DALTON
FULL PAPER

Trihydrogermyl-substituted thiophenes

Frank Riedmiller and Hubert Schmidbaur *

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received 19th May 2000, Accepted 19th September 2000

Treatment of 2-bromo- or 2,5-dibromo-thiophene with equivalent quantities of n-butyllithium at low temperature, followed by bromogermane, afforded 2-germyl- **2** and 2,5-di(germyl)-thiophene **3** in 44 and 82% yields, respectively. The *in situ* Grignard reaction of 2-bromothiophene with tetra(ethoxy)germane and magnesium gave low yields of 2-[tri(ethoxy)germyl]thiophene **1**. Attempts to convert this product into the trihydride using $LiAlH_4$ yielded only traces of **2**. Bis(2-thienyl)germane **4** is available from 2-lithiothiophene and dibromogermane (molar ratio 2 : 1, 64% yield). The products have been characterized by analytical and spectroscopic methods. The ^{73}Ge NMR spectra show only broad resonances without discernible ^{73}Ge–^{1}H coupling owing to the low symmetry of the substituents. The molecular geometries of **2** and **3** have been calculated using standard *ab initio* quantum chemical methods. The results are similar to those for analogous silylthiophenes reported recently. There is no evidence for significant intramolecular Ge · · · S interactions.

Introduction

Silylated thiophenes are an important class of precursor compounds for the production of poly(thiophene) thin films.[1–5] The products have high processability[6] and long-term stability as electrode materials and in optical display devices.[1a] The silyl substituents exert both an electronic effect and good leaving properties in the photo- and electro-chemical oxidative polymerization.[1] The polymerization can be carried out stereoselectively with *e.g.* trimethylsilyl groups in 2 and 5 positions of the heterocycle.[4]

The corresponding *germylated* thiophenes have been investigated much less, but there are encouraging results for a number of model systems.[1] Organogermylthiophenes were the subject of several early preparative studies,[7–9] but with very few exceptions,[1,9a] only partially or fully alkylated germyl substituents were employed which give rise to significant steric and modified electronic effects. The information on simple fully hydrogenated prototypes is very limited.[1]

We have initiated a systematic study of germylated thiophenes bearing simple H_3Ge substituents in the 2 and 2,5 positions. This work follows our earlier investigations of silylated thiophenes with simple H_3Si substituents.[10] Silylated and germylated arenes[10,11] and pyridines[12,13] were also the subject of preceding experimental and structural work, which opened up new preparative routes and provided basic information about structure and bonding in aryl- and heteroarylsilanes and -germanes. Arylgermanes are important precursors for reductive coupling to give extended germane structures.[14]

The structural chemistry of silylated heterocycles has attracted considerable interest because some spectral data suggested *intra*molecular donor–acceptor interactions between the nitrogen/oxygen/sulfur functions of the ring and the silicon atoms in 2 position. Recent crystal structure studies and quantum chemical calculations have shown, however, that there are no significant intra- or inter-molecular interactions of this kind.[10–13] The molecular geometries are governed mainly by the intrinsic electronic configuration of the heterocycles. The effects are common to *all* substituted species (including *e.g.* the methyl derivatives) and not restricted to *silyl* groups. In the present work these studies were extended to the germyl prototypes.

Results and discussion

Preparations and spectroscopy

There are two fundamental pathways for the germylation of arenes or aromatic heterocycles. Both use halogenated precursor molecules which are either subjected to direct nucleophilic substitution with alkali-metal germyls $M^+ GeH_3^-$ or converted first into lithiated (hetero)cycles which then are subjected to electrophilic substitution employing germyl halides $H_3Ge^+ X^-$. Both reaction schemes were applied very successfully to the preparation of the analogous silyl compounds, where reagents like silylpotassium H_3SiK or bromosilane H_3SiBr are available. The former is obtained by reductive cleavage of the Si–Si bond in disilane, while the latter is generated in the regioselective acid cleavage (HBr) of arylsilanes.[15,16] Trifluoromethanesulfonic acid can be employed instead of HBr.[17]

