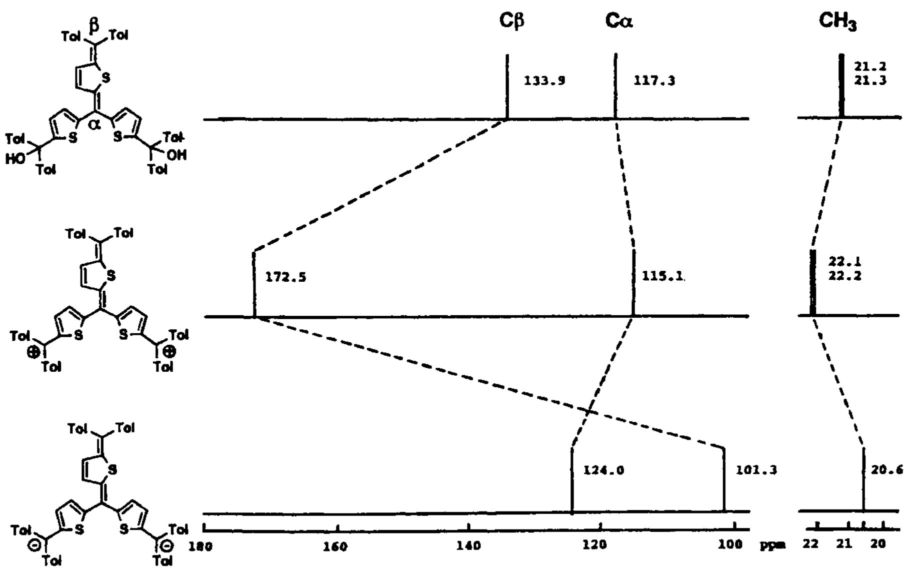
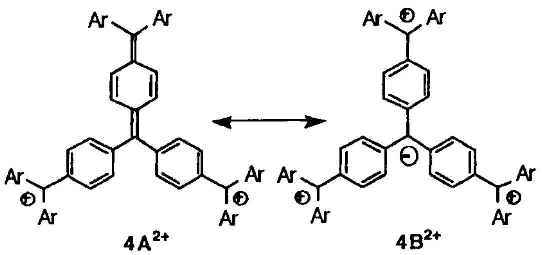


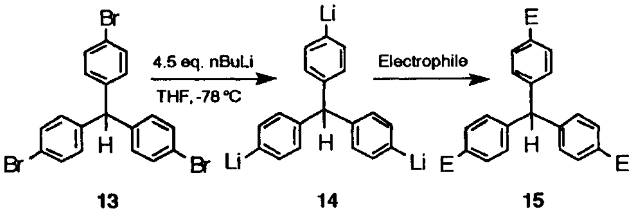
Fig 3 ^{13}C chemical shift change of **10b**, $3b^{2+}$, and $3b^{2-}$.

BENZENE EXTENDED TRIMETHYLENEMETHANE DICATIONS

In view of larger aromatic resonance energy of benzene than thiophene, dication 4^{2+} is expected to show even higher tetrapolar properties, that is, larger resonance contribution of $4B^{2+}$ (Scheme 6).



Scheme 6



Scheme 7

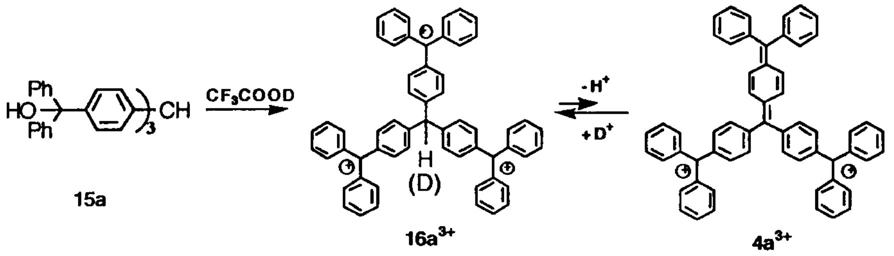
We chose tri(4-bromophenyl)methane **13** as the starting material for the synthesis of **4** and its ionic species and examined the regioselective lithiation of **13** in some detail. It was found that while treatment of **13** with dimsyl anion (NaH/DMSO) affords Cα anion selectively, treatment with excess n-BuLi in THF cleanly does trilithio compound **14** by bromine-lithium exchange. The former reaction is thermodynamically controlled and the latter kinetically controlled. A possible explanation for the highly selective trilithiation is that once one bromine-lithium exchange occurs kinetically, the strong electron-donating *para*-lithio group, decreases the acidity of Cα-proton and hence second and third bromine-lithium exchange proceed even more selectively. No formation of tetralithio compound was observed by use of excess n-BuLi. Reactions of **14** with electrophiles provide a new effective method for the synthesis of substituted triphenylmethanes, including desired triols **15a,b** (Scheme 7 and Table 1, for triols Entry 4 and 5).

