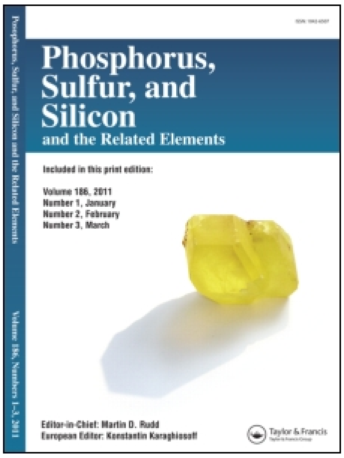

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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE ASYMMETRIC DITHIADIAZENE $BrC_6F_4NSNSC_6H_4NO_2$

Joanna Griffiths[a]; Jeremy M. Rawson[a]
[a] University of Cambridge, Cambridge, United Kingdom

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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE ASYMMETRIC DITHIADIAZENE $BrC_6F_4NSNSC_6H_4NO_2$

Joanna Griffiths and Jeremy M. Rawson
University of Cambridge, Cambridge, United Kingdom

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The asymmetric dithiadiazene $BrC_6F_4NSNSC_6H_4NO_2$ crystallizes in the space group P*-1 and exhibits a 1D polar chain structure linked via structure-directing $Br\cdots O_2N$ synthons.*

Keywords: Crystal engineering; dithiadiazene; fluorination; supramolecular synthons

The design of polar and noncentrosymmetric crystal structures for nonlinear optical (NLO) applications relies on rational crystal engineering strategies to produce materials with desirable properties. Two key features are necessary for SHG (second harmonic generation); firstly a strong molecular hyperpolarisability which is usually afforded by a polar molecule with donor and acceptor groups linked via a π-conjugated spacer group,[1] secondly, these molecules must crystallise in noncentrosymmetric space groups.[2] Our design strategy has focussed on the use of perfluorinated donor (D)—acceptor (A) substituted aromatics, specifically compounds of general formula DC_6F_4A. Results on these single ring systems[3] have shown that the formation of polar chains can be encouraged by the selection of donor and acceptor groups which are well-recognized as forming linear motifs in the solid-state (supramolecular synthons). Perfluorination tends to minimize interactions between these polar chains and so favor the formation of polar acentric structures.[4] As an extension of this work, we have begun an examination of thiazyl chains as π-delocalized spacer groups between donor-acceptor substituted perfluorinated aromatic rings. The extended delocalization is expected to enhance the molecular NLO response.

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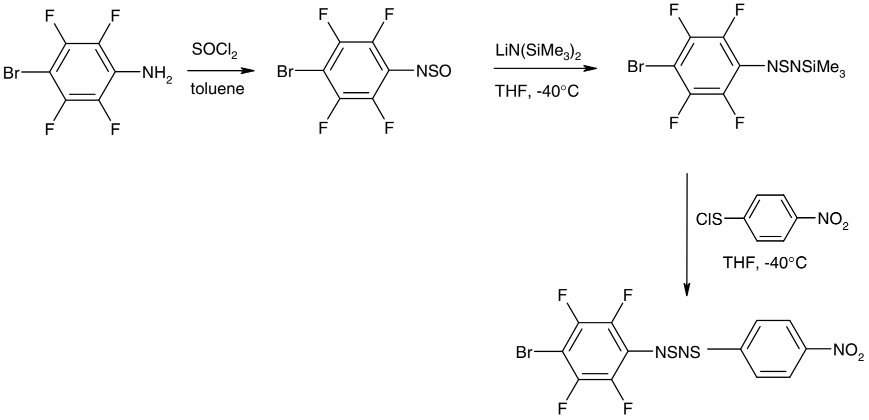
Address correspondence to J. M. Rawson, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK. E-mail: jmr31@cus.cam.ac.uk

RESULTS AND DISCUSSION

Synthetic routes to asymmetric dithiadiazenes are not well documented. Syntheses involving chain-scrambling of symmetrically substituted thiazyl chains have been used with some success,[5] although these reactions have a tendency to be uncontrollable and give a mixture of products. Conversely, a single report indicated that condensation reactions between sulfenyl chlorides (RSCl) and trimethylsilyl protected sulfur diimides can be used to produce asymmetric dithiadiazenes.[5] The methodology detailed in Scheme 1 represents a clean stepwise synthesis of the target compound, $BrC_6F_4NSNSC_6H_4NO_2$ (**1**) in reasonable yield, and has been applied to prepare several other similar compounds in this laboratory.



SCHEME 1 Synthesis of **1**.

