# 1,3,4,6,7,9-Hexamethylbenzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene: a twisted heteroarene†

**Yao-Ting Wu,*[a] Chia-Cheng Tai,[a] Wei-Chih Lin[a] and Kim K. Baldridge*[b]**

***Received 6th February 2009, Accepted 7th April 2009***
***First published as an Advance Article on the web 26th May 2009***
**DOI: 10.1039/b902517k**

1,3,4,6,7,9-Hexamethylbenzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene (**C**-Me) was prepared by palladium-catalyzed methylations of the corresponding hexabromide **C**-Br. The twisted structure of **C**-Me has been confirmed by X-ray crystal analysis. The physical properties of twisted **C**-Me and planar benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene (**C**-H) were studied and compared. Crystal structures are compared to computational structures determined using density functional theory, with both the M06-2X and B3PW91 functionals.

## Introduction

Idealized models for aromatic compounds presume planarity; however, even in simple PAH's the hydrogen atoms would sit at their vdW distances if no molecular distortion were allowed.[1] Bay regions in phenanthrene (**A**-H) represent one simple context where non-ideality is confronted.[2,3] Replacement of the bay hydrogens by any other substituents, such as F, Cl, $CH_3$ or $CF_3$, leads to out-of-plane distortions, ideally along a $C_2$ symmetry path.[4] A high symmetry analog of **A** is triphenylene (**B**-H), idealized $D_{3h}$ in its planar form, but suffering three bay region clashes.[5] Such high symmetry PAHs present a stereochemical issue when forced to distort from planarity in that the fundamental out-of-plane bay-region distortion considered as elementary in **A** can manifest in **B** a $D_3$ state in which each bay-region distortion is of the same helical pitch, or a $C_2$ state if one bay-region distortion adopts an opposite pitch. Crystallographic studies on bay-region substituted **B** reveal twisted structure with a preponderance for $C_2$[6–11] or $D_3$[12] symmetry (Chart 1).

Another aspect of the idealized model of **A** and **B** stems from Clar representation that aromatic sextets are embodied in the flanking or radial rings, respectively.[13] This model raises the question of whether changes in the character of the flanking rings would lead to a different stereochemical outcome in the overcrowded derivatives.[14] Thiophene, a heterocyclic analog of benzene, alters two aspects of the PAH model so far discussed: a) the geometry of the ideal bay region and b) the nature of is aromatic sextet. Whereas derivatives of **B** have been well investigated, trithiophenes **C** have not. Given the importance of thiophene as an element in photoactive and electroactive materials, a comparative study of bay-region substituted analogous is warranted.

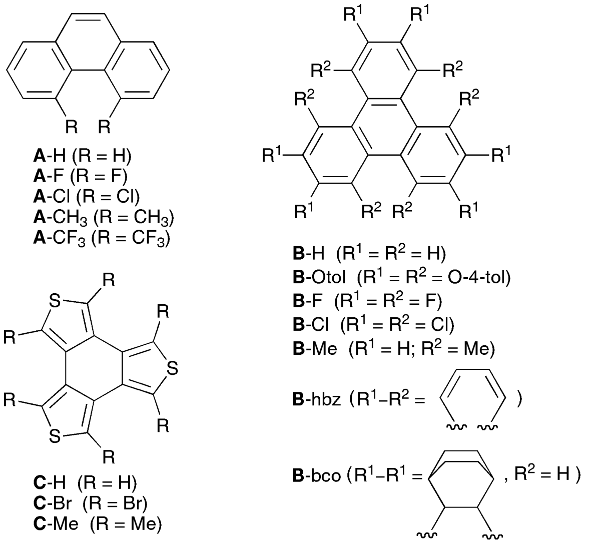


**Chart 1** Examples of overcrowded aromatic compounds.

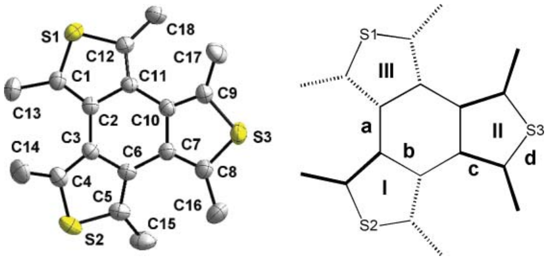
Replacement of three benzene rings with three five-membered heterocycles opens up the bay region through larger angles. Moreover, due to the natural degree of bond localization in thiophene, derivatives of **C** could be viewed geometrically as radialenes. For example benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene, the parent **C**-H, has been characterized as a planar [6]radialene,[15–17] in contrast to other [6]radialenes,[18,19] such as 7,8,9,10,11,12-hexamethyl[6]radialene and its ethyl cognate, which adopt chair conformations. Although derivatives of **B** and **C** can be regarded as triarenocyclohexatrienes, the **B** family does not resemble radialenes from the bond length equality in the *exo* rings, due presumably to the delocalization of the π electrons.[18] Derivatives of **C** containing three thiophenyl subunits, and thiophene-based π-conjugated oligomers potentially have the properties to be organic semiconductors[20] effective as transistors,[21] light-emitting diodes,[22] and photovoltaic cells.[23] Inducing twisted character into derivatives of **C** would lead to differing electronic properties. Herein, we prepared molecules **C**-H and **C**-Me, and compare their structures and physical properties, together with computational predictions.

---

[a] *Department of Chemistry, National Cheng Kung University, No.1 Ta-Hsueh Road, 70101, Tainan, Taiwan. E-mail: ytwuchem@mail.ncku.edu.tw*
[b] *Institute of Organic Chemistry, University of Zurich, Winterthurer-strasse 190, CH-8057, Zurich, Switzerland. E-mail: kimb@oci.unizh.ch*

† Electronic supplementary information (ESI) available: The NMR spectra of **C**-Me and all computational data. CCDC reference numbers 715338 and 715339. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b902517k

**Table 1** The twisted angles and selected bond lengths of **C**-Me



Twisted angles:

| | Dihedral angle (°) | | | "Distortion degree" (°) | |
|---|---|---|---|---|---|
| | Exp. (295 K) | Exp. (100 K) | Calc.[a] | Exp. (295 K) | Exp. (100 K) |
| Planes **I** and **II** | 31.6 | 31.8 | 30.0 [35.0] | 23.7 | 24.0 |
| Planes **II** and **III** | 28.0 | 28.2 | 26.5 [27.8] | 36.5 | 37.5 |
| Planes **III** and **I** | 31.6 | 31.7 | 30.0 [34.7] | 23.0 | 22.8 |

Selected bond lengths and the non-bonded contact distances:[b]

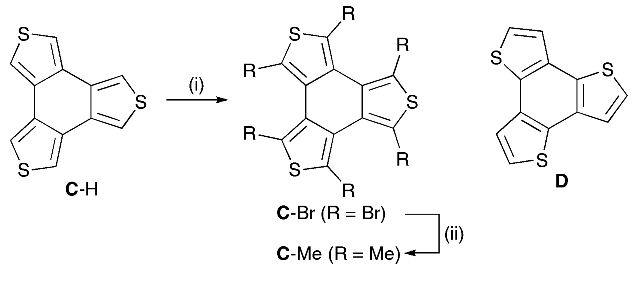
| | C2-C3 | C6-C7 | C10-C11 | C13:C14 | C15:C16 | C17:C18 |
|---|---|---|---|---|---|---|
| 295 K | 1.476 | 1.481 | 1.465 | 3.108 | 3.153 | 3.144 |
| 100 K | 1.485 | 1.479 | 1.478 | 3.114 | 3.154 | 3.158 |
| Calc.[a] | 1.4686 [1.4653] | 1.4686 [1.4653] | 1.4609 [1.4578] | 3.055 [3.1058] | 3.055 [3.1058] | 3.071 [3.1227] |

[a] M06–2X/DZ(2d,p) [B3PW91/DZ(2d,p)] values for $C_2$ structure.

