12. Syntheses and Reactions of Alkylthio- and Arylthio-Substituted 1,6-Methano[10]annulenes

by **Amanda C. Bryant-Friedrich** and **Richard Neidlein***

Pharmazeutisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 364, D–69120 Heidelberg

Dedicated to Professor *Michael Hanack* on the occasion of his 65th birthday

(16.VII.96)

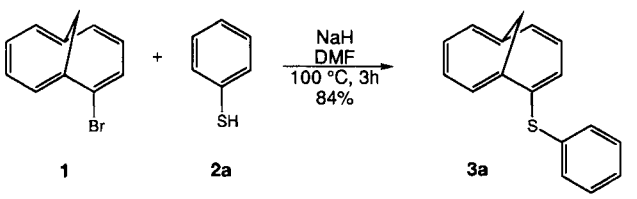
The treatment of bromo-substituted 1,6-methano[10]annulenes with sodium thiolates in DMF provides easy access to alkylthio- and arylthio-substituted 1,6-methano[10]annulenes (*Schemes 2–4*). These compounds are then brominated with *N*-bromosuccinimide (NBS) to study their reactivity in electrophilic substitution reactions (*Schemes 5* and *6*). The resulting brominated thio-1,6-methano[10]annulenes are, in a subsequent reaction, subjected to *Heck* coupling with (4-nitrophenyl)acetylene (**13**) to produce the alkynylated derivatives **14** in reasonable yield (*Scheme 7*).

Introduction. – It was established long ago by *E. Vogel* that electrophilic substitution of 1,6-methano[10]annulene occurs first at the C(2) position [1]. The second substitution occurs at a position dictated by the orientation effects of the first substituent. *Effenberger* and *Klenk* described in detail the directing effect of several electron-donating and electron-withdrawing substitutents [2]. They found that in the bromination of 2-methoxy-1,6-methano[10]annulene, the exclusive product was 2-bromo-5-methoxy-1,6-methano[10]-annulene. The outcome was explained by the same rules that explain the substitution pattern found in electrophilic aromatic substitution of a benzene derivative containing an electron-donating group. When electrophilic attack occurs at C(5), the transition state leading to the formation of the intermediate σ-complex can be most stabilized by an electron-donating group at C(2).

Even though extensive studies have been performed using 2-alkoxy-substituted 1,6-methano[10]annulenes, very little is known concerning other electron-donating groups such as amino or thio, and there are not many examples exploring the properties and reactivities of 1,6-methano[10]annulenes bearing multiple electron-donating groups [3].

Earlier, in the course of our attempts to prepare 2-(thiocyanato)-1,6-methano[10]-annulene, we found that, during column chromatography on alumina, the originally formed thiocyanate was converted to a mixture of diastereoisomeric (±)-*meso*-disulfides [4]. Prompted by data extracted from X-ray structure analysis and NMR spectra concerning the electronic structure of the disulfides, the reactivity of a soft nucleophile, namely, sodium benzenethiolate, towards 2-bromo-1,6-methano[10]annulene (**1**) was investigated (*Scheme 1*). Compound **3a** was isolated in 84% yield after stirring at 100° for 3 h in DMF.

Scheme 1



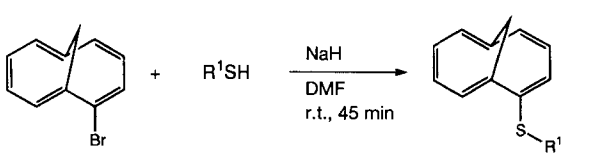
1 2a 3a

Here we investigate the feasibility of this reaction in the synthesis of other thio-substituted 1,6-methano[10]annulene derivatives and their reactivity towards electrophiles. As electrophilic reaction partner we chose, as in earlier studies, *N*-bromosuccinimide (NBS) [5]. It has been proven that bromination of 1,6-methano[10]annulene with NBS is electrophilic and does not follow a radical mechanism [6]. The bromination has also proven to be highly efficient with a large number of substituents on the 1,6-methano[10]annulene ring. Also, in conjunction with our studies concerning alkynylated 1,6-methano[10]-annulene derivatives, we investigate the reactivity of these brominated thio derivatives with (4-nitrophenyl)acetylene in *Heck* couplings [7].

Results and Discussion. – The synthesis of aryl thioethers is not trivial [8]. Aryl halides which are not activated by electron-withdrawing groups usually do not react efficiently with nucleophiles. Therefore, the preparation of aromatic sulfides usually involves high temperatures [9], long reaction times [10], strong bases [11], or catalysts [12]. In the preparation of 1,6-methano[10]annulenyl thioethers, these difficulties were not observed. This is likely the result of lower electron density in the *endo*-region of 1,6-methano[10]-annulene. There is a long-standing hypothesis that the aromatic perimeter of 1,6-methano[10]annulene consists of an intermediate hybridization between sp^2 and sp^3 of the aromatic C-atoms [13]. The C–H bonds of the periphery point downward, *i.e.*, they are in *trans* position relative to the methylene bridge. This may mean that there is considerable π-electron crowding on the side of the methylene bridge which would create low electron density on the opposite side of the molecule making it more susceptible to nucleophilic attack.

Monosubstituted 2-(alkylthio)-1,6-methano[10]annulene derivatives **3b,c** were prepared at room temperature by the addition of 2-bromo-1,6-methano[10]annulene (**1**) to a solution of the thiolate in DMF (*Scheme 2*). The thiolates were formed by the addition of thiols **2b,c** to a suspension of NaH in DMF at room temperature. For compounds **3b** and **3c**, the reaction was carried out at 25° for 45 min. In the case of **3a**, the reaction

Scheme 2

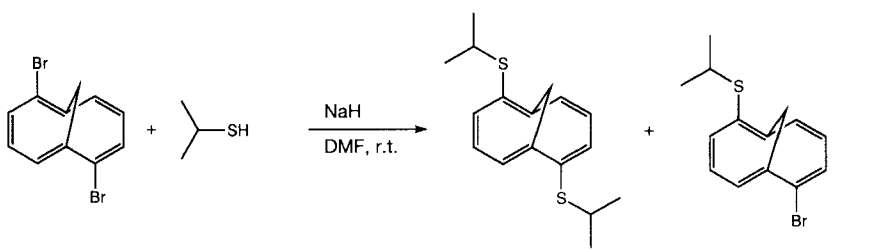


1 **2b** R^1 = i-Pr, **c** R^1 = *t*-Bu → **3b** R^1 = i-Pr (71%), **c** R^1 = *t*-Bu (61%)

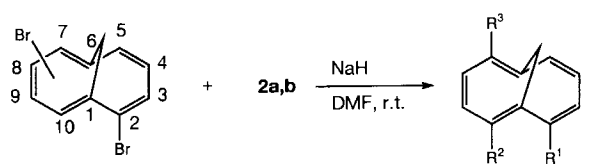
mixture was heated to 100° for 3 h, according to a known literature procedure [4]. These 2-(alkylthio)-1,6-methano[10]annulenes are bright yellow to orange-yellow oils which, contrary to their alkyloxy analogs, are thermally very stable [2].

Bis(thio)- and tetrakis(thio)-1,6-methano[10]annulenes were prepared in the same manner as the monosubstituted derivatives in good-to-satisfactory yields. The reaction times were in some cases considerably longer than in the monosubstituted case. During the synthesis of the disubstituted derivatives, we did run into some unexpected difficulties. In the case of dibromo compound **4a**, when 2.5 equiv. of thiol **2b** were used, and the reaction was conducted at room temperature for only 2 h, the major product (71% yield) was mono(thio)-substituted compound **7a** (*Scheme 3*). The desired bis(thio) derivative **5a** was obtained in only 29% yield. Even when longer reaction times were employed, complete conversion to **5a** was not achieved. In the similar synthesis of bis(thio) compound **5b** from **4b**, this was not the case. The latter was obtained in 59% yield with no detection of monosubstituted product. The reaction of **4a** with 3 equiv. of benzenethiolate delivered compound **6a** in 63% yield, also with no sign of monosubstituted product. However, in the case of the attempted synthesis of bis(thio) compound **6b**, the only product isolated was the mono(thio)-substituted derivative **7b**.

