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Synthesis of tetrakis(2-thienyl)methane

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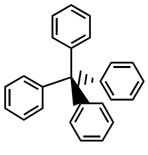
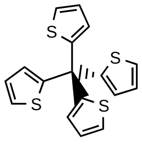
Abstract—Tetrakis(2-thienyl)methane was synthesized for the first time by sodium sulfide induced cyclization of 5,5,5-tris(2-thienyl)pentadiyne which was obtained from tris(2-thienyl)methyl cation, and the molecular structure was elucidated by X-ray analysis for the tetrabromo derivative. © 2002 Elsevier Science Ltd. All rights reserved.

Although tetraphenylmethane **1** has been long known,[1] tetrakis(2-thienyl)methane **2** has remained unknown. Compound **1** and its derivatives have been recently attracting renewed interest as synthons for three dimensionally extended molecules or building blocks for crystal engineering.[2,3] Compound **2** would show wider synthetic application in view of ready functionalization of thiophene at C2 (and C5) position by either electrophilic aromatic substitution or lithiation followed by reaction with electrophiles as well as of synthetic equivalency of thiophene to *n*-butane (or tetramethylene for 2,5-disubstituted thiophenes) through Raney nickel reduction.[4] The combination of the functionalization and desulfurizative Raney nickel reduction on **2** would lead to tetrasubstituted methanes bearing functional groups at the terminal or middle of the alkyl chains. As a part of our studies on thiophene-based novel molecules,[5] we have attempted the synthesis of **2** and here wish to report its first synthesis and some properties.



1



2

A simple logical approach to **2** would be the reaction of tris(2-thienyl)methyl cation **3**[6] with 2-thienylmetal. Nakayama and co-workers have reported that the reaction of **3** with carbon nucleophiles occurs not only at the cation center (Cα-adduct) but also at the 3- and 5-positions of the 2-thienyl group (C3- and C5-adduct).[7] We have at first examined the reaction of **3** with 2-thienyllithium but observed no formation of Cα-adduct **2**. The failure may be ascribed to fairly extensive delocalization of the positive charge into the thienyl groups by taking thiafulvenyl structures as well as steric hindrance at Cα. Another approach would be the application of the thiophene synthesis from butadiynes, namely hydrogen sulfide cyclization of tris(2-thienyl)pentadiyne **9**.[8] Here again, however, the preparation of **9** would need Cα-butadiynylation of **3**. Nevertheless, we expected in this case that ethynylation and butadiynylation might occur at Cα in greater extent than alkylation because of their smaller bulkiness. Therefore, the reaction of **3** with trimethylsilylethynyllithium was first examined to find optimum conditions for the formation of the Cα-adduct. The reactions of **3** and trimethylsilylethynyllithium in ether or THF under varied conditions gave complex mixtures of adducts **4**, **5**, and **6** in only modest yield (<30%) probably due to poor solubility of **3** in these solvents and the yield of **4** was less than 5% (Scheme 1). Adducts **5** and **6** were unstable and mostly decomposed in silica gel column partly isomerizing to thiophene derivatives **7** and **8**.[9] The yield of **4** was improved up to about 30% (70% yield of the adduct mixture) when acetonitrile was used as the major solvent: addition of a solution of trimethylsilylethynyllithium (18 mmol) in ether–hexane (ca. 1:1; 22 ml) to an acetonitrile (100 ml) solution of tetrafluoroborate of **3** (15 mmol; partially suspension) at −50°C and then stirring at room temperature (30 min) gave a mixture of the adducts from which **4**[10] was obtained in 25–30% yield after chromatography on silica gel.

Under similar conditions, the reaction of **3** with trimethylsilylbutadiynyllithium afforded tris(2-

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Keywords: tris(2-thienyl)methyl cation; nucleophilic addition; butadiyne–thiophene transformation; X-ray structural analysis.