[b] Units in Å.

## Results and discussions

Benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene (**C**-H) is easily accessed by Hart's[15] and Weiss'[17] procedures. Treatment of a solution of compound **C**-H in DMF with an excess NBS at ambient temperature, hexabromide **C**-Br was obtained in 50% yield (Scheme 1).[24] The low solubility of **C**-Br in normal organic solvents limited our studies of its structure and physical properties. Therefore, hexamethyl substituted **C**-Me with good solubility is the next choice. The palladium-catalyzed methylations of **C**-Br afforded the desired molecule **C**-Me in 73% yield.



**Scheme 1** Synthesis of the twisted molecule **C**-Me. (i) 8 equiv of NBS, DMF, r.t., 2 d. (ii) cat. Pd($PPh_3$)$_4$, $AlMe_3$, THF, 80 °C, 2 d.

Compounds **C**-H[16,17] and **D**[25] have been determined to have essentially planar structures. Computational analysis also predicts planar structures for these two compounds. An additional six methyl groups in **C**-Me should lead this molecule to be twisted rather than planar due to steric congestion of the adjacent methyl groups. X-Ray quality crystals of **C**-Me were grown from $CH_2Cl_2$/MeOH.[26] The diffraction data were collected at two different temperatures (295 and 100 K), but they did not display significant differences.[27] This compound adopts a conformation with $C_1$ (= approximate $C_2$) symmetry with obvious deviation from planarity (Table 1 and Fig. 1).[28]

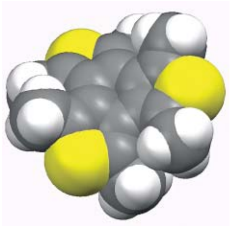


**Fig. 1** The spacefill mode of molecule **C**-Me.

Methyl groups in two thiophene subunits, *i.e.* ring **II** and **III**, present a *"syn"* relationship, and these two thiophene rings are nearly planar. However, ring **I**, where the two methyl substituents adopt an *"anti"* manner, is twisted with a torsion angle 13° (C's C4-C3-C6-C5). The deformation of ring **I** raises mainly from the sterically congested environment.[29] This nonplanarity can be slightly stabilized by an intermolecular S-π interaction. The central six-membered ring of this molecule reveals an unobvious boat conformation, with torsion angles of 17.0, 32.3, −19.5, −8.7, 24.2, and −11.1°. The lengths of $C_{Ar}$–$CH_3$ bonds in **C**-Me are all very similar and are in the range of 1.500 ± 0.003 Å, with mean 1.500 Å. The overcrowded nature of molecule **C**-Me is also evident from the non-bonded contact distances between adjacent methyl substituents. The distance of one non-bonded contact (C13:C14) is shorter than the other two (C15:C16 and C17:C18) and the average of these three distances is 3.135 Å, which is smaller than the sum of the van der Waals radii of two carbons (3.42 Å).[30]

To quantify the deformation, we specify S2, C3 and C6 to define the plane of **I**. The dihedral angles between any two planes are shown in Table 1; the average value is 30.4°. Additionally, due to the nonplanarity of ring **I**, a "distortion degree" between any two rings can be analyzed by their torsion angle. For example, the distortion degree for **I** and **II** involves carbons C5-C6-C7-C8. The distortion degree between plane **II** and **III** is obviously larger than the other two corresponding angles (36.5 vs. 23.7 and 23.0°). Moreover, the largest end-to-end twist (32°) in compound **C**-Me arises from the central "cyclohexane" core and ring **I**, with the contributions of 25° and 7°,[31] respectively. Based on three different definitions, *i.e.* the dihedral angle between two adjacent thiophene planes, the distortion degree and the largest end-to-end twist, the twist angle of this molecule is calculated to be *ca.* 30° away from planarity.

Analysis of the structures of compounds **C**-H, **C**-Me and **D** reveal interesting differences (Table 2). Compounds **C**-H and **C**-Me exhibit radialene-like character, as the bonds in the central six-membered ring are long compared to 'aromatic' C-C bonds in benzene, while lengths of bonds exocyclic to the six-membered ring are more in the range for carbon-carbon double bonds.[16] The twisted nature of **C**-Me manifests in slightly longer bonds **a** and **d** than in planar **C**-H, or even **C**-H in the complex (**C**-H)$_2$(TCNQF$_4$).[32] The bond alternation (ΔL) of the central six-membered ring in **C**-H (1.8–2.7 pm) and **C**-Me (2.3 pm) are also very similar. While compound **C**-H and **C**-Me look essentially like 3 independent thiophenes, compound **D** shows a centralized benzene-like aromatic ring, with isolated double/single bonds in the thiophene rings. Additionally, computation shows compound **D** to be more stable than **C**-H by 9.2 kcal/mol.

To further examine the aromatic character in these two molecules, nucleus-independent chemical shift (NICS) measures[33] were considered for **C**-Me-$C_2$, **C**-H-$D_{3h}$, and **D**-$D_{3h}$, with reference to benzene-$D_{3h}$. Values of NICS(1.5) for the four compounds reveal values of −1.6, −1.6, −6.9, and −7.2, respectively.[34,35] Based on these single points of reference, it would appear that both **C**-H and **C**-Me exhibit a very small chemical shift effect, as compared to benzene, and that **D** would have a chemical shift effect comparable to that in benzene. From the geometric analysis, this analysis would align, particularly for compound **D**. Of course, a much better analysis for this assessment would be a full 3-D plot of the chemical shift field; however, profiles along the central axis perpendicular to the molecular plane suffice (Fig. 2). In particular, the generally accepted NICS(XX-in-plane), NICS(ZZ) and NICS(Iso) curves are depicted. By symmetry, the π part of the NICS(ZZ) term must vanish in the plane. In contrast, the σ component is neglected at distances around 1.0–1.5 Å above the plane,[36] thus the choice to use these as classical measures of NICS for assessing "aromatic" character.