Scheme 3



4a **2b** **5a** (2h: 29%; 14h: 19%) **7a** (2h: 71%; 14h: 47%)

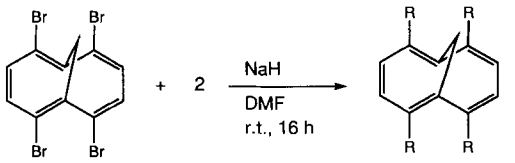


4a 2,7-dibromo
b 2,10-dibromo

5a $R^1 = R^3$ = i-PrS, R^2 = H (29 or 19%)
b $R^1 = R^2$ = i-PrS, R^3 = H (59%)
6a $R^1 = R^3$ = PhS, R^2 = H (63%)
b $R^1 = R^2$ = PhS, R^3 = H (0%)
7a R^1 = i-PrS, R^2 = H, R^3 = Br (21 or 47%)
b R^1 = PhS, R^2 = Br, R^3 = H (–)

Tetrasubstituted derivatives **9a–c** were obtained in satisfactory yield (38, 50, and 50%, resp.), after stirring **8** for 16 h at room temperature (*Scheme 4*). These substances are red to yellow oils which are, with the exception of the tetrakis(*tert*-butylthio)-substituted one, thermally stable.

Scheme 4



8

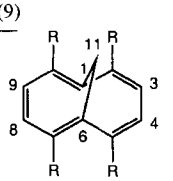
9a R = PhS (38%)
b R = i-PrS (50%)
c R = *t*-BuS (50%)

The special characteristics of this class of 1,6-methano[10]annulene derivatives can be seen by their spectroscopic properties. It has been shown that protons which are *peri* to substituents at the 2-position on the annulene ring are shifted in the ^{1}H-NMR spectra to lower field [14]. This effect is accredited to the steric demand of the substituent which has a deshielding influence on the *peri*-proton. This hypothesis holds true in compounds **3a–c**. In **3c**, where H–C(10) is *peri* to the sterically demanding *t*-Bu group, this proton shows a strong low-field shift appearing at 7.98 ppm. The protons in *peri*-position to sterically less demanding substituents, such as in **3b** and **3a**, show up at higher field (7.89 and 7.72 ppm, resp.). The ^{1}H-NMR spectra of the disubstituted derivatives **5a, b** and **6a** exhibit the same steric effects on the *peri*-protons which also appear at lower field.

In the case of compound **5b**, the ^{13}C-NMR data reveal that there is considerable distortion in the annulene backbone when compared to the parent 1,6-methano[10]annulene backbone. The methylene-bridge C-atom of **5b** appears at 37.0 ppm and the bridgehead atoms C(1) at 121.8 and C(6) at 120.1 ppm. These values are considerably different from those found in 1,6-methano[10]annulene (see *Table*, R = H). This distortion may be explained by the extreme steric crowding in the area of the two isopropylthio substituents. It has been found that in the case of 2,5,7,10-tetraiodo-1,6-methano[10]annulene, the transannular bond distance between C(1) and C(11) and C(6) and C(11) are lengthened due to steric effects from the iodo substituents [15]. This is explained by the fact that the I-atoms seem to flatten the ring causing a longer distance between the bridge and the bridgehead C-atoms. In the case of compound **5b**, it may be that the ring makes an attempt to flatten so that the isopropylthio substituents can reach a conformation which provides minimal steric interaction.

Table. *Selected ^{13}C-NMR Data for Tetrasubstituted 1,6-Methano[10]annulenes* **A**

R	C(1), C(6)	C(11)	C(3), C(4), C(8), C(9)
H	114.9	34.9	126.16
MeSi	132.4	39.7	132.4
I	123.0	36.7	142.3
t-BuS (**9c**)	128.3	39.9	137.6
i-PrS (**9b**)	125.7	39.5	132.5
PhS (**9a**)	124.9	39.8	133.7

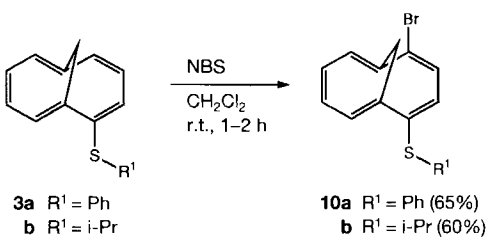


A

The above effect is enhanced in the case of the tetrasubstituted derivatives **9a–c**. It can be inferred by the ^{13}C-chemical-shift values of the bridgehead and bridge C-atoms that the ring system of **9a–c** is considerably distorted as compared to the parent ring system (*Table*). The greater the steric demand of the substituents at positions 2, 5, 7, and 10 of the annulene ring, the higher the chemical-shift values for the above mentioned C-atoms. In the extreme case of 2,5,7,10-tetrakis(trimethylsilyl)-1,6-methano[10]annulene, which, because of steric effects, assumes a polyolefinic structure, C(11) appears at 39.7 ppm [16]. This value is close to those found for the tetrakis(thio)-substituted derivatives **9a–c**. The methylene protons $CH_2(11)$ of **9a–c** (around 0.0 ppm) do not, however, absorb at such low field as in the case of 2,5,7,10-tetrakis(trimethylsilyl)-1,6-methano[10]annulene (1.53 ppm). As seen in the *Table*, the sterically demanding *t*-Bu substituents of **9c** cause the greatest amount of distortion in the annulene backbone. With this amount of distortion, it would be assumed that the protons $CH_2(11)$ of **9c** would also show a more important downfield shift which is not the case ($CH_2(11)$ at −0.09 ppm). However, it could very well be that $CH_2(11)$ is affected in some way by the *t*-Bu groups which could in part orient themselves above the C=C bond plane to avoid undesirable steric interactions.

With the thio-substituted annulene derivatives in hand, we decided to investigate their reactivity toward electrophilic attack. Using NBS as electrophilic reagent, we were successful in preparing the 5-bromo derivatives **10a** and **10b** from the 2-thio-substituted derivatives **3a** and **3b**, respectively (*Scheme 5*). The brominations were carried out in CH_2Cl_2 at room temperature with an equimolar amount of NBS. These compounds are bright yellow oils.

Scheme 5



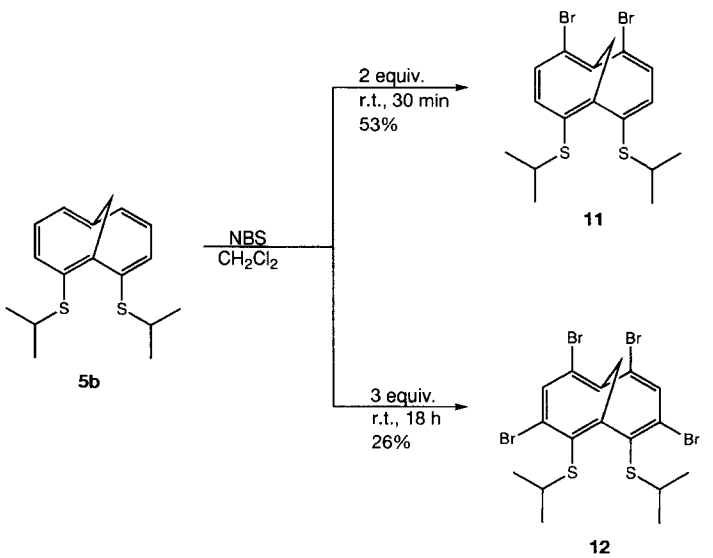
3a R^1 = Ph
b R^1 = i-Pr

10a R^1 = Ph (65%)
b R^1 = i-Pr (60%)

