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THE FIRST DIMERS DERIVED FROM MESOIONIC 1,3-DITHIOLONES

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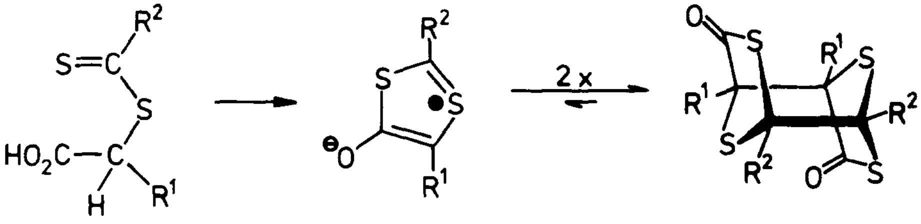
The great synthetical potential of several mesoionic 6π arenes offer, via [3+2] cycloaddition reaction to multiple bonds, valuable entries to heterocyclic systems[1]. In this communication we wish to report on the synthesis, reactions, and X-ray structure determination of a new dimer derived from mesoionic 1,3-dithiolones.

It is known that the anhydrocyclization of α-carboxyethyl dithiobenzoate (**1a**) with acetic anhydride and triethylamine leads to formation of the deep red 1,3-dithiolylium-4-olate **2a**[2].



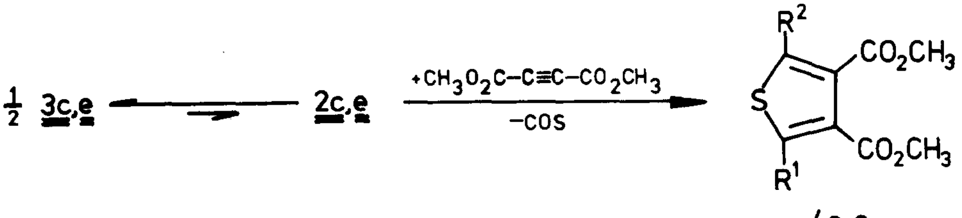
1 **2** **3**

a: $R^1 = CH_3$, $R^2 = C_6H_5$ **b**: $R^1 = C_6H_5$, $R^2 = CH_3$ **c**: $R^1 = C_6H_5$, $R^2 = SCH_2\text{-}CH{=}CH_2$

d: $R^1 = C_6H_5$, $R^2 = SCH_3$ **e**: $R^1 = C_6H_5$, $R^2 = SC_2H_5$

In contrast to this result, the reaction of the isomeric compound **1b** using dicyclohexylcarbodiimide as the cyclization agent proceeds with formation of **3b** (17% colorless needles, mp 162-163.5°C dec.). The dimeric nature of **3b** is consistent with the following spectroscopic data: ir, 1699 cm^{-1} (C=O), nmr, $\tau = 8.17$ (s, 2 CH_3), 3.02-2.59 (m, 2 C_6H_5), ms (70 eV), *m/e* = 416 (5%, M^+), 209 (100), 208 (86). The exact dimer structure is elucidated by X-ray analysis as shown below.

Furthermore, anhydrocyclization of 2c-e using either trifluoroacetic anhydride or dicyclohexylcarbodiimide afford after crystallization the dimers 3c-e, respectively (3c: 57%, mp 102-103°C dec., ir, 1700 cm^{-1} (C=O); 3d: 41%, mp 137-139°C dec., ir, 1715 cm^{-1} (C=O); 3e: 54%, mp 130-131°C dec., ir, 1700 cm^{-1} (C=O)). These latter dimers show in solution an interesting temperature and solvent dependent equilibrium between the deep red or violet mesoionic compound 2 and the colorless dimer 3. For example, a freshly prepared carbontetrachloride solution of 3c exhibits at room temperature a weak absorption band at 518 nm. After short heating, remeasurement at room temperature showed that the extinction coefficient is raised by a factor of 25. In polar solvents, like acetonitrile, the maximum of this long wavelength absorption is shifted to 504 nm and the intensity increases. This negative solvatochromic behavior is in agreement with the relatively high polar ground state of the mesoionic 2[2].



4c,e

Monomers 2c,e, generated in solution from the crystalline dimers 3c,e, show the same ability to [3+2] cycloaddition as does 2a[3]. Thus, the reaction of 3c,e or of 2c,e prepared *in situ*, starting with the precursor 1c,e and dicyclohexylcarbodiimide as the anhydrocyclization reagent, in the presence of dimethyl acetylenedicarboxylate proceed with elimination of COS and formation of the same thiophene derivatives 4c,e, respectively (4c: 37-43%, mp 113-114°C, ir, 1726, 1696 cm^{-1} (C=O); 4e: 88%, mp 120-121°C, ir, 1736, 1699 cm^{-1} (C=O)). The thiophene structures are consistent with spectroscopic data.

