Distorted electron acceptors: an unexpected reaction involving tetramethyl-TCNQ

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Reactions involving the donors N-methyl-2-methylbenzothiazolium – and N-(1-propyl)-2-methylbenzothiazolium iodide with the acceptor 2,3,5,6-tetramethyl-7,7,8,8-tetracyano-p-quinodimethane (TMTCNQ) in the presence of a suitable base lead to the isolation of novel [(Z)-β-(N-alkylbenzothiazol-3-ium-2-yl)-α-cyano-2,3,5,6-tetramethyl-4-styryl]dicyanomethanide chromophores. Under prolonged reaction periods, these first examples of charge transfer compounds incorporating the distorted TMTCNQ electron acceptor, undergo further reaction at the acrylonitrile functionality promoting the synthesis of novel thiomorpholine-based charge transfer compounds via a sulfur mediated cyclisation reaction. This second reaction illustrates a fundamentally new type of TCNQ-based chemistry as confirmed by X-ray crystallography and high-resolution mass spectrometry. A possible reaction mechanism for the formation of the thiomorpholine-based chromophores is considered.
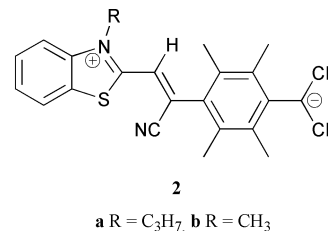
Introduction

The covalent linkage of π-donors to π-acceptors such as 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) through a conjugated π-bridge offers considerable potential for studying intramolecular charge-transfer processes in D-π-A molecules.[1] Systems of this general type are central to studies on chromophores for dyes, non-linear optics and theoretical aspects of charge conduction at the molecular level.[1] The {(Z)-β-[N-(1-hexadecyl)quinolinium-4-yl]-α-cyano-4-styryl}dicyanomethanide C$_{16}$H$_{33}$(4)Q3CNQ **1** zwitterion, produced by the reaction of N-(1-hexadecyl)quinolinium bromide and 7,7,8,8-tetracyano-p-quinodimethane for example, has stimulated a plethora of interest due to its multifunctional properties.[2-8] TCNQ is one of the most attractive electron acceptor molecules and the design and synthesis of TCNQ and DCNQI type electron acceptor molecules as precursors for organic metals have recently been reviewed.[9] Their derivatives have interest and, despite extensive research being carried out in the field of TCNQ-based D-π-A systems,[2-10] very little work has been undertaken utilising functionalised TCNQ acceptors such as the distorted TMTCNQ.[10]

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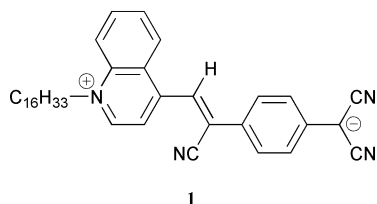
Although TMTCNQ is a relatively weak electron acceptor[11] the introduction of such functionality into the backbone of D-π-A compounds has been shown to markedly affect both their physical and optical properties[5] by altering the degree of charge separation between the donor and acceptor moieties and thus enabling fine tuning of the material's molecular properties for commercial applications.

The synthesis of the {(Z)-β-[N(1-propyl)benzothiazol-3-ium-2-yl]-α-cyano-2,3,5,6-tetramethyl-4-styryl}dicyanomethanide C$_3$H$_7$(2)BT3CNTMQ **2a** zwitterion was attempted as part of a series of studies on π-bridged donor-acceptor molecules of general formula [D$^+$–CH=C(CN)–C$_6$H$_4$–C(CN)$_2$$^-$].[2-5] Reactions between N-alkylated aromatic heterocycles and TCNQ, in the presence of a suitable base, normally yield D-π-A compounds of type **1**.[5,10] Nevertheless, in trying to obtain **2a**, the reaction of equimolar quantities of N-(1-propyl)-2-methylbenzothiazolium iodide with TMTCNQ and piperidine in acetonitrile was found to yield a mixture of C$_3$H$_7$(2)BT3-CNTMQ **2a** and a new chromophore **3**. In this paper we report the one pot preparation of TMTCNQ-based D-π-A analogues of **2** and discuss the subsequent reaction involved in converting **2** to **3** under similar reaction conditions. X-Ray crystallography of the N-methyl analogue of **3** (**3b**) confirms this new TCNQ-based chromophore and a plausible reaction mechanism demonstrates its formation, illustrating a fundamentally new type of reaction undergone by TCNQ-analogues.