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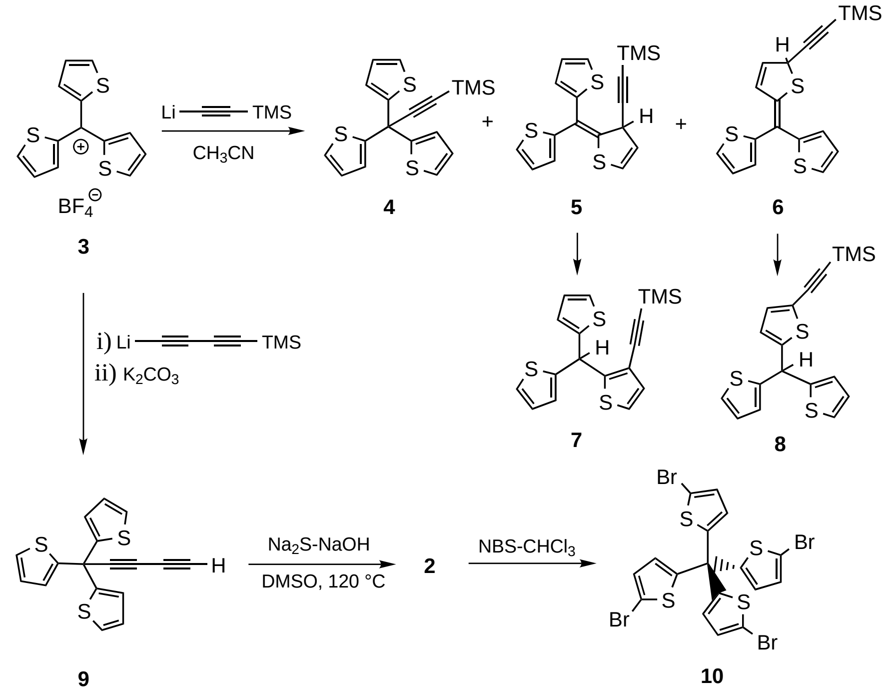

Scheme 1.

thienyl)pentadiyne **9**[10] in 8–12% yield after desilylation of the crude product mixtures with potassium carbonate in methanol–THF (1:1). Heating of **9** with sodium sulfide at 120°C in DMSO–2 M NaOH (pH 10–11) for 16 h afforded the desired tetrathienylmethane **2**[10] in 50–55% yield as a stable colorless crystalline substance (mp 171–172°C). Table 1 lists ^{1}H NMR chemical shifts and UV absorptions of 2-thienylmethanes for comparison. All the thienyl protons move downfield and the UV absorptions show slight red-shift as the number of thienyl group increases.

Upon attempted X-ray structure analysis, the parent compound **2** showed a disorder as to the orientation of thienyl groups in the crystal. Successful X-ray analysis was obtained, however, for tetrabromide **10**[10,11] which was furnished by bromination of **2** with *N*-bromosuccunimide (5.0 equiv./CHCl$_3$; 70% yield), establishing the tetrathienylmethane structure of **2**. Fig. 1 shows ORTEP drawing and Fig. 2 the packing diagram of **10**. Notable features are as follows. First, the bond length around the central carbon C(5) (1.524 Å) is considerably shorter than that of tetraphenylmethane (1.553 Å) and almost the same as that of normal sp^2C–sp^3C bond length such as that of toluene (1.524 Å), probably owing to smaller steric bulkiness of thiophene than benzene. The shortened bond length makes the distances between C2 carbons of 2-thienyl groups [C(4) in the ORTEP drawing] 2.45–2.51 Å that is short enough for possible homoconjugation between thienyl groups at proper conformation. Second, the bond angle at S(1)–C(4)–C(3) (109.2°) is appreciably smaller than that of S(1)–C(1)–C(2) (113.4°), which may also contribute to reducing the steric congestion around the central carbon C(5). Third, each sulfur atom faces C(3)–C(4) bond of another thienyl group, thus being free from disorder in the arrangement by virtue of introduction of the bulky bromine atoms. As for the packing mode, there seems to be no particular intermolecular interactions.

Table 1. ^{1}H NMR chemical shifts[a] and longest absorption maxima[b] of tetra(2-thienyl)methane **2** and the related compounds

Compound	^{1}H NMR chemical shifts δ (ppm)				$\lambda_{\max}$ (nm)	ε
	H-3	H-4	H-5	H-α		
2-MeTh	6.75	6.89	7.07	2.50	234[d]	7590
(2-Th)$_2$CH$_2$	6.87	6.93	7.14	4.33	238	14180
(2-Th)$_3$CH	6.91–7.00[c]	6.91–7.00[c]	7.21	6.11	239	22780
2	7.07	6.98	7.23	–	241	27915

[a] In CDCl$_3$ at 30°C.

[b] In cyclohexane.

[c] Observed as multiplet.

[d] In isooctane, Hartough, H. D. *Thiophene and Its Derivatives*; Interscience: New York; 1952; pp. 101–102.