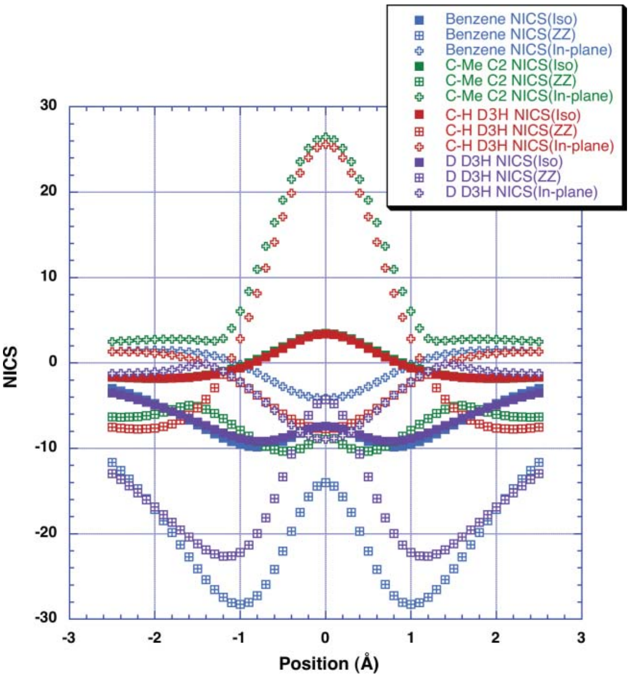


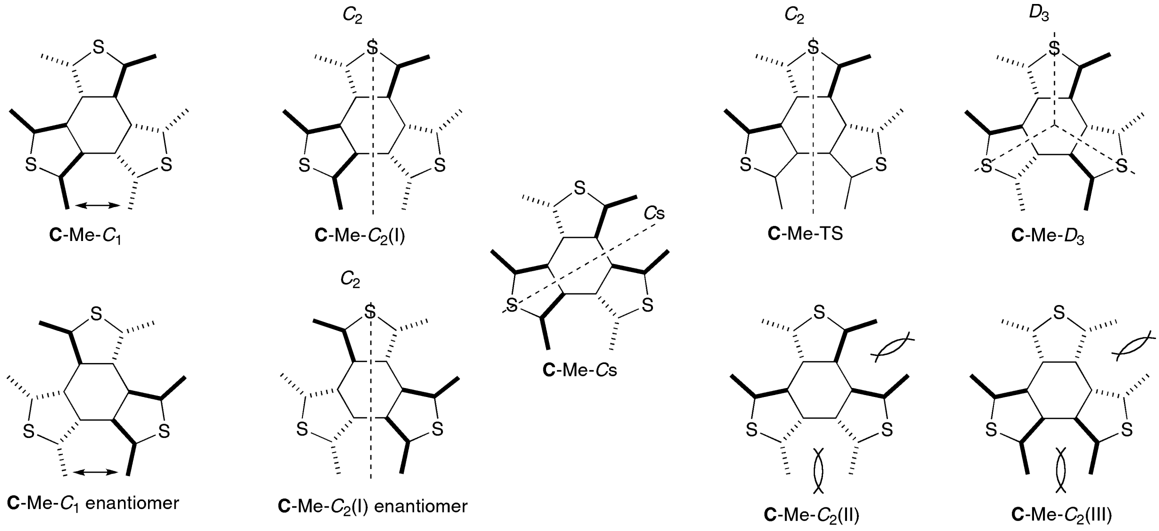
**Fig. 2** NICS analysis for benzene, compounds **C**-H, **C**-Me, and **D**.

Considering aromatic to mean "benzene-like", the comparison between **C**-Me-$C_2$ and **C**-$D_{3h}$ NICS(Iso) curves betray a qualitative difference (*i.e.*, not like benzene),[37] whereas the curve of **D**-$D_{3h}$ betrays a very similar behavior to benzene. The differences can be seen to come from the fact that the NICS(In-plane) contribution dominates the form of the profile for compounds **C**-H and **C**-Me, whereas the NICS(ZZ) component dominates for compounds **D** and benzene. Analysis of the composite (in-plane) and (ZZ) profiles reveal a stronger σ-paramagnetic ring current effect and a weaker π-paramagnetic ring current effect (by NICS(ZZ)) in compounds **C**-H and **C**-Me compared to benzene.

**Table 2** X-Ray and computational comparison of bond lengths in **B**-F, **B**-Me, **C**-H, **C**-Me, and **D**

| Average bond lengths (Å) | | **a** | **b** | **c** | **d** | ΔL[e] |
|---|---|---|---|---|---|---|
| **C**-Me | Exp. (295 K) | 1.474 | 1.451 | 1.370 | 1.722 | 0.023 |
| | Exp. (100 K) | 1.481 | 1.464 | 1.384 | 1.738 | 0.017 |
| | Calc.[a] | 1.469 [1.463] | 1.451 [1.454] | 1.375 [1.382] | 1.721 [1.722] | 0.018 [0.009] |
| **C**-H | Exp.[b] | 1.463 | 1.439 | 1.371 | | 0.018 |
| | Exp.[c] | 1.460 | 1.442 | 1.375 | 1.709 | 0.024 |
| | Calc.[a] | 1.459 [1.454] | 1.439 [1.440] | 1.372 [1.377] | 1.707 [1.708] | 0.020 [0.01] |
| **C**-H complex[d] | Exp.[d] | 1.454 | 1.427 | 1.369 | 1.707 | 0.027 |
| **D** | Calc.[a] | 1.420 | 1.399 | | | 0.021 |
| **B**-F | Calc.[a] | 1.466 | 1.419 | | | 0.047 |
| **B**-Me | Calc.[a] | 1.477 | 1.423 | | | 0.054 |

[a] M06-2X/DZ(2d,p) [B3PW91/DZ(2d,p)] values. [b] Ref. 16. [c] Ref. 17. [d] **C**-H complex: (**C**-H)$_2$(TCNQF$_4$), ref. 32 [e] The bond alternation in bonds **a** and **b**.



**Racemerization process:** between **C**-Me-$C_1$ and its enantiomer

**C**-Me-$C_1$ ⟷ **C**-Me-$C_2$(I) ⟷ **C**-Me-*Cs* ⟷ **C**-Me-$C_2$(I) enantiomer ⟷ **C**-Me-$C_1$ enantiomer

**Interconversion process:** between **C**-Me-$C_1$ and **C**-Me-$D_3$

**C**-Me-$C_1$ ⟷ **C**-Me-$C_2$(I) ⟷ **C**-Me-TS ⟷ **C**-Me-$D_3$

**Chart 2** The possible conformation forms for compound **C**-Me, and their racemization and interconversion processes.

In contrast to known [6]radialenes, **C**-Me exhibits two main differences: a) the central ring in **C**-H is almost planar (2.2°), but that in **C**-Me is twisted (30°). b) Other nonplanar [6]radialenes, such as 7,8,9,10,11,12-hexamethyl[6]radialene,[19a] -hexaethyl[6]radialene,[19b] -hexa(bromomethyl)[6]radialene,[38] -dodecamethyl[6]radialene[39,40] and hexakis(1,3-dithiol-2-ylidene)-cyclohexane,[41] contain a significant chair conformation in the cyclohexane with the average ring torsion angles 46–56°.[18,40] However, the six-membered ring in **C**-Me is a boat form, with the average ring torsion angle only 18.8°.