Table 1. Trilithiation-functionalization of **13**

Entry	Electrophile	15 : E	Yield/%
1	CH_3I	CH_3	90
2	CH_3SSCH_3	SCH_3	81
3	$(CH_3)_3SiCl$	$Si(CH_3)_3$	66
4	$(C_6H_5)_2C{=}O$	$C(OH)(C_6H_5)_2$ **15a**	72
5	$(4\text{-}Cl\text{-}C_6H_4)_2C{=}O$	$C(OH)(4\text{-}Cl\text{-}C_6H_4)_2$ **15b**	59

Differing from the case of thiophene-extended molecules, triol **15a,b** do not undergo dehydration to diol by treatment with dilute acids; therefore generation of dication 4^{2+} from triols **15** were examined. Dissolution of **15a** in trifluoroacetic acid-d$_1$ cleanly afforded trication **16a**$^{3+}$ in yellow-orange solution [^{1}H NMR: δ 8.35 (t, J=7.9 Hz, 6H), 8.00-7.82 (m, 24H), 7.81 (d, J=7.9 Hz, 12H), 6.58 (s, Cα-H)]. However, it was observed that Cα proton slowly undergoes exchange with deuterium of the solvent to suggest intermediary formation of dication **4a**$^{2+}$ (Scheme 8).

Scheme 8



Triol **15a** does not absorb light of visible region, and trication **16a**$^{3+}$ exhibits strong absorption at 444 nm similar to triphenylmethyl cation itrself. When a dichloromethane solution of **15a** is titrated with trifluoroacetic acid, a strong absorption appears at near-infrared region of 1064 nm; however this absorption rapidly reaches maximum, then drops, and almost disappears as the titration proceeds up to about 50% v/v (Figure 4). The new absorption is ascribable to dication **4a**$^{2+}$, and this result indicates that **4a**$^{2+}$ is indeed highly tetrapolar and is prone to be protonated at Cα in trifluoroacetic acid (pKa = 0.3 in H_2O).

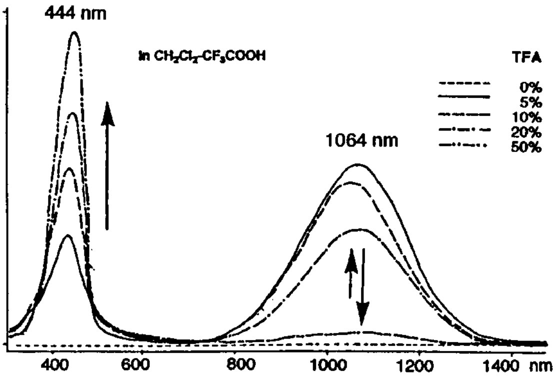


Figure 4. Absorption spectra of equilibroum mixtures of **16a**$^{3+}$ and **4a**$^{3+}$ in CH_2Cl_2 under titration with CF_3COOH.