Brominations of the 2,7- and 2,10-bis(thio)-substituted 1,6-methano[10]annulene derivatives **5a**, **5b**, and **6a** were also attempted. The bromination of 2,7-bis(thio)-substituted derivatives **5a** and **6a** gave di- and tribromo derivatives which could not be separated by flash chromatography. In the case of 2,10-bis(thio) derivative **5b**, when treated with 2 equiv. of NBS, the dibromo derivative **11** was obtained in 53% yield as a red orange oil (*Scheme 6*). When treated with 3 equiv. of NBS in CH_2Cl_2 or nitromethane at room temperature, the only product isolated was the tetrabromo derivative **12** as orange crystals. This outcome may be explained by an increase in electron density in the annulene ring which can be attributed to the addition of the electron-donating Br-substituents '*para*' to the thio groups. It was pointed out in studies by *D'Arcy et al.* [17] that resonance transmission to the C(5) position in the case of 1,6-methano[10]annulenes substituted by electron-donating substituents in the 2-position is very strong. This is in accordance with the electrophilic substitution which occurs at C(5) in 2-methoxy-

and 2-methyl-1,6-methano[10]annulene. These authors also mention that strong resonance effects are also indicated at C(9) but are negated by the polar contribution. In compound **5b**, this polar contribution does not seem to attribute that much, and the C(9) and C(3) positions are also activated, thus allowing electrophilic attack.

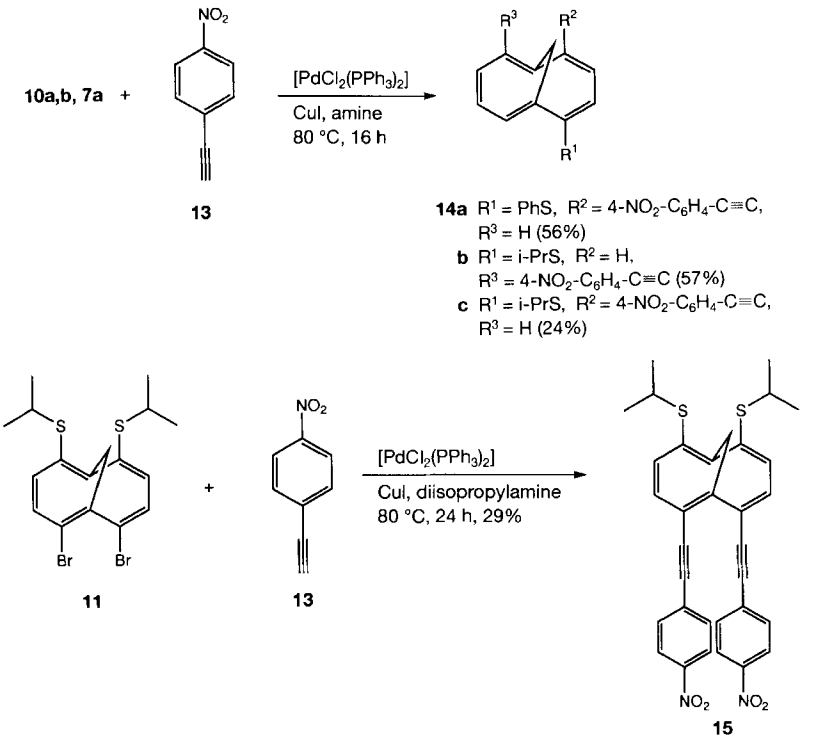
Scheme 6



The spectroscopic data for derivatives **10a,b** show no unexpected surprises. The methylene proton above the substituted ring half in the 2,5-substituted derivatives **10a,b** is deshielded compared to the methylene proton above the unsubstituted ring half. These protons exhibit long-range couplings to ring protons sometimes producing broadened signals or complex coupling patterns. On the other hand, the spectroscopic data for compounds **11** and **12** are somewhat surprising. The signals for the protons of the $CH_2(11)$ bridge of **11** (at 0.15 ppm) indicate some distortion in the annulene ring system. This distortion is enhanced for **12**, its $CH_2(11)$ appearing at 1.54 ppm, a value similar to that for $CH_2(11)$ of 2,5,7,10-tetrakis(trimethylsilyl)-1,6-methano[10]annulene (1.53 ppm). Further investigations concerning the nature of the annulene ring system of compound **12** are currently in progress.

In connection with our ongoing studies of the reactivity of 1,6-methano[10]annulene derivatives toward *Heck* coupling [7], we employed our bromo-thio-substituted derivatives as aromatic coupling partners for the coupling of acetylenes. To investigate potential electronic interactions through the annulene ring system from the electron-donating S-containing substituents, electron-poor (4-nitrophenyl)acetylene (**13**) was used as the alkynyl coupling component. Compounds **10a,b** and **7a** were coupled with **13** in amine solvents using $[PdCl_2(PPh_3)_2]$/CuI as catalyst to give the alkynylated thio-substituted annulene derivatives **14a–c** (*Scheme 7*). Similarly, **11** and **13** yielded **15**. Compounds **14** and **15** are pale-yellow to red solids, and their properties are still under investigation.

Scheme 7



Conclusion. – We have shown that (alkylthio)- and (arylthio)-1,6-methano[10]annulene derivatives can be easily obtained from the reaction of thiolates in DMF with bromo-substituted 1,6-methano[10]annulenes. The steric hindrance of the alkylthio or arylthio group can have some effect on the annulene backbone causing distortion of the ring. These thio-substituted annulene derivatives can be brominated with NBS to give brominated thio-substituted 1,6-methano[10]annulene derivatives which can be successfully employed in *Heck* coupling reactions.

We would like to thank *BASF AG*, *Bayer AG*, and *Hoechst AG*, the *Verband der Chemischen Industrie*, *Fonds der Chemie*, as well as the *Deutsche Forschungsgemeinschaft* for support of this work. Thanks go to *Hewlett-Packard* and *Varian* for providing UV/VIS spectrometers. We would also like to thank Ms. *U. Hertle* and Dr. *W. Kramer* for NMR spectra and Mr. *H. Rudy* and Mr. *P. Weyrich* for mass spectra and elemental analysis.

Experimental Part

General. All reactions were carried out under Ar in dried glassware. Dimethylformamide (DMF), diisopropylamine $(i\text{-Pr})_2NH$, diethylamine (Et_2NH) and triethylamine (Et_3N) were distilled from CaH and stored over molecular sieves. Column chromatography (CC): silica gel (60–200 mesh) from *ICN-Biomedicals*. M.p.: *Reichert* melting-point microscope; uncorrected. UV/VIS Spectra: hexane solns.; *Hewlett-Packard-HP-8453-UV-Vis ChemStation* and *Varian-Cary-2200-UV-Vis* spectrophotometer; in nm (lg ε). IR Spectra: *Perkin-Elmer-PE-1600-FT-IR* spectrophotometer; in cm^{-1}. ^1H-NMR Spectra: at 250.13 MHz on a *Bruker-WM-250* spectrometer and at

299.95 MHz on a *Varian-XL-300* spectrometer; δ in ppm rel. to $SiMe_4$ or residual solvent signals, J in Hz. ^{13}C-NMR Spectra: at 62.89 and 75.4 MHz on the same spectrometers. Mass spectra: *Varian-MAT-311-A* mass spectrometer at 70 eV; m/z (rel. %). Elemental analyses were obtained on a *Foss-Heraeus Vario EL.*

2-(Alkylthio or Arylthio)-1,6-methano[10]annulene Derivatives **3b,c**: *General Procedure.* To a soln. of thiol **2b,c** (1.5 equiv.) in 5 ml of DMF was added NaH (1.5 equiv.) at r.t. The mixture was allowed to stir until gas evolution was at a minimum (10 min). To the thiolate soln. was added 2-bromo-1,6-methano[10]annulene (**1**; 1 equiv.). When the reaction was complete (reaction times and temp. as indicated), it was quenched by the slow addition of H_2O (8 ml). The soln. was then diluted with Et_2O and washed with H_2O. The org. layer was dried ($MgSO_4$) and evaporated and the residue purified by CC (silica gel, hexane).