Many silyl(hetero)arenes can alternatively be prepared in *in situ* Grignard reactions using the corresponding halogeno(hetero)arenes, magnesium and tetra(alkoxy)silanes.[10,12,18]

For germanes the situation is less favourable because digermane Ge_2H_6 as a precursor for $H_3Ge^-K^+$ is not available, and because the dearylation of arylgermanes with HBr is less selective. However, provided that adequate high vacuum facilities for the handling of air-sensitive gases are at hand, bromogermane can be prepared from germane and anhydrous hydrogen bromide with freshly sublimed aluminium tribromide as a catalyst, following a procedure first used by Ebsworth and co-workers.[19] Depending on the molar ratio of the reagents, dibromogermane can also be obtained *via* this route, eqns. (1) and (2). Bromogermane is a colourless, extremely air-sensitive liquid (mp −32 °C, bp 52 °C) which can be stored only at low temperatures without decomposition. Freshly prepared samples are free of redistribution products. Dibromogermane (mp. −15 °C, bp 89 °C) is less susceptible to decomposition.

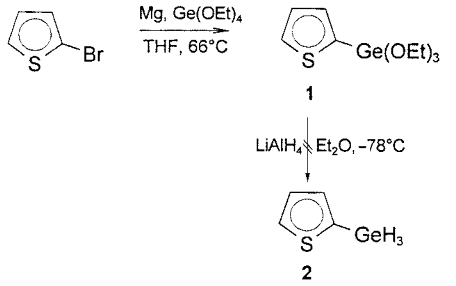
$$GeH_4 + HBr \xrightarrow{[AlBr_3]} H_2 + H_3GeBr \quad (1)$$

$$GeH_4 + 2\,HBr \xrightarrow{[AlBr_3]} 2\,H_2 + H_2GeBr_2 \quad (2)$$

Attempts to prepare 2-germylthiophene *via* the *in situ* Grignard route were not very successful. Treatment of

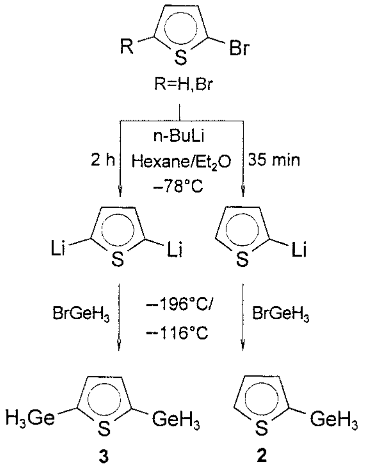
DOI: 10.1039/b004024j

2-bromothiophene with magnesium and tetra(ethoxy)germane in boiling tetrahydrofuran for 24 h gave 2-[tri(ethoxy)germyl]-thiophene **1** in only 33% yield as a light yellow oil. The product was identified by its NMR and mass spectrometric data, which also showed the presence of small amounts of di(ethoxy)-di(2-thienyl)germane. This crude product was treated directly with lithium aluminium hydride in diethyl ether, first at −78 °C and later at 20 °C. After work-up, GC-MS analysis showed that only traces of 2-germylthiophene **2** were formed in this process, eqn. (3). No di(2-thiophenyl)germane was detected.



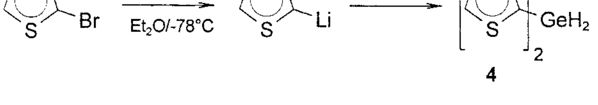
(3)

Much more satisfactory results were obtained *via* the *alternative* route: lithiation of 2-bromothiophene with n-butyllithium at −78 °C in a hexane–diethyl ether mixed solvent (30 min) followed by removal of all solvents in a vacuum at 20 °C gave a colourless residue of LiBr and LiC_4H_4S, which was redissolved/suspended in diethyl ether and treated with equivalent quantities of bromogermane in the temperature range between −196 and −116 °C (45 min) and finally between −78 and 20 °C (35 min). Fractionation of the reaction mixture by trap-to-trap condensation on a vacuum line gave 2-germylthiophene **2** as a colourless liquid in 44% yield (mp −35 °C, bp −20 °C/0.01 Torr). An analogous reaction using 2,5-dibromothiophene and two equivalents of n-butyllithium and bromogermane gave after an optimized reaction time of 2 h at −116 °C colourless 2,5-di(germyl)thiophene **3** in 82% yield (mp. −37 °C, bp 10 °C/0.01 Torr), eqn. (4).



