

## Photomechanical Actuation and Manipulation of the Electronic Properties of Linear $\pi$ -Conjugated Systems

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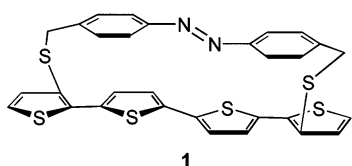
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Dynamic molecular devices capable of converting thermal, chemical, or photochemical energy into motion are a focus of considerable current interest, and a wide range of systems producing longitudinal or rotational motion have recently been reported.<sup>1</sup> Although bulk electrochemical actuators based on volume changes associated with the redox process of conjugated polymers have been extensively investigated,<sup>2</sup> attempts to synthesize molecular  $\pi$ -conjugated dynamic structures remain scarce. A first step in that direction was recently reported by Marsella et al., who investigated tetra[2,3-thienylene] as a basic unit for molecular actuation.<sup>3</sup>

We now report that the covalent fixation of a photostimulable group on two fixed points of an oligothiophene chain allows one to produce conformational changes and thus reversible modifications of the electronic properties of the  $\pi$ -conjugated system.

As the photoactive driving group, we used the azobenzene chromophore which can be reversibly switched between an extended *trans* and a shorter *cis* configuration.<sup>4</sup>



The target compound **1** was synthesized by reacting the deprotected thiolate groups of bis-cyanoethylsulfanyl quaterthiophene<sup>5</sup> with bis-*p*-bromomethylazobenzene.<sup>6</sup>

The structure of **1** was modeled by theoretical calculations based on the density functional method.<sup>7</sup> Becke's three parameter gradient corrected functional (B3lyp) with a polarized 6-31G\* basis for all atoms was used to optimize the geometry and to compute the electronic structure at the minima found. The geometries of the two conformations of **1** and that of models of its two constitutive parts, that is, 3,3''-dimethylsulfanyl-quaterthiophene (**Me4T**) and *para*-dimethyl-azobenzene (**MeAz**), were analyzed independently. Examination of the various minimal energy conformations of **Me4T** shows that the distance (*d*) between the two sulfur atoms serving as anchoring points for the azo group decreases from 12.1 Å for the *syn*-*anti*-*syn* conformation (*SAS*) to 10.8 (*AAA*), 10.7 (*SSA*), 10.3 (*AAS*), and 7.5 Å (*ASA*). Comparison of these data with the distances between the two methyl groups of *trans* and *cis* **MeAz** (12.1 and 8.6 Å) shows that the *SAS* and *ASA* conformations are the best fit for the *trans* and *cis* azo group, respectively.

The optimized geometry of **1** shows that with the *trans* azo group, the 4T chain adopts a *SAS* conformation with *d* = 12.1 Å (Figure 1). *Trans* to *cis* isomerization of the azo group induces a *SAS* to

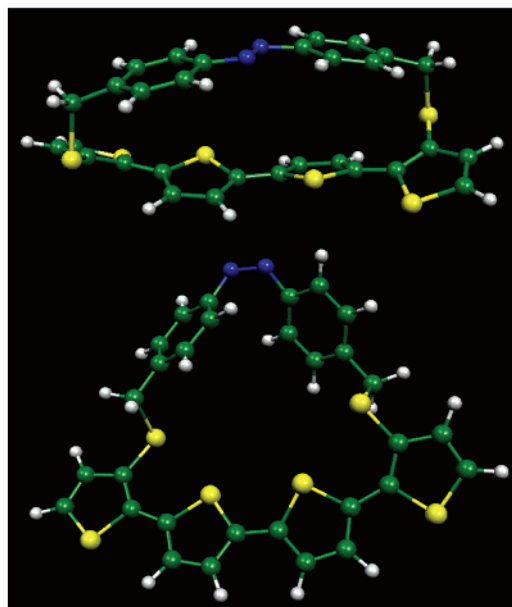


Figure 1. Optimized geometries for compound **1**. Top, 1-*SAS-t*; bottom, 1-*ASA-c*.

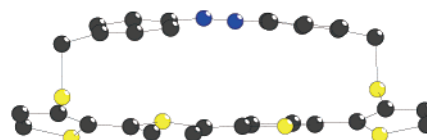


Figure 2. Crystallographic structure of **1** (hydrogens omitted).

