University of Groningen

Donor-acceptor thieno[2,3-b]thiophene systems

Mashraqui, SH; Ashraf, M; Hariharasubrahmanian, H; Kellogg, RM; Meetsma, A; Mashraqui, Sabir H.

Published in:
Journal of Molecular Structure

DOI:
[10.1016/j.molstruc.2003.10.026](https://doi.org/10.1016/j.molstruc.2003.10.026)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2004

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Mashraqui, SH., Ashraf, M., Hariharasubrahmanian, H., Kellogg, RM., Meetsma, A., & Mashraqui, S. H. (2004). Donor-acceptor thieno[2,3-b]thiophene systems: synthesis and structural study of 3-anisyl-4-pyridyl(pyridinium) thieno[2,3-b]thiophenes. *Journal of Molecular Structure*, 689(1-2), 107-113.
<https://doi.org/10.1016/j.molstruc.2003.10.026>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Donor–acceptor thieno[2,3-*b*]thiophene systems: synthesis and structural study of 3-anisyl-4-pyridyl(pyridinium) thieno[2,3-*b*]thiophenes

Sabir H. Mashraqui^{a,*}, Mohamed Ashraf^a, Harini Hariharasubrahmanian^a,
Richard M. Kellogg^b, A. Meetsma^b

^aDepartment of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E), Mumbai 400 098, India

^bDepartment of Chemistry, University of Groningen, Nijenborg 19, Groningen 9747 AG, The Netherlands

Received 25 September 2003; revised 28 October 2003; accepted 30 October 2003

Abstract

Synthesis of a new class of cofacially oriented neutral donor–acceptor thienothiophene, namely 3-anisyl-4-pyridyl thieno[2,3-*b*]thiophenes **7** and its ionic analog **8** has been described to probe the presence of through-space charge transfer interaction. However, structural studies by ¹H NMR and UV–visible data indicate at best rather weak charge transfer interaction. The single crystal X-ray analysis of the ionic donor–acceptor thienothiophene **8** reveals many interesting features, i.e. (i) the donor and acceptor rings are not parallel to each other (ii) the interchromophoric distance is much larger (4.08 Å) than the van der Waals distance and (iii) the torsional angle between the pyridinium ring and the thienothiophene is unusually small, being only 38°. These structural features preclude effective through-space charge transfer interaction in **8**. Conformational analysis of a model system, 3,4-diphenyl thienothiophene indicated that conformations with reduced torsion between the phenyl rings and the thienothiophene plane are possible to maintain a balance between conjugation and steric congestion and the calculated low energy barrier between the high and low energy conformations of the model system suggest the possibility of aryl ring rotations in *peri* disubstituted thienothiophenes.

© 2003 Published by Elsevier B.V.

Keywords: Donor–acceptor thienothiophenes; Synthesis; Charge transfer interaction; Spectral data; Single crystal X-ray

1. Introduction

Charge transfer (c.t.) interaction has been recognized as a key molecular interaction in numerous technological applications such as in developing conducting materials, photonic devices, dyes, sensors and selective chromatographic materials [1]. In addition, the c.t. phenomena are also widely implicated in reaction mechanisms, host–guest interaction, crystal packing and self-organized supramolecular systems [2]. In recent years, several molecular designs which include cyclophanes [3] (A), trypticene analogs [4] (B) and 1,8-diarylnaphthalenes [5] (C) have been developed to entice through-space c.t. interaction by placing donor and acceptor in close proximity to each other (Chart 1). In the case of 1,8-diaryl naphthalenes, several elegant studies have been carried out to demonstrate the presence of

through-space π – π and polar interactions between the closely spaced aryl/heteroaryl groups [6].

