Interannular Contraction upon Oxidation of a Mesoionic Bicyclic Imine

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The bicyclic imine (1) is oxidised exclusively at the thiadiazole ring to give the mono-, di-, and tri-oxides (2), (3), and (4); subtle but marked changes in the pattern of bonding and intramolecular interactions in the X-ray crystal structures of (1)—(4) reflect the increasing contribution of dipolar mesoionic forms [*e.g.* (1a)] along the series, and this in turn is reflected in the formation and chemistry of these oxides.

The reaction of S_4N_4 with phenylacetylene gave the highly rearranged, thermally stable, deep violet product (1) in which both heterocyclic rings and the bridging nitrogen atom are accurately coplanar in the crystalline state.[1] The imine (1) appears to be stabilised by electron delocalisation from the dithiazole to the thiadiazole ring (1a), and this results in the molecular planarity and a close interannular S···N approach (2.70 Å; sum of the van der Waals radii 3.35 Å). Chemical consequences of this delocalisation include the inertness of imine (1) towards cycloaddition with dimethyl acetylenedicarboxylate and dibenzoylacetylene, normally characteristic of mesoionic systems,[2] and the oxidation of (1) exclusively in the (formally more stable) thiadiazole ring.

Imine (1) is converted by dinitrogen tetroxide, N_2O_4, in dichloromethane at −20 °C into the monoxide (2) (90%) and with excess of N_2O_4 at room temperature into the dioxide (3) (55%), together with 3,5-dibenzoyl-1,2,4-thiadiazole (5) (20%). Thiadiazole (5) proved to be an acid hydrolysis

product of the monoxide (2) and is formed from it in high yield (80%) with dilute hydrochloric acid in tetrahydrofuran (THF); see below. Dioxide (3) was inert to further reaction with N_2O_4, but was readily oxidised in high yield (80%) with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane at 0 °C to a trioxide with the unusual hetero-fused oxaziridine structure (4). Compound (4) could also be prepared directly from imine (1) with an excess of MCPBA. Such trioxidation of thiadiazoles is unknown and is presumably another manifestation of the enhanced nucleophilicity of the thiadiazole ring

(1)   (1a)
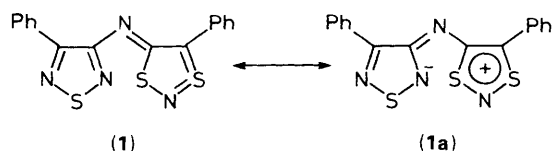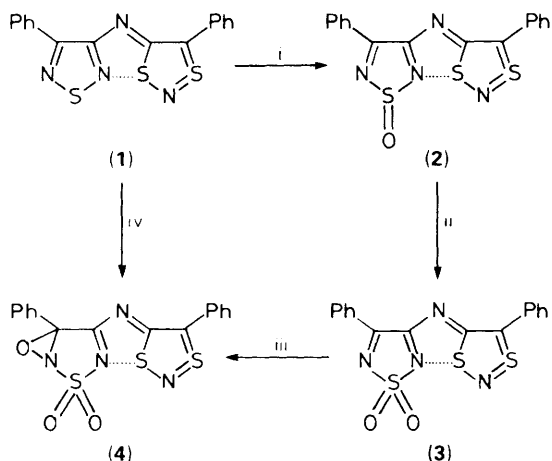
Scheme 1. *Reagents and conditions*: i, N_2O_4, CH_2Cl_2, $-20\,°C$. ii, excess N_2O_4, CH_2Cl_2, $20\,°C$; iii, MCPBA, CH_2Cl_2, $0\,°C$; iv, excess MCPBA, CH_2Cl_2, $0\,°C$.

Table 1. Selected comparative bond lengths for compounds (1)—(4)/Å.