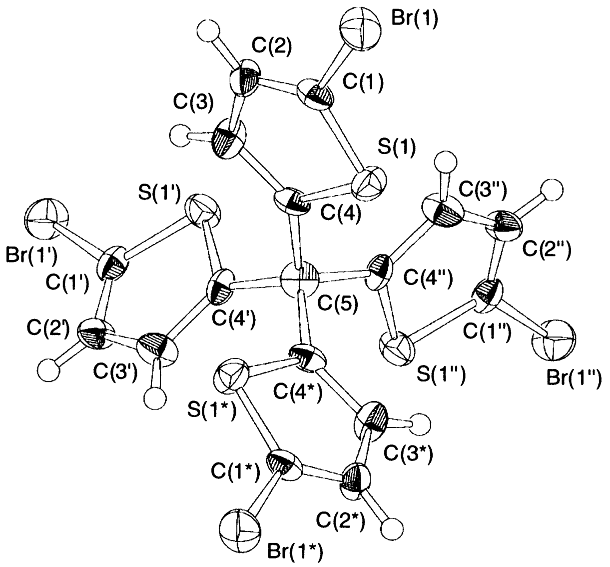

Figure 1. ORTEP drawing of **10** (50% probability). Selected bond lengths (Å) and angles (°): Br(1)–C(1) 1.88(1), S(1)–C(1), 1.70(1), S(1)–C(4) 1.74(1), C(1)–C(2) 1.31(2), C(2)–C(3) 1.41(1), C(3)–C(4) 1.39(2), C(4)–C(5) 1.524(10); C(1)–S(1)–C(4) 91.6(5), S(1)–C(1)–C(2) 113.4(9), C(1)–C(2)–C(3) 113(1), C(2)–C(3)–C(4) 112.5(10), S(1)–C(4)–C(3) 109.2(8), S(1)–C(4)–C(5) 120.3(7); six bond angles around C(5), 110.7(4) (four) and 107.0(7) (two).

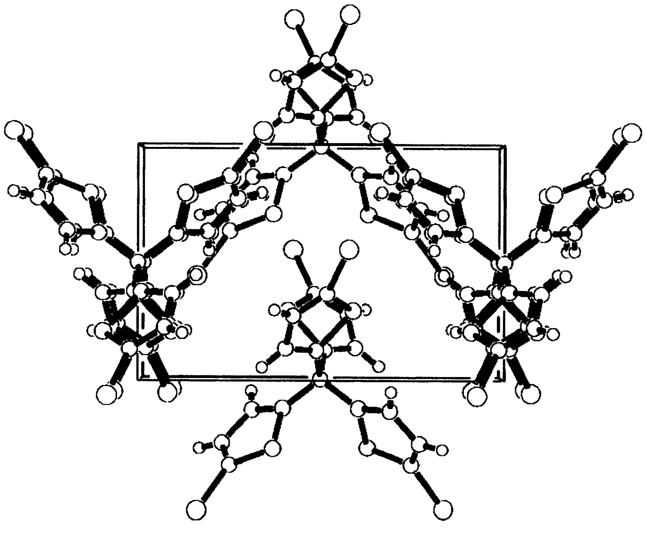

Figure 2. Packing diagram of **10** along *a* axis.

In summary, tetrakis(2-thienyl)methane **2** was here first synthesized, although the yield was poor. Easy transformation of **2** to tetrabromide **10** would promise the synthesis of a good number of its derivatives. The synthesis of those derivatives and their chemistry are in progress, including the Raney nickel reduction to novel tetrasubstituted methanes. In relation to **2**, many other tetrakis(heteroaryl)methanes remain unknown and their synthesis would be of interest from both a synthetic and physicochemical point of view.

