

Generation and Reactions of 2,3-Dibenzylidene-2,3-dihydrothiophene

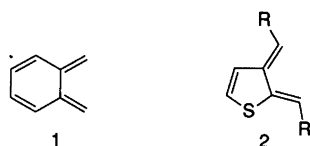
Jan Skramstad and Odd Eriksen*

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo 3, Norway

Skramstad, J. and Eriksen, O., 1991. Generation and Reactions of 2,3-Dibenzylidene-2,3-dihydrothiophene. – Acta Chem. Scand. 45: 919–924.

In this paper are described the synthesis of the highly reactive 2,3-dibenzylidene-2,3-dihydrothiophene (**2**, R = Ph), the determination of the structure of its dimer by single-crystal X-ray diffraction, and the determination of the structures of the products of cycloaddition of **2** to norbornene and styrene by NMR methods.

ortho-Quinonoid compounds such as *o*-xylylene **1** have attracted much recent interest, both spectroscopically¹ and synthetically.² It is noteworthy that a number of intramolecular Diels–Alder reactions of *in-situ* generated *ortho*-quinonoid compounds produce steroids with a high degree of stereochemical control.³



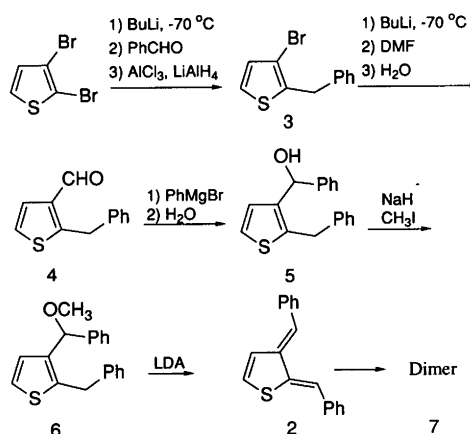
We have for some time been interested in *ortho*-quinonoid thiophenes such as 2,3-dimethylene-2,3-dihydrothiophenes (**2**). Recently several papers have appeared reporting the attempted synthesis of the parent system (**2**, R = H).^{4–7} This prompted us to disclose our results concerning the synthesis of the diphenyl derivative (**2**, R = Ph), the X-ray structure of its dimerization product and some of its other addition reactions.

The phenyl groups at the exocyclic double bonds were introduced in order to stabilize the system and hopefully to be able to make an isolable *ortho*-quinonoid thiophene. We have evidence from our work on cyclopentathiophenes^{8,9} that introduction of phenyl groups have a stabilizing effect on double bonds exocyclic to the thiophene ring.

Result and discussion

Although several methods are available for the synthesis of *ortho*-quinonoid compounds, only a few are practical for the synthesis of heterocyclic analogues. We applied the method developed by Richborn¹⁰ in which a 1,4-elimination of methanol from *ortho*-benzyl substituted benzyl methyl

ethers is accomplished by the use of lithium dialkylamides. Our synthetic approach is outlined in Scheme 1.



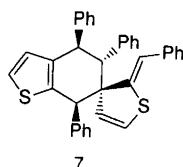
Scheme 1.

2-Benzyl-3-bromothiophene (**3**) was obtained in high yield by the reaction of 2,3-dibromothiophene with butyllithium followed by addition of benzaldehyde. The resulting alcohol was directly reduced to **3** with aluminium chloride and lithium aluminium hydride. 2-Benzyl-3-thiophene-carbaldehyde (**4**) was prepared by reaction of (**3**) with butyllithium and *N,N*-dimethylformamide followed by hydrolysis. Reaction of the aldehyde (**4**) with phenylmagnesium bromide gave 2-benzyl-3-(α -hydroxybenzyl)thiophene (**5**) in 90% yield. Conversion into the corresponding methyl ether was effected by reaction with sodium hydride and methyl iodide. This afforded the key intermediate 2-benzyl- α -methoxybenzylthiophene (**6**) in 76% yield or about 50% based on the starting 2,3-dibromothiophene.

