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PHOTOLYSIS OF 1,12-BIS(DIAZO)-1,12-DIHYDROINDENO[2,3-a]FLUORENE. ESR AND OPTICAL DETECTION OF A σ-TYPE 1,4-BIRADICAL

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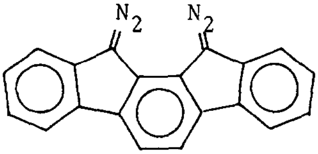
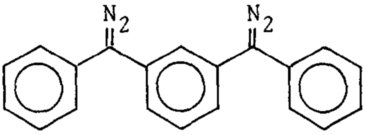
Photolysis of the title bis(diazo) compound in 2-methyltetrahydrofuran glasses at cryogenic temperature has been shown by ESR and UV absorption spectroscopic studies to result in a stepwise cleavage of two nitrogen molecules to give a 1,4-σ-biradical.

Recently there has been much interest in polycarbenes and polyradicals which have high spin ground states due to the topological symmetry of their molecular framework.[2] We now report on the products of photodecomposition of 1,12-bis(diazo)-1,12-dihydroindeno[2,3-a]fluorene (1) which was expected to afford a species having two carbene centers at positions capable of conjugation. The results of this study contrast with and are complementary to the case of 1,3-bis(α-diazobenzyl)benzene (2) and its homologues with regard to both the photolysis and the multiplicity of the resulting polycarbenic species.[3]



1



2

Bis(diazo) compound 1 [green needles; decomp. 155°C; MS, $M^+ = 306$ (2.3%), M^+-28 (100%), M^+-56 (33.7%)] was prepared by oxidation of the bis(hydrazone) of the corresponding bis(ketone)[4] using yellow mercuric oxide in the presence of KOH-MeOH. The UV spectrum of 1 shows characteristically split absorptions at λ_{max} = 490nm ($\varepsilon = 60$) and 570 nm ($\varepsilon = 28$) suggesting a strong through-space interaction between the two diazo groups.

UV irradiation of 1 in 2-methyltetrahydrofuran (= 2-MTHF)-THF (1:1, v/v) glass at 4 K was carried out through a Pyrex filter in an ESR cavity.[5] Signals due to a triplet carbene were observed; since the zero-field parameters ($D = 0.391$ cm^{-1}, $E = 0.0258$ cm^{-1}) are close to those of fluorenylidene ($D = 0.407$ cm^{-1}, $E = 0.027$ cm^{-1}), the monodiazomonocarbene structure 3, resulting from loss of one nitrogen molecule from 1, was assigned. The temperature variation of the triplet siginals in the range 15 ~ 50 K fitted a Curie-Weiss plot suggesting that the triplet is the ground state or is very close to it. At higher temperatures the triplet signals disappeared irreversibly in the dark according to a first order kinetic law with $t_{1/2}$ = 22 min at 55 K. No triplet species were detected when irradiation was carried out at 77 K.

The photolysis of 1 (5.9×10^{-3} M) in the presence of benzophenone (0.12 M) in 2-MTHF-THF glass, however, showed different features. The triplet monocarbene 3 was again detected at temperatures below 60 K. After warming the sample to 80 K in the dark to quench the ESR signals due to the monocarbene, the light was turned on again, and a different set of triplet signals ($D = 0.0739$ cm^{-1}, $E \leq 0.003$ cm^{-1}; accompanied by a $\Delta m = 2$ transition at 1581 gauss) was observed. The new triplet signals disappeared immediately after the light was extinguished, indicating that the triplet is an excited state of a different species (see Figure 1). The results indicate that the nitrogen remaining in 3 is removed thermally to give the bis(carbene) 4 which exists as the singlet 1,4-σ-biradical 5 as a result of conjugation of the p-type electrons on the two carbene centers; the second triplet species is then generated by benzophenone-sensitised excitation of 5.