2-(Isopropylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**3b**). From **1** (1 mmol), after stirring for 45 min at 25°: 154 mg (71%) of **3b**. Bright yellow oil. UV/VIS (hexane): 257 (4.58), 330 (3.77). IR (film): 3322*w*, 3204*w*, 3037*m*, 2958*s*, 2932*s*, 2862*s*, 1507*m*, 1477*m*, 1448*m*, 1380*m*, 1364*m*, 1249*m*, 1240*m*, 1192*m*, 1169*m*, 1154*m*, 1097*m*, 1051*m*, 1017*m*, 995*m*, 904*m*, 874*s*, 764*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.89 (*m*, H–C(10)); 7.39 (*m*, H–C(5), H–C(7)); 7.29 (*d*, ^3J = 9.3, H–C(3)); 7.17 (*m*, H–C(8), H–C(9)); 6.93 (*t*, ^3J = 9, H–C(4)); 3.67 (*sept.*, Me_2CH); 1.35 (*d*, ^2J = 6.6, 3 H, Me_2CH); 1.15 (*d*, ^2J = 6.6, 3 H, Me_2CH); –0.21 (*dd*, ^2J = 9.3, ^4J = 1.2, 1 H–C(11)); –0.44 (*d*, ^2J = 9.3, 1 H–C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.3 (C(2)); 130.5, 129.5, 129.3, 128.2, 127.4, 127.1, 125.7 (C(3), C(4), C(5), C(7), C(8), C(9), C(10)); 117.1, 116.8 (C(1), C(6)); 40.8 (Me_2CH); 35.3 (C(11)); 24.3, 22.5 (Me_2CH). EI-MS: 216 (29, M^+), 173 (100, $[M - Me_2CH]^+$), 141 (68, $[M - Me_2CHS]^+$), 43 (12, Me_2CH^+). HR-MS: 216.0972 ($C_{14}H_{16}S^-$; calc. 216.3464).

2-[(tert-Butyl)thio]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**3c**). From **1** (4.52 mmol), after stirring for 45 min at 25°: 635 mg (61%) of **3c**. Pale yellow oil. UV/VIS (hexane): 258 (4.58), 321 (3.77). IR (film): 3038*m*, 2958*s*, 2920*m*, 2894*m*, 2859*m*, 1676*w*, 1528*w*, 1499*w*, 1471*m*, 1455*m*, 1390*w*, 1362*s*, 1334*w*, 1288*w*, 1250*w*, 1166*s*, 1019*w*, 996*w*, 903*w*, 875*w*, 820*m*, 765*s*, 727*w*, 693*w*, 651*w*, 619*s*, 607*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.98 (*m*, H–C(10)); 7.43 (*m*, H–C(3), H–C(5), H–C(7)); 7.15 (*m*, H–C(8), H–C(9)); 7.01 (*t*, ^3J = 9, H–C(4)); 1.33 (*s*, 3 *t*-Bu); –0.32 (*d*, ^2J = 9.3, 1 H–C(11)); –0.36 (*d*, ^2J = 9.0, 1 H–C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.9 (C(3)); 131.5 (C(2)); 130.6, 129.8, 128.4, 127.0, 125.2 (C(4), C(5), C(7), C(8), C(9), C(10)); 118.8, 116.3 (C(1), C(6)); 47.9 (Me_3C); 35.5 (C(11)); 31.5 (Me_3C). EI-MS: 230 (10, M^+), 174 (32, $[M - t$-Bu]), 141 (100, $[M - t$-BuS]$^+$), 57 (36, *t*-Bu). HR-MS: 230.1129 ($C_{15}H_{18}S^+$; calc. 230.3732).

2,7- and 2,10-Bis(alkylthio or arylthio)-1,6-methano[10]annulene Derivatives **5a,b** *and* **6a**: *General Procedure.* Compounds **5a,b** were prepared as described above for the preparation of the 2-substituted derivatives. However, 2.5 equiv. of thiolate were used. In the case of **6a**, the reaction mixture was heated to 100°.

2,7-Bis(isopropylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**5a**). From **4a** (1 mmol, 300 mg), after stirring at r.t. for 2 h: 210 mg (29%) of **5a**. Bright yellow oil. UV/VIS (hexane): 255 (4.29), 282 (4.28), 352 (3.80). IR (film): 3034*m*, 2958*s*, 2923*s*, 2860*m*, 1521*w*, 1460*m*, 1381*m*, 1364*m*, 1240*m*, 1151*m*, 1051*m*, 1017*w*, 782*w*, 765*s*, 609*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.86 (*d*, ^3J = 8.7, H–C(5), H–C(10)); 7.38 (*d*, ^3J = 9.0, H–C(3), H–C(8)); 7.01 (*t*, ^3J = 9.0, H–C(4), H–C(9)); 3.58 (*sept.*, 2 Me_2CH); 1.32 (*d*, ^3J = 6.9, 6 H, Me_2CH); 1.04 (*d*, ^3J = 6.6, 6 H, Me_2CH); –0.21 (*s*, 2 H–C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 133.8 (C(2), C(7)); 131.7, 130.0, 126.6 (C(3), C(4), C(5), C(8), C(9), C(10)); 119.4 (C(1), C(6)); 41.2 (Me_2CH); 35.9 (C(11)); 24.2, 22.5 (Me_2CH). EI-MS: 290 (52, M^+), 247 (39, $[M - Me_2CH]^+$), 215 (20, $[M - Me_2CHS]^+$), 172 (100, $[M - Me_2CHS - Me_2CH]^+$). HR-MS: 290.1163 ($C_{17}H_{22}S_2^+$; calc. 290.4928).

2-Bromo-7-(isopropylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**7a**) was also obtained from the above reaction: 85 mg (71%). Bright yellow oil. UV/VIS (hexane): 272 (4.44), 340 (3.87). IR (film): 3038*m*, 2957*s*, 2923*s*, 2890*s*, 1521*m*, 1506*w*, 1496*w*, 1457*m*, 1448*m*, 1382*s*, 1364*m*, 1315*w*, 1255*m*, 1240*m*, 1221*w*, 1151*s*, 1051*m*, 1014*m*, 985*w*, 934*w*, 777*m*, 761*s*, 718*m*, 668*m*, 626*m*, 603*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.85 (*d*, ^3J = 8.8, H–C(10)); 7.67 (*d*, ^3J = 9.1, H–C(5)); 7.38 (*dd*, ^3J = 10, H–C(3), H–C(8)); 7.06 (*t*, H–C(4), H–C(9)); 3.62 (*sept.*, Me_2CH); 1.34 (*d*, ^2J = 6.8, 3 H, Me_2CH); 1.12 (*d*, ^2J = 6.5, 3 H, Me_2CH); –0.15 (*m*, 2 H–C(11)). ^{13}C-NMR (63 MHz, $CDCl_3$): 134.9 (C(7)); 131.6, 130.6, 130.1, 129.1, 128.3, 127.1 (C(3), C(4), C(5), C(8), C(9), C(10)); 120.3, 116.8 (C(1), C(6)); 113.0 (C(2)); 41.0 (Me_2CH); 34.8 (C(11)); 24.2, 22.5 (Me_2CH). EI-MS: 294 (35, (^{79}Br)M^+), 251 (62, $[M - Me_2CH]^+$), 219 (54, $[M - Me_2CHS]^+$), 171 (100, $[M - Br - Me_2CH]^+$). HR-MS: 294.0078 ($C_{14}H_{15}BrS^+$; calc. 295.2425).

