New quintet carbenonitrene system formed in the photolysis of 2,6-bis(4,5-dimethoxycarbonyl-1*H*-1,2,3-triazolo)-4-azido-3,5-dichloropyridine

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New triplet pyridyl-4-nitrene, triplet pyridyl-2-imidoylcarbene and quintet 4-nitrenopyridyl-2-imidoylcarbene have been detected by EPR spectroscopy after photolysis of 2,6-bis(4,5-dimethoxycarbonyl-1*H*-1,2,3-triazolo)-4-azido-3,5-dichloropyridine at 77 K.

Recently,[1] azide **1** was synthesised, which is a very interesting compound for photochemical studies. Upon irradiation, this compound can undergo decomposition of the azido group and triazole rings to form nitrene **2**, carbenonitrene **3** and dicarbenonitrene **4**. In the case of a coplanar arrangement of spin carriers in **3** and **4**, these species may have quintet and septet ground spin states, respectively. Thus, only quintet (3-nitrenophenyl)-methylene was isolated in cryogenic matrices.[2] Here, we report on a quintet EPR spectrum formed in the photolysis of compound **1**, which is consistent with expectations for a carbenonitrene system.

Azide **1** was irradiated in degassed frozen solutions of 2-methyltetrahydrofuran (MTHF) with light at $\lambda > 300$ nm for 5 min at 77 K. Upon irradiation, the sample became blue and displayed four signals at 3233, 5197, 6541 and 6765 G in the X-band EPR spectrum (Figure 1). The high-field signals at 5197 and 6765 G lie in regions typical of triplet carbenes[3] and nitrenes[4] and hence can be assigned to isolated triplet imidoyl carbene ($|D/hc|$ = = 0.420 cm^{-1}) and triplet pyridylnitrene ($|D/hc|$ = 0.934 cm^{-1}) units.† In comparison with earlier studied cyclic imidoyl carbenes ($|D/hc|$ = 0.12-0 .17 cm^{-1}),[5] a new acyclic imidoyl carbene has rather large zero-field splitting (zfs) *D*-parameter, which is obviously explained by the effect of a carbomethoxy substituent at this unit. Thus, many carbalkoxy carbenes have zfs values of $|D/hc|$ = 0.61 cm^{-1}.[6] The lower intensity of the carbene signal relative to the nitrene peak is apparently associated with the shorter lifetime of this species. Contrary to nitrenes, many carbenes are unstable even at 77 K and can only be detected by EPR spectroscopy at temperatures below 20 K.[3]

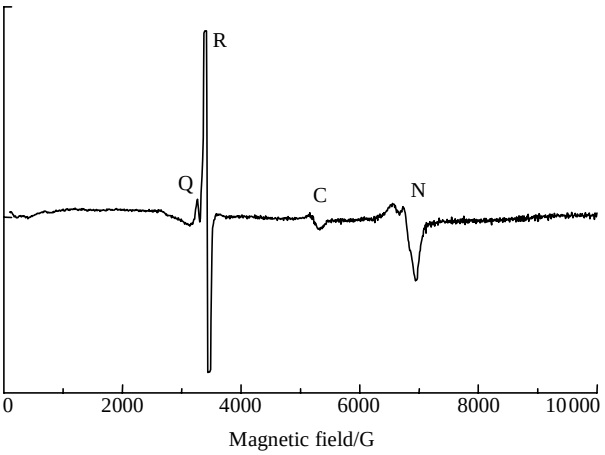


Figure 1 EPR spectrum after the photolysis of azide **1** (ν_0 = 9.560 GHz) with light at $\lambda > 300$ nm for 5 min in MTHF at 77 K. The peaks N, C, Q and R correspond to an isolated triplet nitrene unit, an isolated triplet carbene unit, a quintet carbenonitrene system and a radical from MTHF, respectively.

† According to our observations, the azido group in **1** is more photolabile and decomposes first. On this basis, we excluded imidoyl carbene **5** from further consideration.

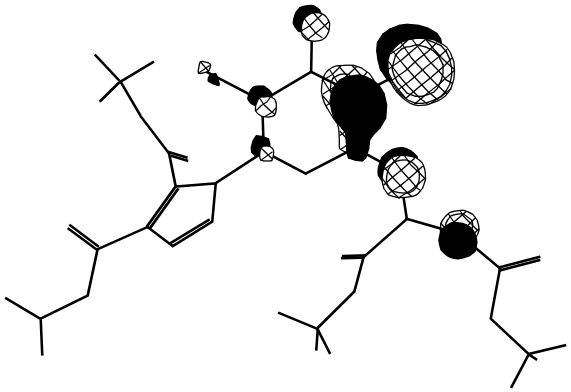
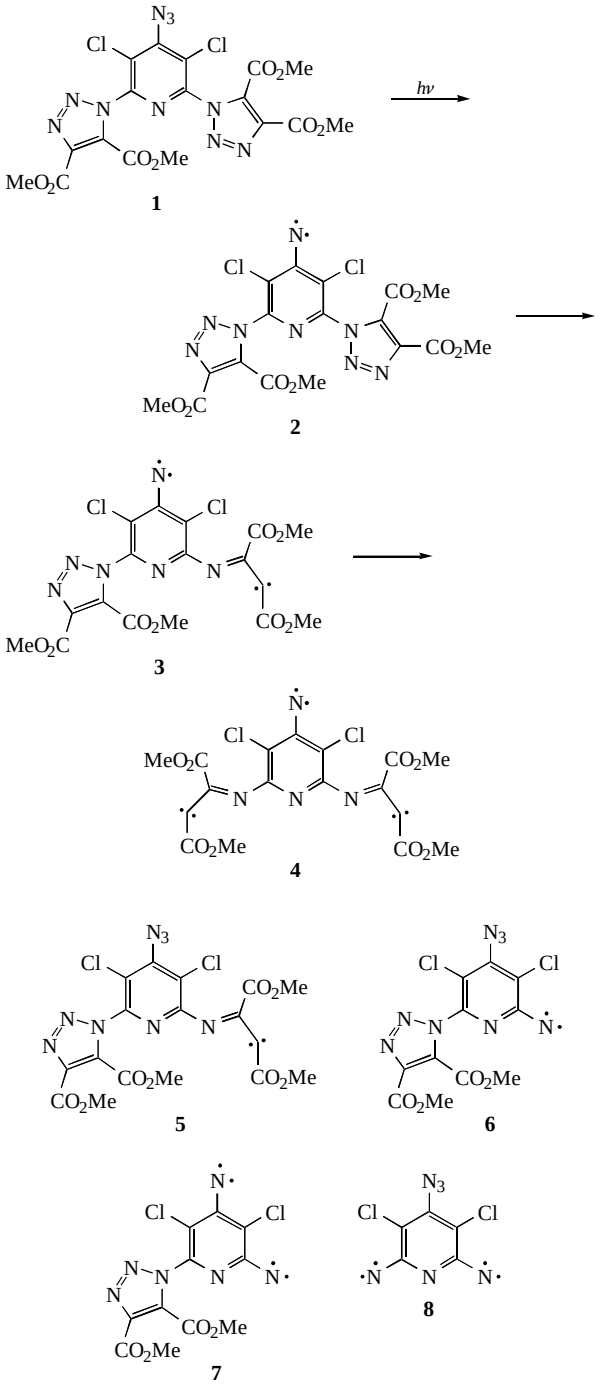


