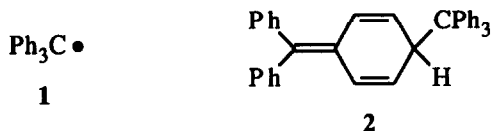


DIMERIZATION OF TRI-2-THIENYLMETHYL RADICAL

Juzo Nakayama,* Akihiko Ishii, Yurie Yamada, Motoaki Sugino, and Masamatsu Hoshino
Department of Chemistry, Faculty of Science, Saitama University,
Urawa, Saitama 338, Japan

Summary: Tri-2-thienylmethyl radical (3), generated by reduction of tri-2-thienylcarbenium tetrafluoroborate (4) with Zn at 65 °C, dimerizes to give 2-(di-2-thienylmethylene)-5-tri-2-thienylmethyl-2,5-dihydrothiophene (5) and a diastereomeric mixture of 5,5'-bis(di-2-thienylmethylene)-2,2',5,5'-tetrahydro-2,2'-bithiophene (6). Each isolated pure dimer thermally dissociates into the radical 3 to give a 1:1 equilibrated mixture of 5 and 6. The radical 3 generated at lower temperatures by reaction of 4 with *t*-BuLi affords 5 as the sole dimer.

In 1968, after the controversy since the beginning of this century,¹ the structure of the dimer of triphenylmethyl radical (1) was determined to be the quinoid structure 2 but not the tetraphenylethane structure by ¹H NMR study.² Meanwhile, any structural proposal for the dimer of tri-2-thienylmethyl radical (3) has not appeared, although properties of 3 were investigated in some detail by ESR and reportedly it dimerized below ca. 15-20 °C.³ We report here the formation, structural elucidation, and mutual interconversion of two isomeric dimers of 3.



The radical 3, generated by reduction of tri-2-thienylmethylcarbenium tetrafluoroborate (4)⁴ in 1,2-dimethoxyethane (DME) at 65 °C for 1 h under nitrogen, dimerized to give a dark blue gum after usual workup. The gum was separated into a sparingly soluble part in carbon tetrachloride and soluble one in the same solvent. The former part, blue-gray powder (mp 132 °C, dec), consists of nearly pure compound I, while the latter is a mixture of compounds II and III containing a small amount of I. Purification of the mixture part by column chromatography gave pure II, though III was contaminated with I.

The ¹H NMR spectrum shows that I has one tri-2-thienylmethyl, two nonequivalent 2-thienyls, and one -CH=CH-CH< system.⁵ The ¹³C NMR spectrum shows two peaks in the sp³ carbon region assigned as quaternary (δ 55.4) and methine (δ 70.3) carbons along with peaks due to sp² carbons. These NMR data are in harmony with two

isomeric dimers **5** and **7** (Th=2-thienyl). Treatment of **1** with *t*-BuOK affords compound **8**.⁶ Therefore, structure of **1** was determined to be the dimer **5**.

Combination of ¹H and ¹³C NMR spectra, which reveal the presence of two nonequivalent 2-thienyls, one -CH=CH-CH< system, and two sp² carbons carrying no hydrogen, indicates **II** to be one of diastereomers of the symmetrical dimer **6** or **9**.⁷ In order to differentiate **6** from **9**, tris(5-deuterio-2-thienyl)carbenium tetrafluoroborate (**4-d**)⁸ was synthesized and treated with zinc powder. The ¹H NMR spectrum of the resulting **II-d** shows the presence of a -CH=CH-CD< system, revealing that it has the structure **6-d**. Thus, the structure of **II** was unambiguously determined to be the dimer **6** arising from coupling at the 5-position of the 2-thienyl group. The ¹H and ¹³C NMR spectra of **III** are very similar to those of **II**.¹⁰ **III-d** obtained from **4-d** also has a -CH=CH-CD< system, and therefore the structure of **III** was determined to be another diastereomeric dimer of **6**.