When an equivalent amount of lithium diisopropylamide (LDA) was added dropwise to **6** in dry hexane at room temperature under nitrogen, the reaction mixture turned

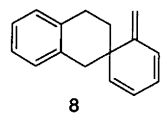
* Present address: Senter for Industriforskning, P.O. Box 124 Blindern, N-0314 Oslo 3, Norway.

red after addition of each drop, but the colour faded away before the next drop was added. When the addition of LDA was complete, the reaction mixture was stirred for 7 h at room temperature. Normal work-up, including preparative TLC, gave the main component (30% isolated yield) as colourless crystals melting at 217–219°C. Mass spectral analysis indicated a dimeric structure with a molecular ion of $m/z = 524$ (see the Experimental). The other products of the reaction were polymeric and were not further studied. Recrystallization from petroleum ether–chloroform gave crystals that melted at 220–222°C which were subjected to X-ray diffraction analysis. This unequivocally established the structure as the spirodimer 4,5,7-triphenyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene-6-spiro-3'-(2'-benzylidene-2',3'-dihydro)thiophene (7).



This is an interesting structure and an interesting result as it throws some light on the reported structures suggested for the dimer of the parent system (2, R = H). Storr *et al.*⁵ picture a dimer formation in which the 2-methylene bond acts as the dienophile whereas van Leusen *et al.*⁶ assign structures for a mixture of dimers in which both the 2- and the 3-methylene bond have played the role of the dienophile. Now that we have established that the diphenyl derivative dimerizes with only the 3-methylene bond acting as the dienophile, it seems reasonable to assume that the unsubstituted compound should behave similarly.

ortho-Xylylene itself (1) is known¹¹ to dimerize to the spiro compound 8 at temperature between –70 and 0°C and to dibenzocyclooctane at temperature between 0 and 200°C. At temperatures above 300°C 1 cyclizes to benzocyclobutene.¹²

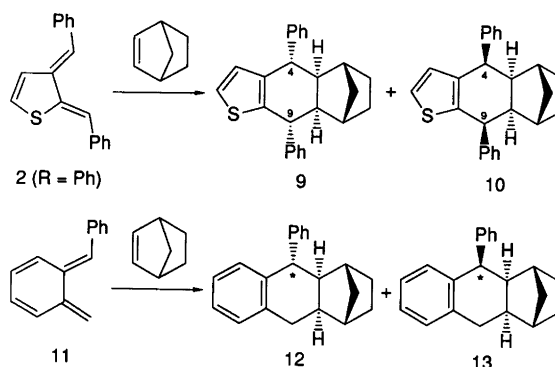


Due to the lower symmetry of 2 (as compared with 1) there is a substantial number of possibilities for the formation of dimers from this system. When also considering the different possible orientations of the phenyl groups in the product, it is remarkable that only one single isomer is observed. This fact indicates that 2 reacts as an *ortho*-quinonoid rather than a diradical. Furthermore it suggests that the dimer formation is governed by orbital symmetry rather than charge. In fact preliminary HOMO–LUMO calculations predict the observed involvement of the 3-methylene bond in preference to the 2-methylene bond

in the cycloaddition of the dienophile to the diene.¹³ Secondary interactions are probably responsible for the observed single product.

Our next step was to try to trap the *ortho*-quinonoid structure 2 with dienophiles. Our strongly basic reaction conditions place limits on the dienophile. However, when 2 was generated in the presence of norbornene, and addition product 9 was isolated in about 40% yield after column chromatography (20% of the spirodimer 7 was also formed).