Figure 2 Orbital density distribution in the SOMO of quintet **3**.

The signal at 3233 G is of considerable interest. Recently,[7] it was found that quintet pyridyl-2,4-dinitrenes display a characteristic EPR signal at about 3000 G ($|D/hc|_{quintet}$ = 0.23 cm^{-1}), and quintet pyridyl-2,6-dinitrene **8** gives a signal at 3345 G ($|D/hc|_{quintet}$ = 0.280 cm^{-1}). According to these data, a signal observed at 3233 G lies at a too high magnetic field to be assigned to quintet 2,4-dinitrene **7**, at least by analogy to the previous work. The peak at 3233 G is also at a significantly lower field than that expected for quintet dinitrene **8**.[7] A reasonable assumption for the carrier of 3233 G is quintet carbenonitrene **3**. Taking into account that many quintet species give, as a rule,[8,9] one or two weak EPR peaks in high magnetic fields, the signal at 6541 G may also have a contribution from putative quintet carbenonitrene **3**. If we assume that this is the highest field transition of quintet **3** and that its second highest field transition is coincident with the carbene peak at 5197 G,‡ we find zfs parameters of $|D/hc|$ = 0.099 cm^{-1} and $|E/hc|$ = 0.0052 cm^{-1}. The *D*-value for **3** thus calculated falls between the relevant values for quintet *m*-phenylenedicarbenes ($|D/hc|$ = 0.070-0 .084 cm^{-1})[8(a),(b)] and quintet *m*-phenylenedinitrene ($|D/hc|$ = 0.156 cm^{-1}),[8(a)] and it is close to the *D*-value reported for (3-nitrenophenyl)methylene ($|D/hc|$ = 0.124 cm^{-1}).[2] The latter displayed a low-field signal at about 3200 G and the highest field transition at 7295 G.

A difference in the EPR characteristics of two quintet carbenonitrenes obviously results from different chemical bonding and spatial arrangements of spin carrier units in these species. The low intensity of EPR signals of **3** can tentatively be explained either by a short lifetime of this species at 77 K or by a low concentration of conformational isomers of **3** with a nearly coplanar arrangement of the carbene and nitrene units. Accord-

‡ The zfs parameters were estimated using the Wasserman procedure.[8(a)] This allowed us to compare the zfs parameters of **3** with those for quintet dicarbenes[8] and quintet dinitrenes.[8(a),9(a)-(c)] The more advanced eigenfield simulation gives higher zfs *D*-values for *meta*-dinitrenes.[7,9(d),(e)] For details of the eigenfield method, see ref. 10. Assuming that $|E/hc|$ = = 0.035 cm^{-1}, in accordance with findings,[7] the approximate zfs for the quintet peak at 3233 G is $|D/hc| \sim 0.27$ cm^{-1} (this is an approximate value because other quintet features are insufficiently pronounced to be adequately identified).



ing to PM3 computations,§ only such conformers (Figure 2) have the SOMO symmetry and high π-orbital densities at both triplet units that are favourable[12] to the high ground spin multiplicity of **3**. Note that the absence of EPR signals for **4** does not exclude the possibility of formation of **4** as low-spin conformers. An EPR study of derivatives of **4** with less bulky triazole substituents at a pyridine ring may be helpful to clarify this uncertainty.

§ The structure of quintet carbenonitrene **3** was calculated with the full optimization of geometry parameters using the PM3 method (UHF, SCF level).[11] Quintet **3** is in the most stable *s*-Z conformation for a carbene moiety, if we consider the mutual arrangement of a carbene unit and a carbomethoxy group. Usually, *s*-Z conformers of carbalkoxy carbenes are the major products of photolysis of diazo precursors.[3]

The quintet carbenonitrene system described represents an unusual quintet heterospin molecule, the high-spin state of which results from the ferromagnetic exchange interaction between remote imidoyl carbene and aryl nitrene units. Despite the lack of a rigid structure, this system has a reasonably long lifetime in an organic glass at 77 K to be observable by EPR spectroscopy.

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