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LETTERS

Unusual Formation of 2,1-Benzisothiazole Derivatives

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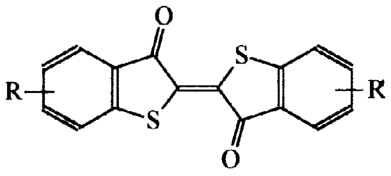
Abstract: Condensation of *N,N*-dimethyl-*p*-nitrosoaniline with 2-thioxo-2*H*-thieno[2,3-*d*]thiazole-6(5*H*)-ones **2a**, **2b** and 2-thioxo-2*H*-thieno[2,3-*d*]-1,3-dithiole-6(5*H*)-one **3**, leads unexpectedly to the formation of 2,1-benzisothiazole derivatives

The photochromic properties of thioindigoids dyes **1** and the nature of the changes they undergo, involving *cis-trans* isomerism, have been the subject of intensive investigation for decades.[1] Recently, the interest in this class of compounds has been renewed and focused in elaboration of photoinduced molecular switches.[2] Within the thioindigo molecule, substituents on the benzene ring do not considerably affect photochromic properties and bring about only small spectral shifts[3] owing to the mainly localized nature of the thioindigo chromophore. In order to investigate properties of the thioindigoid chromophore fused to heterocyclic systems, we elaborated a general synthetic approach for the synthesis of 2-thioxo-2*H*-thieno[2,3-*d*]thiazole-6(5*H*)-ones **2a**, **2b** and 2-thioxo-2*H*-thieno[2,3-*d*]-1,3-dithiole-6(5*H*)-one **3** based on previous works.[4] These compounds, as analogs of benzo[*b*]thiophene-3(2*H*)-one (thioindoxyl) **4**, can serve as key precursors for new class of photochromic compounds.



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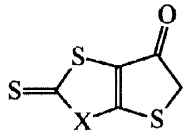
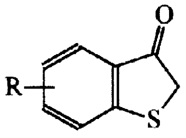


2a X = N-Ph
2b X = N-Naphth-1-yl
3 X = S



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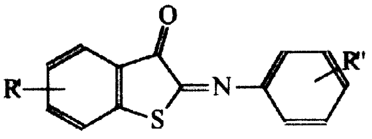

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A typical method for the synthesis of thioindigoid dyes involves the condensation of compounds like thioindoxyl (**4**) with anils like 2-phenyliminoindolin-3-one (isatin-2-anil) **5**.[5] In our attempts to prepare anils derived from **2a**, we observed an unusual behavior. Thus, equivalent amounts of compound **2a** and N,N-

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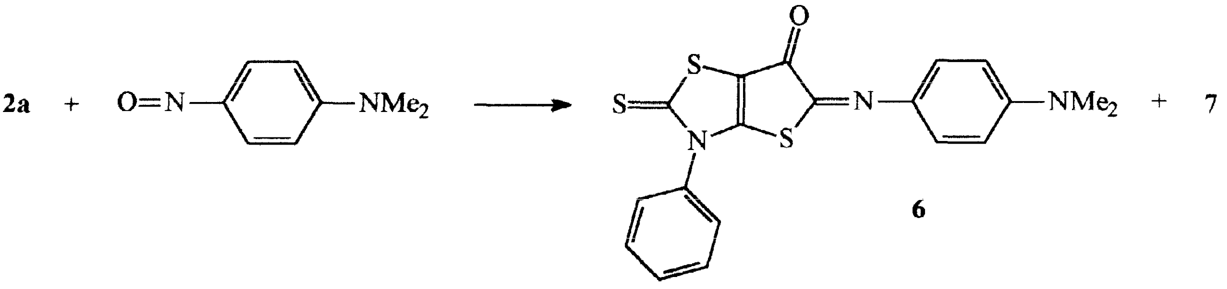
dimethyl-*p*-nitrosoaniline were dissolved in acetic anhydride, a catalytic amount of pyridine was added and the reaction mixture was stirred at room temperature for 15 min. The precipitated mixture of two dark violet products was filtered, dried and chromotographed on silica-gel column using dichloromethane as an eluent. Surprisingly, the expected anil **6** with R_f = 0.2 was obtained as a by-product (12% yield) and identified by spectroscopic means. This compound absorbs at 505nm and its transformation to the corresponding thioindigo derivative is under investigation. According to elemental analysis and mass spectra, the major product 7 with R_f = 0.4 has the same empirical formula as **6**. This product[6] was obtained in 65% yield as green lustrous crystals and possesses a pronounced fluorescence in solutions. The absorption and fluorescence spectra of compound 7 are shown in Figure 1. Of special interest is the large Stokes shift (90nm). Interestingly, 8 aromatic protons together with a singlet peak at 8 ppm, which corresponds to one non-aromatic proton, along with 6 protons of a NMe_2 group can be observed in the H-NMR spectra of compound 7.