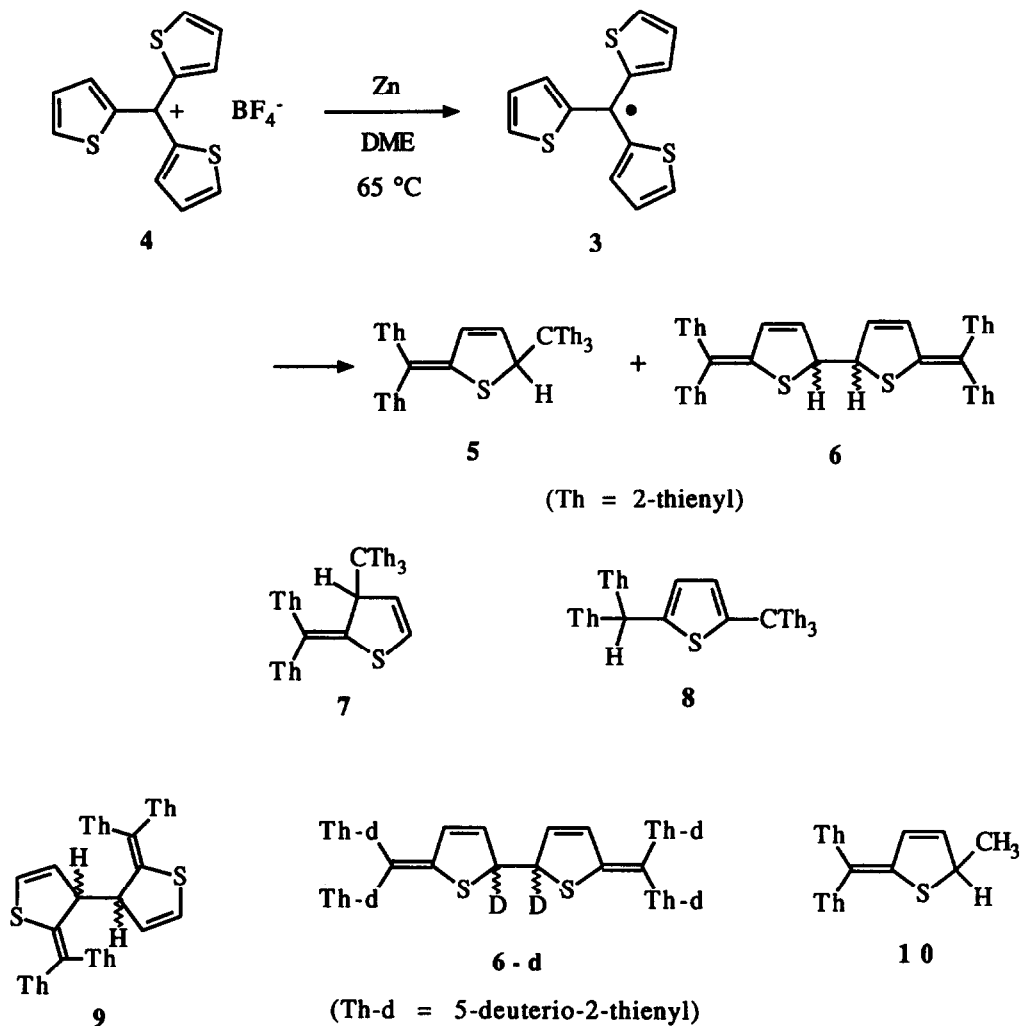
Further support for the structure of **5** and **6** comes from UV-vis spectra. Both in the position of absorption maxima and intensity of molar absorptivities, the spectrum of **5** closely resembles that of compound **10**¹¹ which has the same conjugated system as **5**. The spectrum of **6** (**II**) is similar to those of **5** and **10** in the position of absorption maxima, but its molar absorptivities are about double those of these compounds as expected from its structure.

The low isolated yields of **5** (40-45%) and **6** (**II**) (3%) are probably due to the sensitivity of these compounds to air¹² since the ¹H NMR spectrum recorded immediately after workup showed that dimer formation was nearly quantitative. The ratio of **5** and **6** depends on the reaction time. The reaction at 65 °C for 1 h and 48 h afforded **5** and **6** in the ratios 1:0.5 and 1:0.8, respectively. This may imply that **5** thermally isomerizes to **6**.