ESR characterisation has been reported for a number of biradicals, but most of them are of the π-type.[6] The biradical detected here is of the σ-type and has a fixed geometry, providing an excellent model system for studying the intramolecular interaction of magnetic dipoles.[7] The zero field splitting parameters

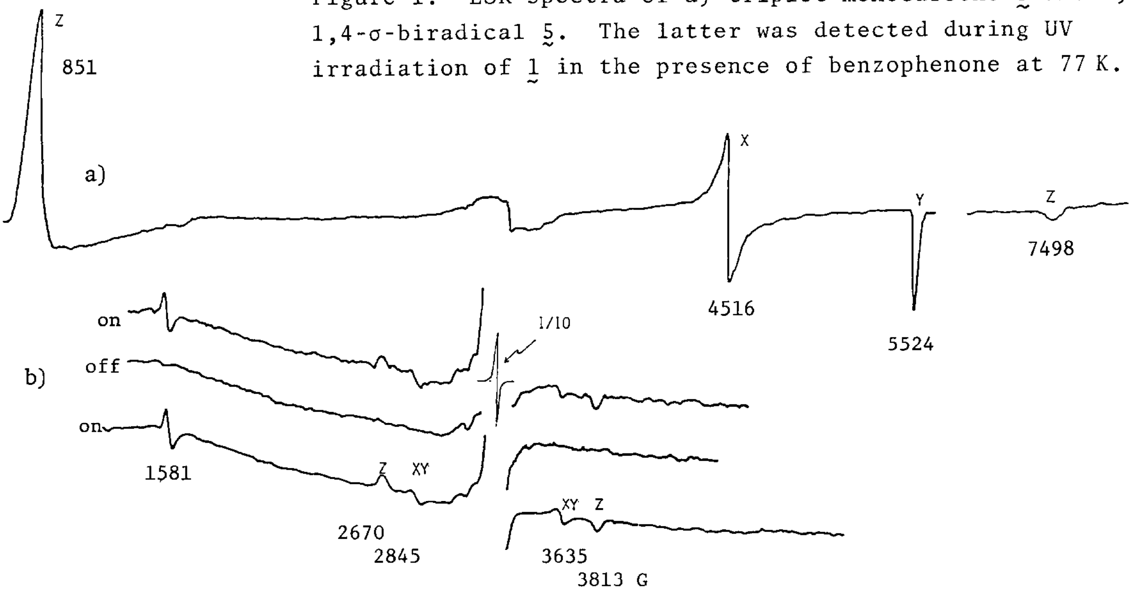


Figure 1. ESR spectra of a) triplet monocarbene 3 and b) 1,4-σ-biradical 5. The latter was detected during UV irradiation of 1 in the presence of benzophenone at 77 K.

for 5 lead to an estimate of the distance between the radical centers of 3.6 Å, based on the point dipole approximation; this estimate is close to the value of the C(1)-C(12) distance of 3.38 Å. The only published example which can be directly compared with 5 is the 1,6-σ-biradical obtained by the photolysis of 1,4-bis(α-diazobenzyl)benzene for which D = 0.0521 and E = 0 cm^{-1}.[8]

The progress of photodecomposition of 1 was also monitored by UV spectroscopy at 77 K. The spectrum obtained during irradiation of 1 in a 2-MTHF-THF-Et$_3$N (1:1:0.1, v/v) glass showed strong absorption with characteristic vibrational structure in the range 350 ~ 400 nm and a broad weak absorption with maxima at 420 and 535 nm (Figure 2). The shorter wavelength band was exactly superimposable on the spectrum of the cyclic azine 6 (orange needles, mp 308 ~ 309.5 °C; MS, M$^+$ = 278.0837) which was a major photoproduct when the photolysis of 1 was conducted in THF at 25 °C. The longer wavelength absorption is probably due to the singlet biradical 5 which is the predominant species generated at 77 K. These observations suggest that formation of 6 may take place by intramolecular cylisation of the singlet monocarbene 3, even at 77 K, competing with intersystem crossing to triplet 3 (Scheme 1). From the absorbance attributed to 6 in the UV spectrum at 77 K, roughly a quater of 3 is diverted to cyclic azine.[9]