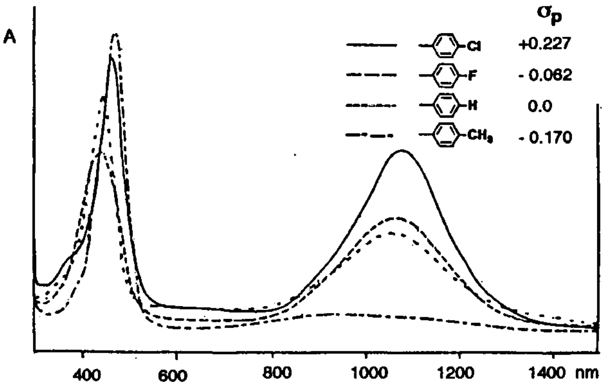


Figure 5. Effects of *para*-substituents on the absorption spectra of 4^{2+} of **16**$^{3+}$ in dichloroacetic acid

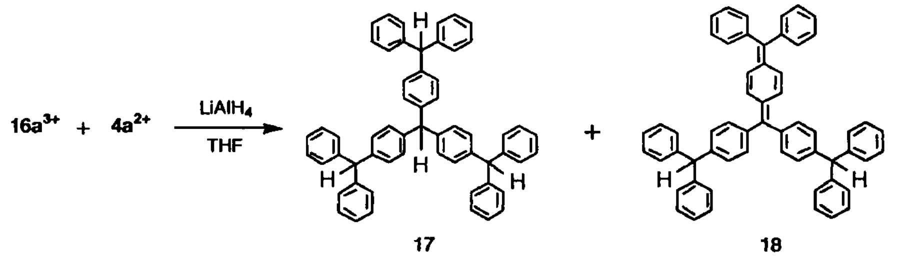
In contrast, thiophene-extended dication **3a**$^{2+}$ is stable in the same solvent. In weaker acid of dichloroacetic acid (pKa = 1.48), **15a** shows absorption of **4a**$^{2+}$ to fair extent in addition to that of **16a**$^{3+}$ (Figure 5). Because of the delicate equilibrium between **4a**$^{2+}$ and **16a**$^{3+}$ in favor of **16a**$^{3+}$ in stronger acid, attempts to isolate the dication salts either by treatment with perchloric acid or tetrafluoroboric acid in acetic anhydride under controlled conditions have failed giving mixtures of dication salt and trication salt in green solids. Attempted purification by recrystalization of the salt mixture was also unsuccessful.

Although yet rather qualitative, effect of *para*-substituents of the terminal phenyl groups on the equilibrium are observable by absorption spectra in dichloroacetic acid (Figure 5). Electron-withdrawing chloro and fluoro groups favor the dication, whereas electron-donating methyl group does the trication. These results suggest possible isolation of dication salts by introduction of proper electron-withdrawing groups, and this is to be examined.

NMR spectra provide confirmative evidence for the formation of dications 4^{2+}. ^{1}H NMR spectra of **15a** in $CDCl_3$-CF_3COOD (9 : 1 v/v) at 30 °C shows the signals of both **16a**$^{3+}$ and **4a**$^{2+}$ in about 1 : 3.5 ratio (Figure 6). The equilibrium is variable with temperature favoring **4a**$^{2+}$ at lower temperature. Thus, **4a**$^{2+}$ is observed more predominantly at -20 °C and the 400 MHz spectrum allows reasonable assignments of the signals (Figure 7). ^{13}C NMR spectrum of the ^{13}C-enriched compound shows C_3 symmetry of the molecule exhibiting Cα at δ 137.3 and Cβ at δ 194.2 ppm (Figure 8). The averaged ^{1}H and ^{13}C chemical shifts of **16a**$^{3+}$ and **4a**$^{2+}$ are as follows; **16a**$^{3+}$: ^{1}H, δ = 7.96; ^{13}C, δ = 145.1 (for sp^2 carbons); **4a**$^{2+}$: ^{1}H, δ = 7.71; ^{13}C, δ = 141.8 ppm. Both ^{1}H and ^{13}C chemical shifts of **4a**$^{2+}$ are higher than those of **16a**$^{3+}$. In particular, the smaller sum of the ^{13}C chemical shifts of **4a**$^{2+}$ than **16a**$^{3+}$ by about 180 ppm agrees with the decrease of one positive charge. The large chemical shift difference between Cα and Cβ (Δδ = 57 ppm) indicates considerable resonance contribution of tetrapolar structure **4B**$^{2+}$ in accordance with the easy protonation at Cα forming trication **16a**$^{3+}$

Reduction of a salt mixture of **16a**$^{3+}$ and **4a**$^{2+}$ with $LiAlH_4$ gave trihydro and dihydro compound, **17** and **18** (Scheme 9). Transformation of these hydrocarbons to dianion, trianion, and tetraanion by base treatment is under examination.

