

## Full Articles

### Ground-state multiplicity of acylnitrenes: computational and experimental studies

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The singlet–triplet energy splitting ( $\Delta E_{ST} = E_S - E_T$ ) was calculated for formylnitrene (**5**) and for the *syn*- and *anti*-rotamers of carboxynitrene HOC(O)N (**6**) by the CCSD(T) method. Extrapolation of  $\Delta E_{ST}$  to a complete basis set was calculated to be negative for **5** and strongly positive for **6**. Similar results were obtained by the G2 procedure. The reason for the dramatic stabilization of the singlet state appeared to be a special bonding interaction between the nitrogen and oxygen atoms, which results in the structure intermediate between those of nitrene and oxazirene. It was found that the B3LYP/6-31G(d) method overestimates  $\Delta E_{ST}$  by  $\sim 9$  kcal mol<sup>-1</sup> for **5** and by  $\sim 7$  kcal mol<sup>-1</sup> for **6**. Taking into account this overestimation and the results of DFT calculations, it was concluded that benzylnitrene has a singlet ground state. It was proved experimentally using photolysis of benzoyl azide in an argon matrix at 12 K that benzylnitrene has a singlet ground state and its structure is similar to that of oxazirene. Nevertheless, these singlet intermediates have low barrier to the aziridine formation, which is traditionally considered to be a typical singlet nitrene reaction.

**Key words:** acyl azides, acylnitrenes, matrix isolation, IR spectroscopy, UV-Vis spectroscopy, quantum chemical calculations, *ab initio* quantum chemical calculations, transition states.

Photolysis of carbonyl azides RC(O)N<sub>3</sub> gives rise to two types of products: (i) isocyanates RNCO (the products of the photo-Curtius rearrangement<sup>1</sup>) and (ii) bimolecular trapping products typical of the reactions of sin-

glet carbonylnitrenes RC(O)N.<sup>2</sup> It has, however, been shown that the yield of isocyanates upon photolysis of a series of carbonyl azides (R = *tert*-butyl, aryl) remains constant ( $\sim 40$ –50%) irrespective of the presence or ab-

sence of nitrene traps.<sup>3–8</sup> Therefore, it was concluded that, even if carbonylnitrenes are formed during photolysis of carbonyl azides, they do not rearrange to isocyanates.<sup>2,4–7</sup>

It was demonstrated<sup>9,10</sup> that direct and triplet-sensitized photolysis of benzoyl azide (**1**) in alkenes produces the same trapping products and that these products are characteristic of reactions of singlet nitrenes. Similar results were obtained for 2-naphthoyl azide and a series of substituted benzoyl azides.<sup>11–13</sup> No nitrene-like triplet ESR spectrum was also detected after benzoyl azide photolysis in glassy matrices.<sup>14,15</sup> Although the authors<sup>11–13</sup> were unable to determine the multiplicity of aroylnitrenes unambiguously by direct spectroscopic observation, they concluded that the sum total of their data left little doubt that aroylnitrenes have singlet ground states.

It is typical of nitrenes to have triplet ground states.<sup>16</sup> The value of the singlet–triplet energy splitting  $\Delta E_{ST} = E_S - E_T$  ( $E_S$  and  $E_T$  are the energies of the singlet and triplet states, respectively) was determined experimentally in only three cases. It was found to be 36 kcal mol<sup>-1</sup> for the simplest nitrene NH,<sup>17</sup> 31 kcal mol<sup>-1</sup> for methylnitrene,<sup>18</sup> and about 18 kcal mol<sup>-1</sup> for phenylnitrene.<sup>19</sup> To understand why aroylnitrenes may have a singlet ground state, we performed DFT calculations of the singlet–triplet splittings for benzoylnitrene (**2**) and 2-naphthoylnitrene (**3**).<sup>20</sup> The resulting  $\Delta E_{ST}$  values were found to be small (~5 kcal mol<sup>-1</sup>), but the triplet states were still lower in energy.<sup>20</sup> The reason for the marked reduction of  $\Delta E_{ST}$  on going from aryl- to aroylnitrenes appeared to be a bonding interaction between the nitrogen and oxygen atoms in the singlet state, resulting in a singlet-state structure which is intermediate between those of a nitrene and an oxazirine.<sup>20</sup>

On the other hand, upon photolysis and thermolysis of azidoformates ROC(O)N<sub>3</sub> (R = Alk, aryl) the major products are derived from capture of acylnitrenes ROC(O)N.<sup>2,21–25</sup> The triplet multiplicity of the ground state of the ethoxycarbonylnitrene EtOC(O)N (**4**) was deduced on the basis of products analysis<sup>2,22,24,25</sup> and proved by ESR spectroscopy.<sup>11,15</sup> A very similar ESR spectrum was recorded<sup>12</sup> upon photolysis of (4-acetylphenoxy)carbonyl azide at 77 K.