*ASA* conformational transition of the 4T chain which reduces *d* to 7.5 Å. Calculations show that the *trans*-azo-*SAS* form (1-*SAS-t*) is more stable than its isomer containing *cis*-azobenzene (1-*ASA-c*) by 52.6 kJ/mol, while the *SAS* to *ASA* transition raises the HOMO level from -5.10 to -5.02 eV and decreases the HOMO-LUMO gap from 3.24 to 3.03 eV.<sup>8</sup>

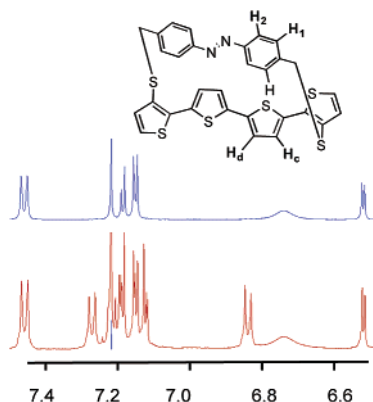
Figure 2 shows the X-ray structure of a single crystal of **1**. The 4T and azo systems are quasi-planar and parallel, the 4T chain presents the expected *SAS* conformation, and the 12.3 Å *d* value is in excellent agreement with the theoretically predicted one (12.1 Å).

Figure 3 shows the aromatic region of the <sup>1</sup>H NMR spectrum of compound **1** in CDCl<sub>3</sub> before and after irradiation with 360 nm monochromatic light.<sup>9</sup> The initial spectrum exhibits two anomalously shielded signals: a broadened singlet at 6.79 ppm assigned to the four benzenic protons at the *ortho* positions of the methylene group of azobenzene (H<sub>1</sub>) and a doublet at 6.58 ppm corresponding to the two hydrogens at the 4' and 3'' positions of the median thiophenes (H<sub>d</sub>).

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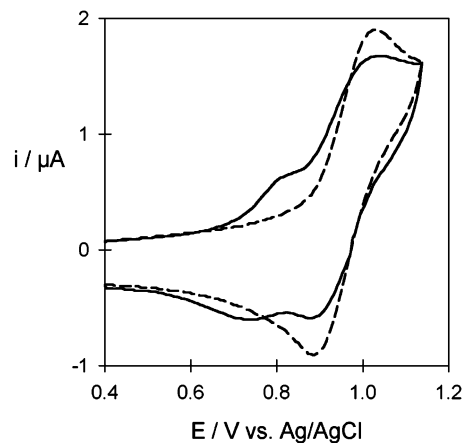
**Figure 3.** Aromatic region of the  $^1\text{H}$  NMR spectrum of compound **1** ( $9 \times 10^{-4}$  M) in  $\text{CDCl}_3$ . Before (top) and after 5 h of irradiation at 360 nm (bottom).

The unusual upfield chemical shifts of these hydrogens are due to their location in the shielding cone of their respective facing thiophenic or benzenic system. The spectrum recorded after irradiation at 360 nm shows new signals associated with the new geometry of the molecule. The chemical shifts of  $\text{H}_1$  and  $\text{H}_d$  protons have been followed by 2D dipole–dipole interactions proton correlation analysis (NOESY). Thus, the broad singlet of the four  $\text{H}_1$  protons at 6.79 ppm becomes a doublet at 7.32 ppm, while the doublet of the  $\text{H}_d$  protons shifts from 6.58 to 7.20 ppm.

The downfield shift of these protons reflects their exit from the shielding cone of the opposite aromatic cycle due to the changes in the geometry of the azo and 4T systems. Before irradiation, the NOESY spectrum shows interactions between  $\text{H}_c$  and  $\text{H}_1$  protons as well as between  $\text{H}_d$  and  $\text{H}_2$ , pointing out the short distances between these various protons. The loss of this correlation after isomerization reflects the increase of the distance between these protons. Integration of the new signals shows that after 5 h of irradiation, 47% of compound **1** has been isomerized. Irradiation at 480 nm allows one to restore the initial spectrum, and the absence of a new signal after a complete forward/backward cycle confirms the photostability of the system.

The CV of **1** shows a reversible oxidation wave ( $E^0 = 0.94$  V) corresponding to the generation of the 4T cation radical (Figure 4).<sup>10</sup> Irradiation at 360 nm produces a decrease of the intensity of this wave with emergence of a new redox system at lower potential ( $E^0 = 0.78$  V). These changes are fully reversible, and the initial CV is restored by irradiation at 480 nm. These results show in agreement with theoretical results that the photoinduced SAS to ASA transition of the 4T chain significantly increases the HOMO level, thus confirming that photomechanical control of the electronic properties of the conjugated system has been achieved.

**Supporting Information Available:** Synthetic procedure and characterization of compound **1**, crystallographic data, tables of bond distances and angles, positional parameters, and general displacement



**Figure 4.** Cyclic voltammogram of **1** ( $5 \times 10^{-4}$  M in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ ;  $100 \text{ mV s}^{-1}$ ). Before irradiation (dashed line) and after 2 h of irradiation at 360 nm (solid line).

parameters for **1** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) This gap value corresponds to the HOMO – LUMO + 1 gap because the LUMO is essentially localized on the azobenzene group.
- (9) Irradiation was performed with a 150 W xenon lamp using band-pass filters.
- (10) A control experiment on *p*-dimethylazobenzene shows that the azo group is electrochemically inert up to +1.70 V versus Ag/AgCl.

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