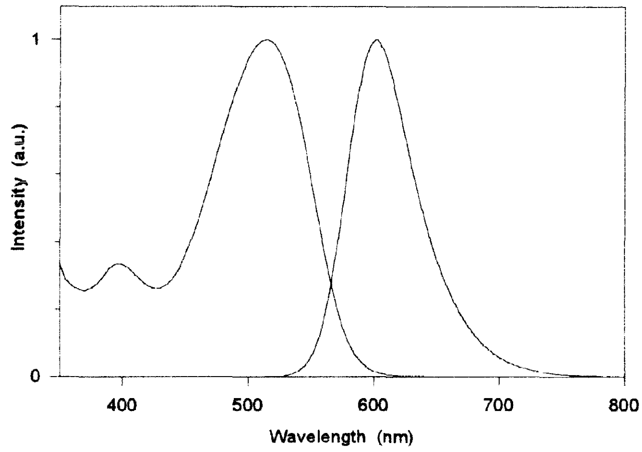
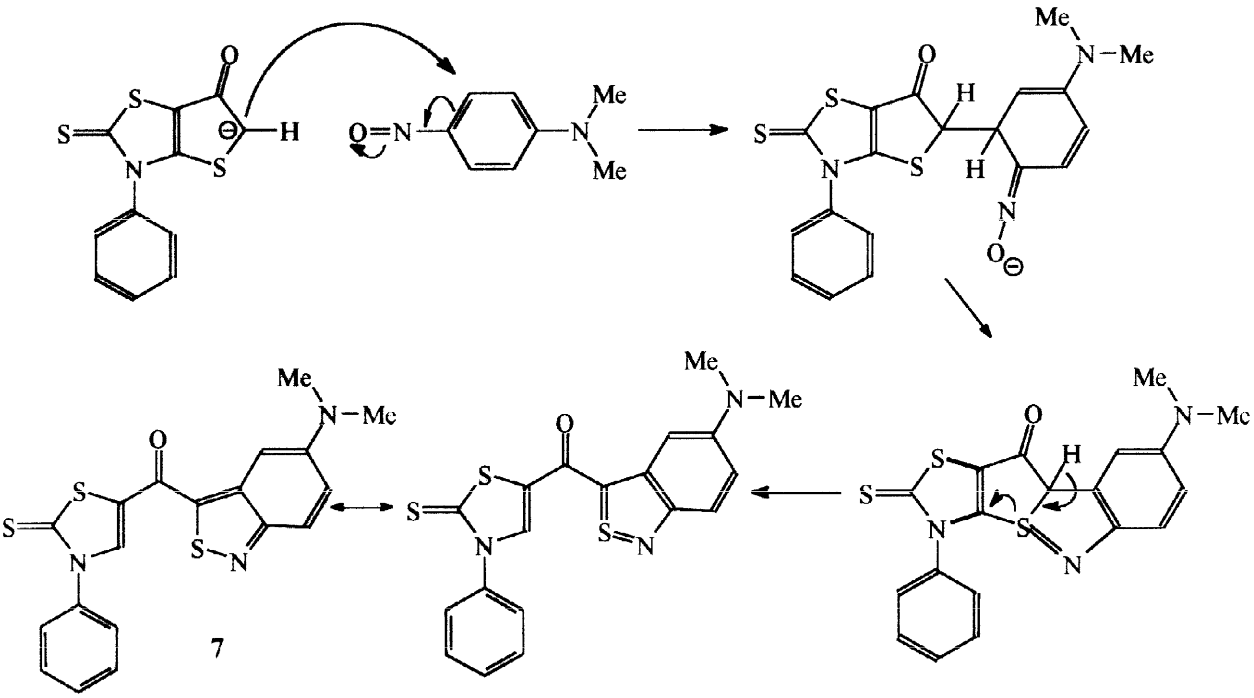