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a R = C$_3$H$_7$, **b** R = CH$_3$

Results and discussion

Our targets were analogues of the prototype molecule **2** for which TCNQ and TCNQF$_4$ derivatives have been previously demonstrated.[5] Introduction of a methyl group into the core structure had been predicted to shift the UV–Vis absorption band bathochromically to longer wavelengths, creating a more efficient NLO response compared to other TCNQ-based chromophores.[5,10]

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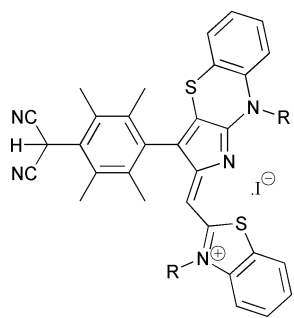
a R = C₃H₇, **b** R = CH₃

a R = C$_3$H$_7$, b R = CH$_3$

Compound **2a** was obtained by reaction of *N*-(1-propyl)-2-methylbenzothiazolium iodide with 2,3,5,6-tetramethyl-7,7,8,8-tetracyano-*p*-quinodimethane (TMTCNQ), in the presence of piperidine, in acetonitrile. The yield obtained after three hours reflux was a disappointing 8%, so as a consequence the reaction time was increased in an attempt to increase substantially the yield, as has been demonstrated[4] for related α-substituted quinolinium adducts of **1**. However, in our case, an increase in reaction time resulted in a loss of yield for **2** (typically down to 3–4%). Further investigations showed that during prolonged reaction periods the reaction conditions facilitate further substitution at the acrylonitrile functionality of **2** resulting in the formation of a new chromophore **3** at the expense of **2**. Subsequent isolation of **3a** by column chromatography and recrystallisation yielded the new chromophore as a red powder. The yield of **3** can be significantly increased when the reagents are allowed to react in a 2 : 1 ratio. Likewise the yield of **2** can be maximised by using a short reaction time (*ca.* 3 hours or less) and a 1 : 1 ratio of reagents. As we were unable to obtain suitable crystals of the *N*-(1-propyl) analogue **3a** for X-ray analysis the *N*-methyl analogue **3b** was synthesised by the reaction of *N*-methyl-2-methylbenzothiazolium iodide with 2,3,5,6-tetramethyl-7,7,8,8-tetracyano-*p*-quinodimethane (TMTCNQ) in a 2 : 1 molar ratio, in the presence of *N*-methylpiperidine, in acetonitrile. After refluxing for 4 days **3b** was isolated in an 8.4% yield. Slow growth of crystals from a dichloromethane solution led to the isolation of deep red plates of **3b**. The structure of **3b** (Fig. 1) clearly illustrates that substitution at the acrylonitrile functionality of the intermediate CH₃(2)BT3-CNTMQ **2b** has occurred. Investigations by ultra-violet–visible
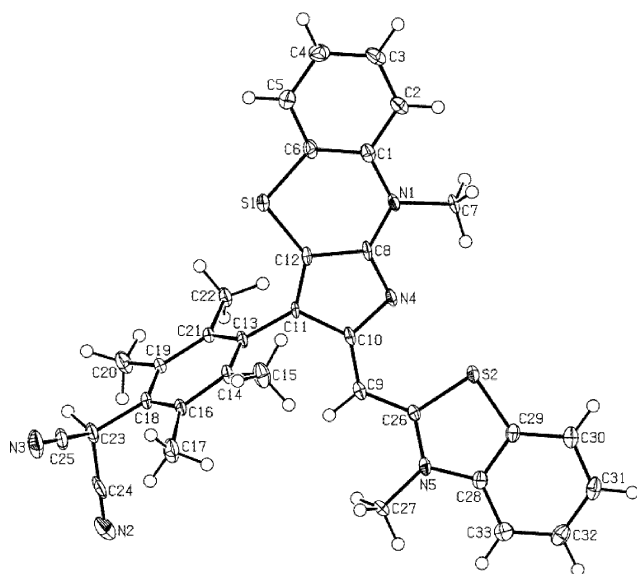