	(1)	(2)	(3)	(4)
S(1)–N(2)	1.609(9)	1.596(3)	1.600(6)	1.594(3)
N(2)–S(3)	1.568(9)	1.629(3)	1.625(5)	1.618(3)
S(3)–C(4)	1.768(9)	1.752(3)	1.733(6)	1.753(3)
C(4)–C(5)	1.437(12)	1.416(4)	1.409(9)	1.414(4)
S(1)–C(5)	1.673(8)	1.663(4)	1.691(4)	1.680(3)
C(4)–N(6)	1.297(11)	1.342(4)	1.351(5)	1.353(4)
N(6)–C(7)	1.410(11)	1.335(4)	1.329(8)	1.316(4)
C(7)–N(8)	1.372(11)	1.329(4)	1.304(8)	1.326(4)
N(8)–S(9)	1.590(8)	1.692(3)	1.645(5)	1.625(3)
S(9)–O(9)	—	1.459(3)	1.423(4)	1.422(3)
S(9)–O(10)	—	—	1.432(4)	1.411(4)
S(9)–N(10)	1.641(9)	1.719(3)	1.668(4)	1.732(3)
N(10)–C(11)	1.374(11)	1.286(4)	1.302(8)	1.468(4)
C(11)–C(7)	1.414(12)	1.510(5)	1.524(6)	1.521(4)
C(5)–C(12)	1.458(12)	1.484(5)	1.470(9)	1.470(4)
C(11)–C(18)	1.487(12)	1.479(5)	1.470(7)	1.483(4)

resulting from a highly dipolar structure. This dipolarity is clearly supported by the results of X-ray crystallographic analysis of compounds (2), (3), and (4).†

Oxidation, and disruption of the aromaticity, of the thiadiazole ring in (1) to give (2) (Figure 1a), produces major

Figure 1. Perspective views with atom numbering for (a) the monoxide (2) and (b) the trioxide (4).

changes in the pattern of bond ordering throughout the molecule (Table 1). In the dithiazole ring there is a greater degree of delocalisation. There is a significant increase in the S(3)–N(2) bond length, 1.629(3) Å, *cf*. 1.568(9) Å in (1), and small reductions in the S(1)–C(5), C(4)–C(5), and C(4)–S(3) distances. The bridging imide C–N bonds virtually equalise at 1.34(1) Å, *cf*. 1.41 and 1.30 Å in (1), indicating a greater contribution of dipolar forms. In the thiadiazole ring the sequence of formal single and double bonds changes: C(7)–C(11), N(8)–S(9), and S(9)–C(10) all increase appreciably and C(7)–N(8) and C(11)–N(10) both decrease. Oxidation of (2) to give (3) does not result in any significant further perturbation in the bond trends. The only noticeable effects are an expected restoration of S(9) to coplanarity with the thiadiazole and dithiazole rings [*cf*. a deviation of 0.21 Å in (2)] and a shortening of all the bonds at the dioxide sulphur S(9). Oxidation of (3) with the formation of the fused oxaziridine–thiadiazole ring in (4) (Figure 1b) produces only a lengthening of the N(10)–C(11) and N(10)–S(9) bonds compared with their values in (3). Planarity of the thiadiazole–dithiazole system is retained. A noticeable trend, after the initial equalisation of the two imide C–N bonds in (2), is a progressive lengthening in (3) and (4) of the bond C(4)–N(6) to the dithiazole ring [with an accompanying shortening of the N-thiadiazole bond, N(6)–C(7)] reflecting the increased electron withdrawal. The effect is such that on reaching (4) the formal double bond to the dithiazole ring [1.353(4) Å] is significantly longer than the formal single bond to the
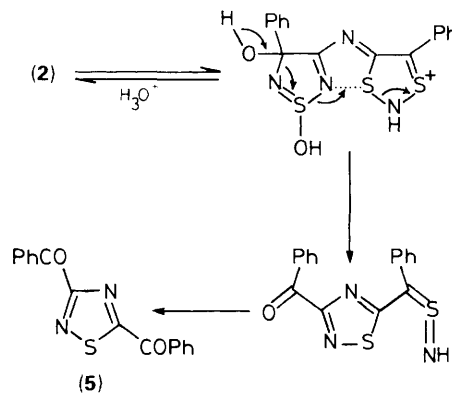
(a)