In analogy to 1,8-diaryl naphthalenes, we envisaged that thieno[2,3-*b*]thiophene framework I, a 10π analog of naphthalene could also be exploited to design potentially interesting intramolecular c.t. systems by placing donor and acceptor at its C3 and C4 (*peri*) positions to create structures of the type II (Chart 1). Based on molecular modelling and analogy to 1,8-diarylnaphthalene systems, we expected the donor and acceptor substituents to occupy near parallel orientation to each other, but orthogonal with respect to the thienothiophene plane in order to minimize steric congestion. We presumed that such geometry would be well suited to exhibit through-space c.t. interaction in systems of type II. Thus, in pursuit of the above goal, we chose our target as the compounds **7/8** having *p*-methoxyphenyl as the donor and pyridine/pyridinium rings as the acceptor substituents attached to the *peri* positions of the thienothiophene framework.

* Corresponding author. Tel.: +912226526119; fax: +912226528547.
E-mail address: sh_mashraqui@yahoo.com (S.H. Mashraqui).

Chart 1. Some novel charge transfer systems.

2. Experimental

The chemicals and solvents for synthesis and column chromatography were purchased from S/D Fine Chemicals and Merck (India) and used as received. Melting points (uncorrected) were determined on a Gallenkamp melting point apparatus. IR spectra were recorded on a Shimadzu FTIR-420 spectrophotometer. ^1H NMR spectra were recorded on a Bruker-AMX-500 spectrometer with TMS as an internal standard. Mass Spectra were recorded on GCMS-QP 5050A Shimadzu spectrophotometer and UV–visible spectra were taken on Shimadzu UV–visible spectrophotometer UV-2100.

1-(4-Methoxyphenyl)3-(3-pyridyl)propane-1,3-dione (3). A solution of 4-methoxyacetophenone **1** (19.5 g, 130 mmol) and ethyl nicotinate **2** (18.0 g, 130 mmol) in dry DMF (50 ml) was added dropwise during 30 min to a stirred suspension of sodium hydride (7.0 g, 260 mmol) in dry DMF (150 ml) at 0°C . The reaction mixture was stirred further at this temperature for 4 h and then allowed to warm-up to room temperature during next 2 h. The contents of the reaction were poured into cold water (1.5 l) and neutralized with acetic acid. The precipitated yellow solid was filtered under suction, washed well with water and air-dried. Crystallization from ethanol gave 19.5 g (66%) of **3**, mp $133\text{--}135^\circ\text{C}$. IR (KBr, $\nu\text{ cm}^{-1}$) 2903, 1620, 1600, 1542, 1421, 1380, 1203, 1075, 860, 802; ^1H NMR (60 MHz, CDCl_3) δ 3.9 (3H, s), 6.5 (2H, s), 7.05–8.80 (8H, m), 9.20 (1H, s). Anal. calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_3$: C, 70.58%; H, 5.09%; N, 5.49%; found: C, 70.83; H, 4.88; N, 5.27.

Ketene thioacetal 4. A solution of diketone **3** (3.75 g, 15 mmol) and freshly distilled carbon disulfide (2.03 ml,

30 mmol) in dry DMF (20 ml) was added at room temperature to a vigorously stirred mixture of dry DMF (20 ml) containing anhyd K_2CO_3 (3.0 g) and a catalytic amount of tetrabutylammonium bromide (100 mg). The addition was completed during 30 min and then ethyl bromoacetate (3.3 ml, 30 mmol) was added dropwise during 30 min. The reaction mixture was stirred for 24 h, diluted with cold 5% cold aq NaOH solution and extracted with diethyl ether. After water washing, the organic extract was dried over anhyd Na_2SO_4 . Removal of the solvent gave a red oil which was subjected to silica gel column chromatography (Eberhardt, Hans (eluant ethyl acetate–petroleum ether 30:70) to afford **4** (60%) as an unstable light yellow oil. IR (oil film, $\nu\text{ cm}^{-1}$): 2830, 1720, 1685, 1620, 1470, 1383, 1185, 1124, 1040, 955. The crude **4** was immediately used as such for the next reaction.