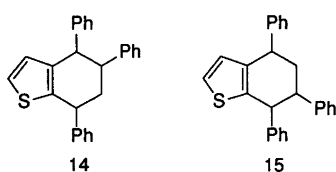
The structure of 9 was established by one- and two-dimensional NMR spectroscopy (see the Experimental). This corresponds to an *exo* addition to the diene. This is also observed in the reaction between *ortho*-xylylene and norbornene.¹⁰ Present as a minor component was an isomer of 9, the NMR spectrum of which indicated a second *exo*-adduct, most likely of structure 10. The coupling constants of the methine protons on the phenyl-bearing carbons gave good evidence for the structural assignments. The chemical shifts and coupling constants for these protons in 9 and 10 are shown in Table 1 together with literature values for the corresponding values for the addition products 12 and 13 from the reaction between the phenyl substituted *o*-xylylene 11 and norbornene.¹⁰



When styrene was used as the trapping reagent, an adduct was isolated in 42% yield. However, in this case a mixture of the two regioisomers 14 and 15 were formed. As

Table 1. The ¹H NMR chemical shifts and coupling constants of the methine protons of compounds 9 and 10 compared with literature values for compounds 12 and 13.

Compound	δ (ppm)	J/Hz	Assignment
9	3.40	10.6	H 4
9	3.58	10.2	H 9
10	4.00	6.6	H 4
10	4.19	6.2	H 9
12	3.4	10	H*
13	4.2	6	H*



a complete preparative separation proved difficult, the structural assignment is based on NMR data for a mixture of the two isomers (see the Experimental). When isoprene or cyclohexene were used as trapping reagents, only the spirodimer **7** was formed.

Experimental

The ^1H NMR spectra were recorded on Varian A 60, Bruker CPX-200 and Bruker WM-400 instruments and the ^{13}C NMR spectra were recorded on Jeol JNM-FX 60 and Bruker WM-400 instruments. The MS spectra were obtained with VG Micromass 7070 F and the GC analyses were carried out with Hewlett-Packard 5700 A with a SP 2100 3% column. IR data were obtained on a Perkin-Elmer 281 B instrument. Melting points are uncorrected.

Reactions were monitored by using Merck precoated

silica gel 60 F 254 plates. Flash liquid chromatography was performed according to literature¹⁴ with Merck silica gel 60, 0.040–0.063 mm.

Commercially available starting materials and solvents were purified and dried when necessary by usual methods. 2,3-Dibromothiophene was prepared according to literature.¹⁵

2-Benzyl-3-bromothiophene (3). Etheral BuLi (300 ml, 1.5 M, 0.45 mol) was cooled to -70°C under nitrogen. A solution of 2,3-dibromothiophene (109 g, 0.45 mol) in diethyl ether (100 ml) was added dropwise. The resulting solution was stirred for 1 h when a solution of freshly distilled benzaldehyde (48 g, 0.45 mol) in *abs. ether* (50 ml) was added over a 1 h period at -70°C . The reaction mixture was stirred for 1 h and warmed to room temperature. The solution was then poured onto ice, the organic layer was separated and the aqueous layer extracted with ether. The ether portions were combined, washed with water and dried with MgSO_4 . Evaporation of the solvent gave 2-(*alpha*-hydroxybenzyl)-3-bromothiophene (121 g) as a crude oil which was used without further purification. The oil (121 g) was dissolved in *abs. ether* (100 ml) and added slowly to an ice-cooled solution of LiAlH_4 (26 g, 0.69 mol) and anhydrous AlCl_3 (90 g, 0.67 mol) in *abs. ether* (350 ml). The reaction mixture was stirred for 10 h at room temperature and then poured onto ice. After separation of the layers, the water layer was extracted several times with ether. The combined ether phase was then washed with aqueous NaHCO_3 and dried with MgSO_4 . Evaporation of the solvent and distillation of the crude product afforded the title compound (96 g, 84% from 2,3-dibromothiophene) as a colourless oil, b.p. $100\text{--}102^\circ\text{C}/0.2\text{ kPa}$.