2,10-Bis(isopropylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**5b**). From **4b** (2.04 mmol), at 25° for 6 h: 592 mg (59%) of **5b**. Bright yellow oil. UV/VIS (hexane): 259 (4.22), 308 (3.75), 376 (3.56). IR (film): 3035*m*, 2957*s*, 2921*s*, 2860*s*, 1902*w*, 1728*w*, 1561*w*, 1527*w*, 1447*s*, 1412*m*, 1379*m*, 1362*m*, 1262*m*, 1239*m*, 1213*m*, 1153*m*, 1102*w*, 1051*m*, 1009*m*, 997*m*, 779*s*, 767*s*, 640*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42 (*d*, ^3J = 9.9, H–C(5), H–C(7)); 7.34 (*d*, ^3J = 9.0, H–C(3), H–C(9)); 7.00 ('*t*', ^3J = 9.3, H–C(4), H–C(8)); 3.46 (*sept.*, 2 Me_2CH); 1.25 (*d*, ^3J = 6.6, 6 H, Me_2CH); 0.997 (*d*, ^3J = 6.6, 6 H, Me_2CH); –0.25 (*s*, 2 H–C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.0 (C(2),

C(10)); 132.0, 128.4, 127.3 (C(3), C(4), C(5), C(7), C(8), C(9)); 121.8, 120.14 (C(1), C(6)); 42.0 (Me_2CH); 37.0 (C(11)); 23.5, 22.1 (Me_2CH). EI-MS: 290 (55, M^+), 247 (100, $[M - Me_2CH]^+$), 215 (5, $[M - Me_2CHS]^+$), 171 (65, $[M - Me_2CHS - Me_2CH]^+$). HR-MS: 290.1163 ($C_{17}H_{22}S_2^+$; calc. 290.4928). Anal. calc. for $C_{17}H_{22}S_2$: C 70.29, H 7.63, S 22.07; found: C 70.39, H 7.69, S 22.13.

2,7-Bis(phenylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**6a**). Stirring at 100° for 4 h gave **6a** (377 mg, 63%). Very bright yellow solid. M.p. 102–103°. UV/VIS (hexane): 258 (4.65), 288 (sh, 4.32), 360 (4.10). IR (KBr): 3038*m*, 2943*m*, 1796*m*, 1577*s*, 1519*m*, 1472*s*, 1435*s*, 1385*m*, 1278*m*, 1247*m*, 1173*m*, 1150*m*, 1083*w*, 1066*w*, 1018*s*, 983*m*, 899*w*, 785*w*, 766*s*, 743*s*, 486*m*, 464*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.78 (*d*, $^3J = 8.7$, H–C(5), H–C(10)); 7.40 (*d*, $^3J = 9.3$, H–C(3), H–C(8)); 7.16 (*m*, 10 arom. H); –0.11 (*s*, 2 H–C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.1 (C(2), C(7)); 131.6 (2 C_{ipso}); 131.9, 130.8, 128.8, 127.9, 127.6, 125.9 (arom. CH); 119.0 (C(1), C(6)); 35.9 (C(11)). EI-MS: 358 (100, M^+), 279 (12, $[M - Ph]^+$), 249 (81, $[M - SPh]^+$), 171 (78, $[M - Ph - SPh]^+$), 139 (51, $[M - 2\ SPh]^+$). Anal. calc. for $C_{23}H_{18}S_2$: C 77.05, H 5.07, S 17.89; found: C 77.31, H 5.17, S 18.10.

2,5,7,10-Tetrakis(alkylthio or arylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaenes **9a–c**: *General Procedure.* To a suspension of NaH (5 equiv.) in 10 ml of DMF, the thiol (5 equiv.) was added. After gas evolution had decreased to a minimum (10 min), the soln. was cooled to 0°, and 2,5,7,10-tetrabromo-1,6-methano[10]annulene (**8**; 1 equiv.) was added in small portions. The mixture was stirred at 0° for 1 h and then at 25° overnight. Compounds **9a** and **9c** were purified by CC (silica gel, pentane) and **9b** by CC (alumina, pentane).

2,5,7,10-Tetrakis(phenylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**9a**). From **8** (155 mg, 0.34 mmol): 74 mg (38%) of **9a**. Orange red crystals. M.p. 139–141°. UV/VIS (hexane): 264 (4.38), 336 (4.05), 434 (2.95). IR (film): 3186*w*, 3071*m*, 2975*w*, 2296*w*, 1576*w*, 1506*w*, 1299*w*, 1271*m*, 1260*m*, 1043*w*, 1021*m*, 1005*w*, 713*m*, 673*m*, 659*m*, 610*s*, 551*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.21 (*m*, 12 arom. H); 7.12 (*s*, H–C(3), H–C(4), H–C(8), H–C(9)); 7.06 (*m*, 8 arom. H); 0.34 (*s*, 2 H–C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.4 (C(2), C(5), C(7), C(10)); 134.0 (C(12)); 133.7 (C(3), C(4), C(8), C(9)); 129.7, 128.9, 128.8, 126.5, 126.4 (arom. CH); 124.9 (C(1), C(6)); 39.8 (C(11)). EI-MS: 574 (100, M^+), 465 (44, $[M - SPh]^+$), 355 (15, $[M - 2\ SPh]^+$), 277 (32, $[M - Ph - SPh]^+$), 246 (14, $[M - 3\ SPh]^+$). HR-MS: 574.0919 ($C_{35}H_{26}S_4^+$; calc. 574.8544).

2,5,7,10-Tetrakis(isopropylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentane (**9b**). From **8** (227 mg, 0.5 mmol): 110 mg (50%) of **9b**. Yellow oil. UV/VIS (hexane): 262 (3.97), 336 (3.75), 420 (3.65). IR (film): 3028*m*, 2959*m*, 2923*s*, 2862*s*, 2362*w*, 1653*w*, 1460*s*, 1447*s*, 1380*s*, 1363*s*, 1312*w*, 1240*m*, 1218*m*, 1193*m*, 1153*m*, 1111*m*, 1050*s*, 1015*s*, 970*m*, 928*w*, 878*w*, 832*m*, 806*m*, 668*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.30 (*s*, H–C(3), H–C(4), H–C(8), H–C(9)); 3.42 (*sept.*, 4 Me_2CH); 1.28, 1.04 (2*d*, $^3J = 6.6$, 4 Me_2CH); 0.04 (*s*, 2 H–C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.2 (C(2), C(5), C(7), C(10)); 132.5 (C(3), C(4), C(8), C(9)); 125.7 (C(1), C(6)); 41.8 (Me_2CH); 39.5 (C(11)); 23.6, 22.2 (Me_2CH). EI-MS: 438 (100, M^+), 363 (6, $[M - Me_2CHS]^+$), 352 (74, $[M - 2\ Me_2CH]^+$), 309 (52, $[M - 3\ Me_2CH]^+$), 267 (43, $[M - 4\ Me_2CH]^+$), 43 (79). HR-MS: 438.1545 ($C_{23}H_{34}S_4^+$; calc. 438.7856).

