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[6,6-Di(5-methylthiophen-2-yl)-2,5-dimethylene-2,5-dihydrothiophene]diylium Derivatives. Stable Trimethylenemethane Dications Extended with Thiophenes

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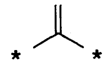
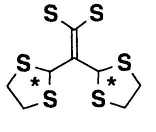
Trimethylenemethane dication derivatives extended with thiophenes are synthesized as stable substances by acid treatment of the precursor diols, showing highly tetrapolar properties and four-stage redox properties with two-electron transfer for each stage.

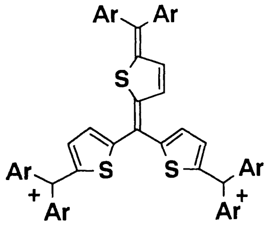
Trimethylenemethane (TMM **1**) and its ionic species $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$ have attracted much attention from theoretical, physicochemical and synthetic points of view.[1] Diradical **1** has been theoretically predicted and experimentally confirmed, though unstable, to be ground state triplet.[2] On the other hand, dianion $\mathbf{1}^{2-}$ was found to be unusually stable for a simple hydrocarbon dianion.[3] The notion of "Y-aromaticity" had been proposed for the stabilization,[4] but recent theoretical studies ascribed the unusual stability to maximally distant localization of the π-electrons by virtue of the D_{3h} symmetry.[5] Dication $\mathbf{1}^{2+}$ itself remains unknown, though some derivatives have been reported. Efforts have been made for stabilization of **1** and its ionic species by introduction of proper substituents such as thio group (e.g. **2**).[6] Hexaaryl substitution on **1** is another possible way of stabilization; however, the resulting steric conjection would hinder coplanarity of the molecules and hence disfavor maximal stabilization through conjugation. Insertion of an aromatic ring into each carbon-carbon bond of **1** should not only widen the conjugated system but also decrease the steric conjection. The Hückel MO calculations predict such molecules to be highly tetrapolar probably owing to the resonance energy of embedded aromatics. Here we wish to report the first synthesis of such molecules, the title dications **3a-c**, which are extended with thiophenes.