Fig. 1 Solid state structure of 2-(4-{2-[(*Z*)-3-methyl-1,3-benzothiazol-3-ium-2-yl)methylidene]-9-methyl-2,9-dihydropyrrolo[3,2-*b*][1,4]benzo-thiazin-3-yl}-2,3,5,6-tetramethylphenyl)malononitrile iodide (**3b**).

(UV–Vis) spectroscopy and thin layer chromatography (TLC) have confirmed that **3a** and **3b** are formed from the intermediates **2a** or **b**, *i.e.* UV–Vis and TLC experiments have demonstrated that **3** [90 : 10 DCM–CH₃OH, R_f = 0.56, (CH₃CN): λ_{max} = 520, 544(CT) nm for **3a**] is only formed once **2** [90 : 10 DCM–CH₃OH, R_f = 0.44, (CH₃CN): λ_{max} = 594(CT) nm for **2a**] is available in solution.

This new type of chromophore is unique in that it is only formed when the TMTCNQ acceptor is used. Reactions utilising other electron acceptors, such as TCNQ or TCNQF₄, only yield compounds of type **2**.[5] A plausible mechanism for the formation of **3** is illustrated in Fig. 2. The distorted nature of
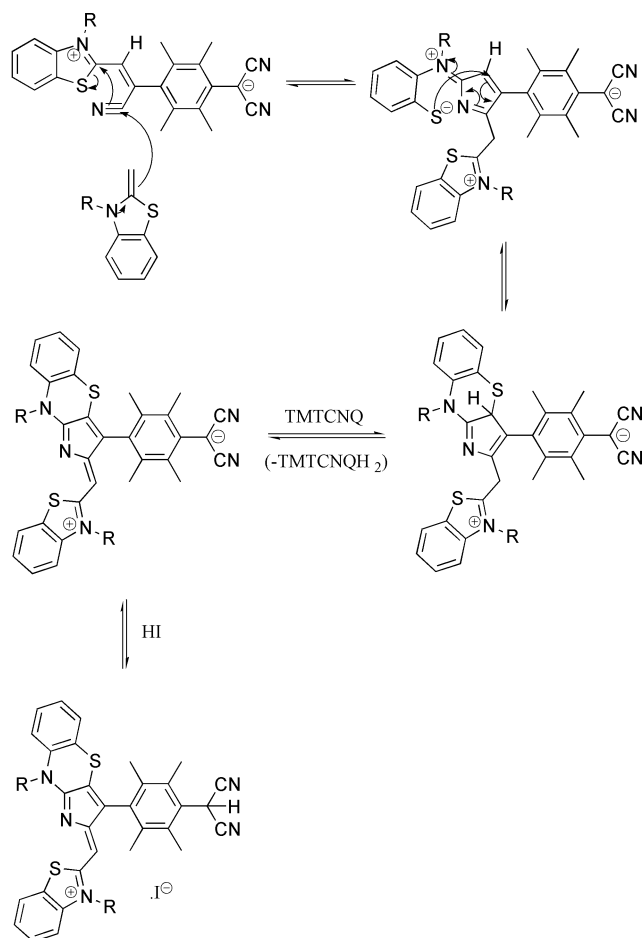