Compound **C**-H has been reported to have π–π stacking and a herringbone pattern.[16,17] However, molecules of **C**-Me are not well organized and each shows the presence of two different intermolecular interactions, *i.e.* $CH_3$-π and S-π types. Two adjacent molecules each provide a methyl group and a thiophene plane (ring **III**) to display the presence of intermolecular $CH_3$-π interactions between C13 and the thiophene plane **III**. The distance between C13 and S1, C1, C2, C11 and C12 is 4.18, 4.07, 3.79, 3.61 and 3.74 Å, respectively. Methyl carbon C13 has a stronger interaction with C11 and C12 rather than C1 and C2. The intermolecular distance of one methyl hydrogen in C13 to this π bond (C's C11 and C12) is *ca.* 2.91 Å, which is in the range of the standard mean value for an interaction of the $CCH_3$-arene type.[42] In this packing pair, there is also an intermolecular interaction between sulfur atom S1 and thiophene ring **I** (containing S2). S1 lies approximately 3.49 Å from the plane **I**. The distance between S1 and S2, and other carbons in ring **I** is *ca.* 3.74 and 3.66–3.77 Å, respectively. These values are slightly longer than the corresponding van der Waals distance.[30] To the best of our knowledge, this kind of S-π interaction is very rare in small molecules, but prevalent in biochemistry.[43] The S-π interaction also plays an important role in protein folding and stabilization. Theoretical investigations of $SH_2$-benzene provided similar results found here with the S-π interaction in **C**-Me.[44]

Chart 2 illustrates the possible conformations for **C**-Me. Each conformation is annotated according to symmetry type and number of methyl-methyl clashes present in the possible structure. Computational studies at all levels of theory (B3PW91, M06-2X or MP2) reveal a single $C_2$-symmetric conformation [that is, **C**-Me-$C_2$(I), **C**-Me-$C_2$(II) and **C**-Me-$C_2$(III), all minimize to the same $C_2$ conformation], as the potential energy minima. Analysis of the racemerization between the two enantiomers, **C**-Me-$C_2$(I), reveals **C**-Me-*Cs* as the transition state responsible for this process. Location of the transition state structure in $C_2$-symmetry (**C**-Me-TS) representing the interconversion between $C_2$ and $D_3$, reveals a barrier to interconversion of 7.3 kcal/mol (Chart 2 and Table 3). A summary of computed relative energies are reported in Table 3.

VT-NMR experiments did not provide enough information for the interconversion processes between any two conformers. When a solution state structure of **C**-Me in $CD_2Cl_2$ was cooled to −90 °C, the peaks of the methyl hydrogen in the $^1$H-NMR spectrum did not significantly become broad. The carbon signals in $^{13}$C-NMR spectrum at −75 °C remained unchanged relative to that at 25 °C. Moreover, a solution state structure of **C**-Me in 1,2-dichlorobenzene-$d_4$ was heated at 170 °C for 6 h to confirm the most thermodynamically stable conformation; a change in the $^1$H-NMR spectrum was not observed. Overall, signals in the temperature range −90 to 170 °C are nearly identical. These NMR studies indicate an equilibrium structure contributed from several conformations, likely since the activation energy for any

**Table 3** Comparison of twisted triphenylene derivatives

| Compound | **B**-F | **B**-Cl | **B**-Otol | **B**-Me | **B**-hbz | | **B**-bco | **C**-Me |
|---|---|---|---|---|---|---|---|---|
| Ground state | $C_2$ | $C_2$ | $C_2$ | $C_2$ | $D_3$ | | $C_2$ | $C_1$ ($\approx C_2$) |
| Observed in solid state | $C_2$ | $C_2$ | $C_2$ | $C_2$ | $C_2$ | $D_3$ | – | $C_1$ ($\approx C_2$) |
| Twisted angle (degree)[a] | 40 | 57 | 45 | 53 | 56 | 24 | 64[e] | 30 |
| The next most stable state | $D_3$ | $D_3$ | – | $D_3$ | $C_2$ | | $D_3$ | $D_3$ |
| Energy difference ($\Delta H$, kcal/mol)[b] | 1.6,[e] 4.9[f] | 1.0,[e] 5.2[h], | – | 5.91,[i] 4.4[f] | 5.0[k] | | 3.6[e] | 6.4,[f] 5.64[m] |
| Racemization barrier (kcal/mol)[c] | 1.96[g] | 7.0[e] | – | 10.93,[i] 14.0,[f] 10.2[j] | 11.5,[e] 11.7[j] | | 6.08[l] | 3.0,[f] 1.61[m] |
| Interconversion barrier (kcal/mol)[d] | 6.57[g] | 26.1[e] | – | 29.4[i] | 22.2,[e] 22.8[j] | | – | 7.3,[f] 5.93[m] |
| Ref. | 7, 9 | 8b | 6 | 9 | 11, 12 | | 9, 10 | This work |

[a] Crystal structure. [b] $\Delta H = H_{\text{(the next most stable state)}} - H_{\text{(ground state)}}$. [c] The barrier for the racemization between the $C_2$-conformer and its enantiomer. [d] The barrier for the interconversion between the ground state and the next most stable state. [e] AM1 values. [f] This work, M06-2X/DZ(2d,p) values. [g] B3LYP/6-311G(d,p) values. [h] HF/STO-3G values. [i] HF/6-31G(d,p) values. [j] Experimental value. [k] B3LYP/cc-pVDZ values. [l] AM1 calculation on a mimic of **B**-bco. [m] This work, B3PW91/DZ(2d,p).

interconversion process is very low,[45] as predicted by computations (Table 3). All methyl groups rapidly flip and display single sharp peaks in the NMR spectra.

Most triphenylene derivatives in Chart 1 and Table 3 show that their $C_2$-conformers are the most thermodynamically stable, rather than the corresponding $D_3$-symmetric forms.[46] As previously noted, "the $C_2$ conformation better preserves the planarity of the three outer rings, while sacrificing the central ring to greater deformation."[1] Compound **C**-Me can be approximately regarded as a "trithiophencyclohexane" based on the crystal structure and the computational analysis, and **C**-Me-$C_2$ should be the thermodynamically most stable conformation. Obviously, the three five-membered heterocycles in molecule **C**-Me create a less overcrowded environment for decreasing the twist and lowering the barrier of the interconversion process.