Fig. 1. Absorption and emission spectra of compound 7

The X-ray structure determination demonstrated that a 1,3-thiazoline-2-thione heterocyclic ring is linked to 2,1-benzisothiazole moiety via a carbonyl group (Figure 2).[7] The known synthetic approaches towards 2,1-benzisothiazole derivatives are limited and requires precursors in which the intramolecular cyclization can brought about by oxidation or reduction.[8] In the present case, the formation of the 2,1-benzisothiazole was initiated, probably, by C-C bond formation which implies a nucleophilic attack of the anion derived from the active methylene compound **2a** on the deactivated aromatic nitroso derivative. Such behavior is unusual and was not observed before.[9] Further intramolecular cyclization and subsequent C-S bond break can afford the 2,1-benzisothiazole derivative (Scheme):



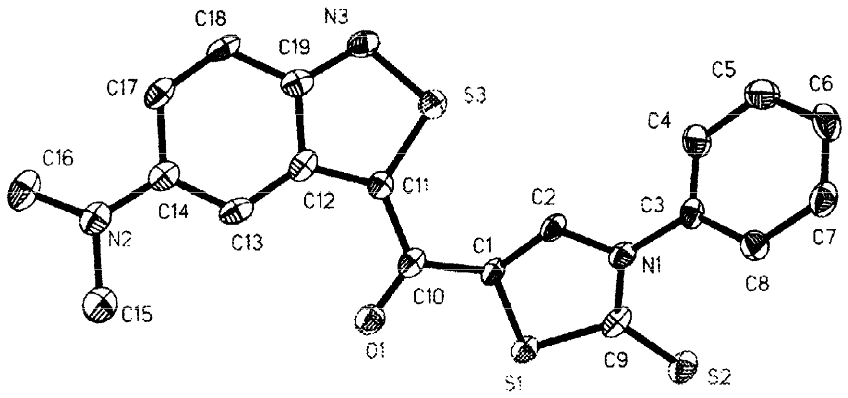


Fig 2. Molecular structure of compound 7

Under the same conditions, compound **2b** and **3** reacted with *N,N*-dimethyl-*p*-nitrosoaniline in a similar manner leading to the formation of the corresponding anils as minor products and the 2,1-benzisothiazole derivatives as the major products. The scope and limitations of this reaction as well as the photophysical properties of the new 2,1-benzisothiazole derivatives are under investigation.

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6. M.p. 212°C; ^{1}H-nmr, $\delta(CDCl_3)$: 3.16 (6H, s, Me_2N); 7.35 (1H, dd, H_3,$^3J_{23}$ = 9.2 Hz, $^4J_{34}$ = 2.7 Hz); 7.5 – 7.6 (5H, m, Ph), 7.73 (1H, dd, H_2, $^5J_{24}$ = 0.5 Hz); 8.03 (1H, s, H_1)
7. X-ray data for a single crystal of 1,3-thiazoline-2-thione (size 0.4x0.25x0.15 mm); $C_{19}H_{15}N_3OS_3$, M= 397.5, monoclinic, space group $P2_1/c$; at 183K, a= 9.115(8), b=26.10(3), c=8.075(7) Å, β= 108.48(3)°, V=1821(6)E^3, Z=4, ρ_c=1.450 Mg/m^3,$\mu(MoK_\alpha)$= 4.03 cm^{-1}. 5275 independent reflections were measured with "Syntex R3 " difractometer ($\lambda(MoK_\alpha)$ = 0.71069, graphite monochromator, $\omega/2\theta$-scan, 2θ<50o) of which 2430 were observed with $F_o>7\sigma(F_o)$. The structure was solved by direct methods and refined by least-squares in anisotropic approximation to R = 8.00, Rw = 7.50. All calculations were carried out using the SHELX -76 and SHELX-86 programs. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.
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