Scheme 9



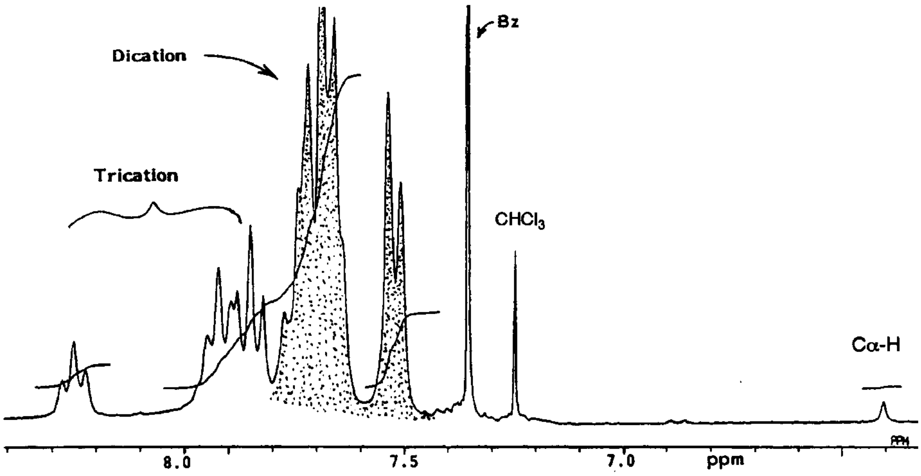


Figure 6. ^1H NMR spectrum (270 MHz) of **15a** in $CDCl_3$-CF_3COOD (9 : 1 v/v) showing the signals of **16a**$^{3+}$ and **4a**$^{2+}$ in about 1 : 3.5 ratio at 30 °C. The dotted signals are of **4a**$^{2+}$.

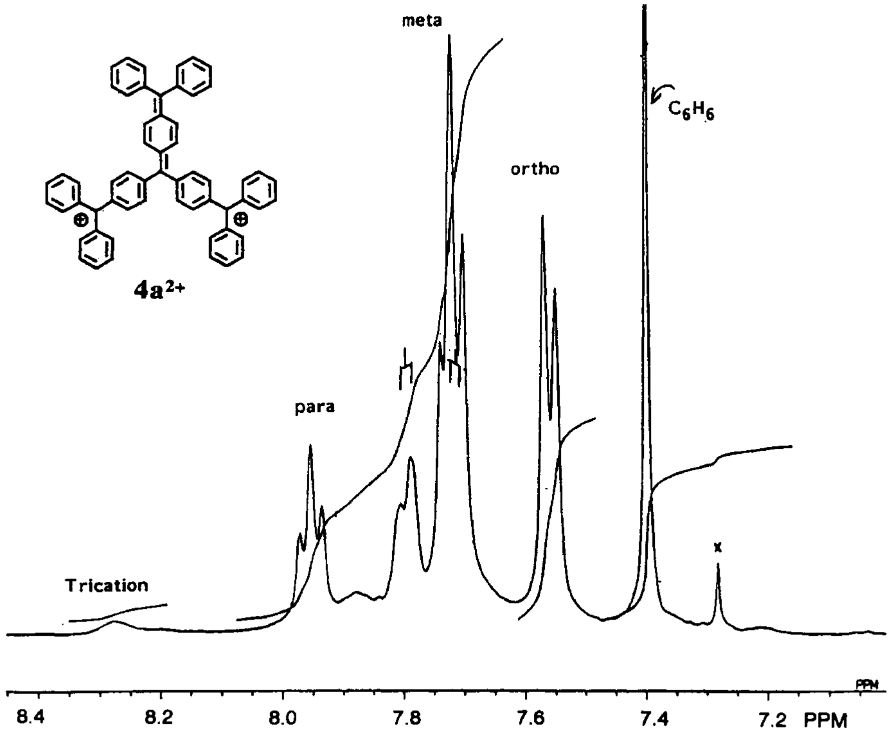


Figure 7. ^1H NMR spectrum of **15a** (400 MHz) in $CDCl_3$-CF_3COOD (9 : 1 v/v) at -20 °C showing **4a**$^{2+}$ as the major component.

