

states of these species.¹⁹ The rather large singlet–quintet energy gap of carbenonitrene **10** suggests that this species is even more photochemically stable than triplet carbenes **14a,b**.

To our knowledge, the rearrangement of **9** into **10** is the first chemical reaction discovered for quintet dinitrenes. The high reactivity of **9** can be rationalised by an analysis of the *D*-values of this ($|D/hc| = 0.247 \text{ cm}^{-1}$) and two other parent **4a** ($|D/hc| = 0.283 \text{ cm}^{-1}$)^{7(b)} and **4c** ($|D/hc| = 0.257 \text{ cm}^{-1}$)^{7(c)} quintet dinitrenes. The smallest *D*-value for **9** indicates that exchange interactions between unpaired electrons of two nitrene units in **9** are the weakest.¹⁵ This is also supported by the results of PM3 computations, which show that the molecule of **9** has the longest N–C=N–C–N distance between two nitrene units and the shortest C(4)–N, C(2)–C(3) and C(6)–C(5) bonds. Obviously, the weakening of conjugation between the nitrene units and the pyridine ring in quintet pyridyl-2,6-dinitrenes, as in the case of triplet pyridyl-2-nitrenes, favours the localization of spin density on the nitrene centres, thus increasing their reactivity. As has been noted earlier, the border between ‘stable’ and ‘reactive’ triplet pyridyl-2-nitrenes lies in the region of nitrenes with $|D/hc| = 1.04\text{--}1.05 \text{ cm}^{-1}$. Judging on results of the photolysis of **4a**, **4c** and **9**, a similar border between ‘stable’ and ‘reactive’ quintet pyridyl-2,6-dinitrenes lies in the region of nitrenes with $|D/hc| = 0.25\text{--}0.26 \text{ cm}^{-1}$. Taking into account small magnitudes of the *D*-parameters of quintet dinitrenes, it is reasonable to assume that even very small changes in the *D*-values of quintet pyridyl-2,6-dinitrenes (much smaller than in the case of triplet nitrenes)¹ evidence for essential changes in the reactivities of such species.

We are grateful to Professor P. M. Lahti (University of Massachusetts, Amherst) for EPR simulations of quintet dinitrene **9** and to Professor M. S. Platz (Ohio State University, Columbus) for helpful discussions.

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Received: 1st February 2001; Com. 01/1765

Are aroylnitrenes species with a singlet ground state?

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DOI: 10.1070/MC2001v01n03ABEH001376

The B3LYP calculations of the properties of singlet and triplet benzoylnitrenes and naphthoylnitrenes testify to the stabilization of the ¹A' state relative to the ³A'' state due to the intermediacy of an NCO structure between nitrene and oxazirene in the ¹A' state.

Nitrenes are the key intermediates of azide photolysis and thermolysis. It is well known¹ that alkyl- and aryl nitrenes have a triplet ground state. The case with aroylnitrenes^{1–4} is more complicated and inconsistent. Taking into account that aroylnitrenes have a singlet ground state, Melvin and Schuster⁵ proposed acetyl-substituted aroyl azides as potential photolabeling agents.

Nitrenes, as well as better studied carbenes, have a nontrivial electronic structure with two valence electrons, which are distributed between two nonbonding molecular orbitals (NBMOs). In carbenes, one of the NBMOs is a pure *p*-AO; the second

hybridised σ orbital exhibits a considerable *2s* character and thus a much lower energy. The ground state of the parent carbene CH₂ is a triplet state. The singlet state, in which both of the nonbonding electrons occupy the σ NBMO, is only 38 kJ mol⁻¹ higher in energy. Phenyl⁶ and methyl⁷ substituents reduce ΔE_{ST} by 20–30 kJ mol⁻¹, and halogens make a singlet state to be the ground state.⁸

Unlike carbenes, in the parent nitrene NH, both of the NBMOs are pure *p*-AOs. Lower Coulomb repulsion in a triplet state cannot be compensated by occupation of the lower MO by two electrons in a singlet state, as in the case of carbene. Therefore,

To predict the electronic absorption spectra of these intermediates, the time-dependent DFT calculations²⁵ at the B3LYP/6-31+G* level were performed. The near-UV and visible spectrum of the species in the ¹A' state has transitions at 532 ($f=0$) and 306 nm ($f=6\times 10^{-3}$) in the case of benzoylnitrene. The spectrum of naphthoylnitrene has two transitions with non-zero intensities at 319 ($f=3.4\times 10^{-3}$) and 313 nm ($f=1.5\times 10^{-2}$). This is in agreement with the fact that no intermediates with absorption in the region 350–600 nm were observed upon photolysis of benzoyl and naphthoyl azides.^{3,5}

This work was supported by the Russian Foundation for Basic Research (grant no. 01-03-32864), the Ministry of Higher Education of the Russian Federation and the Swiss National Science Foundation (SCOPES 2000–2003, grant no. 7SUPJ062336).

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Received: 14th September 2000; Com. 00/1701

New type of pyrimidinophanes with α,ω -bis(uracil-1-yl)alkane and bis(uracil-5-yl)methane units

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DOI: 10.1070/MC2001v011n03ABEH001440

New pyrimidinophanes containing four uracil units connected with methylene bridges through the N(1) and C(5) atoms of pyrimidine rings were obtained by treatment of 1,4-bis(3,6-dimethyluracil-1-yl)butane with paraform.

Macrocyclic compounds consisting of purine and pyrimidine bases are interesting model objects for the study of stacking structures in nucleic acids and can serve as precursors for host-guest molecules. While purinophanes of different types have been synthesised and well studied, pyrimidinophanes have been

reported only recently.^{2–6} In the course of an investigation aimed at the creation of effective macrocyclic complexing agents, T. Itahara^{2,5} elaborated a direct method of pyrimidinophane preparation. These pyrimidinophanes, which were synthesised for the first time previously,^{7–10} consisted of two uracil or 2,4-dithio-