

Dithiatetrazocines and Dithiadiazolium Salts

Mehul Amin and Charles W. Rees

Department of Chemistry, Imperial College of Science, Technology, and Medicine, London SW7 2AY, U.K.

Benzamidine and sulphur dichloride give the dithiadiazolium salt (2) as well as dithiatetrazocine (1), though better syntheses for both are reported; the first heterocyclic (7) and unsymmetrical (10) derivatives of dithiatetrazocine are described, and one dimethylamino substituent, in (10), is shown to be sufficient to destroy the planarity of the dithiatetrazocine ring.

In an attempted synthesis of a linear polymeric conductor analogous to polysulphur nitride, Woodward and co-workers condensed benzamidine with sulphur dichloride.¹ The reaction was complex, giving none of the desired polymer but a small amount (7.4%) of 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine (1), a new planar, delocalised 10 π aromatic system. A few other aryl and alkyl substituted derivatives, with similar properties and structures, were made in the same way.^{1,2} *N,N*-Dimethylguanidine and sulphur dichloride gave the analogous 3,7-bis(dimethylamino) compound (9) but this had a very different ultraviolet spectrum, and *X*-ray diffraction showed that the heterocyclic ring was now folded about the S...S axis with an interplanar angle of 101°. Thus the electron-rich planar dithiatetrazocine ring was destabilised by the two strongly electron releasing groups and had distorted to a structure with partial S...S bonding.

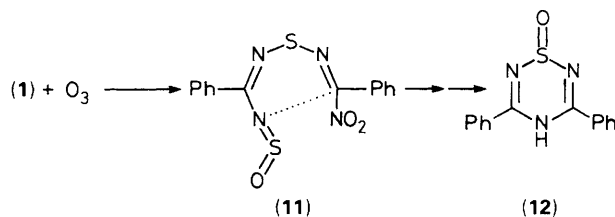
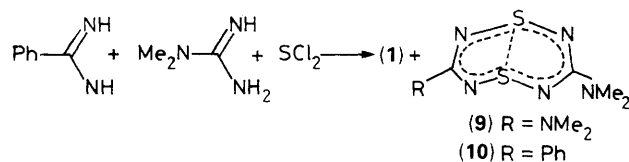
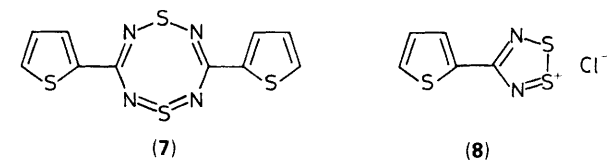
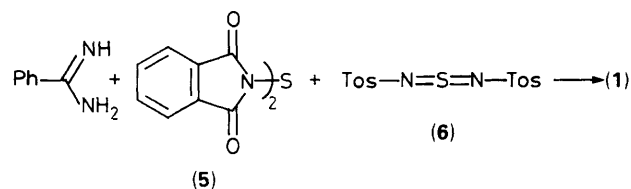
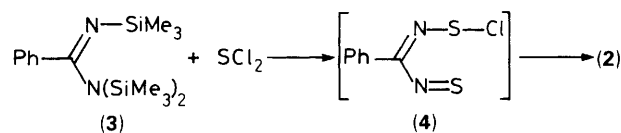
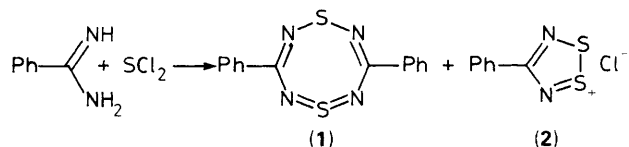
In a detailed reinvestigation of the reaction of benzamidine with sulphur dichloride we were unable to increase the yield of dithiatetrazocine (1), but we uncovered a new product, the yellow air-sensitive 4-phenyl-1,2,3,5-dithiadiazolium chloride (2) (15%), identical with an authentic specimen.³ If benzamidine is replaced by its tris(trimethylsilyl) derivative (3), or if sulphur dichloride is replaced by disulphur dichloride, the yield of dithiadiazolium chloride (2) is much improved (60 and 54% respectively), and the latter reaction provides a particularly convenient route to it which compares favourably with literature methods.^{3,4} Benzamidine and its silyl derivative are possibly converted into the dithiadiazolium salt *via* intermediate (4), which can cyclise and ionise to the 6 π aromatic cation.