3-(4-Methoxyphenyl)4(3-pyridyl)thienof[2,3-b]thiophene-2,5-diethylester (5). The crude **4** (1.53 g, 3 mmol, purity ca. 90%) was dissolved in absolute ethanol (5 ml) and added dropwise at 0°C during 10 min to a stirred solution of sodium ethoxide (prepared from 230 mg Na) in absolute ethanol (20 ml). The reaction was stirred at this temperature for 30 min and then poured over crushed ice. A yellowish brown solid which separated out was filtered and washed thoroughly with water. The crude solid was purified by repeated crystallization from ethyl acetate–petroleum ether (1:3) to provide **5** as a light yellow solid, mp $115\text{--}118^\circ\text{C}$ in 50% yield. IR (KBr, $\nu\text{ cm}^{-1}$) 2905, 1703, 1680, 1605, 1580, 1504, 1460, 1410, 1382, 1220, 1165, 840. ^1H NMR (200 MHz, CDCl_3) δ 1.02 (3H, t), 1.05 (3H, t, $J = 7.5\text{ Hz}$), 4.1–4.2 (4H, two q, $J = 7.5\text{ Hz}$), 6.40 (2H, d, $J = 8\text{ Hz}$), 6.66 (2H, d, $J = 8\text{ Hz}$), 6.87 (1H, m), 7.17 (1H, d, $J = 6.5\text{ Hz}$), 8.1 (1H, s), 8.27 (1H, d, $J = 6.5\text{ Hz}$).

Anal. Calcd for $C_{24}H_{21}NO_5S_2$; C, 61.67%; H, 4.50%; N, 2.99%; S, 13.70%. Found. C, 61.93; H, 4.34; N, 2.95; S, 13.46.

Preparation of the diacid 6. The diester **5** (1.0 g, 2.27 mmol) was dissolved in 20 ml of DMSO containing 10% aq KOH (10 ml) and the reaction mixture heated at 100 °C for 10 h. The reaction was cooled, diluted with water and acidified with conc. HCl to ca. pH 3. The precipitated diacid **6** was obtained as a light brown solid in 85% yield, mp 235–240 °C. IR (KBr, ν cm⁻¹) 3400, 3060, 1683, 1622, 1580, 1507, 1485, 1341, 1300, 1218, 1155, 1103, 998, 880. Anal. Calcd for $C_{20}H_{13}NO_5S_2$; C, 58.39%; H, 3.16%; N, 3.40%; S, 15.57%. Found. C, 58.55; H, 3.35; N, 3.22; S, 15.38.

3-Anisyl-4-pyridyl thieno[2,3-*b*]thienophene (7). The diacid **6** (400 mg, 0.97 mmol) was taken in a Slenck tube and heated for 10 min in a silicone oil-bath kept at 240–250 °C under N₂ atmosphere. The reaction mixture, which had turned dark brown was cooled to room temperature, extracted with chloroform and filtered to remove a small amount of insoluble residue. The filtrate was concentrated and the crude product purified by SiO₂ column chromatography using petroleum ether as an eluant to provide the required product **7** as a pale yellow solid, mp 77–79 °C in 32% yield. IR (KBr, ν cm⁻¹) 2980, 1605, 1403, 1350, 1178, 1112, 1003, 920, 840, 821. For ¹H NMR (200 MHz, DMSO-*d*₆) see Table 1. MS (EI, 70 eV, *m/z* (%)) 323 (M⁺, 100), 293 (45), 279 (17), 246 (11), 149 (15), 132 (9). UV–visible (CH₃CN, λ , nm ($\epsilon_{\max}$)) 236.5 (20,000), 277 (9000). Anal. calcd for $C_{18}H_{13}NOS_2$; C, 16.87%; H, 4.02%; N, 4.33%; S, 19.81%. Found. C, 16.91; H, 3.88; N, 4.56; S, 20.13.