The conjugation between any two thiophenyl planes can be examined by UV spectroscopy. In general, breaking the planarity of a polyaromatic compound would lead to a decrease in π-orbital conjugation, shifting the absorption $\lambda_{\max}$ to shorter wavelength. However, UV spectra of compounds **C**-H and **C**-Me in $CH_2Cl_2$ do not show significant differences; Even their extinction coefficients are very similar. Only $\lambda_{\max}$ of the twisted molecule **C**-Me reveals slight bathochromic shifts (Fig. 3). This result perhaps comes from the contributions of two factors: 1) the weak electron-donating property of methyl groups; 2) low conjugation (interactions) between any two thiophene rings. The second factor is more important than the first. Therefore, a planar or a twisted structure would not affect their absorption band $\lambda_{\max}$ to a large degree. Although previous investigations have also reported the central six-membered ring in compound **C**-H to be lacking in aromatic character and the interaction between any two thiophene rings is low,[47] we provide here a direct evidence to confirm these two properties. In addition, compounds **C**-Me and **C**-H do not exhibit obvious luminescence either in solid or solution.

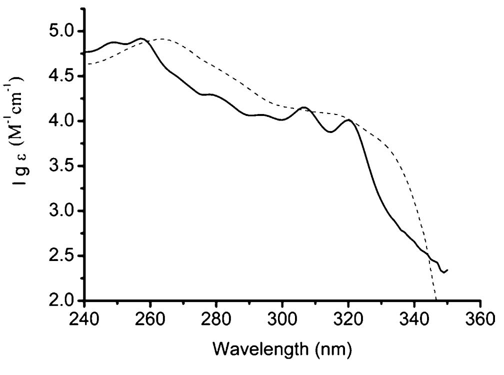


**Fig. 3** UV spectra of compounds **C**-Me (dashed line) and **C**-H (solid line). [**C**-Me] and [**C**-H] = $10^{-5}$ M in $CH_2Cl_2$.

Cyclic voltammetric (CV) analyses of compounds **C**-Me and **C**-H show two irreversible oxidation waves.[48] In contrast to **C**-H, the twisted molecule **C**-Me has slightly lower oxidation potentials (Fig. 4a). As expected, the weak electron-donating nature of the six methyl substituents lead **C**-Me to have a lower oxidation potential.[49] From the oxidation potential $E_{\text{onset}}$, the calculated HOMO potential is close to the computational values (see supporting information). It is also worth noting that, when the

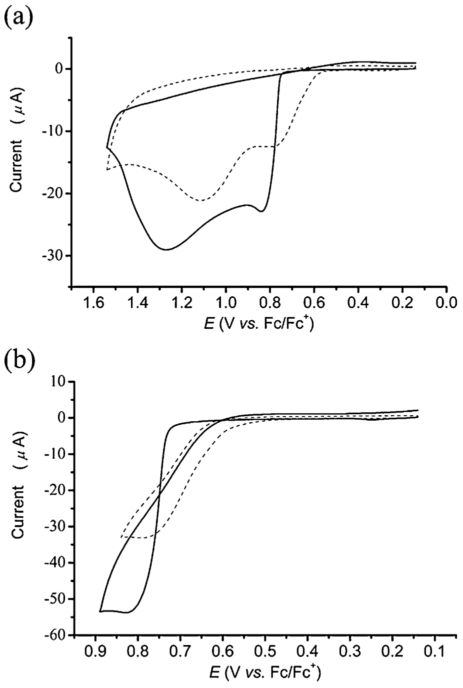


**Fig. 4** Cyclic voltammograms of **C**-Me (dashed line) and **C**-H (solid line) in different potential ranges. (a) 0–1.5 V. (b) 0–0.9 V. Experimental conditions: Compounds (concentration *ca.* $10^{-3}$ M) in background electrolyte solution of 0.1 M N(*n*-Bu)$_4$OCl$_4$ in $CH_2Cl_2$. Working electrode: platinum, reference electrode: Ag/AgNO$_3$ (0.1 M AgNO$_3$ and 0.1 M N(*n*-Bu)$_4$OCl$_4$ in acetonitrile), counter electrode: platinum wire. Scan rate: 50 mV/s.

potential for compounds **C**-Me and **C**-H was scanned positively from the rest-potential and reversed at *ca.* 0.9 V, only the latter showed a classic nucleation loop behavior (Fig. 4b).[50,51] This indicates that compound **C**-H could form a polymer film at low oxidation potential and the polymerization process for **C**-Me is not significant arising from its overcrowded environment.

## Conclusion

The structure of compound **C**-Me has been characterized as a twisted heteroarene *ca.* 30° away from planarity. This molecule and its planar analogue **C**-H do not exhibit in their physical properties, in particular UV and CV, significant differences. We provide strong evidences indicating that 1) compounds **C**-H and **C**-Me both have [6]radialene character, 2) their central "cyclohexane rings" lack aromaticity and 3) the conjugation between any adjacent thiophene rings is low. Synthesis of heterocyclic bowls of the sumanene type from compound **C**-Br and internal alkynes under catalysis of palladium complexes are in progress.

## Experimental

### General

$^1$H and $^{13}$C NMR: Bruker AMX 300 (300 and 75.5 MHz). EI-MS: Finnigan MAT 95 spectrometer (70 eV). MS: Bruker Daltonics Apex II30. UV: Agilent 8453 UV-Visible Spectrophotometer. Melting points were determined with a Büchi melting point apparatus B545 and are uncorrected. Chromatography: Merck silica gel 60 (230–400 mesh). Solvents for chromatography were technical grade and freshly distilled before use. The electrochemical experiments were accomplished by Princeton Applied Research Corporation (PAR) model 263A potentiostat controlled by PAR model 270 software. A three-electrode cell was used for the electrochemical experiments.

### Computational method

The conformational analyses of the molecular systems described in this study, including structural and orbital arrangements as well as property calculations, were carried out using the Gaussian98[52] and GAMESS[53] software packages. Structural computations of all compounds were performed using density functional methods (DFT), including the Becke's 3 parameter functional[54] in combination with nonlocal correlation provided by the Perdew-Wang 91 expression[55,56] with both local and nonlocal terms, B3PW91, and Truhlar and Zhao's M06-2X functional.[57] Dunning's correlation consistent basis set, cc-pVDZ, a [3s2p1d] contraction of a (9s4p1d) primitive set, as well as the Dunning/Huzinaga double-ζ polarized sets, DZ(2d,p) and DZ+(2d,p), were also employed.[58] Full geometry optimizations were performed and uniquely characterized *via* second derivatives (Hessian) analysis to determine the number of imaginary frequencies (0 = minima; 1 = transition state). Comparison of results with and without diffuse functionality indicated little to no effect. With regard to the DFT functional, improved functionals, such as the M06 series of Truhlar have been shown to superior to most other conventional functionals, including B3PW91, across 4 large databases of most every molecular construct. We have found very similar results from these two functionals for the types of molecules considered in this work, and have chosen to emphasize the M06 results, as we have found them to have greater predictability.[57,59–61] Nucleus-independent chemical shifts (NICS) properties,[33] including NICS(Iso),[62,63] NICS(In-plane), and NICS(ZZ)[36] values, were computed using the GIAO method.[64,65] A NICS-scan[66] was carried out for several molecules considered here. The isotropic chemical shift values are separated into their in-plane (NICS(Iso) and out-of-plane (NICS(ZZ) components, by consideration of the eigenvalues of the chemical shift tensors. The NICS(ZZ) values, more closely related to the current density, reflect the magnetic response of a molecule toward a magnetic field applied perpendicular to the plane (*i.e.*, z direction), and are therefore considered primarily associated with the π contribution. Visualization and analysis of structural (including representation of 3D molecular orbitals) and property results were obtained using QMView[67] and MacMolPlt.[68]

### Benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene (C-H)

Similar to the Hart's procedure,[15] 1,3,4,6,7,9-hexahydro-2,5,8-trithiatrindene (505 mg, 2.00 mmol) in *o*-xylene (150 mL) was treated with DDQ (1.70 g, 7.50 mmol), and heated at 150 °C under argon for 26 h. After cooling down to room temperature, the solvent was removed under reduced pressure and the residue was subjected to chromatography on silica gel. Elution with hexane/$CH_2Cl_2$ (10:1) afforded 251 mg (51%) of **C**-H as a colorless solid, m.p. 232–233 °C. (Lit.: 234–235 °C[17]; 236–238 °C[15]). $^1$H- and $^{13}$C-NMR spectra are identical to ref. 17

### 1,3,4,6,7,9-Hexabromobenzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene (C-Br)

To a solution of compound **C**-H (1.20 g, 4.87 mmol) in DMF (50 mL) at room temperature was added NBS (6.94 g, 39.0 mmol) in five portions within 5 min. The reaction mixture was stirred under nitrogen at the same temperature for 2 d. The suspension was diluted with MeOH (100 mL), and the precipitate was collected by filtration. The red-brown solid was washed with MeOH (25 mL × 2), water (10 mL) and finally with $Et_2O$ (10 mL). After drying, 1.76 g (50%) of **C**-Br was obtained as a yellow-orange solid [m.p. 153–155 °C (dec.)], which was directly used without any further purification. MS (70 eV), *m*/*z* (%): 724/722/720/718/716 (2/4/5/4/1) [$M^+$]. Due to the extremely low solubility in organic solvents, the $^{13}$C-NMR spectrum of **C**-Br was not recorded.

### 1,3,4,6,7,9-Hexamethylbenzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene (C-Me)

A mixture of compound **C**-Br (360 mg, 0.50 mmol) and $Pd(PPh_3)_4$ (289 mg, 0.25 mmol) in THF (5 mL) in a Schlenk tube at ambient temperature was treated with a 2.0 M solution of $AlMe_3$ in heptane (2.5 mL, 5.00 mmol). The suspension was heated under nitrogen at 100 °C for 36 h. After cooling down to room temperature, the solution was quenched with a saturated aqueous solution of $MgSO_4$ (20 mL) and extracted with $CH_2Cl_2$ (30 mL × 3). The combined organic phases were dried over $MgSO_4$ and filtrated, and the solvent of the filtrate was removed under reduced pressure. The residue was subjected to chromatography on silica gel. Elution with hexane/$CH_2Cl_2$ (1:8) afforded 122 mg (73%) of **C**-Me as a colorless solid, m.p. 162–170 °C (dec.). $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta = 2.61$ (s, 18 H, $CH_3$). $^{13}$C NMR (75.5 MHz,

$CDCl_3$, plus DEPT, ppm): $\delta = 18.2$ (+, $CH_3$), 128.4 ($C_{quat}$), 132.2 ($C_{quat}$). MS (70 eV), *m/z* (%): 330 (100) [$M^+$], 315 (48) [$M^+ - CH_3$], 297 (22), 282 (17), 269 (15), 221 (13), 165 (15), 132 (13), 84 (16). HRMS (EI) calcd for $C_{18}H_{18}S_3$: 330.0571; found: 330.0569. *Note: This compound slowly decomposes on contact with air at room temperature. It should be stored at low temperature in inert gas atmosphere.*

## Acknowledgements

Part of this work was supported by the National Science Council of Taiwan (NSC 94-2113-M-006-019). K.K.B. is grateful to the Schweizerischer Nationalfonds for support of this work. We also thank Prof. S.-L. Wang and Ms. C.-Y. Chen (National Tsing-Hua University, Taiwan) for the X-ray structure analyses, and Prof. Jay S. Siegel (University of Zurich) for valuable discussions over the course of this work.

## Notes and references

1 For a review on twisted acenes, see: R. A. Pascal, Jr., *Chem. Rev.*, 2006, **106**, 4809.

2 (*a*) Phenanthrene (**A**-H) is apart from the small displacements from exact planarity, see: J. Trotter, *Acta Crystallogr.*, 1963, **16**, 605; (*b*) M. I. Kay, Y. Okaya and D. E. Cox, *Acta Crystallogr.*, 1971, **B27**, 26.

3 The subtle deviations from planarity of phenanthrene (**A**-H), triphenylene (**B**-H) and benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophene (**C**-H) could be due to intermolecular solid-state effects. The calculated optimized structures of these PAHs are planar.

4 Some 4,5-disubstituted phenanthrenes (**A**-F, **A**-Cl, **A**-$CH_3$ and **A**-$CF_3$) deviate significantly from planarity, see: R. Cosmo, T. W. Hambley and S. Sternhell, *J. Org. Chem.*, 1987, **52**, 3119.

5 (*a*) F. R. Ahmed and J. Trotter, *Acta Crystallogr.*, 1963, **16**, 503; (*b*) A. Klug, *Acta Crystallogr.*, 1950, **3**, 165.

6 Dodecakis(4-tolyloxy)triphenylene (**B**-Otol): C. S. Frampton, D. D. MacNicol and S. J. Rowan, *J. Mol. Struct.*, 1997, **405**, 169.

7 (*a*) Perfluorotriphenylene (**B**-F): M. B. Hursthouse, V. B. Smith and A. G. Massey, *J. Fluorine Chem.*, 1977, **10**, 145; (*b*) M. Weck, A. R. Dunn, K. Matsumoto, G. W. Coates, E. B. Lobkovsky and R. H. Grubbs, *Angew. Chem.*, 1999, **111**, 2909; M. Weck, A. R. Dunn, K. Matsumoto, G. W. Coates, E. B. Lobkovsky and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 1999, **38**, 2741.

8 (*a*) Perchlorotriphenylene (**B**-Cl): K. Shibata, A. A. Kulkarni, D. M. Ho and R. A. Pascal, Jr., *J. Am. Chem. Soc.*, 1994, **116**, 5983; (*b*) K. Shibata, A. A. Kulkarni, D. M. Ho and R. A. Pascal, Jr., *J. Org. Chem.*, 1995, **60**, 428.

