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Synthesis and structures of thieno[2,3-*b*]thiophene incorporated [3.3]dithiacyclophanes. Enhanced first hyperpolarizability in an unsymmetrically polarized cyclophane

Sabir H. Mashraqui,[a,*] Yogesh S. Sangvikar[a] and Auke Meetsma[b]

[a]*Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz-E, Mumbai 400098, India*
[b]*Department of Chemistry, University of Groningen, Nijenborg 4, 9747 AG, Groningen, The Netherlands*

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Abstract—Dithiacyclophanes incorporating thieno[2,3-*b*]thiophene have been synthesized, in order to investigate the nonlinear optical properties of donor–acceptor cyclophane **7**. Cyclophane **7** displayed significantly higher first hyperpolarizability β (21.6×10^{-30} esu) compared to model **10** (9.58×10^{-30}esu). Relatively higher β in **7** presumably arises from an extra electron redistribution arising from through-space charge transfer, a feature lacking in **10**. Moreover, the thermal decomposition temperature of **7** (300 °C) is higher than that reported for the NLO prototype DANS (295 °C).

Designing organic molecules exhibiting large molecular nonlinearity has been a challenging subject to access materials for application in opto-electronic fields.[1,2] Besides a high molecular nonlinear optical (NLO) response, many optical applications also require materials to possess good thermal stability and transparency in the fundamental region of emission.[3] Traditionally, cyclophanes have been extensively probed for their molecular structures and unique spectral and chemical properties.[4–6] On account of co-facially locked conformations and short inter-chromophoric distances, cyclophanes also serve as ideal platforms to study transmission of the electronic effects of substituents across π-stacked rings.[7] Recently, in a series of elegant papers, Bazan et al.[8–11] have shown that octupolar cyclophanes not only show higher nonlinear optical coefficients relative to open models, but they also conform to nonlinearity/transparency trade-off. A multi-dimensional tunnelling barrier provided for an increased π-electron distribution has been invoked as one of the important factors for the improved NLO properties in these cyclophanes. However, to our knowledge, NLO properties of unsymmetrically polarized cyclophanes have not yet been reported.

Here, we report the synthesis of dithia-bridged cyclophanes **3**–**7** incorporating thieno[2,3-*b*]thiophene as one of the rings and investigated their structures, including the linear and nonlinear optical properties of donor–acceptor cyclophane **7**. The thienothiophene ring, included in a cyclophane framework for the first time, was specifically chosen to provide a handle to create the unsymmetrically polarized cyclophane **7**. The synthetic route implemented towards **3**–**7** is depicted in Scheme 1. The known thienothiophene diester **1**[12] was readily converted into dibromide **2** (79%) by radical bromination using NBS/dibenzoyl peroxide. High dilution coupling of **2** with *m*-xylylenedithiol in refluxing 1:1 alcohol–benzene, followed by chromatographic purification over SiO_2, afforded the desired dithia[3.3]cyclophane diester **3** in 47% yield as a colourless crystalline solid. Ester hydrolysis of **3** gave diacid **4** (95% yield), which on decarboxylation (Cu/quinoline, 200 °C, 10 min) gave the dithiaphane **5** in 40% yield. To access donor–acceptor cyclophane **7**, formylation of **5** under standard Vilsmeier–Hack conditions ($DMF/POCl_3$) provided mono-aldehyde **6** (57% yield), which was condensed with malononitrile (DMF/piperidine) to afford the target molecule **7** as a deep yellow solid in 39% yield.

Keywords: Cyclophanes; Thieno[2,3-*b*]thiophene; X-ray structures; UV–vis; First hyperpolarizability; Through-space charge redistribution.