*2,5,7,10-Tetrakis[(*tert*-butyl)thio]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene* (**9c**). From **8** (100 mg, 0.22 mmol): 55 mg (50%) of **9c**. Yellow oil. UV/VIS (hexane): 279 (4.20), 333 (3.81), 414 (3.52). IR (film): 3033*w*, 2962*s*, 2921*s*, 2855*s*, 1471*m*, 1454*w*, 1389*w*, 1362*s*, 1216*w*, 1162*s*, 1001*w*, 819*m*, 710*w*, 564*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.48 (*s*, H–C(3), H–C(4), H–C(8), H–C(9)); 1.19 (*s*, *t*-Bu); –0.09 (*s*, 2 H–C(11)). ^{13}C-NMR (75 MHz, $CDCl_3$): 137.6 (C(3), C(4), C(8), C(9)); 134.0 (C(2), C(5), C(7), C(10)); 128.3 (C(1), C(6)); 48.7 (Me_3C); 39.9 (C(11)); 31.4 (Me_3C). EI-MS: 494 (36, M^+), 438 (4, $[M - t\text{-Bu}]^+$), 381 (4, $[M - 2\ t\text{-Bu}]^+$), 325 (22, $[M - 3\ t\text{-Bu}]^+$), 270 (34, $[M - 4\ t\text{-Bu}]^+$), 57 (100, $t\text{-Bu}^+$). This compound was too unstable for further characterization.

2-Bromo-5-(phenylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**10a**). To a soln. of **3a** (426 mg, 1.70 mmol) in 25 ml of CH_2Cl_2 was added NBS (363 mg, 2.04 mmol). The mixture was stirred for 2 h at 25°, then H_2O was added (25 ml). The aq. layer was extracted with CH_2Cl_2, the org. phase dried and evaporated, and the residue purified by CC (silica gel, hexane): **10a** (365 mg, 65%). Bright yellow oil. UV/VIS (hexane): 265 (4.66), 296 (sh, 4.10), 350 (3.884). IR (film): 3042*m*, 2946*m*, 1937*w*, 1856*w*, 1580*s*, 1515*w*, 1477*s*, 1439*s*, 1381*m*, 1305*w*, 1254*m*, 1220*w*, 1189*m*, 1140*m*, 1099*m*, 1085*m*, 956*m*, 909*m*, 891*s*, 807*s*, 739*s*, 706*s*, 689*s*, 647*m*, 630*s*, 612*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.69 (*m*, $^3J = 6.9$, $^4J = 1.2$, H–C(7), H–C(10)); 7.27 (*m*, 9 arom. H); 0.03 (*m*, $^2J = 10$, $^4J = 1.2$, 1 H–C(11)); –0.4 (*d*, $^2J = 10$, 1 H–C(11)). ^{13}C-NMR (63 MHz, $CDCl_3$): 138.2, 132.6 (C(5), C(12)); 131.0, 129.8, 129.4, 128.8, 128.8, 128.8, 128.4, 126.1 (arom. CH); 119.3, 118.7 (C(1), C(6)); 113.1 (C(2)); 34.9 (C(11)). EI-MS: 328 (42, (^{79}Br)M^+), 251 (13, $[M - Ph]^+$), 249 (46, $[M - Br]^+$), 219 (55, $[M - PhS]^+$), 139 (100, $[M - Br - PhS]^+$). HR-MS: 329.6093 ($C_{17}H_{13}BrS^+$; calc. 329.2597).

2-Bromo-5-(isopropylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**10b**). To a soln. of **3b** (120 mg, 0.55 mmol) in 5 ml of CH_2Cl_2 was added NBS (99 mg, 0.55 mmol) at 0°. The mixture was stirred at 0° for 1 h, then H_2O (25 ml) was added. The aq. phase was extracted with CH_2Cl_2 (50 ml), the org. phase dried (Na_2SO_4) and evaporated, and the residue chromatographed (silica gel, hexane): **10b** (97 mg, 60%). Bright yellow oil. UV/VIS (hexane): 263 (4.24), 284 (4.00), 339 (3.49). IR (film): 3040*m*, 2958*s*, 2923*s*, 2861*s*, 1517*m*, 1458*m*, 1445*m*, 1380*m*, 1364*m*, 1254*m*,

1241*m*, 1189*m*, 1154*m*, 1140*m*, 1100*m*, 1050*m*, 1003*m*, 981*m*, 955*m*, 890*s*, 706*s*, 718*m*, 668*m*, 626*m*, 603*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.84 (*m*, H–C(7)); 7.67 (*m*, H–C(10)); 7.29 (*m*, H–C(8), H–C(9)); 7.17 (*dd*, ^3J = 9.9, H–C(3), H–C(4)); 3.65 (*sept.*, ^2J = 6.6, Me_2CH); 1.35 (*d*, ^2J = 6.9, 3 H, Me_2CH); 1.15 (*d*, ^2J = 6.3, 3 H, Me_2CH); –0.05 (*dt*, ^2J = 9.9, 1 H–C(11)); –0.42 (*d*, ^2J = 9.9, 1 H–C(11)). ^{13}C-NMR (63 MHz, $CDCl_3$): 135.0 (C(5)); 131.2, 130.0, 129.6, 129.0, 128.7 (C(3), C(4), C(7), C(8), C(9), C(10)); 120.2, 118.1 (C(1), C(6)); 113.1 (C(2)); 40.9 (Me_2CH); 34.9 (C(11)); 24.3, 22.5 (Me_2CH). EI-MS: 294 (44, (^{79}Br)M^+), 251 (99, $[M - Me_2CH]^+$), 219 (61, $[M - Me_2CHS]^+$), 171 (100, $[M - Br - Me_2CH]^+$). HR-MS: 294.0179 ($C_{14}H_{15}BrS^+$; calc. 295.2425).

2,10-Dibromo-5,7-bis(isopropylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**11**). To a soln. of **5b** (147 mg, 0.51 mmol) in 40 ml CH_2Cl_2 was added NBS (180 mg, 1.01 mmol). The mixture was stirred for 30 min, then H_2O (10 ml) was added. The aq. phase was extracted with CH_2Cl_2 (25 ml), the combined phase dried (Na_2SO_4) and evaporated, and the residue purified by CC (silica gel, hexane): **11** (121 mg, 53%). Dark orange yellow oil. UV/VIS (hexane): 278 (4.14), 320 (3.87), 401 (3.87). IR (film): 3037*w*, 2960*s*, 2922*s*, 2862*m*, 1735*w*, 1719*w*, 1701*w*, 1685*w*, 1654*w*, 1636*w*, 1560*w*, 1546*w*, 1496*w*, 1458*m*, 1448*m*, 1381*m*, 1363*m*, 1240*m*, 1221*m*, 1185*m*, 1153*m*, 1110*w*, 1050*m*, 1007*s*, 947*m*, 927*w*, 878*w*, 816*m*, 793*m*, 761*w*, 689*w*, 668*w*, 635*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.34, 7.21 (*d*, ^3J = 10.5, H–C(3), H–C(4), H–C(8), H–C(9)); 3.44 (*sept.*, ^2J = 6.6, 2 Me_2CH); 1.30 (*d*, ^2J = 6.9, 6 H, Me_2CH); 1.04 (*d*, ^2J = 6.3, 6 H, Me_2CH); 0.15 (*s*, 2 H–C(11)). ^{13}C-NMR (63 MHz, $CDCl_3$): 136.2 (C(5), C(7)); 134.0, 132.6 (C(3), C(4), C(8), C(9)); 127.3 (C(6)); 116.3 (C(1)); 114.5 (C(2), C(10)); 41.6 (Me_2CH); 37.9 (C(11)); 23.7, 22.3, (Me_2CH). EI-MS: 448 (82, (^{79}Br)M^+), 405 (15, $[M - Me_2CH - Me_2CHS]^+$), 283 (45, $[M - 2\ Me_2CH - Br]^+$), 43 (100, Me_2CH). HR-MS: 447.9354 ($C_{17}H_{20}Br_2S_2^+$; calc. 448.285).

