Photochemical isomerization of a $C_2N_4S_2$ ring into a diazene

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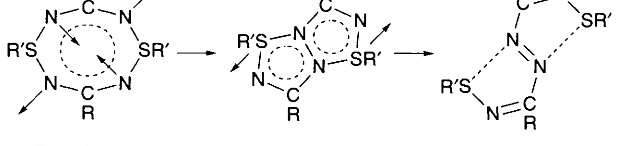
The eight-membered rings $(ArC)_2N_4(SPh)_2$ [Ar = 4-XC_6H_4 (X = Br, CF_3)] undergo photoisomerization to the purple diazenes PhSN=C(Ar)N=NC(Ar)=NSPh by a first-order process that is thermally symmetry-forbidden, but photochemically allowed.

Photoisomerization is a common process for heterocyclic compounds.[1] Cyclic C–N systems containing two-coordinate sulfur have been studied extensively[2,3] and the structures and characteristic reactions of these π-electron-rich systems are readily understood in terms of frontier-orbital concepts.[3] Molecular rearrangements, including ring expansion and contraction, are frequently observed. However, photochemical studies of CNS systems have been limited to the isomerization of 1,3,2,4-dithiadiazolyl radicals[4] and the photolytic generation of unstable molecules, *e.g.* N_2S.[5]

Although C–N heterocycles containing three-coordinate sulfur are readily accessible,[6–10] investigations of their reactivity patterns have received comparatively little attention and no photochemical transformations have been described. Eight-membered rings of the type **1** (see Scheme 1) are obtained from the reaction of $ArCN_2(SiMe_3)_3$ (Ar = aryl) with PhSCl (1 : 3 molar ratio) under kinetically controlled conditions[11,12] and, in one case, a sixteen-membered ring $(4\text{-}BrC_6H_4C)_4N_8(SPh)_4$ has been isolated and structurally characterized.[13] The major products of this reaction, however, are the intensely coloured diazenes of type **2**.[11,14] In this communication we report a novel, photochemical isomerization of the eight-membered rings **1b** and **1c** into the corresponding diazenes **2b** and **2c**. A combination of kinetic experiments and density functional theory (DFT) calculations have shown that this is a unimolecular, photochemically symmetry-allowed process.

Two observations led us to investigate the effect of UV irradiation on the $C_2N_4S_2$ rings **1b** and **1c**. First, exposure of pale yellow crystalline samples of **1b** to daylight for several days produced a purple taint. Secondly, a melting point determination of **1b** resulted in the formation of a purple melt at *ca.* 190 °C. In both cases the purple chromophore was identified as the diazene **2b** (λ_{max} 543 nm, $\varepsilon = 1.7 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$).

The transformation of **1b** into **2b** occurs at a convenient rate under the influence of UV irradiation to allow the kinetics of the process to be determined. When a toluene solution of **1b** (4.0×10^{-5} mol dm^{-3}) was irradiated with UV light (Xe lamp with a 313 nm filter) for *ca.* 90 min, the absorption at *ca.* 290 nm, attributable to **1b**, decreased steadily while the absorption at 543 nm characteristic of **2b** increased. Kinetic data were obtained from plots of absorbance (at 543 nm) *vs.* irradiation time. The experiment was repeated for several different interference filters and a plot of the slope of the absorbance (at 543 nm) with time *vs.* intensity of irradiation gave a straight line consistent with a first-order, *i.e.* intramolecular, reaction with a rate constant of $1.43 \pm 0.03 \times 10^{-11}$ mol s^{-1} and a quantum yield of 0.09. The eight-membered ring **1c** undergoes a similar isomerization to the corresponding diazene **2c**. Significantly, however, the sixteen-membered ring $(4\text{-}BrC_6H_4C)_4N_8S_4Ph_4$ is not converted into **2b** upon photolysis suggesting that a ring-opening process is not involved in the transformation to the diazene.



1a; R = R′ = H
1b; R = 4-BrC_6H_4, R′ = Ph
1c; R = 4-$CF_3C_6H_4$, R′ = Ph

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2a; R = R′ = H
2b; R = 4-BrC_6H_4, R′ = Ph
2c; R = 4-$CF_3C_6H_4$, R′ = Ph
2d; R = R′ = 4-MeC_6H_4

Scheme 1

In order to understand this photochemical process, density functional theory (DFT) calculations[15] were carried out for the model systems **1a** and **2a**. Based on the known X-ray structures of **1b** (C_{2v})[12] and **2d** (C_{2h}),[16] the structures of **1a** and **2a** were fully optimized. The total reaction enthalpy for the isomerization of **1a** into **2a**, calculated as the difference of total bonding energy, was found to be −154.7 kJ mol^{-1}. The driving force is the formation of a very stable N=N bond at the expense of *elongation* of two S–N bonds. A recent X-ray structural determination of **2d** has revealed a closed *cis, trans, cis* structure with weak intramolecular S···N interactions [*d*(S–N) = 2.61 Å].[16]