MS [IP 70 eV; m/z (% rel. int.)]: 254/52 (31/32, M^+), 173 (100, $M-\text{Br}$). ^1H NMR (60 MHz, CDCl_3): δ 4.0 (2 H, s), 6.8 (1 H, d, J 6 Hz), 7.0 (1 H, d, J 6 Hz), 7.2 (5 H, s). ^{13}C NMR (15 MHz, CDCl_3): δ 35.09 (CH_2), 109.29 (C-Br), 123.97, 126.70, 128.58, 129.88, 138.52, 139.04.

2-Benzyl-3-thiophenecarbaldehyde (4). BuLi in hexane (25 ml, 1.5 M, 38 mmol) and *abs. ether* (50 ml) was cooled to -70°C under nitrogen. 2-Benzyl-3-bromothiophene (**3**) (9.5 g, 38 mmol) in *abs. ether* (60 ml) was added dropwise, and the reaction mixture was stirred for 1 h. *N,N*-Dimethylformamide (DMF) (3.0 g, 41 mmol) in ether (10 ml) was added dropwise, and the solution was stirred for 1 h at -70°C . The solution was warmed to room temperature and poured onto ice. The organic layer was separated and the water layer was extracted with ether. The combined ethereal solutions were dried over MgSO_4 , filtered and the solution evaporated to dryness. Distillation of the crude product afforded 6.5 g (85%) of the title product, b.p. $114\text{--}116^\circ\text{C}/0.3\text{ kPa}$.

IR (film): 1710 cm^{-1} (s, C=O). MS [IP 70 eV; m/z (% rel. int.)]: 202 (100, M^+), 201 (63, $M-1$), 173 (15). ^1H NMR (60 MHz, CDCl_3): δ 4.5 (2 H, s), 7.1 (1 H, d, J 6 Hz), 7.3 (5 H, s), 7.4 (1 H, d, J 6 Hz), 10.1 (1 H, s).

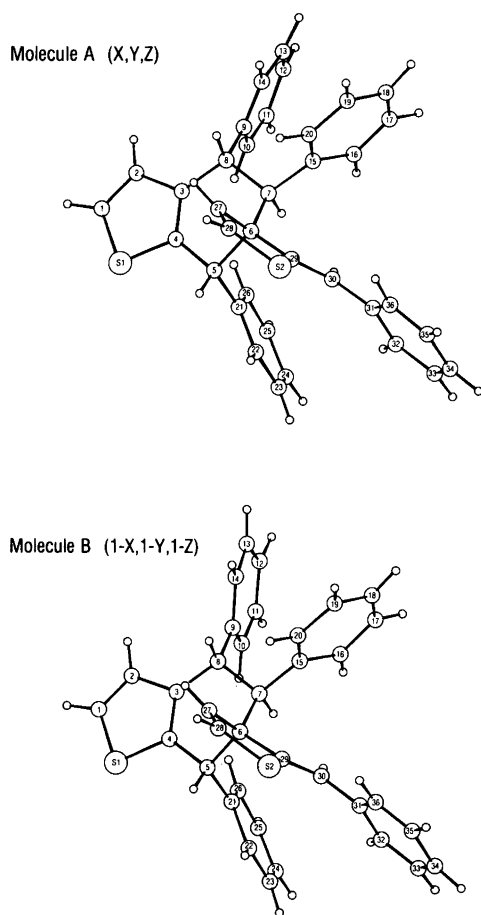


Fig. 1. Plots of the two molecules A and B of the spiro-dimer **7**.