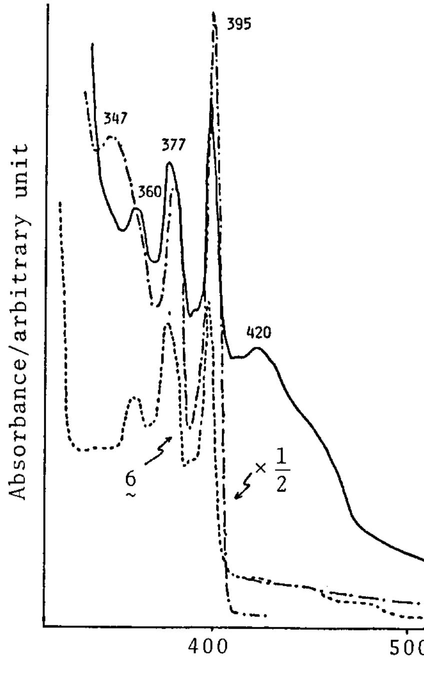
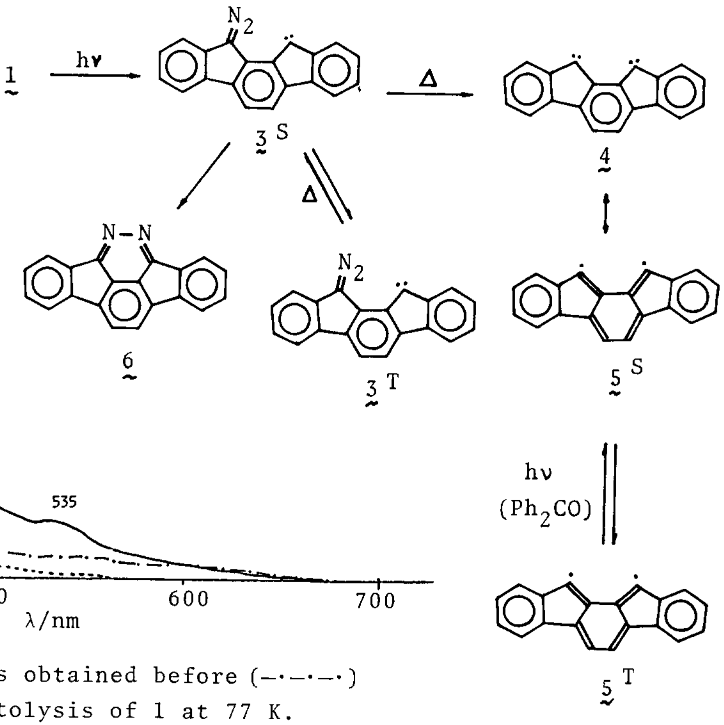


Figure 2. UV absorptions obtained before (—·—·—·) and after (———) the photolysis of 1 at 77 K. Absorptions due to authentic 6 (------) are also given.

Scheme 1



This picture is in sharp contrast to the case of 1,3-bis(α-diazobenzyl)-benzene **2** from which, in a glassy matrix, two nitrogen molecules are removed by one photon to give directly the bis(carbene) in its quintet ground state.[3] The difference is not surprising, however, when the exothermicity of the photodecomposition and the thermal stability of the monocarbenes derived from the two precursors are taken into account. The photodecomposition of diazodiphenylmethane is reported to be an exothermic process;[10] if the energy liberated from one diazo-moiety in **2** were efficiently transferred to the adjacent chromophore in a rigid matrix or in a single crystal, the second nitrogen molecule could be removed thermally. Such is apparently the case for **2** but not for **1**. Alternatively, the different behaviour of the two bis(diazo)-compounds may be associated with the lifetime of the monocarbenes; the delocalized monocarbene **3** is sufficiently long-lived to be detected by ESR spectroscopy below 60 K whereas the lifetime of the monocarbene from **2** is so short that it cannot be detected by CW ESR spectroscopy even at 4 K.

References and Notes

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7) Although the agreement of the experimental D value with the calculated one is reasonably well, there still remains a possibility that the observed triplet biradical is π-π* in nature.
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