3,5,7,9-Tetrabromo-2,10-bis(isopropylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**12**). To a soln. of 503 mg (1.73 mmol) of **5b** in 60 ml of CH_2Cl_2 was added NBS (3 equiv., 924 mg, 5.19 mmol). The mixture was stirred for 2 days at r.t., then H_2O (60 ml) was added. The aq. phase was extracted with CH_2Cl_2 the org. phase dried ($MgSO_4$) and evaporated, and the residue absorbed on *Celite*. Chromatography (silica gel, hexane/AcOEt 100:1) gave **12** (273 mg, 26%). Red orange crystals. M.p. 150–151°. UV/VIS (hexane): 276 (4.01), 315 (3.78), 334 (3.63), 435 (3.37). IR (KBr): 2963*m*, 2920*m*, 2861*w*, 1653*w*, 1560*m*, 1507*m*, 1442*m*, 1382*m*, 1364*m*, 1326*m*, 1258*m*, 1237*m*, 1208*m*, 1170*m*, 1152*w*, 1092*m*, 1045*s*, 1032*s*, 1106*m*, 996*m*, 930*s*, 855*s*, 801*m*, 703*m*, 658*m*, 546*m*, 501*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.55 (*s*, H–C(4), H–C(8)); 3.3 (*sept.*, ^2J = 6.6, 2 Me_2CH); 1.54 (*s*, 2 H–C(11)); 1.23 (*d*, ^2J = 6.6, 6 H, Me_2CH); 0.82 (*d*, ^2J = 6.6, 6 H, Me_2CH). ^{13}C-NMR (63 MHz, $CDCl_3$): 137.3 (C(4), C(8)); 134.8 (C(2), C(10)); 133.5, 126.8, 120.4, 115.4 (C(1), C(3), C(5), C(6), C(7), C(9)); 41.3 (Me_2CH); 36.7 (C(11)); 24.6, 21.8 (Me_2CH). EI-MS: 606 (21, (^{79}Br)M^+), 564 (12, $[M - 2\ Me_2CH]^+$), 520 (19, $[M - 2\ Me_2CH]^+$), 484 (6, $[M - Me_2CHS]^+$), 439 (13, $[M - 2Me_2CH - Br]^+$), 361 (14, $[M - 2\ Me_2CH - Br]^+$), 43 (100, Me_2CH^+). HR-MS: 606.4736 ($C_{17}H_{18}Br_4S_2^+$; calc. 606.0772).

2,4-[(Nitrophenyl)ethynyl]-5-(phenylthio)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**14a**). A soln. of **10a** (242 mg, 0.74 mmol) in Et_3N (10 ml) was degassed, and $[PdCl_2(PPh_3)_2]$ (4 mol-%, 22 mg, 0.03 mmol) and CuI (2 mol-%, 3 mg, 0.015 mmol) were added. To this yellow mixture was added (4-nitrophenyl)acetylene (**13**; 2 equiv., 216 mg, 1.47 mmol) in small portions. The mixture was stirred at 80° for 4 h, then cooled to r.t., and evaporated, and the residue dissolved in CH_2Cl_2, absorbed on *Celite* and chromatographed (silica gel, hexane/AcOEt 95:5): **14a** (163 mg, 56%). Orange yellow crystals. M.p. 129–131°. UV/VIS (hexane): 266 (4.22), 384 (4.12). IR (film): 3043*w*, 2900*w*, 2850*w*, 2200*m*, 1589*s*, 1559*m*, 1512*s*, 1477*s*, 1437*m*, 1340*s*, 1306*s*, 1254*m*, 1188*m*, 1173*m*, 1107*m*, 1022*m*, 996*m*, 847*s*, 825*m*, 818*m*, 742*m*, 715*m*, 688*m*, 634*m*, 502*w*, 473*w*, 427*w*, 417*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.20 (*dt*, ^3J = 9, ^4J = 2.1, 2 H_m to C≡C); 7.77 (*m*, ^3J = 8.7, ^4J = 1.2 Hz) and 7.71 (*m*, ^3J = 8.7, ^4J = 1.2, each 1 H, C(7), H–C(10)); 7.65 (*dt*, ^3J = 8.7, ^4J = 2.1, 2 H_o to C≡C); 7.24 (*m*, 7 arom. H); 7.20 (*dd*, H–C(3), H–C(4)); 0.25 (*d*, 1 H–C(11)); –0.34 (*d*, ^2J = 9.3, 1 H–C(11)). ^{13}C-NMR (63 MHz, $CDCl_3$): 146.8 (C_p to C≡C); 138.0, 135.7 (C(5), C_{ipso} of PhS); 130.1 (C_{ipso} of $NO_2C_6H_4$); 131.9, 131.7, 129.5, 129.2, 129.1, 129.0, 128.8, 128.4, 128.0, 126.5, 123.6 (arom. CH); 121.8 (C(2)); 118.1, 117.3 (C(1), C(6)); 92.8, 91.3 (C≡C); 35.4 (C(11)). EI-MS: 395 (80, M^+), 349 (4, $[M - NO_2]^+$), 317 (79, $[M - Ph]^+$), 286 (100, $[M - PhS]^+$), 271 (15, $[M - PhNO_2]^+$), 239 (92, $[M - PhS - NO_2]^+$). HR-MS: 395.1127 ($C_{25}H_{17}NO_2S^+$; calc. 395.4623).

2-(Isopropylthio)-7-[(4-nitrophenyl)ethynyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**14b**). As described for **14a**, with **7a** (188 mg, 0.74 mmol) (i-Pr)$_2$NH (5 ml), $[PdCl_2(PPh_3)_2]$ (2 mol-%, 6 mg, 0.01 mmol), CuI (2 mol-%, 2 mg, 0.01 mmol), and **13** (1.5 equiv., 93 mg, 0.63 mmol) (at 25° for 1 h and overnight at 80°). CC (silica gel, hexane/AcOEt 100:1): **14b** (87 mg, 57%). Orange crystals. M.p. 138–140°. UV/VIS (hexane): 275 (4.46), 388.0 (4.37). IR (film): 3036*w*, 2960*m*, 2924*m*, 2862*w*, 2363*w*, 2198*s*, 1592*s*, 1515*s*, 1490*w*, 1443*w*, 1403*w*, 1380*w*, 1365*w*, 1340*s*, 1099*m*, 1285*w*, 1253*w*, 1174*w*, 1106*m*, 1051*w*, 853*m*, 781*m*, 764*s*, 807*s*, 749*s*, 690*w*, 610*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.21 (*dt*, ^3J = 9, 2 H_m to C≡C); 7.93 (*d*, ^3J = 8.7, H–C(10)); 7.76 (*d*, ^3J = 8.7, H–C(5)); 7.66 (*dt*, ^3J = 9, 2 H_o to C≡C); 7.51 (*d*, ^3J = 9.6, 1 H); 7.39 (*d*, ^3J = 9.6, 1 H); 7.14 (*d*, ^3J = 9.2, 1 H); 7.05 (*t*, ^3J = 9.2, 1 H); 3.66 (*sept.*, Me_2CH); 1.39 (*d*, ^3J = 6.9, 3 H, Me_2CH); 1.12 (*d*, ^3J = 6.6, 3 H, Me_2CH); –0.10 (*d*, ^2J = 8.4,

1 H–C(11)); –0.19 (*d*, ^2J = 9.6, 1 H–C(11)). ^{13}C-NMR (63 MHz, $CDCl_3$): 146.6 (C_p of $NO_2C_6H_4$); 134.9 (C(2)); 130.2 (C_{ipso} of $NO_2C_6H_4$); 132.5, 131.8, 131.4, 131.1, 128.8, 127.1, 127.0, 123.5 (arom. CH); 120.1, 119.5, 117.9 (C(1), C(6), C(7)); 92.8, 91.0 (C≡C); 41.1 (Me_2CH); 35.4 (C(11)); 24.2, 22.5 (Me_2CH). EI-MS: 361 (51, M^+), 318 (100, $[M - Me_2CH]^+$), 286 (38, $[M - Me_2CHS]^+$), 272 (26, $[M - Me_2CH - NO_2]^+$), 239 (55, $[M - PhNO_2]^+$). HR-MS: 361.1135 ($C_{22}H_{19}NO_2S^+$; calc. 361.4631).