2-Benzyl-3-(α -hydroxybenzyl)thiophene (5). The Grignard reagent prepared from bromobenzene (2.1 g, 13 mmol) and magnesium (0.5 g, 20 mmol) in ether (5 ml) was added dropwise to an ice-cooled solution of the aldehyde (4) (2.4 g, 12 mmol) in ether (10 ml). The reaction mixture was hydrolysed with saturated aqueous NH_4Cl and extracted several times with ether. The combined ethereal solutions were washed with aqueous NaHCO_3 , dried over MgSO_4 and evaporated. The crude product was purified by flash liquid chromatography with petroleum ether–diethyl ether (1:1 v/v) as the eluent. Evaporation of the solvent gave 3.0 (90%) of the title compound as a colourless oil. IR (film): 3600–3150 cm^{-1} (s, OH). MS [CI isobutane; m/z (rel. int.)]: 281 (1, $M^+ + 1$), 280 (2, M^+), 263 (100), 262 (50). ^1H NMR (60 MHz, CDCl_3): δ 2.6–2.9 (1 H, br s, centred at δ 2.75, OH), 4.3 (2 H, s), 5.9 (1 H, s), 6.9 (1 H, d, J 5 Hz), 7.1 (1 H, d, J 5 Hz), 7.2–7.4 (10 H, m).

2-Benzyl-3-(α -methoxybenzyl)thiophene (6). The alcohol 5 (8.6 g, 30 mmol) and sodium hydride (hexane washed) (2.2 g, 90 mmol) were stirred in ether (100 ml) under nitrogen until the evolution of gas ceased. A large excess of methyl iodide (17 g, 100 mmol) was added, and the reaction mixture stirred overnight at room temperature. The excess hydride was quenched by slow addition of dilute hydrochloric acid. The organic layer was separated and washed neutral with water. The ethereal solution was dried over MgSO_4 and then evaporated to dryness. The product was purified by flash liquid chromatography with toluene as the eluent. This gave 6.9 g (76%) of the title product as a colourless oil.

MS [IP 70 eV; m/z (% rel. int.)]: 263 (21, $M^+ - \text{OCH}_3$), 262 (100, $M^+ - \text{CH}_3\text{OH}$). ^1H NMR (60 MHz, CDCl_3): δ 3.5 (3 H, s), 4.4 (2 H, s), 5.5 (1 H, s), 7.1 (1 H, d, J 5 Hz), 7.2 (1 H, d, J 5 Hz), 7.3–7.5 (10 H, m).

Preparation of lithium diisopropylamide (LDA) solutions. To a mechanically stirred solution of $n\text{-BuLi}$ in hexane (2.5 ml, 1.6 M, 4 mmol) was slowly added diisopropylamine (0.5 g, 5 mmol) under nitrogen. After the mixture has been stirred for 0.5 h at room temperature, additional hexane (10 ml) was added to give a clear, pale yellow solution. In the following procedures the amount of this standard solution is given in ml for each experiment.

Generation of 2,3-dibenzylidene-2,3-dihydrothiophene (2 $R=\text{Ph}$) and formation of a spiro-dimer (7). To a solution of 2-benzyl-3-(α -methoxybenzyl)thiophene (6) (1.3 g, 4 mmol) in dry hexane (10 ml) was added a solution of LDA in hexane (13 ml) over a period of 5 h at room temperature. After the reaction mixture had been stirred for 12 h, it was poured onto water, extracted with ether and the ether layer was dried (MgSO_4). After filtration and evaporation of the solvent, the residue was subjected to preparative TLC with toluene as the eluent. This afforded 400 mg (30%) of the spiro-dimer 7 as white powder of m.p. 217–219°C. An

analytical sample melted at 220–222°C (from petroleum ether–chloroform).

MS [IP 70 eV; m/z (% rel. int.)]: 524 (2, M^+), 343 (14), 262 (100). MS [CI methane; m/z (rel. int.)]: 525 (11, $M^+ + 1$), 524 (12, M^+). ^1H NMR (400 MHz, CDCl_3): δ 3.48 (1 H, d, J 11.1 Hz, H5), 4.31 (1 H, s, H7), 4.38 (1 H, d, J 11.1 Hz, H4), 4.73 (1 H, s, H6'), 6.4–7.3 (24 H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 51.36 (C4), 52.20 (C5), 54.44 (C7), 67.02 (C6), 123.72, 124.37, 125.82, 126.10, 126.14, 126.47, 127.08, 127.49, 127.60, 127.85, 128.10, 128.85, 129.44, 129.91, 136.97, 138.53, 139.07, 139.11, 139.67, 140.16, 143.32.