9 1,4,5,8,9,12-Hexamethyltriphenylene (**B**-Me): Y. Wang, A. D. Stretton, M. C. McConnell, P. A. Wood, S. Parsons, J. B. Henry, A. R. Mount and T. H. Galow, *J. Am. Chem. Soc.*, 2007, **129**, 13193.

10 Perbicyclo[2.2.2]octenetriphenylene (**B**-bco): This compound has been prepared, but its structure has not been characterized by X-ray analysis, see: T. Nishinaga, R. Inoue, A. Matsuura and K. Komatsu, *Org. Lett.*, 2002, **4**, 1435.

11 (*a*) $C_2$-Hexabenzotriphenylene (**B**-hbz-$C_2$): D. Péna, D. Pérez, E. Guitián and L. Castedo, *Org. Lett.*, 1999, **1**, 1555; (*b*) D. Péna, A. Cobas, D. Pérez, E. Guitián and L. Castedo, *Org. Lett.*, 2000, **2**, 1629.

12 $D_3$-Hexabenzotriphenylene (**B**-hbz-$D_3$): L. Barnett, D. M. Ho, K. K. Baldridge and R. A. Pascal, Jr., *J. Am. Chem. Soc.*, 1999, **121**, 727.

13 E. Clar, *The aromatic sextet*, Wiley: London, 1972.

14 The term "overcrowding" was first introduced by Bell and Waring to define aromatic systems, which adopt nonplanar forms to accommodate certain hydrogen atoms (*e.g.*, hydrogen atoms at positions 4 and 5 in dibenzo[*c*,*g*]phenanthrene), see: F. Bell and D. H. Waring, *J. Chem. Soc.*, 1949, 2689.

15 H. Hart and M. Sasaoka, *J. Am. Chem. Soc.*, 1978, **100**, 4326.

16 The average dihedral angle in the central six-membered ring is only 2.2° for compound **C**-H, see: A. Patra, Y. H. Wijsboom, L. J. W. Shimon and M. Bendikov, *Angew. Chem.*, 2007, **119**, 8970; A. Patra, Y. H. Wijsboom, L. J. W. Shimon and M. Bendikov, *Angew. Chem., Int. Ed.*, 2007, **46**, 8814.

17 M. E. Weiss, *Dissertation*, Universität GH Essen, 2000.

18 (*a*) Reviews: H. Hopf and G. Maas, *Angew. Chem.*, 1992, **104**, 953; H. Hopf and G. Maas, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 931; (*b*) H. Hopf, G. Maas, in *The Chemistry of Dienes and Polyenes* (Ed.: Z. Rappoport,), Vol. 1, J. Wiley, & Sons: Chichester, 1997, pp. 927.

19 (*a*) W. Marsh and J. D. Dunitz, *Helv. Chim. Acta*, 1975, **58**, 707; (*b*) P. G. Jones, P. Bubenitschek, T. Höpfner and H. Hopf, *Acta Crystallogr.*, 1997, **C53**, 920; (*c*) C. Domene, P. W. Fowler, L. W. Jenneskens and E. Steiner, *Chem.–Eur. J.*, 2007, **13**, 269.

20 (*a*) Reviews, see: G. Zotti, B. Vercelli and A. Berlin, *Acc. Chem. Res.*, 2008, **41**, 1098; (*b*) Y. Le, Y. Umemoto, M. Nitani and Y. Aso, *Pure Appl. Chem.*, 2008, **80**, 589; (*c*) G. Horowitz, P. Delannoy, in *Handbook of Oligo- and Polythiophenes* (Ed.: D. Fichou,), Wiley-VCH: Weinheim, 1999, pp. 283; (*d*) P. Bäuerle, in *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner,), Wiley-VCH: Weinheim, 1998, pp. 105.

21 (*a*) Y. Ie, Y. Umemoto, M. Okabe, T. Kusunoki, K.-i. Nakayama, Y.-J. Pu, J. Kido, H. Tada and Y. Aso, *Org. Lett.*, 2008, **10**, 833; (*b*) K. H. Kim, Z. Chi, M. J. Cho, J.-I. Jin, M. Y. Cho, S. J. Kim, J.-s. Joo and D. H. Choi, *Chem. Mater.*, 2007, **19**, 4925; (*c*) C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, 2002, **14**, 99; (*d*) H. E. Katz, A. J. Lovinger and J. G. Laquindanum, *Chem. Mater.*, 1998, **10**, 457; (*e*) F. Garnier, R. Hajlaoui, A. El Kassmi, L. Laigre, G. Horowitz, W. Porzio, M. Armanini and F. Provasoli, *Chem. Mater.*, 1998, **10**, 3334; (*f*) Review, see: H. E. Katz, A. Dodabalapur, Z. Bao, in *Handbook of Oligo- and Polythiophenes* (Ed.: D. Fichou,), Wiley-VCH: Weinheim, 1999, pp. 459.

22 (*a*) J. M. Hancock, A. P. Gifford, R. D. Champion and S. A. Jenekhe, *Macromolecules*, 2008, **41**, 3588; (*b*) A. Cravino, S. Roquet, O. Aleveque, P. Leriche, P. Frere and J. Roncali, *Chem. Mater.*, 2006, **18**, 2584; (*c*) U. Mitschke and P. Bäuerle, *J. Mater. Chem.*, 2000, **10**, 1471; (*d*) Review, see:Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1.

23 (*a*) N. Leclerc, A. Michaud, K. Sirois, J.-F. Morin and M. Leclerc, *Adv. Funct. Mater.*, 2006, **16**, 1694; (*b*) R. de Bettignies, Y. Nicolas, P. Blanchard, E. Levillain, J.-M. Nunzi and J. Roncali, *Adv. Mater.*, 2003, **15**, 1939; (*c*) D. Fichou, *J. Mater. Chem.*, 2000, **10**, 571; (*d*) N. Noma, T. Tsuzuki and Y. Shirota, *Adv. Mater.*, 1995, **7**, 647; (*e*) Review, see: J. Roncali, *Chem. Soc. Rev.*, 2005, **34**, 483.

24 Tribromobenzo[1,2-*c*:3,4-*c*′:5,6-*c*″]trithiophenes can be prepared in the similar manner, see: K. Imamura, K. Takimiya, Y. Aso and T. Otsubo, *Chem. Commun.*, 1999, 1859.

25 Y. Nicolas, P. Blanchard, E. Levillain, M. Allain, N. Mercier and J. Roncali, *Org. Lett.*, 2004, **6**, 273.

26 Compound **C**-Me: $C_{18}H_{18}S_3$, monoclinic crystals of space group $C2/c$, unit cell dimensions: $a = 20.700(3)$, $b = 8.1002(11)$, $c = 19.248(3)$ Å, $\alpha = 90$, $\beta = 94.392(2)$, $\gamma = 90$ °, $V = 3217.9(7)$ Å$^3$. CCDC 715338 and 715339†.