(4)

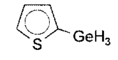
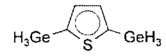
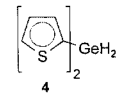
Treatment of 2-lithiothiophene with dibromogermane in the molar ratio 2 : 1 under similar conditions afforded bis(2-thienyl)-germane **4** in 64% yield (colourless liquid, mp 24 °C, bp 0 °C/0.01 Torr), eqn. (5).



(5)

All three germylthiophenes were identified through their NMR, IR and mass spectra (after GLC separation). Elemental analysis data are available for 2-germyl- and 2,5-di(germyl)-thiophene. The ^1H and ^{13}C NMR spectra showed the expected resonance patterns already documented for the analogous silyl compounds.[10–13] In all three cases ^{73}Ge resonances were observed as broad signals without discernible ^{73}Ge–^1H splitting (Table 1). This result is at variance with the findings for related arylgermanes (aryl = phenyl, mesityl, *etc.*) where doublet, triplet and quartet splittings were clearly resolved.[11] This difference may be ascribed to the reduced symmetry of the substituents (thienyl *vs.* phenyl) which leads to large electrical field gradients at the germanium nucleus. The mass spectra of all compounds show the molecular ions with the expected isotope distribution. In the gas phase IR spectra characteristic $GeH_{2/3}$ stretching vibrations are observed. The IR spectra have also been calculated in quantum chemical studies and there is a very satisfactory agreement between experimental and calculated spectra (see below, Experimental section and Fig. 3).

Table 1 ^{73}Ge and ^1H NMR data [δ] and IR bands of *ortho*-germylthiophenes **2**–**4** in C_6D_6 at 21 °C

Compound	$\delta(^{73}Ge)$	$\delta(^1H)$ for GeH functions	$\nu(Ge-H)/cm^{-1}$
 GeH3 S **2**	−214.0	4.20	2093
 H3Ge GeH3 S **3**	−208.0	4.24	2083
 GeH2 S 2 **4**	−124.2	5.21	2091

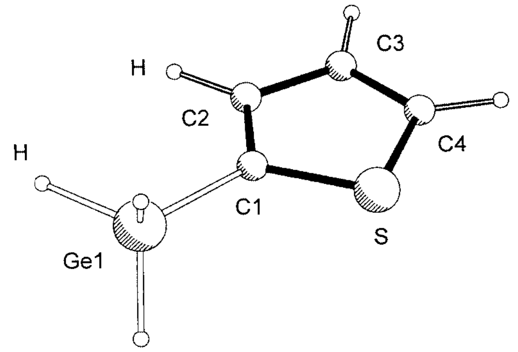


Fig. 1 Molecular structure of 2-germylthiophene **2** as calculated by *ab initio* quantum chemical methods (MP2/6-31G*) with atomic numbering. The ground state conformation has mirror symmetry with the Ge–H and C2–H hydrogen atoms in the *Z* configuration.

In contrast to the experiments with the analogous silylthiophenes and -pyridines,[10,12] all attempts to grow single crystals of compound **3** from the melt by low temperature techniques were unsuccessful. The crystals turned out to be twinned or irregular otherwise and no structure refinement could be carried out. The structures of **2** and **3** were therefore calculated in order to provide preliminary geometrical data.