Preparation of the *N*-methyl pyridinium salt 8. The thieno[2,3-*b*]thienophene **7** (50.0 mg) was dissolved in dry acetonitrile (2.0 ml) and freshly distilled CH₃I (0.35 ml) was added. The reaction mixture was kept at room temperature for 48 h whereby yellow crystals were deposited. The solvent was removed by decantation, the crystals washed with little cold acetonitrile and then dried over KOH under vacuum to give **8** in almost quantitative yield, mp 210–215 °C (dec). IR (KBr, ν cm⁻¹) 3007, 1600, 1433, 1378, 1330, 1176, 1121, 1020, 929, 843, 821. For ¹H NMR (200 MHz, DMSO-*d*₆) see Table 1. UV–visible (CH₃CN, λ , nm ($\epsilon_{\max}$)) 244 (42,000), 285 (11,000). Anal. calcd for $C_{19}H_{16}NOS_2I$; C, 49.03; H, 3.44; N, 3.01; S, 13.76; I, 27.31. Found. C, 49.34; H, 3.22; N, 2.87; S, 13.98; I, 27.66.

The crystal structure of 8. The crystal, a parallelepiped of approximate size 0.25 × 0.30 × 0.30 mm³ was used for characterization and data collection. Unit cell parameters and orientation matrix were determined from a least squares treatment of SET 4 setting angles of 22 reflections in the range 16.49 < θ < 21.84°. The structure was solved by Patterson methods using the DIRDIF program.

Table 1

¹H NMR spectral assignments for **7** and **8**

Type of protons	Chemical Shifts in δ		$\Delta\delta$
	7	8	
H(a)	7.52 (s, 1H)	7.64 (s, 1H)	0.12
H(b)	7.72 (s, 3H)	8.05 (s, 3H)	0.33
H(2')	8.27 (s, 1H)	8.67 (s, 1H)	0.40
H(4')	7.34 (d, 1H, $J = 8$ Hz)	8.22 (d, 1H, $J = 8$ Hz)	0.88
H(5')	7.08 (t, 1H, $J = 8$ Hz)	7.88 (t, 1H, $J = 8$ Hz)	0.80
H(6')	8.37 (d, 1H, $J = 5$ Hz)	8.82 (d, 1H, $J = 8$ Hz)	0.45
H(2)	6.63 (d, 1H, $J = 8$ Hz)	6.75 (d, 1H, $J = 8$ Hz)	0.12
H(3)	6.92 (d, 1H, $J = 8$ Hz)	7.00 (d, 1H, $J = 8$ Hz)	0.08
O–CH ₃	3.70 (s, 3H)	3.77 (s, 3H)	0.07
N–CH ₃	–	4.05 (s, 3H)	

3. Results and discussion

The synthetic strategy towards the target structures **7** and **8** (Scheme 1) entail as the key step the double Dieckman cyclization [7] on the oxo-ketene dithioacetals intermediate **4**. To start with, we prepared the known diketone **3** more conveniently by condensing *p*-methoxyacetophenone **1** with nicotinate ester **2** using NaH as the base instead of NaNH₂ reported in the Patent [8]. The condensation of **3** with CS₂ under anhydrous K₂CO₃/DMF conditions followed by treatment with two equivalents of ethyl bromoacetate provided ketene dithioacetal **4** as an oil. The treatment of **4** with sodium ethoxide in absolute alcohol led to a spontaneous cyclization to afford the desired thienothienophene diester **5** in 50% yield as a yellow crystalline solid, mp 115–118 °C. Base catalyzed hydrolysis of **5** (KOH in aq DMSO) afforded upon acidification diacid **6** in excellent yield. Finally, thermal decarboxylation of **6** followed by SiO₂ chromatographic purification of the crude gave the target thienothienophene **7** in 32% yield, mp 77–79 °C, M⁺ at *m/z* 323. To enhance the acceptor character of the pyridyl ring, the compound **7** was quaternized with CH₃I to obtain *N*-methyl pyridinium salt **8**. The latter was expected to exhibit c.t. interaction which could be evaluated in comparison to the neutral **7** as the reference standard.