Acknowledgements

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References

1. Gomberg, M. *Ber. Dtsch. Chem. Ges.* **1897**, *30*, 2043–2047.
2. (a) Desiraju, G. R. *Crystal Engineering*; Elsevier: New York, Amsterdam, 1989; (b) MacNicol, D. D.; Toda, F.; Bishop, R. *Comprehensive Supramolecular Chemistry*; Pergamon: New York, 1996; Vol. 6.
3. (a) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696–4698; (b) Desiraju, G. R. *Chem. Commun.* **1997**, 1475–1482; (c) Sengupta, S.; Sadhukhan, S. K. *Tetrahedron Lett.* **1999**, *40*, 9157–9161; (d) Galoppini, E.; Gilardi, R. *Chem. Commun.* **1999**, 173–174; (e) Wang, S.; Oldham, W. J., Jr.; Hudack, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695–5709; (f) Jetti, R. K. R.; Xue, F.; Mak, T. C. W.; Nangia, A. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1223–1232.
4. Reviews: (a) Hauptmann, H.; Walter, W. F. *Chem. Rev.* **1962**, *62*, 347–404; (b) Pettit, G. R.; van Tameln, E. E. *Org. React.* **1962**, *12*, 356–529.
5. (a) Kawase, T.; Muro, S.; Kurata, H.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1992**, 778–779; (b) Kawase, T.; Ueno, N.; Oda, M. *Tetrahedron Lett.* **1992**, *33*, 5405–5408; (c) Kawase, T.; Kurata, H.; Morikawa, T.; Oda, M. *Tetrahedron Lett.* **1993**, *34*, 3449–3452; (d) Kawase, T.; Ohsawa, T.; Enomoto, T.; Oda, M. *Chem. Lett.* **1994**, 1333–1336; (e) Kurata, H.; Kawase, T.; Oda, M. *Chem. Lett.* **1994**, 2219–2222; (f) Oda, M.; Kawase, T.; Wei, C. *Pure Appl. Chem.* **1996**, *68*, 267–274; (g) Kurata, H.; Baba, H.; Oda, M. *Chem. Lett.* **1997**, 571–572; (h) Enomoto, T.; Kawase, T.; Kurata, H.; Oda, M. *Tetrahedron Lett.* **1997**, *38*, 2693–2696; (i) Kurata, H.; Monden, M.; Kawase, T.; Oda, M. *Tetrahedron Lett.* **1998**, *39*, 7135–7138; (k) Kurata, H.; Inase, M.; Oda, M. *Chem. Lett.* **1999**, 519–520; (l) Kurata, H.; Nakaminami, H.; Matsumoto, K.; Kawase, T.; Oda, M. *Chem. Commun.* **2001**, 529–530.
6. (a) Taddei, F.; Spagnolo, P.; Tiecco, M. *Org. Magn. Reson.* **1970**, *2*, 159–164; (b) Varea, T.; Medio-Siomon, M.; Abarca, B.; Ballesteros, R.; Asensio, G.; Garcia-Grancla, S.; Perez-Carreno, E.; Gomez-Beltran, F. *Chem. Commun.* **1993**, 1476–1477.
7. Ishii, A.; Nakayama, J.; Endo, Y.; Hoshino, M. *Tetrahedron Lett.* **1990**, *31*, 2623–2626.
8. Kagan, J.; Arora, S. K. *J. Org. Chem.* **1983**, *48*, 4317–4320 and references cited therein.
9. Compounds **7** and **8** were obtained as a hardly separable mixture and their structures were tentatively assigned from a ^{1}H NMR spectrum of the mixture.
10. **4**: Colorless needles; mp 77.5–79.0°C; ^{1}H NMR: δ (400 MHz, $CDCl_3$) 7.23 (dd, $J=5.0$, 1.4 Hz, 3H), 6.97 (dd, $J=3.7$, 1.4 Hz, 3H), 6.91 (dd, $J=5.0$, 3.7 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR: δ (67.8 MHz, $CDCl_3$) 149.90, 126.40, 126.29, 125.47, 108.21, 89.83, 46.24, −0.25. **9**: Colorless needles, mp 87.5–88.5°C; ^{1}H NMR: δ (270 MHz, $CDCl_3$)

7.26 (dd, $J=5.3$, 1.3 Hz, 3H), 7.02 (dd, $J=3.6$, 1.3 Hz, 3H), 6.94 (dd, $J=5.3$, 3.6 Hz, 3H), 2.30 (s, 1H); ^{13}C NMR: δ (67.8 MHz, $CDCl_3$) 148.59, 126.85, 126.47, 125.91, 78.23, 69.80, 69.40, 67.53, 45.92. **2**: ^{1}H NMR: δ (270 MHz, $CDCl_3$) 7.23 (dd, $J=5.1$, 1.1 Hz, 4H), 7.07 (dd, $J=3.6$, 1.1 Hz, 4H), 6.98 (dd, $J=5.1$, 3.6 Hz, 4H); ^{13}C NMR: δ (67.8 MHz, $CDCl_3$) 152.67, 127.78, 126.29, 125.19, 53.19; MS (EI) m/z 344 (M^+, 41), 261 (M^+–Th, 27), 178 (M^+–2Th, 37); anal. calcd for $C_{17}H_{12}S_4$: C, 59.26, H, 3.51. Found: C, 59.11, H, 3.52. **10**: Colorless prisms; mp 249.5–250.5°C; ^{1}H NMR: δ (270 MHz, $CDCl_3$) 6.94 (d, $J=4.0$ Hz, 4H), 6.78 (d, $J=4.0$ Hz, 4H); ^{13}C NMR: δ (67.8 MHz, THF-d_8) 151.27, 129.88, 128.50, 112.76, 53.80.

11. Crystallographic data of **10**: $C_{17}H_8Br_4S_4$, FW = 660.11, tetragonal, space group $P\bar{4}2_1c$ (#114), $a=11.514(1)$, $c=7.358(2)$ Å, $Z=2$, $V=975.5(3)$ Å^3. The measurement was performed with Rigaku AFC5R diffractometer; radiation MoKα ($\lambda=0.71069$ Å); of a total of 710 reflections collected, 660 were unique ($R_{\mathrm{int}}=0.000$) for $2\theta<55.02°$. The structure was solved by the direct method using SHELXS-86 with a GOF 1.53. Final residuals are $R=0.081$, $R_w=0.116$, and $R_1=0.049$. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 177658.