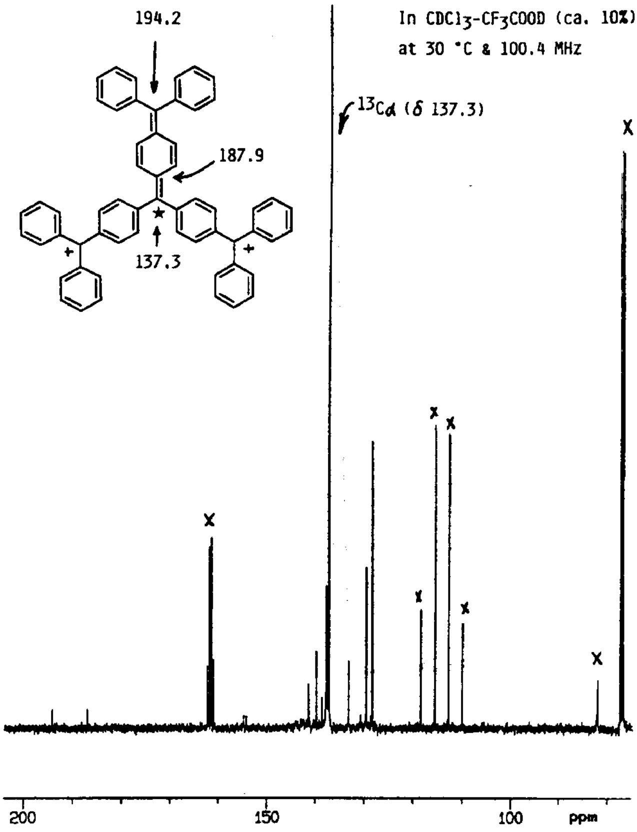


Figure 8. ^{13}C NMR spectrum of ^{13}C-enriched **4a**$^{2+}$ in $CDCl_3$-CF_3COOD (9 : 1 v/v).

Table 2. Redox potentials of **3a**$^{2+}$, **3b**$^{2+}$, and related triarylmethyl cations.

Compound	E_1	E_2	E_3	E_4
Hexaphenyl- **3a**$^{2+}$	1.21	-0.26	-1.20	-1.98
Hexa(p-tolyl)- **3b**$^{2+}$	1.15	-0.15	-1.15	-1.83
Tris(2-thienyl)methyl cation		0.02	-1.22	
Triphenylmethyl cation		0.15	-1.31	

V vs Ag/AgCl, 0.1 M nBu_4NClO_4 in CH_2Cl_2 at -60 °C, 100 mV/sec

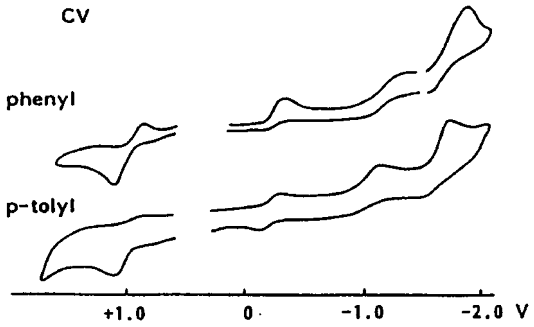
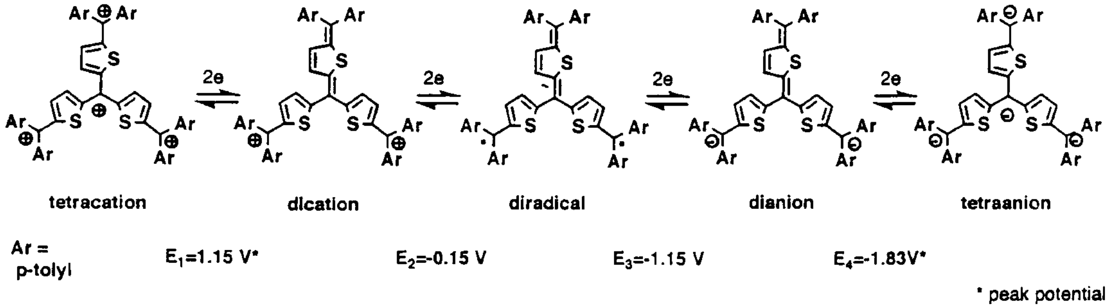