Fig. 2 Synthesis of 2-(4-{2-[(*Z*)-3-alkyl-1,3-benzothiazol-3-ium-2-yl)methylidene]-9-alkyl-2,9-dihydropyrrolo[3,2-*b*][1,4]benzothiazin-3-yl}-2,3,5,6-tetramethylphenyl)malononitrile iodide **3** from {(*Z*)-β-[*N*-(1-propyl)benzothiazol-3-ium-2-yl]-α-cyano-2,3,5,6-tetramethyl-4-styryl}dicyanomethanide.

the TMTCNQ acceptor, allows further nucleophilic attack at the acrylonitrile backbone to occur forming a new pyrrole-based heterocycle. A sulfur mediated ring expansion[12] then affords the thiomorpholine system through intramolecular rearrangement. Compound **3** is finally afforded *via* a TMTCNQ-based re-aromatisation reaction in which hydride abstraction affords the new π-bridge between C9–C26 further increasing the conjugation within the chromophore. The final feature of this unique reaction is the protonation of the dicyanomethanide swallowtail by the presence of HI yielding an iodide salt. Such an observation is unusual in TCNQ-based zwitter-ions, as the intramolecular charge-transfer pathway is removed.

X-Ray crystallography

The single crystal X-ray structure of **3b** (Fig. 1) is comprised of two essentially planar moieties (the planarity is only broken by the swallowtail cyano groups and some hydrogen atoms)

orientated at a dihedral angle of 69.48(13)° with respect to each other. The geometry of the molecule is otherwise unremarkable. The supramolecular assembly formed by intermolecular interactions is that of two interwoven planes of sheets that both pack parallel to the thiomorpholine moiety of the molecule. These sheets interact with each other through 'out of plane' cyano and methyl groups to form the parallel sheet structure (Donor ⋯ Acceptor distances: C5–H5 ⋯ N2 = 2.552(6) Å and C7–H7 ⋯ C28/C33 ring centroid = 3.043(6) Å). Two discrete sheet structures then interweave with each other by means of an interaction to a thiomorpholine ring centroid (C31–H31 ⋯ S1 ring centroid = 3.162(5) Å). The crystal structure is then completed by binding the I⁻ anion and dichloromethane solvent (C01–H01B ⋯ N2 = 3.282(6) Å, C23–H23 ⋯ I1 = 3.653(5) Å and C27–H27C ⋯ Cl2 = 3.549(6) Å).

Conclusion

The use of TMTCNQ as an electron acceptor in reactions involving *N*-alkylated heterocycles, in the presence of a suitable base, not only yields the normal D-π-A compounds of type **2** but due to the steric nature of the acceptor molecule enables further reaction to occur at the acrylonitrile functionality of **2**, thereby producing a new type of TCNQ-based chromophore **3** whose structure has been confirmed crystallographically.

Experimental

General

All melting points are uncorrected. IR spectra were recorded on an ATI Mattson Genesis series FTIR instrument in the range 4000 cm⁻¹ to 500 cm⁻¹ and are for KBr discs. UV–Vis spectra were recorded using a Hitachi U-2000 Spectrophotometer in the range 210–1100 nm, using a 1 cm path length quartz cell. ^{1}H spectra were recorded using a Bruker AC400 NMR spectrometer. Coupling constant (J) values where illustrated are given in Hertz (Hz). Mass spectra were recorded using a VG Micromass 7070F mass spectrometer using EI/FAB modes of ionisation. FAB-HRMS mass spectra and elemental analysis were obtained courtesy of the Analytical Services at the University of Sheffield. *N*-Methyl-2-methylbenzothiazolium iodide was prepared by the standard literature method.[13] *N*-(1-Propyl)-2-methylbenzothiazolium iodide was obtained commercially from Sigma-Aldrich. 2,3,5,6-Tetramethyl-7,7,8,8-tetracyano-*p*-quinodimethane (TMTCNQ) was prepared by the standard literature method.[11]