Actually, heating a solution of **5** in DME at 65 °C for 1 h and 48 h afforded **5** and **6** in the ratios 1:0.54 and 1:0.8, respectively, and heating **5** in refluxing DME for 1 h a 1:1 mixture. On the other hand, heating a solution of **6** (pure diastereomer **II**) at 65 °C for 48 h also afforded a 1:1 mixture of **5** and **6**. These observations clearly show that the both dimers thermally dissociate into the radical **4** to afford an equilibrated 1:1 mixture ultimately, though **5** is the kinetically favored dimer. In fact, **5** is isolated as the sole dimer in 36% yield, when **3** is generated at room temperature in ether by single electron transfer reaction from *t*-BuLi to the salt **4**.¹³

In summary, dimerization of **4** between the radical center and the sterically less hindered 5-position of 2-thienyl having a high spin density initially affords the kinetically favored dimer **5**, which is then thermally equilibrated with another dimer **6**. No hexa-2-thienylethane was formed as no hexaphenylethane formed from **1**. Despite the fact that **4**, in which thiophene rings are more coplanar than benzene rings in **1**¹⁴ and its electron spin density is effectively delocalized over the whole molecule,^{3c} seems to be a more stable radical than **1**, the formation of easily isolable

dimers leads to the conclusion that, in triarylmethyl radicals, the relative stability of the radical and dimer is controlled much more by steric hindrance than by electron delocalization.