Quantum chemical studies

Ab initio quantum chemical calculations (MP2/6-31G*) of the molecular structures of compounds **2** and **3** led to the results illustrated in Figs. 1 and 2. The conformation of minimum energy for molecule **2** converged for a model with mirror symmetry (point group C_s) with one hydrogen atom of the germyl group in the *Z* configuration relative to the hydrogen atom of the neighbouring ring carbon atom. However, the corresponding *E* configuration is only 0.53 kcal mol^{-1} higher in energy. With low barriers between these two conformations, the germyl group has free rotation about the Ge–C axis. Molecule **3** has an energy minimum for a model with the symmetry of

Table 2 Selected bond lengths [Å] and angles [°] of compounds **2** and **3** as calculated on the MP2/6-31G* level of theory for the ground state conformations. For atomic numbering see Figs. 1 and 2

	$2\text{-}H_3GeC_4H_3S$ **2** $C_s(Z)$	$2,5\text{-}(H_3Ge)_2C_4H_2S$ **3** $C_{2v}(Z)$
S–C1	1.724	1.722
C1–C2	1.386	1.387
C2–C3	1.416	1.413
C3–C4	1.377	
Ge1–C1	1.926	1.928
Ge1–H	1.552/1.549	1.552/1.549
C1–S–C4	92.82	93.71
S–C1–C2	109.96	109.79
S–C4–C3	111.43	
S–C1–Ge1	124.27	124.31
C2–C1–Ge	125.76	125.90
C1–Ge–H	107.17/111.32	107.22/111.12
H–Ge–H	109.36/108.32	109.46/108.43

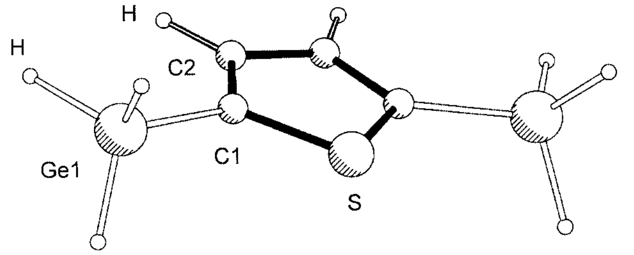


Fig. 2 Calculated molecular structure of 2,5-di(germyl)thiophene **3** with atomic numbering. The ground state conformation (C_{2v} symmetry) is the same as for **2**.

point group C_{2v} and two Ge–H hydrogen atoms again in the Z configuration.

The Ge–H bond lengths show only very minor variations (2 × 1.552 and 1 × 1.549 Å for each GeH_3 group). The germanium atoms have tetrahedral co-ordination with only small deviations of the H–Ge–H and H–Ge–C angles from the ideal values. Neither the overall geometry of the molecules nor natural bond order (NBO) analysis shows any significant direct Ge · · · S donor/acceptor interactions ("through space"). The angles C–C–Ge and S–C–Ge are very similar and show no bending of the germanium atoms towards the sulfur atom (Table 2). [Note that DFT calculations often fail to reproduce long-range interactions. Therefore this alternative was not probed.]

Vibrational frequency calculations for molecule **3** at the HF level led to a pattern which to a first approximation (after applying the usual scale factor of 0.9 to the frequencies) is in good agreement with the experimental findings (Fig. 3).

Conclusion

Fully hydrogenated germylthiophenes are readily prepared from 2-lithio- or 2,5-dilithio-thiophene and bromogermane as stable, highly volatile liquids. Their spectroscopic properties and calculated electronic and molecular structures suggest simple monomeric molecules with no unusual intra- or intermolecular Ge · · · S interactions. The basic characteristics resemble those of the corresponding trihydrosilylated thiophenes. Both series of compounds qualify as precursors for the generation of polythiophene thin films.

Experimental

General methods

All experiments were routinely carried out in an atmosphere of dry nitrogen using Schlenk techniques or in a high vacuum line.