* Corresponding author. Fax: +91 022 6528547; e-mail: sh_mashraqui@yahoo.com

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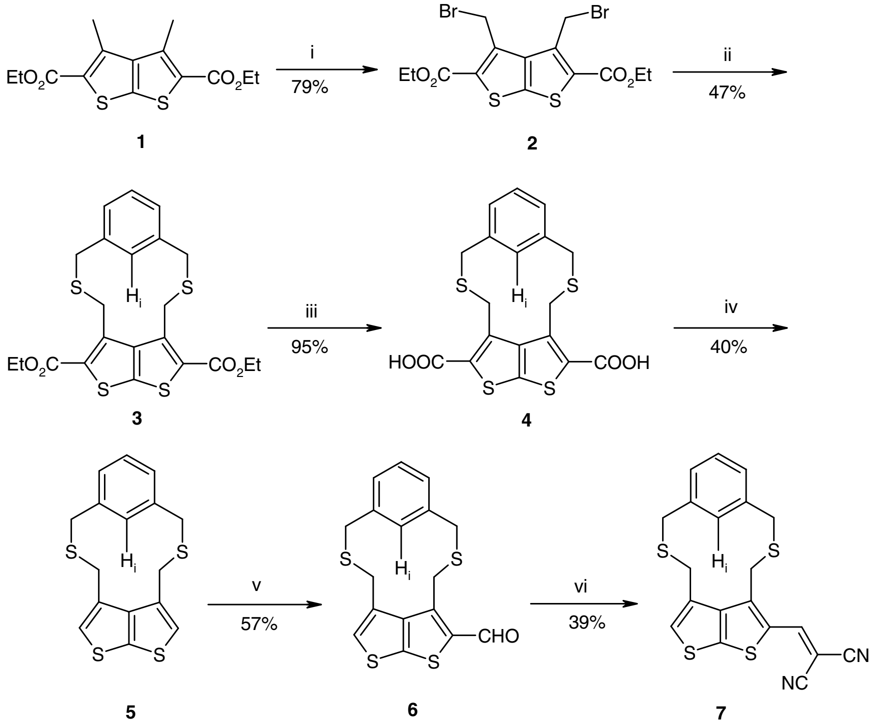


Scheme 1. Synthesis of dithia-cyclophanes **3**–**7**. Reagents and conditions: (i) NBS/CCl_4 $(PhCOO)_2$, Δ, 1 h. (ii) *m*-Xylylenedithiol/anhyd K_2CO_3/DMF, 80–90 °C, 18 h. (iii) 20% KOH/ethanol, Δ, 4 h. (iv) Cu/quinoline, 200 °C, 10 min. (v) DMF/$POCl_3$, 0 °C–rt, 4 h. (vi) $CH_2(CN)_2$, DMF/piperidine, 70–80 °C, 5 h.

The ^1H NMR spectral data for **3**–**7** are collected in Table 1. For symmetrical cyclophanes **3**–**5**, the bridged CH_2 protons appear as sharp singlets, whereas unsymmetrical cyclophanes **6** and **7** displayed four well-resolved singlets corresponding to four non-equivalent CH_2 groups. The singlets associated with the bridged CH_2's in **3**–**7** are consistent with free bridge inversion at ambient temperature on the ^1H NMR time scale. Variable temperature NMR spectra scanned down to −55 °C did not reveal either signal splitting or line broadening of CH_2 singlets, implying unhindered conformational interconversion even at lower temperatures. The existence of free conformational rotation in **3**–**7** is consistent with low energy barriers associated with many known [3.3]cyclophanes.[13]

The internal proton H_i of the *meta*-bridged ring for **5**–**7**, as expected of a cyclophane framework,[14] appears markedly upfield (δ 6.30–6.68) relative to the chemical shift position of the corresponding proton in *m*-xylene at δ 7.00. However, in contrast, H_i of **3** and **4** resonates at significantly lower field at δ 7.76 and δ 7.77. Rather than being subjected to upfield shielding effects, the H_i in **3** and **4** seems to be experiencing some degree of deshielding from the facing thienothiophene ring.

The unprecedented downfield shift of H_i in cyclophane **3** necessitated an examination of its molecular structure, together with that of **5** for comparison, by X-ray crystallographic analysis.[15] The ORTEP plots of **3** and **5** are depicted in Figures 1 and 2, respectively. The angles of inclination between the mean plane of the phenyl ring in relation to that of the thienothiophene plane in **3** and **5** were found to be 74.29(4)° and 27.50(5)°, respectively. Thus, while **3**, with C2 and C5 ester substituents,