Red needle-like crystals of **1** suitable for x-ray diffraction studies were grown from a concentrated THF solution at 4°C. The asymmetric unit contains a single molecule, which is essentially planar. Within the structure, molecules are linked into polar chains by $Br\cdots O_2N$ synthons ($d_{Br\cdots O}$ = 3.118 Å, compared to the sum of the van der Waals radii 3.08–3.38 Å). Hydrogen bonding between a nitro group in one chain and aromatic protons in an adjacent chain ($d_{C-H\cdots O}$ = 2.509 Å, 146.8°) results in the antiparallel chain alignment seen in Figure 1.

Successive layers also align antiparallel, with short $S\cdots N$ contacts between layers ($d_{S\cdots N}$ = 3.411 Å, compared to the sum of the van der Waals radii 3.20–3.63 Å) being reinforced by $\pi_F\cdots\pi_H$ stacking.

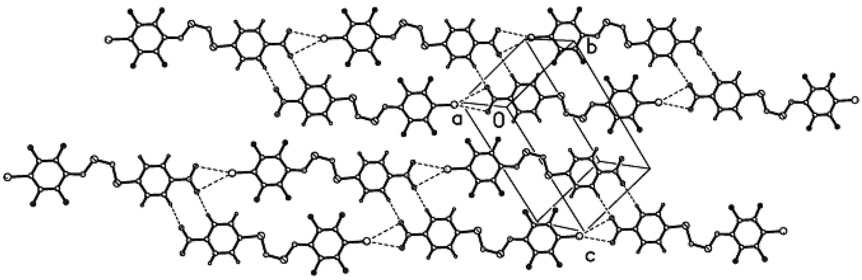


FIGURE 1 Single layer illustrating antiparallel chains in **1**.

CONCLUSIONS

Whilst the formation of one-dimensional polar chains is encouraged through the use of the structure-directing $Br\cdots O_2N$ synthon, interactions between polar chains generate a centric structure which is therefore NLO inactive. Key intermolecular interactions promoting the centric structure are $\pi_F\cdots\pi_H$ and C—H···O interactions. Current attempts to synthesize perfluorinated derivatives in which these features are absent are underway.

EXPERIMENTAL

Crystal data for **1**: $C_{12}H_4BrF_4N_3O_2S_2$, $M = 442.21$, triclinic, space group P-1, $a = 7.5372(15)$, $b = 7.9664(16)$, $c = 13.805(3)$ $\alpha = 103.79(3)$, $\beta = 90.42(3)$, $\gamma = 114.63(3)$, $U = 726.4(3)$ Å^3, $T = 180(2)$K, $Z = 2$, D = 2.022 Mg/m^3. Of 8474 reflections measured, 3315 were unique (R(int) = 0.0435) and were used in all calculations. The final $wR2 =$ 0.0794 (all data), $R1$ [$F^2 > 2\sigma(F^2)$] = 0.0326. CCDC ******

Preparation of $BrC_6F_4NSNSC_6H_4NO_2$

$SOCl_2$ (1.8 ml, 2.716 g, 22.8 mmol) in toluene (20 ml) was added dropwise to a rapidly stirred solution of p-$BrC_6F_4NH_2$ (5.56 g, 22.8 mmol) in toluene (20 ml) to yield a yellow precipitate. The suspension was heated to reflux for 5 h then solvents were removed in vacuo to yield p-BrC_6F_4NSO as a yellow crystalline solid which was used without further purification. A solution of p-BrC_6F_4NSO (2.90 g, 10 mmol) in THF (20 ml) was added dropwise to a stirred solution of $LiN(SiMe_3)_2$ (1.67 g, 10 mmol) in THF (20 ml) at −40°C to form a deep red solution. After stirring for 1 h, the reaction mixture was allowed to warm to 0°C and stirred for a further 1 h. After cooling again to −40°C, a solution of p-$O_2NC_6H_4SCl$ (1.85 g, 10 mmol) in THF (20 ml) was added dropwise to the stirred reaction mixture to give a red/brown precipitate. After warming to room temperature and stirring for a further 16 h, the reaction mixture was filtered to remove insoluble impurities. The solvents were removed from the filtrate in vacuo to give the **1** as a red/brown solid (1.24 g, 27.9%). Anal. Calc. for $C_{12}H_4F_4O_2BrN$: C 32.6, H 0.9, N 9.5. Found: C 32.4, H 0.9, N 9.5. EI-MS: 442.9, 440.9 (M+). UV-vis ($CHCl_3$): 457.9 nm, $\varepsilon = 7.4 \times 10^4$ mol dm^{-3} cm^{-1}.

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