3.1. Structural study: ¹H NMR and UV analysis of **7** and **8**

The presence of intramolecular c.t. interaction involving the overlap of the HOMO of the π -rich anisyl donor to

Scheme 1. Synthesis of thienothiophene **7** and its ionic salt **8**. Reagents and conditions: (i) NaH/DMF, 0 °C–RT, 6 h; (ii) CS₂/Anhyd.K₂CO₃, RT, 1 h, then 2eq BrCH₂CO₂C₂H₅, RT, 24 h; (iii) C₂H₅ONa/C₂H₅OH, 0 °C, 1 h; (iv) DMSO + aq KOH, 100 °C, 10 h; (v) Δ, 240–250 °C, 10 min, N₂ atm and (vi) CH₃I/CH₃CN, RT, 48 h.

the LUMO π -deficient pyridinium ring would be expected to diminish the electron density around the anisyl ring in the ionic compound **8** in comparison to the neutral **7**. The reduced electron density would reflect itself in the deshielding of the anisyl protons in **8** relative to that of the neutral **7**. Accordingly, the magnitude of $\Delta\delta$ (the deshielding coefficient) [9] could at least provide a qualitatively indication of the c.t. interaction in pyridinium salt **8**.

The ¹H NMR chemical shift assignments for **7** and **8** together with deshielding coefficient $\Delta\delta$ are summarized in Table 1. It can be seen that all the protons attached to the pyridinium ring in **8** are downfield shifted in the range from 0.40 to 0.88 δ relative to **7** so also the thienothiophene protons Ha and Hb experience downfield shift by 0.33 and 0.12 δ , respectively, with respect to the compound **7**. These downfield shifts are a direct consequence of the presence of the positively charged pyridinium ring in **8**. More importantly, in context to the c.t. interaction, H2 and H3 protons of anisyl group as well as the methoxyl protons in **8** also experience downfield shift, though by a small margin of only 0.08 and 0.12 δ , respectively. As stated above, these downfield shifts form the basis for evaluating the degree of c.t. interaction. Unfortunately, the magnitude of $\Delta\delta$ for the protons associated with the anisyl ring is rather small (0.08–0.12 δ) to indicate the presence of significant through-space c.t. in **8** relative to **7** [10].

The UV spectrum of compound **7** was found to exhibit a strong band at 236.5 nm ($\epsilon_{\max}$ 2.0×10^4) and a weak band at 277 nm ($\epsilon_{\max}$ 9×10^3) which tapers-off at 320 nm (Fig. 1). In comparison to **7**, in the case of corresponding ionic salt **8**,

the shorter wave length absorption band is slightly red shifted with marked enhancement in its intensity ($\lambda_{\max}$ 244 nm; $\epsilon_{\max}$ 4.2×10^4). Though, not well defined, there is also present a longer wavelength absorption in **8**, which is relatively broad and extends up to 370 nm. However, no new absorption band at longer wavelength arising out of the c.t. interaction between the donor anisyl ring and the acceptor pyridinium ring could be observed for **8**. Nevertheless, the presence of a broad band extending up to 370 nm in **8** could be indicative of a modest c.t. Earlier, we

Fig. 1. UV–visible spectra of **7** (plot I) and **8** (plot II) in CHCl₃.

reached similar conclusion on the basis of ^1H NMR spectral analysis.

