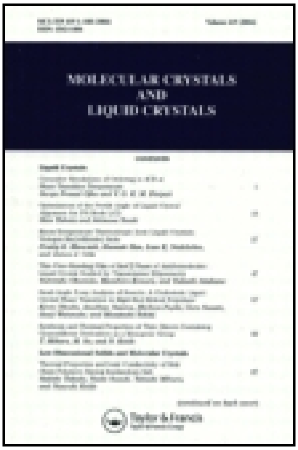

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# Bis (DIAZINO) Tetrathiafulvalenes and Similar π-Donors

G. C. Papavassiliou [a] , S. Y. Yiannopoulos [a] & J. S. Zameounis [a]

[a] Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation, 48, Vass. Constantinou Ave., Athens, 116/35, Greece

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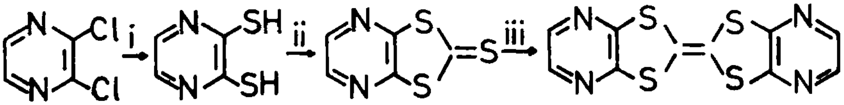
# BIS (DIAZINO) TETRATHIAFULVALENES AND SIMILAR π-DONORS

G.C.PAPAVASSILIOU, S.Y.YIANNOPOULOS,AND J.S.ZAMBOUNIS, Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation, 48, Vass. Constantinou Ave., Athens 116/35, Greece.

Bis(pyrazino) tetrathiafulvalene (BPTTF), bis(quinoxalino)tetrathiafulvalene (BQTTF), bis (pyrimidino) tetrathiafulvalenes (BPMTTFs), bis (pyridazino)tetrathiafulvalenes (BPDTTFs), bis(pyrazino) tetraselenafulvalene(BPTSF) and bis(quinoxalino) tetraselenafulvalene (BQTSF) were prepared. These compounds were found to be π-donors and gave C.T. salts. The perchlorate salt of BPTTF was found to be a 3-D conductor.

Substituted derivatives of tetrathiafulvalene and tetraselenafulvalene (π-donors) with a benzene-ring are described in [1],[2] (and refs.therein). In this paper the preparation of some tetrathia(selena)fulvalenes with a 1,2-diazine (:pyridazine)-ring (I), 1,3-diazine (:pyrimidine)-ring (II), and 1,4-diazine (:pyrazine)-ring (III) is described. Also, a number of C.T. complexes of these compounds and preliminary results concerning their properties are described. The new compounds were prepared using the ortho-dichloroderivatives of the corresponding diazine as starting materials [3]-[7]. The following scheme shows the method of the preparation of bis (pyrazino) tetrathiafulvalene (BPTTF):



(III-1a) (III-2a) (III-3a) (III-4a)

i. KHS, $H_2O$; ii. $SCCl_2$ in $C_6H_6$(or $H_2O$); iii. $(EtO)_3P$

2,3-dimercaptopyrazine (III-2a) (mp>245°C) was prepared by refluxing aqueous solutions of KHS (or NaHS)* with 2,3 dichloropyrazine (III-1a)[3] for 1h followed by filtration and $CH_3COOH$ addition to the filtrate. The crude product was disolved in water made alkaline by addition of NaOH. On acidifying with $CH_3COOH$ the pure product (III-2a) that was formed, was separated by filtration washed with water and dried in air. Pyrazine-2,3-trithiocarbonate (III-3a) was prepared by treating a suspension of (III-2a) in benzene with $SCCl_2$. The resulting solution of (III-3a) was concentrated to a small volume. The crystals obtained after cooling were washed with ethanol and dried (mp=170°C). Compound (III-3a) can be also prepared by using aqueous solutions of (III-2a) [8], instead of benzene-suspensions, followed by extraction with benzene. BPTTF(III-4a) was prepared by refluxing solutions of (III-3a) in $(EtO)_3P$ followed by concentration, filtration, and washing with ethanol. Yellow crystals of (III-4a) (mp=303°C) gave satisfactory analytical results and UV($CH_3CN$) bands at 395, 300(sh), 277nm.

Refluxion of aqueous solutions of KHS (or NaHS)* with 2,3-dichloroquinoxaline (III-1′a) [4] yields 2,3-dimercaptoquinoxaline (III-2′a) (mp=290-5°C). Treatment of (III-2′a) with $SCCl_2$ in benzene yields quinoxaline-2,3-trithiocarbonate (III-3′a) (mp=180-5°C). Refluxion of (III-3′a) with $(EtO)_3P$ in benzene yields purple crystals of bis (quinoxalino) tetrathiafulvalene (III-4′a, BQTTF) (mp>310°C), which gave satisfactory analytical results and UV($CH_2Cl_2$) bands at 445, 300(sh), 265 nm.

By similar methods and starting from 4,5-dichloropyrimidine (II-1′a)[5], 3,4-dichloropyridazine (I′-1a) [6] and 4,5-dichloropyridazine (I-1a) [7], a mixture of cis- and trans-bis (pyrimidino)tetrathiafulvalenes (II-4a′,II-4a′′), a mixture of cis-and trans-bis(3,4 pyridazino)tetrathiafulvalenes(I′-4a′,I′-4a′′)and bis (4,5--pyridazino)tetrathiafulvalene(I-4a)were prepared,respectively.Last compound has been prepared by Gorgues et al[9]with an alternative method. Also,starting from (III-1a) and (III-1′a) and using NaHSe[10] (or KHSe)*,bis (pyrazino)tetraselenafulvalene (BPTSF) and bis(quinoxalino)tetraselenafulvalene(BQTSF) were prepared,respectively. In this case the yield of the reaction with $(EtO)_3P$ (or $Ph_3P$) was poor.

The new compounds were found to be π-donors and gave charge transfer complexes.BPTTF,for example,reacts with bromine to give $(BPTTF)Br_3$,which is a semiconductor. This salt react with $Bu_4N$ $Ni(dmit)_2$(where dmit=4,5-dimercapto-1,3-dithiole-2-thione)to give a complex salt of BPTTF which is a conductor.Also C.T. complexes of BPTTF with $ClO_4$, $BF_4$,and $PF_6$ were prepared using standard electrochemical techniques (see[11]and refs.therein).The perchlorate salt of BPTTF is crystallized in elongate rhombohedrals with a copper-black luster.Preliminary conductivity measurements on these crystals showed a 3-D conductivity.Perhaps,this is due to intermolecular S-N and/or S-S contacts.Details on the preparations of the above and similar donors and their C.T. salts will be described in a future paper.

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* By refluxing with aqueous solutions of NaHS or NaHSe, a large amount of the required compound precipitated. Dilution with aqueous solutions of NaOH and reprecipitation with $CH_3COOH$ yielded the pure product.