The results of a X-ray analysis of the dimer 3b show that only one of four possible head to head and head to tail dimerization pathways is realized. 3b (*M* = 416.61) crystallizes in the orthorhombic space group D_{2h}^{14} - P_{bcn} with four molecules per unit cell. Accurate unit cell constants, a = 9.251 (3), b = 14.240 (2), c = 13.996 (1) Å, were calculated from 75 Bragg angles (CuK$_\alpha$, λ = 1.54178 Å, 20°C) by a least-squares technique. The calculated density of 1.501 [gcm^{-3}] agrees well with the observed density of 1.50 [gcm^{-3}] (floatation). A total of

2240 reflections ($1^{\circ} < 2\theta \leq 154^{\circ}$) were measured on a CAD-4 diffractometer using Ni-filtered CuK_{α} radiation and the ω-2θ scan technique. The intensity data were corrected for absorption and the small random fluctuations of the three monitor reflections; then they were converted into structure factor amplitudes. Only the 1944 reflections with $I \geq 2\sigma(I)$ were used in the structure determination and refinement. The coordinates of the sulfur atoms were obtained from a sharpened Patterson map. A subsequent Fourier calculation revealed positions for the C and O atoms. After several cycles of refinement using anisotropic temperature factors, hydrogen atoms were located as residual electron density on a difference Fourier map. The hydrogen atoms were given isotropic temperature factors and included in the next cycles of refinement. The function minimized in the least-squares refinement was $\Sigma w\Delta^2$ where $\Delta = ||F_o|-|F_c||$ and $w = (\sigma(|F_o|))^{-2}$. Isolated spherical atom scattering factors[4], dispersion corrections included for S atoms[5], were used for all atoms except H[6]. The structure, the nonhydrogen atoms of which are shown in the FIGURE 1, converged with $R = \Sigma\Delta/\Sigma|F_o| = 0.038$ and $R_w = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2} = 0.042$.

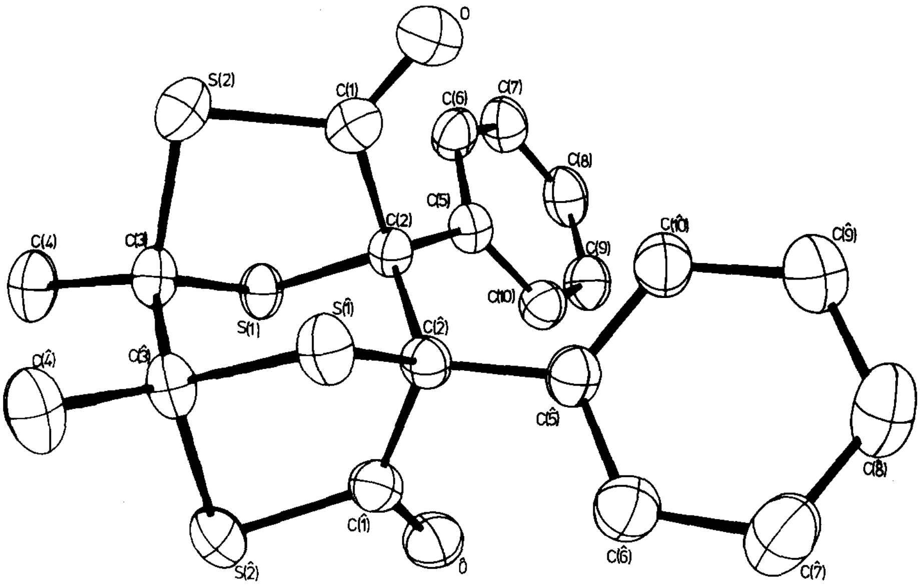


FIGURE 1. Molecular structure and numberig scheme for 3b

Our X-ray analysis determined 3b as head to tail dimer with no unusually short intermolecular contacts. The dimer possesses crystallographic $2(C_2)$ symmetry, the two fold axis bisecting the $C(2) - C(\hat{2})$ and $C(3) - C(\hat{3})$ bonds. These bridge bonds are remarkably long, 1.583 (2) and 1.578 (3) Å, respectively. The tricyclic compound contains five-membered rings in the envelope conformation and a eight-membered ring in the chair form. A complete discription of the structure will be published elsewhere.

Formation of the dimer **3b** by way of $C(2) - C(\hat{2})$, $C(3) - C(\hat{3})$ bridging is perhaps surprising because $C(2) - C(\hat{3})$, $C(3) - C(\hat{2})$ bridging might have been predicted from considerations of the dipole moment2) in the monomer.

Since, this surprisingly easy dimerization of **2** is, according to the rules of conservation of orbital symmetry[7], not allowed for a concerted thermal $[{}_{\pi}4_{s} + {}_{\pi}4_{s}]$ cycloaddition reaction, we presume that these dimers are formed by a two step mechanism. To our knowledge, compounds of type **3** are the first reported dimers derived from five-membered mesoionic 6π arenes.

All new compounds described showed satisfactory analytical results.

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