3.2. X-ray crystal structural analysis of pyridinium salt **8**

In order to understand the underlying reasons for the weak through-space c.t. interaction in **8**, we carried out its single crystal X-ray analysis [11]. The ORTEP diagram of the X-ray structure of **8** is shown in Fig. 2. The crystallographic data are summarized in Table 2. Several interesting structural features become readily apparent from the X-ray structural analysis. The torsional angle ϕ , of the anisyl ring (involving C(4), C(3), C(7) and C(12)) is found to be 50.9° whereas for the pyridinium ring, the ϕ encompassing C(4), C(5), C(13) and C(14) is only 38.1° . The torsional angle, being a measure of deviation away from coplanarity, indicates the anisyl ring to be more out of plane than the pyridinium ring (50.9° vs 38.1°) with respect to the plane of thienothiophene framework. Consequently, there exists reasonably good possibility for appreciable through-bond overlap between the π -deficient pyridinium ring and the π -rich thienothiophene ring. Indeed, this energy stabilizing interaction could well be the driving force for the much reduced torsion between the pyridinium ring and thienothiophene ring compared to the torsion of the π rich anisyl ring.

Another important structural feature born out from the X-ray crystal structure of **8** is the shorter C–C bond distance between the thienothiophene and pyridinium rings

Fig. 2. ORTEP plot of the crystal structure of **8**. Selected (i) interatomic distances (Å): S(1)–C(1), 1.709; S(1)–C(6), 1.728; S(2)–C(1), 1.722; S(2)–C(2), 1.734; C(2)–C(3), 1.357; C(5)–C(6), 1.358; C(3)–C(7), 1.491; C(5)–C(13), 1.480; (ii) bond angles ($^\circ$): S(1)–C(1)–S(2), 133.8; C(4)–C(3)–C(7), 124.5; C(3)–C(4)–C(5), 137.2; C(4)–C(5)–C(13), 127.1 and (iii) torsion angle ($^\circ$): C(4)–C(3)–C(7)–C(12), -50.9 ; C(4)–C(5)–C(13)–C(14), -38.1 ; S(2)–C(1)–C(4)–C(5), 3.8 .

Table 2

Summary of crystallographic data and refinement details

Empirical formula	$[\text{C}_{19}\text{H}_{16}\text{NOS}_2]^+\cdot\text{I}^-$
Formula mass	465.38
Crystal color and habit	Yellow, block
Crystal size (nm^3)	$0.25 \times 0.30 \times 0.30$
Crystal system	Monoclinic
a (Å)	8.816(1)
b (Å)	14.411(1)
c (Å)	15.174(1)
β ($^\circ$)	106.685(7)
V (Å 3)	1846.7(3)
Z	4.0
ρ_{calcd} (g/cm^3)	1.674
$F(000)$	920
μ (cm^{-1})	0.71 (Mo K α)
$2\theta_{\text{max}}$ ($^\circ$)	55.0 ($I > 3.0\sigma$)
No. of reflections	4039
R_{int}	0.025
No. of parameters	341
R	0.043
R_w	0.094
GO F	1.312

(i.e. C(5)–C(13)) is 1.48 Å compared to that between anisyl and thienothiophene ring, C(3)–C(7) distance being 1.491 Å. The shorter C–C bond between the pyridinium ring and the thienothiophene ring further supports the existence of through-bond orbital overlap between these two rings. The bond angle C(4)–C(3)–C(7) between the anisyl and thienothiophene rings is found to be 124.5° whereas the bond angle C(4)–C(5)–C(13) between the pyridinium and the thienothiophene rings is 127.1° (the ideal sp^2 angle is 120°). Consequently, the anisyl and pyridinium rings are not parallel but tilted away from each other by an angle of 11.6° . In addition to this tilt, the van der Waals distance of 4.08 Å between the anisyl ring and the pyridinium ring is found to be much too large (for the cofacial 1,8-diaryl naphthalenes, the separation between aryl rings is 3.48 Å) [5] to allow for effective intramolecular c.t. to occur in **8**.