Table 1. ^1H NMR spectra (400 MHz; $CDCl_3$) of cyclophanes **3**–**7**

3	δ 1.39 (6H, t, $J = 7$ Hz), 3.91 (4H, s), 3.98 (4H, s), 4.37 (4H, q, $J = 7$ Hz), 7.12 (2H, d, $J = 7$ Hz), 7.26 (1H, t, $J = 7$ Hz), *7.76 (1H, s)*
4	δ 3.86 (4H, s), 3.92 (4H, s), 7.17 (2H, d, $J = 7$ Hz), 7.26 (1H, t, $J = 7$ Hz), *7.77 (1H, s)*, 13.46 (2H, s)
5	δ 3.53 (4H, s), 3.62 (4H, s), *6.30 (1H, s)*, 7.28 (2H, d, $J = 7$ Hz), 7.42 (1H, t, $J = 7$ Hz), 7.66 (2H, s)
6	δ 3.49 (2H, s), 3.62 (2H, s), 3.68 (2H, s), 4.0 (2H, s), *6.60 (1H, s)*, 7.25 (1H, d, $J = 8$ Hz), 7.29 (1H, $J = 8$ Hz), 7.43 (1H, t, $J = 8$ Hz), 7.74 (1H, s), 10.69 (1H, s)
7	δ 3.48 (2H, s), 3.61 (2H, s), 3.73 (2H, s), 3.93 (2H, s), *6.68 (1H, s)*, 7.23 (1H, d, $J = 8$ Hz), 7.26 (1H, d, $J = 7$ Hz), 7.31 (1H, s), 7.45 (1H, dd, $J = 7$ and 8 Hz), 7.75 (1H, s)

The internal proton H_i is italicized.

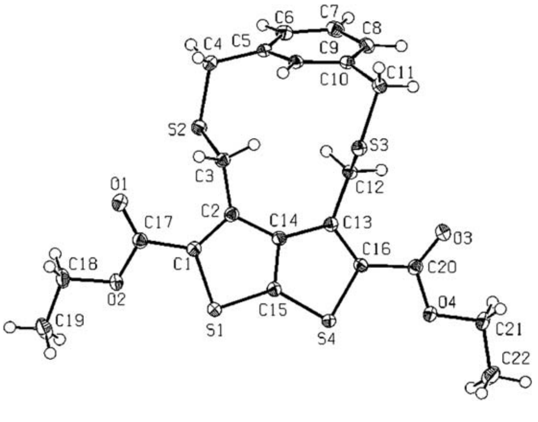


Figure 1. ORTEP plot of cyclophane **3**.

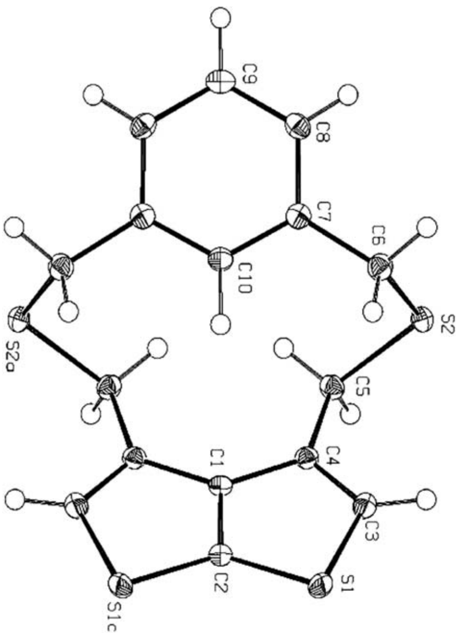


Figure 2. ORTEP plot of cyclophane **5**.

adopts an edge to face conformation, molecule **5** lacking ester substituents possesses a partially stacked geometry. The thia-bridges in molecules **3** and **5** are *anti* oriented and the bridge S…S distances are 5.1502(11) Å and 6.3236 (8) Å, respectively. The bridging angles, S3, C11, C9 and S3, C12, C13 for **3** are 112.07° and 110.95°, respectively; however, for **5** the corresponding angles (S2, C6, C7 and S2, C5, C4) are appreciably larger, being 115.01° and 114.79°, respectively. Shorter S.…S distance and smaller bridging angles for **3** relative to those noted for **5** indicate the presence of a significantly constricted cavity in **3** in comparison to that of **5**. This is most likely the consequence of the steric compression of C2 and C5 ester substituents on the bridge methylenes in **3**. Thus, while the *phane* cavity **5** is large enough to accommodate the facing phenyl ring, in the case of **3**, relatively constricted cavity forces the phenyl ring to move out of the *phane* cavity. The H_i in **3** is consequently facing the edge of thienothiophene ring, a feature which could conceivably induce some degree of deshielding effect on this proton (downfield location at δ 7.76). As far as we are aware, cyclophane **3** constitutes the first example of a *phane* structure wherein the internal proton of the facing ring is subjected to a deshielding effect.