1: * = •
$\mathbf{1}^{2-}$: * = -
$\mathbf{1}^{2+}$: * = +

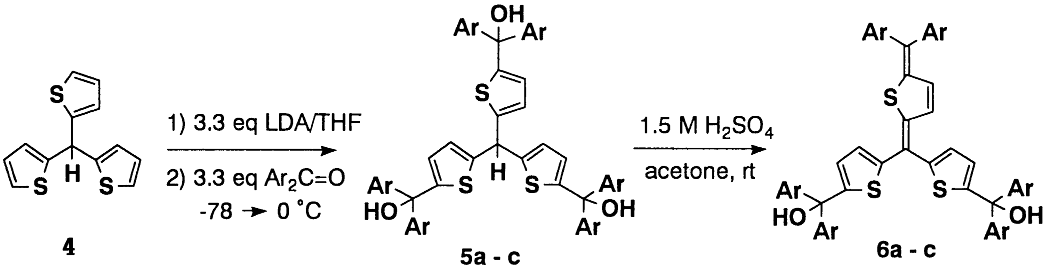


2: * = + or •

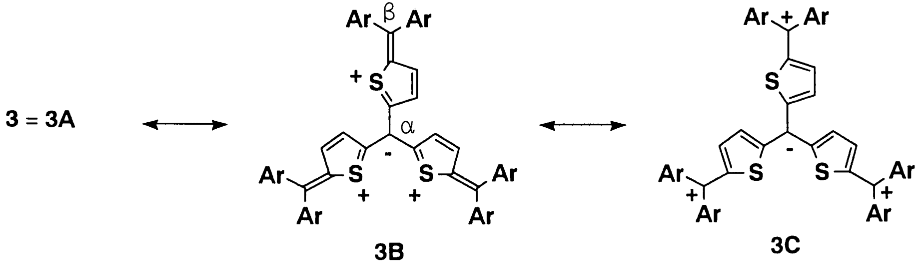


3; **a** : Ar = C_6H_5, **b** : Ar = p-Me-C_6H_4
c : Ar = p-F-C_6H_4

Tri(2-thienyl)methane (**4**) was recently reported to be regioselectively lithiated at the central methyne carbon (Cα) with butyllithium-tetramethylethylenediamine in THF.[7] More recently we have reported that di(2-thienyl)methane can be regioselectively lithiated at either C5-position of the thienyl group or Cα-position depending on bases, additives, and solvents.[8] We here found that although lithium diisopropylamide (LDA) produces Cα-anion of **4** almost selectively,[9] there is a smooth equilibrium with a small amount of C5-anion probably by mediation of diisopropylamine and only C5-anion is reactive enough towards diaryl ketones. Thus, treatment of **4** with five equivalents of diaryl ketones in the presence of five equivalents of LDA at -78 to 0 °C afforded triols **5a-c** in good yields (Scheme 1).[10] Further treatment of **5a-c** with 1.5 M H_2SO_4 in acetone at room temperature effected smooth dehydration to afford diols **6a-c**[11] in good yields from **4** (79%, 80%, and 67%, respectively).



Scheme 1.



Upon dissolution in trifluoroacetic acid or treatment with tetrafluoroboric acid in acetic anhydride, diols **6a-c** afforded dications **3a-c** as green, stable substances.[12] The electronic spectra of **3a-c** show strong absorptions at about 800 nm with appreciable bathochromic shift by the methyl groups for **3b** (Table 1).

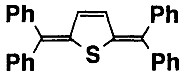
^1H and ^{13}C NMR spectra of **3a-c** at 30 °C show two sets of signals for the six terminal aryl groups with some broadening for **3b**. On the other hand, the three embedded thienyl groups are observed to be equivalent. Similar behaviors have also been observed for the dication of thiophene analogue of Chichibabin's hydrocarbon **8**.[13] These results point to a considerable resonance contribution of tetrapolar structure **3B** responsible for the restricted rotation of the diarylmethylene groups. The variable temperature ^1H NMR spectra for the two methyl signals of **3b** (δ = 2.62 and 2.67; T_c = 38 ± 1 °C) and their computer simulation (nine data points at 10-40 °C) gave the activation parameters for the bond rotation ($\Delta H^{\neq}$ = 15.5 ± 0.1 kcal/mol, $\Delta S^{\neq}$ = 1.6 ± 0.1 eu). The proton signals of **3a** and **3c** begin to broaden above about 35 °C and 45 °C, respectively, to suggest slightly higher activation energies for the bond rotation.[14] The electron-releasing methyl groups should increase the contribution of another tetrapolar structure **3C**, which makes the bond rotation easier. The tetrapolar property of **3a-c** is clearly shown in the ^{13}C chemical shifts (Table 1): while the methyne carbons (Cβ) of diarylmethylene groups are observed at low field of about δ 175, the central carbons (Cα) are at substantially high field of about δ 115 which is even higher than those of precursor diols **6a-c** (ca. δ 117). Apart from the positive charge in aryl groups, the large difference alone in the chemical shifts between Cα and Cβ (Δδ = 60 ppm for **3a**) evidences a large charge separation in the molecules (The Δδ corresponds to difference in charge density of roughly 0.38 unit[15]).

Cyclic voltammetry of **3a** and **3b** show four reversible or quasi-reversible redox waves between +1.1 and -1.8 V (Table 1). Comparison with the redox potentials of the related compounds **7**[16] and **8**[13] leads to a conclusion that E^1 (ca. +1.1 V) and E^4 (ca. -1.8 V) of **3a-c** should correspond to the formation of tetracations and tetraanions, respectively. This, together with D_{3h} symmetry of TMM and the similar experimental results on hexathio analogue **2**,[6] strongly suggests that each redox wave of **3a** and **3b** involves two-electron transfer (or in more rigorous sense, probably two sequential one-electron transfer with small difference in potential). Accordingly, the fairly low E^2 and E^3 similar to the reduction potentials of triphenylmethyl cation (0.19 and -1.05 V[17]) suggest good thermodynamic stability of the corresponding diradicals and dianions.