3.3. Energy minimization on model 3,4-diphenyl thieno[2,3-*b*]thiophene

In order to shed light on the conformational aspect of *peri* substituted thienothiophenes, we have also carried out energy minimization on a model system, namely 3,4-diphenyl thieno[2,3-*b*]thiophene (**9**) using PM3 Hamiltonian within the MOPAC 93 program [12]. The heat of formation ΔH_f in kcal/mol was calculated by keeping one phenyl ring stationary while rotating the other phenyl ring about the thienothiophene-phenyl bond in steps of 5° each. Fig. 3 shows the plot of change in ΔH_f with change in the torsional angle. The lowest energy structure (105.74 kcal/mol) corresponds to a dihedral angle of 85° (structure **9a**) which gives a near parallel orientation of the two aryl rings

Fig. 3. Energy minimization of model system, 3,4-diphenyl-thieno[2,3-*b*]thiophene.

on the thienothiophene framework. On other hand, the conformation **9b** having a dihedral angle of 190° (one phenyl ring perpendicular to the another) occupies the highest energy maximum, corresponding to ΔH_f of 110.46 kcal/mol. Interestingly, conformational energy is found to vary by no more than 1 kcal/mol on changing the torsion angle from 85° to 45° . Therefore, at least theoretically this result implies that minimum energy conformations of **9** with reduced torsion are possible, presumably to achieve balance between the conjugative tendency towards coplanarity and steric hindrance. In the light of this observation, it appears reasonable to assume that the tendency of the ionic **8** in comparison to the model system **9** to tend towards coplanarity would be even more pronounced to achieve direct π conjugation between the acceptor pyridinium and the donor thienothiophene rings.

Further, in view of relatively large interchromophoric distance (ca. 4.08 Å), couple with the reduced dihedral angle between the pyridinium and thienothiophene rings, the presence of rather weak through-space c.t. interaction in **8** is not entirely unexpected. In the case of 1,8-diphenyl naphthalene, House et al. [5] have calculated free energy of rotation of phenyl rings to be approximately 15 kcal/mol and the distance between the cofacial rings in this molecule in the lowest energy conformation to be 3.59 Å. Relatively, greater inter-ring separation of 4.08 Å in **8** compared to 3.59 Å for 1,8-diaryl naphthalenes together with low energy barrier (ca. 5 kcal/mol) between the lowest and the highest energy conformations **9a** and **9b** seem to suggest that the conformational ring rotation of

the *peri* substituents in thienothiophenes would be relatively less energy demanding [6] than reported for 1,8-diaryl naphthalenes.

4. Conclusion

In a quest to find molecular systems with a potential to show intramolecular c.t. interaction, we have successfully carried out the synthesis of novel donor acceptor thienothiophene **7** and its ionic analog **8**. However, the structural analysis by high resolution ^1H NMR and UV–visible absorption spectra reveal rather weak through bond c.t. interactions in **8**. An X-ray crystal structure of **8** reveals key structural features that work against appreciable through-space c.t. interaction. Conformational energy minimization carried out on a model system, 3,4-diphenyl thienothiophene indicated a low energy barrier to aryl ring rotation in *peri* substituted thienothiophene relative to analogous 1,8-diaryl naphthalenes. Work is currently in progress to study conformational behavior and to evaluate nonlinear optical properties of donor–acceptor thienothiophenes.

Acknowledgements

S.H.M. thanks CSIR, New Delhi, India for a generous research grants and for awarding junior research fellowship to M.A.