A unimolecular transformation of **1a** into **2a** would occur with conservation of the only common symmetry element (the C_2 axis) (Scheme 1). The process starts with an a_2 normal vibrational mode of the ring. Along the C_2 pathway there is a bicyclic transition state (**3**), from which two S–N bonds are elongated while the N=N bond is formed. DFT calculations revealed that the isomerization involves an a–b HOMO–LUMO crossing. For **1a** the HOMO (11b) and LUMO (12a) energies are −5.54 and −3.06 eV, respectively; the corresponding values for **2a** are −5.66 eV for the HOMO (12a) and −4.29 eV for the LUMO (11b). Consequently, despite the strongly exothermic character of the isomerization, it will not occur spontaneously because it is thermally a symmetry-forbidden process. However, UV light can provide the energy necessary to overcome the activation barrier, since the process is photochemically allowed.

A qualitative explanation of the photochemical process can be provided in terms of the crucial MOs involving the reactive S–N centres. Only the relevant contributions to those functions are shown in Fig. 1. As the antipodal N atoms of the $C_2N_4S_2$ ring approach each other, two in-phase combinations of p orbitals (I-**1a** and II-**1a**, a symmetry) will lead to the formation of σ and π bonding orbitals, respectively, driving the system towards the transition state **3**. Geometric distortions to form transannular S···S bonds are common in S–N systems involving two-coordinate sulfur, *e.g.* S_4N_4,[17] 1,5-$(Ph_3PN)_2S_4N_4$,[18] 1,5-$(Me_2NC)_2N_4S_2$,[19] and 1,5-$R_4P_2N_4S_2$ (R = alkyl, aryl).[20] Simultaneously, an out-of-phase combination of p orbitals (III, b symmetry) will rise in energy to form the π* orbital. This implies a HOMO–LUMO crossing along the reaction pathway; the transformation in the ground state is, therefore, symmetry-forbidden. UV irradiation can promote one electron into the σ*(N–S) LUMO (IV-**1a**) making the process allowed.

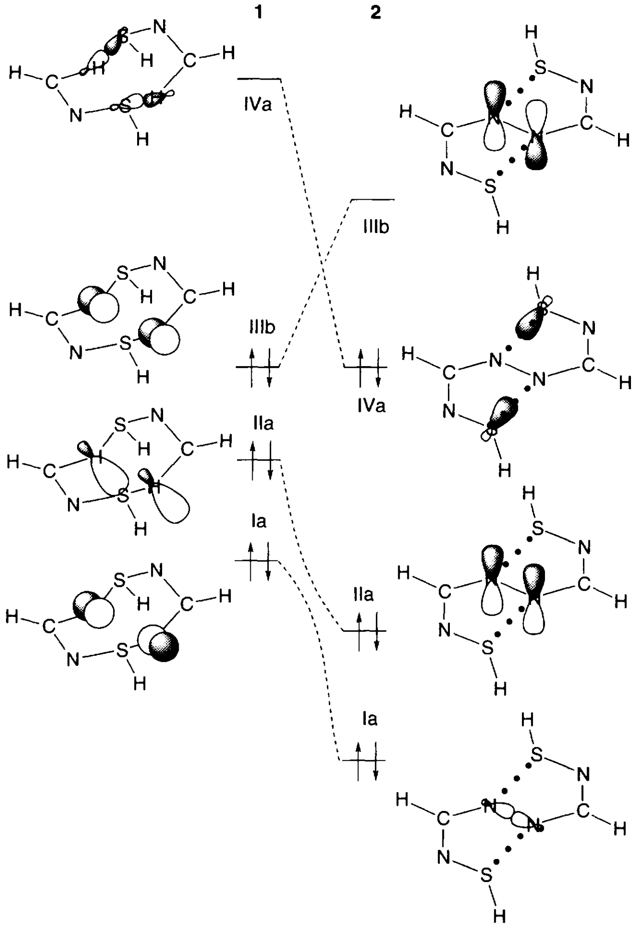

Fig. 1 Qualitative correlation diagram for the isomerization of $(HC)_2N_4(SH)_2$ **1a** into HSN=C(H)N=NC(H)=NSH **2a** based on the calculated energies of MOs I–IV

In view of the ease with which chalcogen–nitrogen heterocycles undergo molecular rearrangements, the novel photochemical process reported here is likely to be the forerunner of other unexpected transformations. Photochemical studies of these electron-rich ring systems merit more attention than they have heretofore been accorded.

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