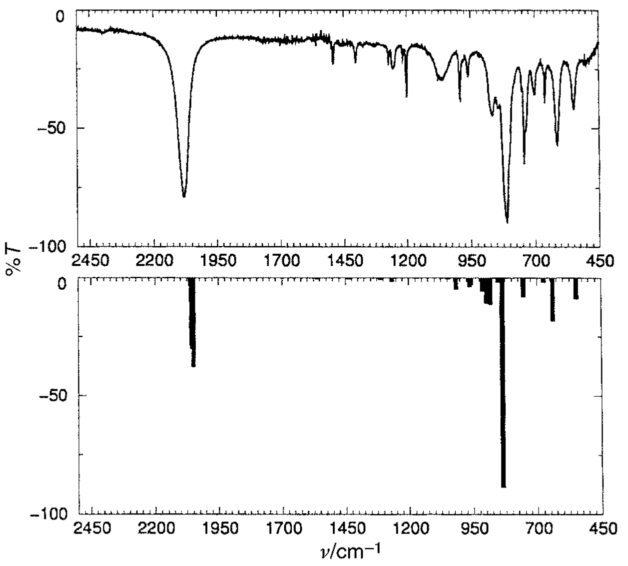


Fig. 3 Experimental (gas phase) (above) and calculated (HF level of theory) (below) IR spectrum of 2,5-di(germyl)thiophene **3** (2450–450 cm^{-1} region) [ν(GeH) 2083; δ(GeH) 887 cm^{-1}].

Otherwise standard equipment was used throughout. Glassware was oven-dried and filled with nitrogen. Solvents were appropriately dried, distilled and saturated with nitrogen. Bromo- and dibromo-germane were prepared following literature procedures.[19] All other reagents were commercially available. NMR spectra (JEOL-JNM-LA 400) were obtained (at 21 °C) from samples dissolved in C_6D_6 sealed into glass tubes, mass spectra with an analytical GLC-MS Hewlett Packard 5890 Series II/HP MS 5971 A system (EI, 70 eV; column HP1, crosslinked methylsilicon gum 12 m × 0.2 mm, thickness of film 0.33 µm) and IR spectra with a Midac FT-IR Prospect system. Microanalyses were performed in an in-house service laboratory.

Preparations

2-[Tri(ethoxy)germyl]thiophene 1. Magnesium turnings (0.5 g, 0.020 mol) suspended in tetrahydrofuran (10 mL) were activated with a few drops of dibromoethane. As a reaction became discernible upon warming, 3.4 g of tetra(ethoxy)germane dissolved in 20 mL of thf were added, followed by 10% of a solution of bromothiophene (1.7 g, 0.010 mol) in thf (10 mL). As the exothermic reaction proceeded the rest of the solution was slowly added (1 h) to maintain boiling of the reaction mixture. Boiling was continued under reflux for *ca.* 90 min until no 2-bromothiophene remained (GLC). The thf solvent was removed in a vacuum and the residue extracted with 15 mL of pentane. The extract was filtered and the solvent removed in a vacuum to leave a yellow oil which consisted of 94% 2-[tri(ethoxy)germyl]thiophene **1** and 6% di(ethoxy)di(2-thienyl)germane (by GLC-MS) (yield 0.9 g, 33%). $(EtO)_3GeC_4H_3S$: ^1H NMR δ 1.46 (t, $^3J_{HH} = 7$, 9 H, Me), 3.55 (q, $^3J_{HH} = 7$ Hz, 6 H, OCH_2), 6.96, 7.08, 7.37 (m for H^4, H^3, H^5, respectively); MS (EI, 70 eV) *m/z* 292 [M^+], 247 [$M^+ - EtO$, 100%], 202 [$M^+ - 2EtO$], 157 [$M^+ - 3EtO$], 113 [$GeOEt^+$] and 83 [$C_4H_3S^+$]. $(EtO)_2Ge(C_4H_3S)_2$: MS (EI, 70 eV) *m/z* 327 [M^+], 282 [$M^+ - EtO$], 246 [$M^+ - C_4H_3S$], 237 [$M^+ - 2EtO$], 201 [$M^+ - C_4H_3S - EtO$], 157 [$M^+ - C_4H_3S - 2EtO$] and 82 [C_4H_3S].