{(*Z*)-β-[*N*-(1-Propyl)benzothiazol-3-ium-2-yl]-α-cyano-2,3,5,6-tetramethyl-4-styryl}dicyanomethanide C₃H₇(2)BT3CNTMQ (2a)

N-(1-Propyl)benzothiazolium iodide (0.29 g, 0.94 mmol) was refluxed with piperidine (0.08 g, 0.94 mmol) in acetonitrile (30 cm³) for twenty minutes and cooled. 2,3,5,6-Tetramethyl-7,7,8,8-tetracyano-*p*-quinodimethane (0.25 g, 0.94 mmol) was added and the mixture refluxed for three hours. After cooling at 0 °C for 24 hours the resulting yellow–brown powder was filtered off, washed with diethyl ether (3 × 25 cm³) and purified by column chromatography (90 : 10 dichloromethane–methanol, R_f = 0.44) to yield 0.040 g (10%) of a canary yellow powder (mp >300 °C). IR (KBr): 3447 (O–H str), 2960, 2930, 2873 (C–H str), 2157, 2099 (C≡N str), 1564 (C=C str), 1508 (Ar C=C str) cm⁻¹; ^{1}H NMR (d₆-DMSO): δ = 1.1 (t, 3H, CH₃–R, *J* = 12.5), 1.9 (m, 2H, R–CH₂), 2.3 (s, 12H, 4CH₃), 5.0 (t, 2H, CH₂N⁺, *J* = 12.5), 7.9 (t, 1H, Ar–H, *J* = 5), 8.0 (t, 1H, Ar–H, *J* = 5), 8.4 (d, 1H, Ar–H, *J* = 5), 8.55 (d, 1H, Ar–H, *J* = 5), 8.95 (s, 1H, π-bridge-H); MS (70 eV): *m/z* = 424 (6%, M⁺), 382 (84%, M⁺ − CH₂CN), 367 (22%, M⁺ − CH₃CN–CH₃), 318 [9%, M⁺ − R–C(CN)₂], 43 (100%, CH₃CN); UV–Vis (CH₃CN):

λ_{max} = 594(CT) nm (found: C, 71.3; H, 5.62; N, 12.21%. C₂₆H₂₄N₄S·CH₃OH requires C, 71.03; H, 6.18; N, 12.27%).

2-(4-{2-[(*Z*)-3-Propyl-1,3-benzothiazol-3-ium-2-yl)methylidene]-9-propyl-2,9-dihydropyrrolo[3,2-*b*][1,4]benzothiazin-3-yl}-2,3,5,6-tetramethylphenyl)malononitrile iodide (3a)

N-(1-Propyl)-2-methylbenzothiazolium iodide (0.29 g, 0.94 mmol) was refluxed with piperidine (0.08 g, 0.94 mmol) in acetonitrile (30 cm³) for twenty minutes and cooled. 2,3,5,6-Tetramethyl-7,7,8,8-tetracyano-*p*-quinodimethane (0.25 g, 0.94 mmol) was added and the mixture refluxed for 6 hours. After cooling at 0 °C for 24 hours the resulting red powder was filtered off, washed with diethyl ether (3 × 25 cm³) and purified by column chromatography (90 : 10 dichloromethane–methanol, R_f = 0.56) followed by recrystallisation from acetonitrile–diethyl ether to yield 0.050 g (8.4%) of a brick red powder (mp >300 °C). IR (KBr): 2923, 2869 (C–H str), 2151, 2089 (C≡N str), 1671, 1563 (C=C str), 1506 (Ar C=C str) cm⁻¹; ^{1}H NMR (d₆-DMSO): δ = 0.80 (t, 3H, CH₃–R–N), 1.20 (t, 3H, CH₃–R–N⁺), 1.80 (m, 2H, R–CH₂–NCH₂–N), 2.05 (m, 2H, R–CH₂–CH₂–N⁺), 2.10 (s, 6H, 2CH₃–Ar), 2.35 (s, 6H, 2CH₃–Ar), 3.40 [s, 1H, CH(CN)₂], 4.60 (t, 2H, R–CH₂–N), 4.90 (t, 2H, R–CH₂–N⁺), 6.30 (s, 1H, Alkene–H), 7.35–8.40 (m, 8H, Ar–H); MS (FAB): *m/z* = 614 (100%, M⁺ + H), 572 (6%, M⁺ − R), 507 [5%, M⁺ − R–C(CN)₂]; UV–Vis (CH₃CN): λ_{max} = 520, 544(CT) nm; FAB-HRMS, *m/z* calcd. For [(3a) + H⁺ − I⁻ − CH₂Cl₂]: 614.241215. (Found: 614.242632; found: C, 58.99; H, 4.97; N, 9.16%. C₃₇H₃₆N₅S₂I requires C, 59.9; H, 4.89; N, 9.44%).