(b)
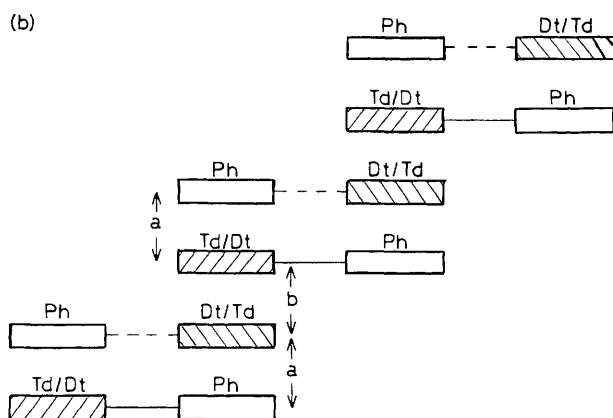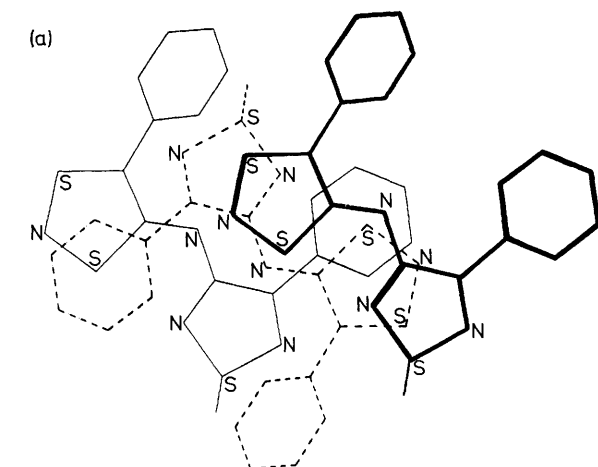
Figure 2. (a) Skeletal (plan) [the stack sequence from the top down is: heavy–broken–light outline] and (b) schematic (elevation) representations of the continuous stepped stacking of the molecules of (2) in the crystal. Interplanar separations a = 3.43, b = 3.36 Å.

thiadiazole ring [1.316(4) Å]. An interesting parallel trend within (1) → (4) is a marked shortening of the interannular S–N distance. Although the differences within (2) → (4) are small, 2.566 → 2.497 Å, the changes are in the same sense and when (1) is considered (2.695 Å) the overall effect is significant. Thus the heterocyclic rings are held coplanar and progressively closer as dipolar contributions, analogous to (1a), become more important.

With one exception, (2), where one of the phenyl rings is coplanar with the dithiazole ring, the phenyl rings are inclined by varying degrees to the thiadiazole–dithiazole plane.‡ The

Scheme 2

coplanarity of one of the phenyl rings in (2) does not affect the geometry of the thiadiazole ring.§ It does, however, play an important role in the intermolecular packing interactions. In crystals of (1) continuous stacks with partial thiadiazole and dithiazole ring overlap, and *vice versa*, are present; the interplanar separations are 3.55 Å. In (2) the pattern is different with pairs of centrosymmetrically related molecules displaying thiadiazole and dithiazole overlap (interplanar separation 3.43 Å) and with the coplanar phenyl ring of a lattice translated molecule lying directly beneath and parallel to a dithiazole ring at a separation of 3.36 Å. These combined interactions produce a continuous stepped layer structure (Figure 2). In (3) and (4) no such interactions are present.

A comparison of the thermolyses of the oxides is instructive. Dioxide (3) is very stable, being unchanged after 1 h at 280 °C, but monoxide (2) was deoxygenated smoothly to imine (1) at 250 °C. Trioxide (4) was least stable and was quantitatively deoxygenated to dioxide (2) in boiling bromobenzene for 4 h; this is unusual for oxaziridines, which normally rearrange thermally to nitrones or amides.

The most striking consequence of coulombic attraction between the heterocyclic rings is seen in the ready acidic hydrolysis of monoxide (2) to 3,5-dibenzoyl-1,2,4-thiadiazole (5) (Scheme 2). In this unusual reaction the thiadiazole and dithiazole rings are both destroyed and a new thiadiazole ring, the incipient central 'ring' of the monoxide, is formed.

References

1 S. T. A. K. Daley and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1987, 207; S. T. A. K. Daley, C. W. Rees, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1984, 57.
2 H. Gotthardt, *Chem. Ber.*, 1972, **105**, 188 and 196.

‡ The dihedral angles between the phenyl rings and their associated thiadiazole and dithiazole rings in these structures are: (1) 31 and 27°; (2) 2 and 41°; (3) 16 and 47°; (4) 44 and 40°.

§ This coplanarity gives rise to a short intramolecular contact, 2.27 Å, between the *ortho* ring hydrogen atom and the imine nitrogen N(6). The C⋯N distance is 2.97 Å.