2-Germylthiophene 2. *Method (a).* The product of the above reaction [2-tri(ethoxy)germylthiophene and di(ethoxy)di(2-thienyl)germane (94:6), 0.9 g] was dissolved in diethyl ether (25 mL) and dropped slowly into a suspension of lithium aluminium hydride (0.4 g, 0.016 mol) in diethyl ether (25 mL) at −78 °C. After 2 h the reaction mixture was allowed to warm to

20 °C and the solvent removed in a vacuum. Extraction of the residue with pentane and GC-MS analysis showed that only traces of 2-germylthiophene **2** is produced [MS (EI, 70 eV): *m*/*z* = 160, 159, 158 for M^+; 85 for H_3Ge^+, *etc*.]. No di(2-thienyl)germane was detected. For NMR data see the following preparation.

Method (b). To a solution of n-butyllithium (13.7 mL, 1.6 M, 0.022 mol) in 50 mL of hexane–diethyl ether at −78 °C a solution of 2-bromothiophene (3.6 g, 0.022 mol) in 20 ml of diethyl ether was added dropwise with stirring. After 35 min at −78 °C the reaction mixture was allowed to warm to room temperature. The formation of a white precipitate was observed. All volatile components (solvents and bromobutane) were removed in a vacuum. The residue was dissolved in 20 mL of diethyl ether, the flask connected to a STOCK vacuum line and evacuated while cooling the solution to −196 °C. 3.4 g of bromogermane (0.022 mol) followed by 10 mL of diethyl ether were condensed into the flask at −196 °C, and the reaction mixture was allowed to warm to −116 °C with stirring. After stirring for 45 min at −116 °C and for 15 min at −78 °C the formation of a white solid was observed. Subsequently, the mixture was allowed to warm to room temperature under nitrogen and the gaseous components were removed in a vacuum. Product **2** was isolated by fractional trap to trap distillation (−11, −20, −196 °C) as a colourless liquid collected at −20 °C (mp −35 °C, yield 1.5 g, 44%). ^{1}H NMR: δ 4.20 (s, 3 H, GeH_3), 6.86 (dd, $^3J_{HH} = 5/3.5$, 1 H, H^4), 7.01 (d, $^3J_{HH} = 3.5$, 1 H, H^3) and 7.14 (d, $^3J_{HH} = 5$ Hz, 1 H, H^5). ^{13}C NMR: δ 126.2 (dqd, $^2J_{CH} = 10$, $^2J_{CGeH} = 7.5$, $^3J_{CH} = 5$, C^2 *ipso*), 128.4 (ddd, $^1J_{CH} = 167$, $^2J_{CH} = 10$, 6 Hz, C^4), 131.4 (ddd, $^1J_{CH} = 184$, $^2J_{CH} = 10$, $^3J_{CH} = 5$, C^5) and 136.7 (ddq, $^1J_{CH} = 167$, $^2J_{CH} = 6$, $^3J_{CGeH} = 3$ Hz, C^3). ^{73}Ge NMR: δ −214.0 (br s, GeH_3). MS (EI, 70 eV): *m*/*z* = 160 [$M^+ + 1$], 159 [M^+, 100%], 158 [$M^+ - H$], 85 [$M^+ - GeH_3$], 74 [GeH_2], 131, 119, 107, 95 and 54. IR (gas): 3084 [m, $\nu(CH)_{aryl}$], 2093, 2063 [s, ν(GeH)], 1652/1467 /1260 [s, ν(C=C)], 890, 835 cm^{-1} [s, δ(GeH)]. Found: C, 30.0; H, 3.6. Calc. C, 30.3; H, 3.8%.