X-Ray crystallographic structure determination of the spiro-dimer 7. Monoclinic symmetry, space group $P2_1/a$, cell dimensions: $a = 7.534$, $b = 19.579$, $c = 36.220$ Å, $\beta = 92.79^\circ$; $Z = 8$. All reflections with $2D < 45^\circ$ were considered, yielding about 9200 reflections, 6597 of which were treated as observed ($I > 2CI$). The e.s.d. of the observations were taken as that due to counting statistics plus an additional term $(0.02 I)^2$ due to experimental instability. The coefficient 0.02 was derived from the variances observed for three test reflections measured periodically throughout the experiment.

The quality of the data were rather poor, having an expectation value of $R = 0.072$. All experiments were carried out on an automatic Syntex P1 diffractometer using graphite monochromated Mo K-radiation.

The phase problem was readily solved by direct methods (MULTAN), and after a few Fourier syntheses all non-hydrogen atoms were located. Least-squares refinement was performed using reciprocal variances of the observations as weights, and several models were tried (in all cases hydrogen-atom contributions were calculated from hydrogen atoms with fixed parameters), including anisotropic thermal parameters and/or constraints. The best result was obtained with anisotropic thermal parameters for the sulphur atoms, and isotropic thermal parameters for the carbon atoms. Final $R = 0.197$, $R_w = 0.215$ and $S = 5.41$. There were clearly systematic differences in $F_o - F_c$, depending especially on H.

Since the investigations were undertaken primarily to establish the configuration of the compound, the results are useful in spite of the rather unsatisfactory precision obtained.

The dimerization reaction creates four chiral centres, and four pairs of enantiomers are thus possible. In addition there are four possible constitutions, depending on the positions of the reacting double bonds relative to the sulphur atoms. A mixture of these possible constitutions would manifest itself as disorder of the sulphur positions in the thiophene rings. No such disorder was found, and *it may thus safely be concluded that the title compound is specifically created in the synthesis used. The same is true for the different pairs of enantiomers, as only one pair is found, in spite of the fact that there are two independent molecules in*

the asymmetric unit. The existence of both enantiomers is ascertained by the centrosymmetric space group. The relationship between the two independent molecules and the derived structural parameters will be briefly discussed below.

The two molecules are approximately related by the following symmetry operations:

$$\begin{aligned} X_a &= 1.439 - X_b & (X_a + X_b &= 1.4385 \pm 0.0387) \\ Y_a &= Y_b & (Y_a - Y_b &= -0.00076 \pm 0.00380) \\ Z_a &= Z_b - 0.5 & (Z_a - Z_b &= -0.50017 \pm 0.00209) \end{aligned}$$

The r.m.s. deviations given correspond to 0.29, 0.074 and 0.076 Å, respectively. The nature of the deviations is mainly that of a small relative rotation around the crystallographic *b*-axis (ca. 4°) and an even smaller rotation around the *c*-axis (ca. 2.5°). In addition there is only one significant difference in the molecular parameters, namely a rotation of one of the phenyl groups by 15°. Average structural parameters are given in Table 2. The e.s.d.s are estimated from half-normal probability plots based on the hypothesis that the two molecules are identical, and – for distances and bonding angles – the external e.s.d.s derived by averaging all phenyl groups. The derived e.s.d.s are: bonding distances; 0.018 Å; bonding angles; 1.3° and torsional angles 1.6°. For the phenyl groups the e.s.d.s are 0.0004 Å in bonding and 0.3° in angles (24 individual measurements). The e.s.d.s in the individual measurements are very similar in the two types of derivation: 0.025 vs. 0.031 (bond) and 1.8 vs. 1.8 (angles) as derived from half-normal probability plot and averaging of phenyl parameters, respectively.