27 The crystal structure presented in this context is generated from the diffraction data collected at 295 K unless stated otherwise.

28 Mainly, the methyl groups C13 and C14 break the perfect $C_2$ symmetry.

29 It was observed that a highly congestive thiophene, such as 3,4-di-(*tert*-butyl)-2,5-bis(triisopropylsilyl)thiophene, is twisted with a torsion angle 14° from the central four carbon atoms, see: J. Nakayama, T. Yu, Y. Sugihara, A. Ishii and S. Kumakura, *Heterocycles*, 1997, **45**, 1267.

30 Y. V. Zefirov, *Crystallog. Rep.*, 1997, **42**, 111. The sum of van der Waals radii of two atoms is as follows: C–C: 3.42 Å; S–S: 3.68 Å; S–C: 3.55 Å.

31 The end-to-end twist of ring **I** was determined by the torsion angle (C's C3-C6-C5-C4).

32 T. Sugano, T. Hashida, A. Kobayashi, H. Kobayashi and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2303.

33 P. V. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao and N. J. R. van Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317.

34 Z.-H. Li, D. Moran, K.-N. Fan and P. v. R. Schleyer, *J. Phys. Chem. A*, 2005, **109**, 3711.

35 A. Hirsch, Z. Chen and H. Jiao, *Angew. Chem.*, 2001, **113**, 2916; A. Hirsch, Z. Chen and H. Jiao, *Angew. Chem., Int. Ed.*, 2001, **40**, 2834.

36 P. W. Fowler and E. Steiner, *Mol. Phys.*, 2000, **98**, 945.

37 J. Juselius and D. Sundholrn, *Phys. Chem. Chem. Phys.*, 1999, **1**, 3429.

38 A. Stanger, N. Ashkenazi, R. Boese, D. Bläser and P. Stellberg, *Chem. Eur. J.*, 1997, **3**, 208.

39 G. Wilke, *Angew. Chem.*, 1988, **100**, 189; G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 185.

40 T. Höpfner, P. G. Jones, B. Ahrens, I. Dix, L. Ernst and H. Hopf, *Eur. J. Org. Chem.*, 2003, 2596.

41 T. Sugimoto, Y. Misaki, T. Kajita, Z. Yoshida, Y. Kai and N. Kasai, *J. Am. Chem. Soc.*, 1987, **109**, 4106.

42 (*a*) The standard mean value (2.75 ± 0.1 Å) of the distance for the type $CH_3$/planar arene, see: O. Takahashi, Y. Kohno, S. Iwasaki, K. Saito, M. Iwaoka, S. Tomoda, Y. Umezawa, S. Tsuboyama and M. Nishio, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 2421; (*b*) The standard mean value (2.87 ± 0.13 Å) of the distance for the type $sp^3$-CH/fullerene, see: H. Suezawa, T. Yoshida, S. Ishihara, Y. Umezawa and M. Nishio, *CrystEngComm*, 2003, **5**, 514; (*c*) Review for crystallographic study see: M. Nishio, *CrystEngComm*, 2004, **6**, 130; (*d*) For computational study see: P. Hobza and Z. Havlas, *Chem. Rev.*, 2000, **100**, 4253.

43 Interactions between cysteine and aromatics are frequently found in crystal structures from the Brookhaven Protein Data Bank.

44 In the optimized structure of $H_2S$–benzene complex, the sulfur atom lies 3.6 Å from the central of the benzene with a total interaction energy (or stabliization energy) of −1.12 kcal/mol, see: A. L. Ringer, A. Senenko and C. D. Sherrill, *Protein Sci.*, 2007, **16**, 2216.

45 The interconversion (or racemization) barriers of **C**-Me is much smaller than 10.2 kcal/mol, which is determined from **B**-Me with a coalescence temperature of −55 °C, see ref. 9.

46 Compound **B**-Me contains three non-equivalent molecules in the solid state. One of them is not perfect $C_2$-conformer, and it should be $C_1$. The slight deformation breaks the perfect symmetry. In contrast, **B**-F and **B**-Cl in solid state are perfect $C_2$-conformers.

47 P. Rademacher, C. Heinemann, S. Jänsch, K. Kowski and M. E. Weiss, *Spectrochim. Acta, Part A*, 2000, **56**, 1179.

48 Oxidation potentials of **C**-Me and **C**-H are lower than their isomer **D**, see ref. 25 The oxidation potential of **D** ($E_{pa} = 1.55$ V) was measured in the following conditions: 0.1 mM of **D** in 0.2 M $(n\text{-Bu})_4NPF_6/CH_2Cl_2$, Pt electrodes, Ag/AgCl as a reference, Pt wire as counter electrode, scan rate 100 mV/s).

49 (*a*) It has been observed that 2,5-dimethylthiophene has a much lower oxidation potential than thiophene. The oxidation potential of thiophene ($E_p = 2.06$ V vs. SSCE) was determined in 0.1 M solution of $(n\text{-Bu})_4BF_4$ in acetonitrile by a Pt electrode, see: R. J. Waltman, J. Bargon and A. F. Diaz, *J. Phys. Chem.*, 1983, **87**, 1459; (*b*) The oxidation potential of 2,5-dimethylthiophene ($E_{onset} = 1.20$ V vs. SCE) was determined in solution of $NaClO_4$ in methanol by a Pt electrode, see: K. Yoshida, T. Saeki and T. Fueno, *J. Org. Chem.*, 1971, **36**, 3673.

50 R. Borjas and D. A. Buttry, *Chem. Mater.*, 1991, **3**, 872.

51 Cyclic voltammetric (CV) analysis of compound **C** has been studied, see: ref. 16.

52 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. J. Montgomery, 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, 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, J. A. Pople, *Gaussian98, Revision A.6*, Pittsburgh PA, 1998.

53 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, Jr, *J. Comput. Chem.*, 1993, **14**, 1347.

54 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

55 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 6671.

56 J. P. Perdew, K. Burke and Y. Wang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 16533.

57 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

58 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007.

59 Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput.*, 2008, **4**, 1849.

60 Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157.

61 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2006, **110**, 13126.

62 P. v. R. Schleyer, H. Jiao, N. J. R. van Hommes, V. G. Malkin and O. L. Malkina, *J. Am. Chem. Soc.*, 1997, **119**, 12669.

63 P. v. R. Schleyer, M. Manoharan, Z.-X. Wang, B. Kiran, H. Jiao, R. Puchta and N. J. R. van Eikema Hommes, *Org. Lett.*, 2001, **3**, 2465.

64 K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251.

65 R. Ditchfield, *J. Chem. Phys.*, 1972, **56**, 5688.

66 A. Stanger, *J. Org. Chem.*, 2006, **71**, 883.

67 K. K. Baldridge and J. P. Greenberg, *J. Mol. Graphics*, 1995, **13**, 63.

68 B. M. Bode and M. S. Gordon, *J. Mol. Graphics Modell.*, 1998, **16**, 133.