2,5-Di(germyl)thiophene 3. A procedure analogous to that described for 2-lithiothiophene above was used, with 1 equivalent of 2,5-dibromothiophene (1.7 g, 0.007 mol) and 2 equivalents of n-butyllithium (8.7 mL, 1.6 M, 0.014 mol). The reaction time was optimized to 2 h (determined by quenching of small amounts with chlorotrimethylsilane and GC-MS analysis). The cooled ether suspension (−78 °C) of the 2,5-dilithiothiophene was added dropwise to a solution of bromogermane (2.2 g, 0.014 mol) in 50 mL of diethyl ether at −116 °C with stirring. The product **3** was separated by fractional trap to trap distillation (10, −196 °C) and collected at −196 °C as a colourless, air-sensitive liquid (mp −37 °C, yield 1.4 g, 82%). ^{1}H NMR: δ 4.24 (s, 6 H, GeH_3) and 7.07 (s, 2 H, $H^{3,4}$). ^{13}C NMR: δ 133.1 (dqd, $^2J_{CH} = 10$, $^2J_{CGeH} = 7.5$, $^3J_{CH} = 5$ Hz, $C^{2,5}$) and 138.0 (ddq, $^1J_{CH} = 167$, $^2J_{CH} = 6$, $^3J_{CGeH} = 3$ Hz, $C^{3,4}$). ^{73}Ge NMR: δ −208.0 (br s, GeH_3). MS (EI, 70 eV): *m*/*z* 236 [$M^+ + 2$], 234 [M^+], 159 [$M^+ - GeH_3$], 157 [$M^+ - GeH_2$, 100%], 85 [$M^+ - 2GeH_3$], 74 [GeH_2^+], 201, 178, 148, 131, 99 and 53. IR (gas): 3064 [m, $\nu(CH)_{aryl}$], 2083 [s, ν(GeH)], 1493/1404/1257 [s, ν(C=C)], 887, 816 cm^{-1} [s, δ(GeH)]. Found: C, 20.1; H, 3.3; Calc. C, 20.6; H, 3.4%.

Bis(2-thienyl)germane 4. A procedure analogous to that described for 2-germylthiophene **2** was used, with 2 equivalents of 2-bromothiophene (3.0 g, 0.018 mol) and n-butyllithium (11.5 mL, 1.6 M, 0.018 mol) and 1 equivalent of dibromogermane (2.2 g, 0.009 mol) in 50 mL of diethyl ether at −100 °C. The product **4** was separated by fractional trap to trap distillation (0, −10, −196 °C) and collected at 0 °C as a colourless, air-sensitive oil (mp 24 °C, yield 1.4 g, 64%). ^{1}H NMR: δ 5.21 (s, 2 H, GeH_2), 6.85 (dd, $^3J_{HH} = 5/3.5$, 2 H, H^4), 7.11 (d, $^3J_{HH} = 3.5$, 2 H, H^3) and 7.14 (d, $^3J_{HH} = 5$ Hz, 2 H, H^5). ^{13}C-{^{1}H} NMR: δ 126.6 (C^2 *ipso*), 127.8 (C^4), 130.7 (C^5) and 136.7 (C^3). ^{73}Ge NMR: δ −124.2 (br s, GeH_2). MS (EI, 70 eV): *m*/*z* 242 [$M^+ + 1$], 241 [M^+], 166 [$M^+ - GeH_2$], 157 [$M^+ - C_4H_3S$, 100%], 82 [$M^+ - GeH_2 - C_4H_3S$], 74 [GeH_2^+], 131, 107, 97 and 52. IR (gas): 3080 [m, $\nu(CH)_{aryl}$], 2091 [s, ν(GeH)] and 879 cm^{-1} [s, δ(GeH)].

Ab initio calculations

Ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 program.[20] Geometry optimizations (SCF and MP2 level of theory) and vibrational frequency calculations (SCF/6-31G*) were performed from analytical first and second derivatives. Calculations were undertaken at the SCF level using the standard 3-21G*[21,22] and 6-31G*[23–25] basis sets, the larger basis sets being used for calculations at the MP2 level of theory. Further geometry optimizations have been carried out at the MP2/6-31G* (FC) level of theory (Frozen Core configurations for heavy atoms). NBO calculations were undertaken with the NBO 3.0 facilities built into GAUSSIAN 94.[26,27]

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie. The authors are grateful to Dr N. W. Mitzel and M. Busold for help with the quantum chemical calculations.