The high e.s.d.s precluded nearly any conclusions with respect to molecular parameters other than pure conformation. However, it seems that the rehybridization of C6 from sp² to sp³ effectively disrupts the conjugation of the thiophene ring, as the C–S distances in this ring are substantially longer than in the other ring.

An analysis of the C–C bonding distances with respect to different kinds of bond give the following average values (e.s.d. in average) (e.s.d. in individuals): C=C, 1.350(9) (26); C–C_{phenyl}, 1.395(4)(31); C_{sp}²–C_{sp}², 1.482(9)(17); C_{sp}²–C_{sp}³, 1.531(7)(26); C_{sp}³–C_{sp}³, 1.565(19)(46), e.s.d.s refer to last digit given. All distances in Å.

Generation of 2,3-dibenzylidene-2,3-dihydrothiophene (2, R = Ph) and formation of cycloadducts 9 and 10 with bicyclo[2.2.1]hept-2-ene (norbornene). To a solution of **6** (1.3 g, 4 mmol) and norbornene (7.5 g, 80 mmol) in dry hexane (20 ml) was added a solution of LDA in hexane (13 ml) over a period of 1 h at room temperature under nitrogen. The reaction mixture was stirred until TLC indicated complete consumption of **6**. The solution was then poured onto ice and extracted with ether. The ethereal solution was washed with water, dried over MgSO₄ and evaporated to dryness. The residue was subjected to flash chromatog-

Table 2. Bonding distances, angles and torsional angles^a in **7**. The values given are average values for the two independent molecules A and B. E.s.d.s calculated from the normal distribution/equality assumption are: 0.018 Å, 1.3° and 1.6° for the three types of parameter respectively. The e.s.d. in bonding, as derived from position e.s.d. (neglecting covariance), is 0.025 Å. The sign of torsional angles refers to molecule A at (X, Y, Z).

Bond	Distance	Bond	Distance
S1–C1	1.721	C8–C9	1.531
S1–C4	1.692	C1–C2	1.346
C2–C3	1.491	C3–C4	1.374
C4–C5	1.545	C5–C6	1.610
C6–C7	1.564	C7–C8	1.520
C8–C3	1.525	S2–C28	1.763
S2–C29	1.780	C27–C28	1.324
C6–C27	1.517	C29–C6	1.521
C29–C30	1.355	C30–C31	1.473
C5–C21	1.519	C7–C15	1.562
Bonding	Angle	Bonding	Angle
C1–S1–C4	92.0	S1–C1–C2	112.8
C1–C2–C4	111.6	S2–C3–C4	109.9
C3–C4–S1	113.6	C2–C3–C8	127.0
S1–C4–C5	121.9	C4–C5–C21	109.8
C6–C5–C21	117.2	C6–C7–C15	114.0
C8–C7–C15	110.0	C7–C8–C9	112.5
C3–C8–C9	112.0	C8–C3–C4	122.7
C3–C4–C5	124.5	C4–C5–C6	106.6
C5–C6–C7	107.1	C6–C7–C8	111.3
C7–C8–C3	111.4	C8–C9–C10	122.6
C8–C9–C14	118.5	C7–C15–C16	118.3
C7–C15–C20	120.7	C5–C21–C22	117.3
C5–C21–C26	122.8	C30–C31–C32	119.3
C27–C6–C29	106.7	C6–C27–C28	114.6
C27–C28–S2	115.0	C28–S2–C29	91.5
S2–C29–C6	110.6	C5–C6–C27	105.5
C5–C6–C29	109.2	C7–C6–C27	115.3
C7–C6–C29	112.9	S2–C29–C30	123.7
C6–C29–C30	125.6	C29–C30–C31	129.7
C30–C31–C36	124.1		
Torsional	Angle	Torsional	Angle
C1–C2–C3–C4	–2.4	C2–C3–C4–S1	1.1
C3–C4–S1–C1	0.3	C4–S1–C1–C2	–1.8
S1–C1–C2–C3	2.7	C2–C3–C8–C9	–45.0
C9–C8–C7–C15	58.5	C15–C7–C6–C29	–46.3
C29–C6–C5–C21	–53.5	C21–C5–C4–S1	77.1
C29–C6–C27–C28	–13.3	C6–C27–C28–S2	8.1
C27–C28–S2–C29	–0.1	C28–S2–C29–C6	–7.8
S2–C29–C6–C27	12.7	C28–S2–C29–C30	175.0
S2–C29–C30–C31	2.5	C4–C5–C21–C26	33.1
C6–C5–C21–C22	89.3	C29–C30–C31–C36	31.2
C8–C3–C4–C5	–8.7	C3–C4–C5–C6	27.7
C4–C5–C6–C7	–54.5	C5–C6–C7–C8	68.4
C6–C7–C8–C3	–47.3	C7–C8–C3–C4	17.2
C8–C7–C15–C16	–99.9	C6–C7–C15–C20	–56.6
C3–C8–C9–C10*	–42.3/–55.5		
C7–C8–C9–C14*	–92.1/–109.3		