Since dithiatetrazocine (1) formally contains one divalent and one tetravalent sulphur, we investigated the reaction of benzamidine with mixtures of sulphur transfer agents of the type R₂N-S-NR₂ and RN=S=NR. We found the best combination to be bis(phthalimido) sulphide (5)⁵ and bis(*p*-tolylsulphonyl)sulphurdiimide (6) (Tos = *p*-MeC₆H₄SO₂),⁶ which are easy to make and purify, and are stable. Addition of benzamidine in dichloromethane to a stirred slurry of the sulphide (5) in dichloromethane at room temperature, followed by slow addition of sulphurdiimide (6) gave dithiatetrazocine (1) (10%). The work up is simple since no base is required and no sulphur is formed to complicate the chromatography.

When 2-thienylamidine was treated with sulphur dichloride in dichloromethane at 0 °C in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the red crystalline air-sensitive dithiadiazolium salt (8), m.p. 162–164 °C, was the major product (70%) together with the orange-yellow 3,7-di(2-thienyl)-1,5,2,4,6,8-dithiatetrazocine (7), m.p. 271–273 °C, (7%). The u.v. spectrum of the latter has a complex long-wavelength absorption pattern [λ_{max} (EtOH) 271, 318, 351, and 447 nm] similar to that of the diphenyl compound (1), indicating the same planar structure for the dithiatetrazocine ring.

We also made the first unsymmetrically substituted dithiatetrazocine (10) by treating a mixture of benzamidine and

N,N-dimethylguanidine with sulphur dichloride in dichloromethane at 0 °C in the presence of DBU. This gave 3,7-diphenyl-(1) (10%), 3,7-bis(dimethylamino)-(9) (5%), and 3-dimethylamino-7-phenyl-dithiatetrazocine (10), m.p. 182–183 °C, (3%). The unsymmetrical compound (10) has a u.v. spectrum (λ_{max} 250 nm) similar to that of the bis-amine (9), completely lacking the long-wavelength absorptions of (1) and (7), indicating the same folded structure for (10) as for (9); thus one dimethylamino substituent is sufficient to buckle the dithiatetrazocine ring.



Woodward and co-workers¹ had shown that the diphenyl compound (**1**) was thermally stable, resistant to nucleophiles, and not oxidised by *m*-chloroperbenzoic acid (MCPBA). We find that it is also stable to dinitrogen tetroxide, chloramine-T, diazomethane, norbornadiene, and triphenylphosphine, all in accord with its 10 π aromatic nature. However, it could be cleaved with anhydrous hydrazine and 10% palladium on charcoal at room temperature to give benzamidine (75%) and sulphur. On treatment with ozone in dichloromethane at -78°C it gave 3,5-diphenyl-1,2,4,6-thiatriazine 1-oxide (**12**), m.p. $156\text{--}158^{\circ}\text{C}$ (38%) and the 1,1-dioxide, m.p. $>310^{\circ}\text{C}$, (5%), possibly by ozonolysis of an S–N bond to give the nitrosulphinylamine (**11**),⁷ which cyclises by nitrite displacement, is oxidised further, and finally hydrolysed to give (**12**).

Since the dithiatetrazocine ring was so resistant to MCPBA and N_2O_4 , we hoped to oxidise the thiophene rings in compound (**7**) to the sulfoxide or sulphone and to degrade these rings further, as an approach to the parent dithiatetrazocine. However, attempted oxidation of (**7**) with MCPBA in boiling 1,2-dichloroethane, or with N_2O_4 , gave no *S*-oxides and (**7**) was recovered in high yield. Similarly, attempted nitration of (**7**) with nitronium tetrafluoroborate in aceto-

nitrile left the starting material unchanged. This inertness was surprising since the ' π -excessive' dithiatetrazocine ring was not expected to be a strongly electron withdrawing substituent on the thiophene ring.

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References

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