2-(Isopropylthio)-5-[(4-nitrophenyl)ethynyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**14c**). As described for **14a**, with **10b** (86 mg, 0.30 mmol), $(i\text{-Pr})_2NH$ (5 ml), $[PdCl_2(PPh_3)_2]$ (5 mol-%, 11 mg, 0.01 mmol), and CuI (5 mol-%, 3 mg, 0.01 mmol), and **13** (1.1 equiv., 49 mg, 0.33 mmol) (at 25° for 1 h and overnight at 80°). CC (silica gel, hexane/AcOEt 100:1): **14c** (26 mg, 24%). Pale yellow solid. M.p. 143–145°. UV/VIS (hexane): 278 (4.37), 373 (4.27). IR (KBr): 3036*w*, 2925*s*, 2854*m*, 2200*w*, 1772*w*, 1734*m*, 1700*m*, 1695*w*, 1684*w*, 1653*w*, 1591*m*, 1559*w*, 1512*s*, 1457*w*, 1345*s*, 1286*m*, 852*m*, 764*m*, 749*m*, 686*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.23 (*dt*, ^3J = 8.7, ^4J = 2.1, 2 H_m to C≡C); 7.87 (*d*, ^3J = 8.7, H–C(10)); 7.76 (*d*, ^3J = 8.7, H–C(7)); 7.68 (*dt*, ^3J = 8.7, 2 H_o to C≡C); 7.30 (*m*, H–C(3), H–C(4), H–C(9), H–C(8)); 3.68 (*sept.*, Me_2CH); 1.37 (*d*, ^3J = 6.9, 3 H, Me_2CH); 1.15 (*d*, ^3J = 6.9, 3 H, Me_2CH); 0.05 (*d*, ^2J = 10.2, 1 H–C(11)); –0.34 (*d*, ^2J = 9.6, 1 H–C(11)). ^{13}C-NMR (63 MHz, $CDCl_3$): 146.7 (C_o of $NO_2C_6H_4$); 137.8 (C(2)); 130.3 (C_{ipso} of $NO_2C_6H_4$); 131.9, 131.1, 129.5, 129.2, 128.8, 128.1, 128.0, 123.6 (arom. CH); 120.9, 118.9, 116.9 (C(1), C(6), C(5)); 93.1, 91.0 (C≡C); 41.1 (Me_2CH); 35.4 (C(11)); 24.4, 22.6 (Me_2CH). EI-MS: 361 (74, M^+), 318 (100, $[M - Me_2CH]^+$), 286 (79, $[M - Me_2CHS]^+$), 272 (28, $[M - Me_2CH - NO_2]^+$), 239 (55, $[M - PhNO_2]^+$), 43 (37). HR-MS: 361.1135 ($C_{22}H_{19}NO_2S^+$; calc. 361.4631).

2,10-Bis(isopropylthio)-5,7-bis[(4-nitrophenyl)ethynyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**15**). As described for **14a**, with **11** (99 mg, 0.22 mmol), $(i\text{-Pr})_2NH$ (5 ml), $[PdCl_2(PPh_3)_2]$ (2 mol-%, 6 mg, 0.01 mmol), CuI (2 mol-%, 3 mg, 0.01 mmol), and **13** (2.5 equiv., 81 mg, 0.55 mmol) (overnight at 80°). CC (silica gel, hexane): **15** (37 mg, 29%). Dark red crystals. M.p. 164–165°. UV/VIS (hexane): 294 (4.30), 337 (4.14), 464 (4.13). IR (KBr): 2964*m*, 2952*w*, 2931*w*, 2201*m*, 1593*s*, 1559*w*, 1521*s*, 1490*m*, 1441*m*, 1382*m*, 1343*s*, 1281*m*, 1235*m*, 1173*m*, 1154*m*, 1107*m*, 1046*m*, 995*m*, 853*s*, 831*w*, 796*w*, 749*m*, 686*w*, 668*m*, 656*w*, 601*w*, 545*w*, 438*w*, 419*w*, 405*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.24 (*m*, 4 H_m to C≡C); 8.01 (*d*, ^3J = 8.4, 1 H); 7.70 (*m*, 4 H_o to C≡C); 7.44 (*d*, 2 H); 3.56 (*sept.*, 2 Me_2CH); 1.37 (*d*, ^3J = 6.9, 3 H, Me_2CH); 1.10 (*d*, ^3J = 6.3, 3 H, Me_2CH); 0.18 (*s*, 2 H–C(11)). ^{13}C-NMR (63 MHz, $CDCl_3$): 146.7 (C_p of $NO_2C_6H_4$); 139.2 (C(2), C(10)); 130.2 (C_{ipso} of $NO_2C_6H_4$); 135.2, 131.8, 130.6, 123.3 (arom. CH); 125.0 (C(7), C(5)); 122.2, 119.2 (C(1), C(6)); 94.3, 93.9 (C≡C); 42.2 (Me_2CH); 37.7 (C(11)); 23.9, 22.4 (Me_2CH). EI-MS: 580 (59, M^+), 537 (14, $[M - Me_2CH]^+$), 495 (17, $[M - 2\,Me_2CH]^+$), 43 (37). HR-MS: 580.1492 ($C_{33}H_{28}N_2O_4S^+$; calc. 580.7262).

REFERENCES

[1] E. Vogel, *Chimia* **1968,** *22,* 21

[2] F. Effenberger, H. Klenk, *Chem. Ber.* **1976,** *109,* 769.

[3] C. Radke, R. Neidlein, *Chem.-Ztg.* **1984,** *108,* 110; G. Hartz, R. Neidlein, *ibid.* **1984,** *108,* 366; A. Johmann, R. Neidlein, *Monatsh. Chem.* **1991,** *122,* 215; T. Köhler, R. Neidlein, *Arch. Pharm.* **1985,** *318,* 1126.

[4] T. Constantinescu, C. Krieger, H.-P. Deigner, R. Neidlein, *Z. Naturforsch., B* **1990,** *45,* 1582.

[5] E. Vogel, W. A. Böll, *Angew. Chem.* **1964,** *76,* 784; *ibid. Int. Ed.* **1964,** *3,* 642.

[6] S. Ross, M. Finkelstein, R. Peterson, *J. Am. Chem. Soc.* **1958,** *80,* 4327.

[7] U. Kux, Dissertation, Universität Heidelberg, 1993.

[8] T. Nakazawa, N. Hirose, K. Itabashi, *Synthesis* **1989,** 955.

[9] P. Cogolli, F. Maiolo, L. Testaferri, M. Tingoli, M. Tiecco, *J. Org. Chem.* **1979,** *44,* 2642.

[10] L. Testaferri, M. Tiecco, M. Tingoli, D. Chianelli, M. Montanucci, *Synthesis* **1983,** 751.

[11] J. Bradshaw, J. South, R. Hales, *J. Org. Chem.* **1972,** *37,* 2381.

[12] T. Migita, T. Shimizu, Y. Asami, J. Shiobara, Y. Kato, M. Kougi, *Bull. Chem. Soc. Jpn.* **1980,** *53,* 1385.

[13] R. Gleiter, M. Böhm, E. Vogel, *Angew. Chem.* **1982,** *94,* 925; *ibid. Int. Ed.* **1982,** *21,* 922.

[14] W. Klug, Dissertation, Universitat Köln, 1972.

[15] K. Sturm, F. Wudl, J. Lex, *J. Org. Chem.* **1991,** *56,* 957.

[16] R. Neidlein, W. Wirth, A. Gieren, V. Lamm, T. Hübner, *Angew. Chem.* **1985,** *97,* 580; *ibid. Int. Ed.* **1985,** *24,* 587.

[17] B. D'Arcy, W. Kitching, H. Olszowy, P. Wells, *J. Org. Chem.* **1982,** *47,* 5232.