^aTorsional angles marked with an asterisk (*) represents the only significant difference between the two structures A and B and both angles are given.

raphy with petroleum ether–diethyl ether (1:1, v/v) as the eluent to give 550 mg (40%) of the adduct **9** (m.p. 185–188°C) and 200 mg (20%) of the dimer **7**. MS [IP 70 eV; m/z (% rel. int.)]: 357 (20, M^+), 356 (79), 262 (100). ^1H NMR (400 MHz, CDCl_3): δ 1.1 (3 H, m, H6, H7, H10), 1.5 (2 H, m, H6, H7), 1.9 (1 H, m, H10), 2.1 (4 H, m, H4a, H5, H8a, H8), 3.4 (1 H, d, J 10.6 Hz, H4), 3.6 (1 H, d, J 10.2 Hz, H9), 6.4 (1 H, d, J 5.0 Hz, H3), 6.9 (1 H, d, J 5.0 Hz, H2), 7.2–7.4 (10 H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 29.89 (C6, C7), 33.98 (C10), 41.23/41.27 (C5/C8), 46.82 (C9), 47.17 (C4), 53.67 (C4a, C8a), 120.81 (C2), 126.63, 126.92, 127.25, 128.50, 128.57, 129.06, 129.22, 140.62, 141.43, 143.52, 144.16.

Generation of 2,3-dibenzylidene-2,3-dihydrothiophene (2, R = Ph) and formation of the cycloadducts 14 and 15 with 1-phenylethene (styrene). To a solution of **6** (1.3 g, 4 mmol) in 1-phenylethene (20 ml) was added a solution of LDA in hexane (13 ml) over a period of 1 h at room temperature under nitrogen. The reaction mixture was stirred until TLC analysis indicated full conversion of **6**. The solution was evaporated to dryness under reduced pressure, and the residue was dissolved in ether and washed until neutral to litmus with water. The ethereal solution was dried over MgSO_4 and evaporated to dryness. The crude product was purified by flash chromatography with petroleum ether–toluene (1:2, v/v) as the eluent. This gave 620 mg (42%) of the title compound with m.p. 60–69°C which was pure according to TLC, but which according to NMR spectroscopy consisted of a mixture of regioisomers.

MS [IP 70 eV; m/z (% rel. int.)]: 366 (1, M^+), 262 (100). ^{13}C NMR (100 MHz, CDCl_3): aliphatic carbons for the two regioisomers: δ 33.36 (CH_2), 45.31 (CH), 46.70 (CH), 47.87 (CH); 38.74 (CH_2), 40.95 (CH), 45.45 (CH), 49.99 (CH).

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