For comparison of linear and nonlinear optical properties of **7**, a reference model, 2-dicyanovinyl-3,4-dimethylthienothiophene **10**, was also synthesized starting from the known **8**[16] by following the sequence shown in Scheme 2. The UV–visible spectra of **7** and the reference model, 2-dicyanovinyl-3,4-dimethylthienothiophene **10**, recorded in $CHCl_3$ are depicted in Figure 3. The absorption maximum for **7** appeared at 390 nm with molar absorption coefficient ε_{max} of 3.90×10^4 M^{-1}. The corresponding values of λ_{max} and ε_{max} for the model **10** are 380.5 nm and 2.0×10^4 M^{-1}, respectively. In comparison to **10**, a red shift in the absorbance maxima together with significantly higher ε_{max} observed for the case of **7** is presumably a consequence of intramolecular charge transfer (ICT) across the donor phenyl ring to the acceptor dicyanovinyl-substituted thienothiophene chromophore in the former system.[17,18] The presence of ICT also finds support in the downfield shift of H_i in **7** ($\Delta\delta$ 0.30) compared to the chemical shift position of this proton in cyclophane **5**, which is devoid of the acceptor chromophore.[19]

The first hyperpolarizability β for **7** and **10**, measured by hyper-Rayleigh scattering technique[20] in $CHCl_3$ solvent, was found to be 21.6 and 9.58×10^{-30} esu, respectively, with respect to *p*-nitroaniline as the reference standard ($\beta = 16 \times 10^{-30}$ esu). Although the increment in λ_{max} in going from model **10** to cyclophane **7** is only 10 nm, it is noteworthy that the increase in nonlinearity for **7** amounts to nearly twice that observed for **10**. For model **10**, which lacks a through-space charge transfer component, the only contributing factor to β stems from essentially one dimensional charge delocalization. However, in the case of **7**, in addition to direct through-bond delocalization, larger β relative to **10** can be understood in

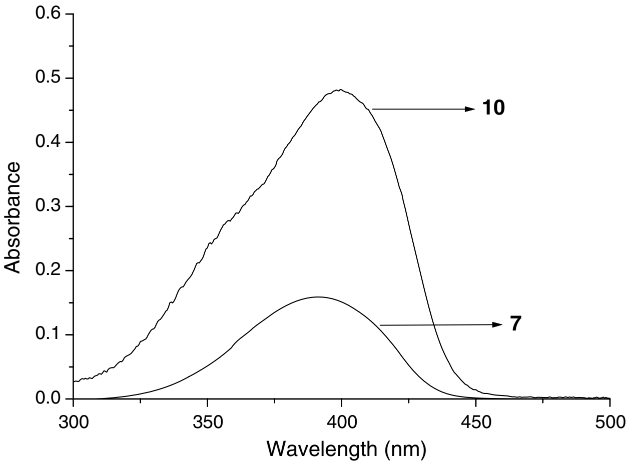
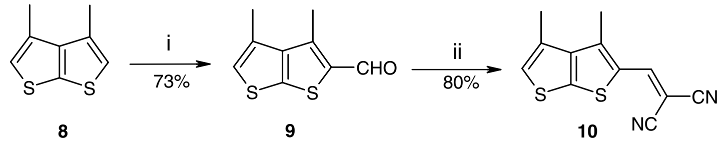


Figure 3. UV–vis molar absorbance spectra of cyclophane **7** and model **10** ($CHCl_3$).



Scheme 2. Synthesis of reference model **10**. Reagents and conditions: (i) DMF/$POCl_3$, 0 °C–rt, 4 h. (ii) $CH_2(CN)_2$, DMF/piperidine, 70–80 °C, 5 h.

terms of an extra contribution to the nonlinearity coefficient arising from the through-space charge redistribution.[21] Furthermore, a small bathochromic shift in **7** relative to **10** means that transparency/nonlinearity trade-off is not seriously compromised. The thermal stability of **7** and model **10** measured by differential scanning calorimetry indicated thermal decomposition temperatures (T_g) of 300 and 325 °C, respectively. For the NLO prototype DANS,[22] the T_g is 295 °C. Thus, the thermal stability of cyclophane **7** is quite appreciable, which is a useful parameter for device applications.

To our knowledge, cyclophane **7** represents the first example of an unsymmetrically polarized *phane* exhibiting enhanced β on account of through-space charge transfer contribution. Although, the β value of **7** is moderate by current standards, nevertheless, the present results demonstrate that unsymmetrically polarized cyclophanes could offer a useful design strategy to access higher nonlinearity and thermally robust NLO systems.

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Supplementary data

Full experimental procedures, characterization data (^{1}H and ^{13}C NMR spectra) of all new compounds, energy minimized structures of **3**, **5** and **7**, UV–vis spectra of **7** and **10** and NOE experiments of **3** and **5** are included. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.05.098.

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