2-(4-{2-[(*Z*)-3-Methyl-1,3-benzothiazol-3-ium-2-yl)methylidene]-9-methyl-2,9-dihydropyrrolo[3,2-*b*][1,4]benzothiazin-3-yl}-2,3,5,6-tetramethylphenyl)malononitrile iodide (3b)

N,2-Dimethylbenzothiazolium iodide (2.25 g, 7.73 mmol) was refluxed with *N*-methylpiperidine (0.38 g, 3.87 mmol) in acetonitrile (125 cm³) for twenty minutes and cooled. 2,3,5,6-Tetramethyl-7,7,8,8-tetracyano-*p*-quinodimethane (1.00 g, 3.87 mmol) was added and the mixture refluxed for 4 days. After cooling at 0 °C for 24 hours the resulting red powder was filtered off and purified by column chromatography (90 : 10 dichloromethane–methanol, R_f = 0.58) to yield 0.222 g (8.4%) of red plates (mp 198–200 °C). IR (KBr): 3019 (Ar C–H str), 2975, 2944 (C–H str), 2158, 2092 (C≡N str), 1528 (C=C str), 1479 (Ar C=C str) and 1216 (C–S str) cm⁻¹; ^{1}H NMR (d₁-CDCl₃): δ = 2.18 (s, 6H, 2CH₃–Ar), 2.58 (s, 6H, 2CH₃–Ar), 3.85 [s, 1H, CH(CN)₂], 4.25 (s, 3H, CH₃–N), 4.49 (s, 3H, CH₃ − N⁺), 6.19 (s, 1H, Alkene-H), 7.2–8.38 (m, 8H, Ar–H); UV–Vis (CH₃CN): λ_{max} = 512, 548(CT) nm; FAB-HRMS, *m/z* calcd. For [(3b) + H⁺ − I⁻ − CH₂Cl₂]: 559.185863, found: 559.186440 (found: C, 56.72; H, 4.6; N, 9.79%. C₃₃H₂₈N₅S₂I requires C, 57.80; H, 4.11; N, 10.21%).

X-Ray crystallography †

A suitable crystal was selected and data collected on a Nonius KappaCCD area detector at the window of a Nonius FR591 rotating anode ($\lambda_{Mo-K\alpha}$ = 0.71073 Å). The structure was solved and refined using the SHELX[14] suite of programs. Hydrogen atoms were placed in idealised positions and their parameters tied to the values of the parent atom. Crystal data: C₃₃H₂₈N₅S₂·I·CH₂Cl₂, Mr = 770.55, T = 100(2) K, monoclinic, space group $P2_1/n$, a = 7.9977(16), b = 14.986(3), c = 27.776(12) Å, β = 95.75(3)°, V = 3312.3(12) Å³, ρ_{calc} = 1.545 g cm⁻³, μ = 1.287 mm⁻¹, Z = 4, reflections collected: 32635, independent reflections: 7272 (R_{int} = 0.0877), final R indices [$I > 2\sigma I$]: R1 = 0.0538, wR2 = 0.1419, R indices (all data): R1 = 0.0734. wR2 = 0.1526.

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