References

1 (*a*) S. K. Ritter and R. E. Noftle, *Chem. Mater.*, 1992, **4**, 872; (*b*) S. K. Ritter and R. E. Noftle, *Inorg. Chim. Acta*, 1999, **287**, 232 and references therein.

2 C. Visy, J. Kukkari and J. Kankare, *J. Electroanal. Chem. Interfacial Electrochem.*, 1996, **401**, 119.

3 E. M. Genies and F. El Omar, *Electrochim. Acta*, 1983, **28**, 547.

4 M. Lemaire, W. Buchner, R. Garreau, H. A. Hoa, A. Guy and J. Roncali, *J. Electroanal. Chem. Interfacial Electrochem.*, 1990, **281**, 293; J. Roncali, A. Guy, M. Lemaire, A. Garreau and H. A. Hoa, *J. Electroanal. Chem. Interfacial Electrochem.*, 1991, **312**, 277.

5 J.-L. Sauvajol, C. Chorro, J.-P. Lere-Porte, R. J. P. Corriu, J. J. E. Moreau, Ph. Thepot and M. Wong Chi Man, *Synth. Met.*, 1994, **62**, 233; J.-P. Lere-Porte, J. J. E. Moreau and J.-L. Suavajol, *J. Organomet. Chem.*, 1996, **521**, 11.

6 S. Hotta, *Synth. Met.*, 1991, **22**, 103.

7 J. Barrau, G. Rima, A. Akkari and J. Satge, *Inorg. Chim. Acta*, 1997, **260**, 11.

8 N. Kakimoto, K. Sato, T. Takada and M. Akiba, *Heterocycles*, 1989, **29**, 2115.

9 (*a*) E. Lukevits, R. Y. Strukovich and O. A. Pudova, *Zh. Obshch. Khim.*, 1988, **58**, 815; (*b*) E. Lukevits, O. A. Pudova, Y. Popelis and N. P. Erchak, *Zh. Obshch. Khim.*, 1981, **51**, 115; (*c*) E. Lepins, I. Zicmane, L. M. Ignatovich and E. Lukevits, *J. Organomet. Chem.*, 1990, **389**, 23; (*d*) I. Mazeika, S. Grinberga, M. Gavars, A. P. Gaukhman, N. P. Erchak and E. Lukevits, *Org. Mass Spectrom.*, 1993, **28**, 1309.

10 F. Riedmiller, A. Jockisch and H. Schmidbaur, *Organometallics*, 1999, **18**, 2760.

11 F. Riedmiller, G. L. Wegner, A. Jockisch and H. Schmidbaur, *Organometallics*, 1999, **18**, 4317.

12 F. Riedmiller, A. Jockisch and H. Schmidbaur, *Organometallics*, 1998, **17**, 4444.

13 F. Riedmiller, A. Jockisch and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1999, **54**, 13.

14 S. M. Katz, J. A. Reichl and D. H. Berry, *J. Am. Chem. Soc.*, 1998, **120**, 9844 and references therein.

15 F. Feher, P. Plichta and R. Guillery, *Tetrahedron Lett.*, 1970, **51**, 4443.

16 L. G. L. Ward, *Inorg. Synth.*, 1968, **11**, 159.

17 A. R. Bassindale and T. Stout, *J. Organomet. Chem.*, 1984, **271**, C1; W. Uhlig and C. Tretner, *J. Organomet. Chem.*, 1994, **467**, 31; W. Uhlig, *Chem. Ber.*, 1996, **129**, 733.

18 H. G. Woo, J. F. Walzer and T. D. Tilley, *Macromolecules*, 1991, **24**, 6863; K. J. Shea and D. A. Loy, *Chem. Mater.*, 1989, **1**, 572; D. R. Anderson and J. M. Holovka, *J. Chem. Soc.*, 1965, 2269.

19 J. E. Bentham, S. Cradock and E. A. V. Ebsworth, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 1077.

20 Calculations were performed using standard methods implemented in GAUSSIAN 98: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

21 W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.*, 1982, **104**, 5039.

22 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

23 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

24 M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163.

25 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.

26 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.

27 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735.