References

- [1] (a) R. Foster, Organic Charge Transfer Complexes, Academic Press, London, 1969.
 (b) J.M. Williams, J.R. Ferraro, Introduction to Synthetic Electrical Conductors, Academic Press, Orlando, FL, 1987.
 (c) M.R. Wasielewski, Chem. Rev., 435, 1992, pp. 92.
 (d) H.S. Nalwa, S. Miyata, Nonlinear Optics of Organic Molecules and Polymers, CRC Press, Boca Raton, 1997.
- [2] (a) J.M. Lehn, Supramolecular Chemistry, Concept and Perspective, VCH, New York, 1995.
 (b) P.R. Ashton, J.F. Stoddart, D.J. Williams, Angew. Chem. Int. Ed. Engl., 1550, 1988, pp. 27.
 (c) B. Dietrich, P. Viout, J.-M. Lehn, Macrocyclic Chemistry, VCH, Weinheim, 1995.
 (d) D.O.A. Dougherty, Science, 271, 1996, pp. 163.
 (e) N. Martin, P. Bando, K. Davidov, J.L. Segura, C. Seone, A. Gonzalez, J.M. Pingarron, Synth. Met., 1721, 1993, pp. 56.
 (f) J. Laxmikanth, K. Bhanuprakash, Ind. J. Chem., 114, 2000, pp. 39A.
 (g) G.R. Desiraju, Angew. Chem. Int. Ed. Engl., 1485, 1995, pp. 34.
 (h) J.F. Stoddart, S.A. Nepogodiev, Chem. Rev., 393, 1998, pp. 30.
- [3] F. Vogtle, Cyclophane Chemistry, Wiley, Chichester, 1993.
- [4] T. Nakazawa, I. Murata, J. Am. Chem. Soc. 1996 (1997) 99.
- [5] (a) H.O. House, D. Koepsell, W. Jaeger, J. Org. Chem. 1003 (1972) 37.
 (b) R.L. Clough, P. Mison, J.D. Roberts, J. Org. Chem. 2252 (1976) 41.
 (c) H.O. House, W.J. Campbell, M. Gall, J. Org. Chem. 1815 (1970) 35.
- [6] (a) R. Clough, J.D. Roberts, J. Am. Chem. Soc. 1018 (1976) 98.
 (b) J.A. Zoltewicz, N.M. Maier, W.M.F. Fabian, J. Org. Chem. 7018 (1996) 61.
- (c) A. Bahl, W. Grahn, S. Staddler, F. Feiner, G. Bourhill, C. Brauchle, A. Reisner, P.G. Jones, Angew. Chem. Int. Ed. Engl. 1485 (1995) 34.
- (d) N. Kaneta, F. Mitamura, M. Uemura, Y. Murata, K. Komatsu, Tetrahedron Lett. 5385 (1996) 37.
- (e) F. Cozzi, M. Cinquini, R. Annunziata, T. Dwyer, J.S. Siegel, J. Am. Chem. Soc. 5729 (1992) 114.
- (f) S. Cohen, M. Rabinovitz, J. Phys. Org. Chem. 435 (1993) 6.
- (g) S. Lavier, J.A. Zoltewich, J. Org. Chem. 7227 (2001) 66.
- [7] (a) S.H. Mashraqui, H. Hariharasubramanian, Synth. Commun. 1695 (2000) 30.
 (b) S.H. Mashraqui, H. Hariharasubramanian, S. Kumar, Synthesis (1999) 2030.
 (c) A.M.M. El-Saghier, Bull. Chem. Soc. Jpn 2011 (1993) 66.
- [8] H. Eberhardt, R. Albert, Ger. Offen., 2,105,672 (CA, 77, P151957h).
- [9] B.J. Whitlock, W.H. Whitlock Jr., J. Am. Chem. Soc. 838 (1983) 105.
- [10] In contrast, for stacked cyclophanes and 1,8-diaryl naphthalenes, the shielding effects on account of charge transfer interactions range from 0.50 to 1.5 δ or more. For examples, see P.M. Keehn, S.M. Rosenfeld, Cyclophanes, vol. I, Academic Press, New York, 1983, and Ref. [2].
- [11] X-Crystallographic data for **8** have been deposited with the Cambridge Data base (Deposited Data-CCDC 191022).
- [12] The MOPAC 93 program (Fujista Ltd) was used for the energy minimization. The visualization was done using the Spartan v 4.0 (Wavefunction Inc.) on a Silicon Graphics Indigo computer running the Irix v 5.3 OS as well as CS Chem3D Pro (Cambridge Soft Corp.) on a Macintosh Performa 636 CD computer.