Figure 9. Cyclic voltammograms of **3a**$^{2+}$ (upper) and **3b**$^{2+}$ (lower).

REDOX PROPERTIES OF THIOPHENE EXTENDED DICATIONS

Extended triemthylenemethanes **2** are expected to show good amphoteric properties beween dications and dianions. Cyclic voltammetry of thiophene-extended dications **3a**$^{2+}$ and **3b**$^{2+}$ in CH_2Cl_2 exhibit four reversible and quasi reversible waves bettween +1.3 ~ -2.0 V (Figure 9 and Table 2). The second and third potentials (E_2 and E_3) are comparable to the redox potentials of triphenylmethyl cation and tri(2-thienyl)methyl cation which correspond to reduction to their radicals and anions. Accordingly, we at present assume that each wave of **3**$^{2+}$ involves two electron transfer, E_2 and E_3 correspond to formation of diradicals **3** and dianions **3**$^{2-}$, and hence E_1 and E_4 correspond to the formation of tetracation **3**$^{4+}$ and tetraanion **3**$^{4-}$, respectively (Scheme 10). The low potential of E_2 suggests ready reduction of **3a**$^{2+}$ to diradical **3a**.

Scheme 10



METAL REDUCTION OF THIOPHENE EXTENDED DICATIONS - ATTEMPTS TO GENERATE DIRADICALS

Reduction of **3a**$^{2+}$ with zinc metal in degassed acetnitrile was traced by absorption spectra to show sharp appearance of an absorption at 569 nm with disappearance of the absorption of **3a**$^{2+}$ at 769 nm (Figure 10). Although ESR spectra of the solution show the presence of radical species, the results have not so far been clear enough. More study has to be done.

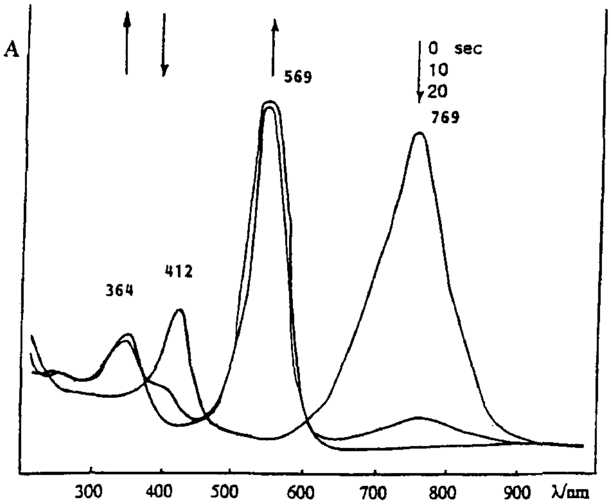


Figure 10. Absorption spectral change of **3a**$^{2+}$ upon zinc reduction in degassed CH_3CN as a function of contact time.

CONCLUDING REMARKS

We have nearly established the synthetic ways for trimethylenemethanes extended with aromatic rings. Dications and dianions here described are indeed highly tetrapolar molecules with strong and very long wavelength absorption in near infrared region. We can envision a good variety homolugues and expect emerging of interesting molecules from structural and physicochemical points of view. The present synthetic methods should also be applicable to the synthesis of such molecules, and their synthetic and physicochemical studies are in progress.

Acknowledgements

This work was supported by Grant-in-Aids for Scientific Research (No. 05403007, 07216247 and 06804038) from the Ministry of Education, Science and Culture, Japan. Thanks are also due to Sumitomo Foundation for partial financial support.

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