References and Notes

1. For a review see: McBride, J. M. *Tetrahedron* 1974, 30, 2009.
2. (a) Lankamp, H.; Nauta, W. T.; MacLean, C. *Tetrahedron Lett.* 1968, 249. See also: (b) Guthrie, R. D.; Weisman, G. R. *Chem. Commun.* 1969, 1316. (c) Staab, H. A.; Brettschneider, H.; Brunner, H. *Chem. Ber.* 1970, 103, 1101. (d) Volz, H.; Lotsch, W.; Schnell, H.-W. *Tetrahedron* 1970, 26, 5343.
3. (a) Mangini, A.; Pedulli, G. F.; Tiecco, M. *Tetrahedron Lett.* 1968, 4941. (b) Lunazzi, L.; Mangini, A.; Pedulli, G. F.; Tiecco, M. *Gazz. Chim. Ital.* 1971, 101, 10. (c) Pedulli, G. F.; Zannoni, C.; Alberti, A. *J. Magn. Resonance* 1973, 10, 372. (d) Bernardi, F.; Guerra, M.; Pedulli, G. F. *Tetrahedron* 1976, 32, 951.
4. 4 was prepared by reaction of tri-2-thienylmethanol^{3a} with HBF₄ in Ac₂O. 4: mp 128 °C (dec). Anal. calcd for C₁₃H₉S₃BF₄: C, 44.84; H, 2.61. Found: C, 44.78; H, 2.81.
5. ¹H NMR (CDCl₃, 400 MHz) δ 5.89 (triplet-like, *J*=2.5 Hz, 1H), 6.29 (dd, *J*=6.4, 2.9 Hz, 1H), 6.46 (dd, *J*=6.4, 2.0 Hz, 1H), 6.92 (dd, *J*=3.5, 1.0 Hz, 1H), 6.95 (dd, *J*=5.0, 3.6 Hz, 3H), 6.98 (dd, *J*=4.9, 4.0 Hz, 1H), 7.00 (dd, *J*=5.2, 3.5 Hz, 1H), 7.03 (dd, *J*=3.6, 1.1 Hz, 3H), 7.10 (broad d, *J*=3.2 Hz, 1H), 7.17-7.26 (m, 4H containing 3H for Th₃C which appear at δ 7.25 as dd, *J*=5.0, 1.1 Hz), 7.31 (dd, *J*=5.2, 1.0 Hz, 1H); ¹³C NMR (CDCl₃, 100.6 MHz) δ 55.4 (s), 70.3 (d), 116.7 (s), 125.3 (d), 125.5 (d), 126.0 (d), 126.6 (d), 127.06 (d), 127.15 (d), 127.4 (d), 128.2 (d), 134.8 (d), 135.0 (d), 142.45 (s), 144.52 (s), 145.3 (s) (two peaks due to =CH- and =C< cannot be detected because of overlapping with other peaks). UV-vis (CH₂Cl₂) λ_{max}/nm, (ε) 362 (sh, 25000), 353 (28000). MS *m/z* 261 (Th₃C, base peak).
6. 8: mp 146 °C (EtOH); ¹H NMR (CDCl₃, 400 MHz) δ 6.00 (s, 1H), 6.77 (d, *J*=3.7 Hz, 1H), 6.88 (d, *J*=3.7 Hz, 1H), 6.89-6.91 (m, 2H), 6.93 (dd, *J*=4.9, 3.7 Hz, 2H), 6.97 (dd, *J*=4.9, 3.6 Hz, 3H), 7.06 (dd, *J*=3.6, 1.0 Hz, 3H), 7.20 (dd, *J*=4.9, 1.2 Hz, 2H), 7.22 (dd, *J*=4.9, 1.0 Hz, 3H); ¹³C NMR (CDCl₃, 100.6 MHz) δ 42.6 (d), 53.3 (s), 124.8 (d), 125.2 (d), 125.8 (d), 126.4 (d), 126.6 (d), 127.2 (d), 127.8 (d), 146.6 (s), 147.0 (s), 151.5 (s), 152.4 (s) (one =C< carbon cannot be detected because of overlapping with other peaks); MS *m/z* 522 (M⁺, 100), 489 (7), 439 (13), 343 (62), 261 (34), 179 (31); exact mass for C₂₆H₁₈S₆ 521.9733, found 521.9769.
7. 6 (II): ¹H NMR (CDCl₃, 400 Hz) δ 4.86 (s, 2H), 6.21 (d, *J*=6.5 Hz, 2H), 6.55 (d, *J*=6.5 Hz, 2H), 6.99 (dd, *J*=3.7, 1.0 Hz, 2H), 7.02 (dd, *J*=5.1, 3.8 Hz, 2H), 7.04 (dd, *J*=5.3, 3.7 Hz, 2H), 7.13 (dd, *J*=3.8, 1.0 Hz, 2H), 7.28-7.30 (m, 2H), 7.35 (dd, *J*=5.3, 1.0 Hz, 2H); ¹³C NMR (CDCl₃, 100.6 MHz) δ 63.2 (d), 116.8 (s), 125.5 (d), 126.1 (d), 126.6 (d), 127.1 (d), 127.3 (d), 128.2 (d), 133.9 (d), 135.3 (d), 142.2 (s), 144.0 (s), 145.1 (s). MS *m/z* 261 (Th₃C, base peak). UV-vis (CH₂Cl₂) λ_{max}/nm, (ε) 372 (57000), 357 (56000). MS *m/z* 261 (Th₃C, base peak).
8. 4-d was obtained by reaction of diethyl carbonate with 5-deuterio-2-thienyllithium which was prepared by treatment of 2,5-dideuteriothiophene⁹ with BuLi.
9. Dawson, R. M.; Gillis, R. G. *Aust. J. Chem.* 1972, 25, 1221.
10. 6 (III): ¹H NMR (CDCl₃, 400 MHz) δ 4.73 (s, 2H), 6.22 (d, *J*=6.3 Hz, 2H), 6.57 (d, *J*=6.3 Hz, 2H), 7.01 (dd, *J*=3.5, 1.1 Hz, 2H), 7.03 (dd, *J*=5.2, 3.7 Hz), 7.05 (dd, *J*=5.2, 3.5 Hz, 2H), 7.13 (dd, *J*=3.7, 0.9 Hz, 2H), 7.30 (dd, *J*=5.2, 0.9 Hz, 2H), 7.36 (dd, *J*=5.2, 1.1 Hz, 2H).
11. 10: UV-vis (CH₂Cl₂) λ_{max}/nm, (ε) 362 (sh, 25000), 351 (29000). For the preparation of 10, see the preceding paper.
12. The both dimers turn to highly colored polar materials during column chromatography or even on standing in the air.
13. See the preceding paper. See also: (a) Bilevitch, K. A.; Pubnov, N. N.; Okhlobystin, O. Y. *Tetrahedron Lett.* 1968, 3465. (b) Diachkovskii, F. S.; Bubnov, N. N.; Shilov, A. E. *Doklady Akad. Nauk S.S.S.R.* 1958, 123, 870. (c) Price, C. C.; Follweiler, D. H. *J. Org. Chem.* 1969, 34, 3202.
14. The calculated twist angle of aromatic rings is 25.5° for 3^{3d} and 30° for 1.¹⁵
15. Kirste, B.; Harrer, W.; Kurreck, H. *J. Am. Chem. Soc.* 1985, 107, 20.