Tetrahedron Letters No. 43, pp. 3999 - 4002, 1971. Pergamon Press. Printed in Great Britain.

Dithiopyrylium Dication

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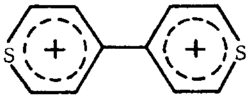
(Received in Japan 13 September 1971; received for publication in UK 22 September 1971)

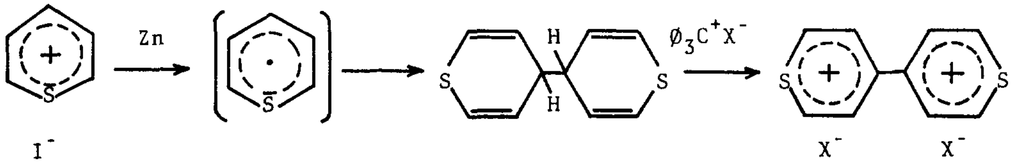
The present communication reports the first synthesis of dithiopyrylium dication (I), in which two thiopyrylium rings (II)[1) are directly connected by a covalent C-C bond each other. This novel hetero-aromatic system (I) is iso-π-electronic to ditropylium dication recently synthesized by Vol'pin et al.[2) I is anticipated to be less stable than II, because the unstabilization due to the repulsion of two positive charges would outweigh the stabilization due to π-electron conjugation between both the rings. We have succeeded in the synthesis of I by the treatment of dithiopyranyl, prepared from II and zinc, with the Doering reagent[3) in acetonitrile.



I

II

To a suspension of excess zinc in acetonitrile was added a solution of thiopyrylium iodide in acetonitrile at 0° under a nitrogen atmosphere. After filtration of the unreacted zinc, the filtrate was treated at 0° with triphenylmethyl fluoroborate, the iodide and the perchlorate followed by addition of anhydrous ether to give γ,γ'-dithiopyrylium difluoroborate Ia (yield; 24%), the diiodide Ib (27%) and the diperchlorate Ic (26%), respectively. The decomposition occured at 165° for Ia and 188° for Ib, and Ic was explosive. These dications are considerably stable in the air, but rapidly decompose in water. The route of the formation of γ,γ'-dithiopyrylium dication is shwon in the following scheme.



I_a: $X=BF_4$
I_b: $X=I$
I_c: $X=ClO_4$

The elemental analysis of Ia shows a good accord with the assigned formula. Found: C, 33.10; H, 2.22; S, 17.67. Calcd. for $C_{10}H_8S_2B_2F_8$: C, 32.82; H, 2.19; S, 17.51. The mass spectra of Ia and Ib showed a strong peak at m/e 192, corresponding to the molecular ion of dithiopyrylium dication. Other prominent fragment peaks were observed at m/e 160 and 128, which correspond to the fragments formed by the loss of the sulfur atom from the dication. The proton magnetic resonance (pmr) spectrum of I in trifluroacetic acid (Figure Ia) showed an AB quartet, indicating that I is the γ,γ'-dication. In the Figure Ia, the lower field two peaks at τ -0.37 (J=9.8 Hz, 4H) are assigned to the α-protons and the higher field two peaks at τ 0.65 (J=9.8 Hz, 4H) to the β-protons, both of which are shifted by 0.20~0.25 ppm downfield with respect to the α- and β-protons of thiopyrylium cation (Figure Ib).[4] The observed low field shifts would be reasonably accounted for by a strong electron-withdrawing nature of the thiopyrylium cation.

It should be mentioned that no appreciable quantity of α,α'- and α,γ'-dications could be detected in the reaction product as judged by the pmr spectrum. This would be explained by assuming that α,α'- and α,γ'-dications are less stable than γ,γ'-dication because of much more repulsion between the rings in the former compounds. Thus α,α'- and α,γ'-dications would not be obtained, even though α,α'- and α,γ'-dithiopyranyls might be formed besides γ,γ'-dithiopyranyl.[5]

Characteristics of I are now under investigation in this laboratory.

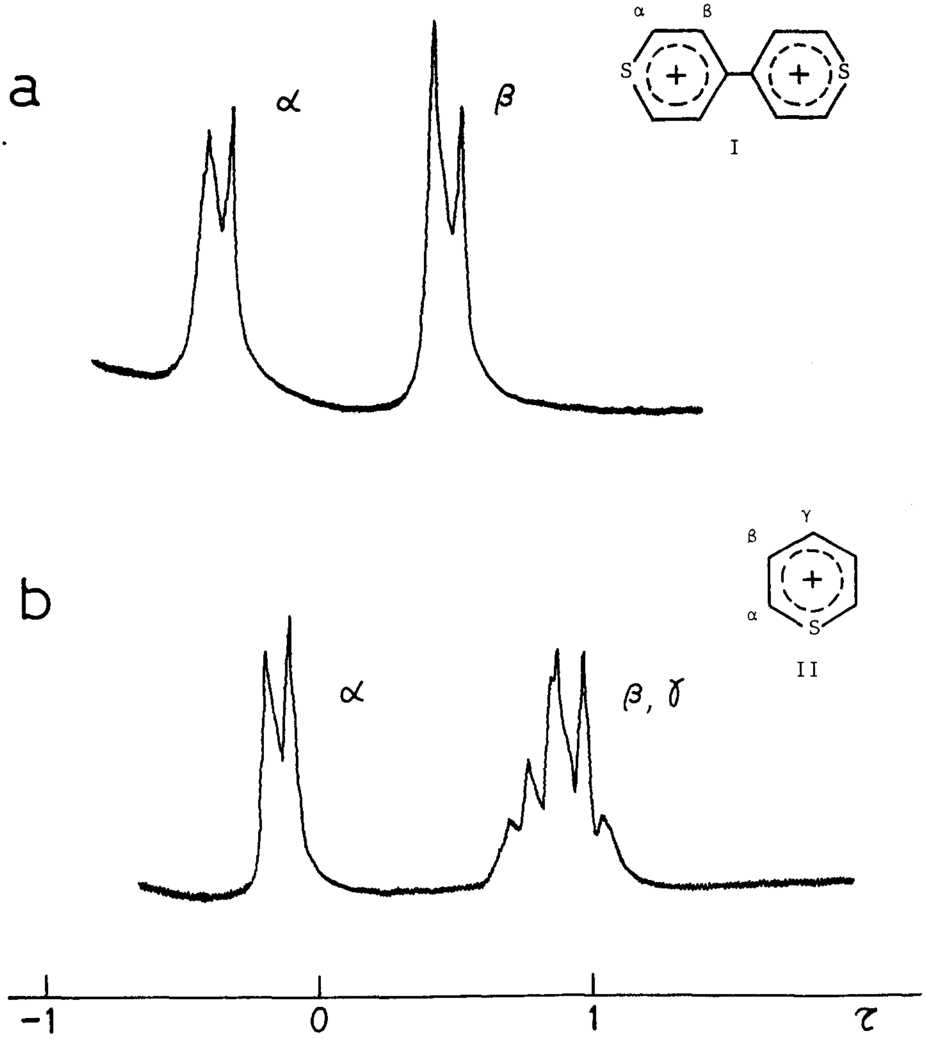


Fig. 1. The pmr spectra of I and II

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(5) The observation of thiopyranyl radical and its reactivity are under investigation. In the dimerization of 2,4,6-triphenylthiopyranyl radical, α,α'- and α,γ'-dithiopyranyls were obtained besides γ,γ'-dithiopyranyl.