Table 1. Selected physical data of **3a-c** and related compounds

Compound	UV-Vis[a] (λmax/nm (log ε))	^{13}C-NMR[b] (δ ppm)		Redox Potentials[c,d] (V)			
		Cα	Cβ	E^1	E^2	E^3	E^4
3a	423 (4.51) 779 (4.74)	115.8	175.9	1.09	-0.12	-1.13	-1.83
3b	436 (4.24) 813 (4.96)	115.1	172.5	1.05	-0.11	-1.09	-1.79
3c	425 (4.45) 789 (4.76)	117.3	174.8	1.10	0.02	-1.15	-1.90
7[e]				1.01	0.86	-1.64	-1.86[f]
8				0.72	0.49	-1.44	-1.70[g]

a) In CH_2Cl_2. b) In CF_3COOD at 67.8 MHz. c) V vs Ag/AgCl in 0.1 M n-Bu_4NClO_4/CH_2Cl_2 at -60 °C, sweep rate at 100 mV/sec. d) E^1 and E^2 are half wave potentials, and E^3 and E^4 are peak potentials for **3a~c**. e) Ref. 16. f) Unpublished data measured in DMF in our laboratory. g) Ref. 13.



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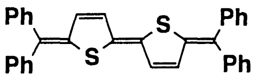

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9) Cα anion of **4**: ^{1}H NMR (270 MHz, THF-d_8) δ = 6.10 (3H, dd, J = 4.95, 1.32 Hz), 6.33 (3H, dd, J = 3.63, 1.32 Hz), 6.60 (3H, dd, J = 4.95, 3.63 Hz); ^{13}C NMR (DMSO-d_6) δ = 77.24, 107.39, 110.05, 126.39, 151.34.

10)The diarylhydroxymethyl groups are introduced one by one, because quenching of the lithiation mixture with AcOD yields **4** with monodeuteration mostly at Cα.

11)**6a**: orange prisms, mp 104-105 °C; ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 80.11, 80.20, 116.95, and 29 signals from 126.55 to 152.77; **6b**: orange prisms, mp 73-74 °C; ^{13}C NMR, δ = 21.02, 21.20, 21.32, 79.85, 79.96, 116.53, and 29 signals from 126.28-153.00; **6c**: orange prisms, mp 53-54 °C; ^{13}C NMR, δ = 79.39, 79.46, 116.86, and 32 signals from 114.73-164.10 containing splitting by the fluorine atoms.

12)**3a** (fluoroborate): green needles, mp 149-150 °C; ^{1}H NMR (270 MHz, CF_3COOD), δ = 7.51 (6H, d, J = 8.25 Hz), 7.64-7.69 (18H, m), 7.85 (6H, t-like), 7.87 (3H, d, J = 5.19 Hz), 8.12 (3H, d, J = 5.19 Hz); **3b**: green fine needles, mp 174-174 °C; ^{1}H NMR (0 °C), δ = 2.62 (9H, s), 2.67 (9H, s), 7.49-7.53 (12H, m), 7.54 (6H, d, J = 8.25 Hz), 7.66 (6H, d, J = 8.25 Hz), 7.85 (3H, d, J = 4.95 Hz), 8.14 (3H, d, J = 4.95 Hz); **3c**: green fine needles, mp 174 °C dec.; ^{1}H NMR, δ = 7.30 (12H, m), 7.53 (4H, m), 7.66 (4H, m), 7.82 (3H, d, J = 5.30 Hz), 8.02 (3H, d, J = 5.30 Hz).

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14)Detailed measurements for activation parameters of **3b** and **3c** were difficult because of complex ^{1}H signals and use of CF_3COOD as the solvent.

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