Recently,<sup>26</sup> a laser flash photolysis study of EtOC(O)N was carried out in order to determine the absolute rates of spin relaxation and of the reaction of this intermediate with tetramethylethylene (TME). The formation of triplet ethoxycarbonylnitrene was registered ( $\lambda = 400$  nm,  $\tau = 1.5$   $\mu$ s in CF<sub>2</sub>CICFCI<sub>2</sub> at 298K) and a reduction of its yield and a shortening of its lifetime in the presence of TME observed. It was deduced that singlet ethoxycarbonylnitrene has a lifetime between 2 and 10 ns in CF<sub>2</sub>CICFCI<sub>2</sub> at room temperature.<sup>26</sup>

In order to understand the proposed difference in the ground-state multiplicity of two types of acylnitrenes,

RC(O)N and ROC(O)N, we performed high-level quantum chemical calculations of  $\Delta E_{ST}$  values for two model compounds, formylnitrene HC(O)N (**5**) and carboxynitrene HOC(O)N (**6**). In addition, we calculated barriers to the reactions of singlet acylnitrenes with ethylene. The multiplicity and the structure of the ground state of benzoylnitrene were also proved experimentally.<sup>27</sup>

## Experimental

**Spectroscopy in argon matrices.** A gaseous mixture of 1 part of benzoyl azide in 1000 parts of argon (mixed with 10% of N<sub>2</sub> to improve the optical properties of the matrix) was slowly deposited on a CsI plate at 19 K. Photolysis of benzoyl azide was performed with a low-pressure mercury lamp (254 nm) or a medium-pressure Hg/Xe lamp with a 313-nm interference filter. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda-900 spectrometer (200–1000 nm). IR spectra were measured on a Bomem DA3 interferometer (4000–500 cm<sup>-1</sup>) with an MCT detector.

**Quantum chemical calculations.** The B3LYP/6-31G(d) calculated geometries of singlet and triplet molecules **2** and **5** were taken from our previous computational study<sup>20</sup> and those of other compounds discussed in this paper were computed by the same method. The geometries of the model compounds **5** and **6** were reoptimized at the CCSD(T)/cc-pVTZ level. All B3LYP calculated structures were ascertained to be minima on the potential energy surfaces by the second derivative calculations, which also yielded harmonic frequencies (for comparison with experimental spectra) and zero-point vibrational energies, which were taken into account in the singlet–triplet splitting calculations. The stability of the SCF solutions for the nitrenes was tested by CIS calculations. If no precautions were taken, the wave function for triplet formylnitrene invariably converged to that of the excited state. Reoptimization of the wave function using the "stable=opt" procedure (GAUSSIAN-98 suite of programs) was required to obtain the geometric parameters and energy characteristics of the lowest triplet state.

The  $\Delta E_{ST}$  values for formylnitrene and carboxynitrene were also evaluated at the CCSD(T) levels<sup>28–30</sup> using Dunning's correlation-consistent basis sets ranging from double to quadruple-zeta quality.<sup>31</sup> Extrapolation to a complete basis set was performed using exponential Dunning–Feller formula.<sup>32–34</sup> All these calculations were performed with the GAUSSIAN-98 suite of programs,<sup>35</sup> except for the geometry optimizations of the two model compounds at the CCSD(T)/cc-pVTZ level which were carried out with the ACES II program.<sup>36</sup>

In addition, the singlet and triplet states of formylnitrene and carboxynitrene molecules were characterized in accordance with the G2 procedure.<sup>37</sup> As mentioned above, reoptimization of the triplet formylnitrene wave function to the lowest triplet state was necessary. It should be noted that geometry optimization of singlet formylnitrene at the HF/6-31G(d) level failed due to an inevitable convergence to the isocyanate. In order to overcome this obstacle, we calculated the zero-point vibrational energy correction for formylnitrene at the MP2(full)/6-31G(d) level of theory.

Location of the transition states of the reactions of singlet acylnitrenes with ethylene was carried out at the B3LYP/6-31G(d) level using the synchronous transit-guided

quasi-Newton method<sup>38</sup> as implemented in the GAUSSIAN-98 suite of programs.<sup>35</sup> In addition to second derivative calculations, all transition-state structures were subjected to intrinsic reaction coordinate (IRC) calculations<sup>39</sup> to identify the minima they interconnect.

The excited state energies of benzoylnitrene were calculated with the B3LYP/6-31G(d) geometry by the CASSCF/CASPT2 procedure<sup>40</sup> using the ANO-S basis set.<sup>41</sup> In order to arrive at a satisfactory description of all excited states at the CASPT2 level (*i.e.*, remove intruder states), it was necessary to resort to the level-shifting technique,<sup>42</sup> whereby it was carefully assured that no artifacts are introduced. All CASSCF/CASPT2 calculations were carried out with the MOLCAS 4 suite of programs.<sup>43</sup>

## Results and Discussion

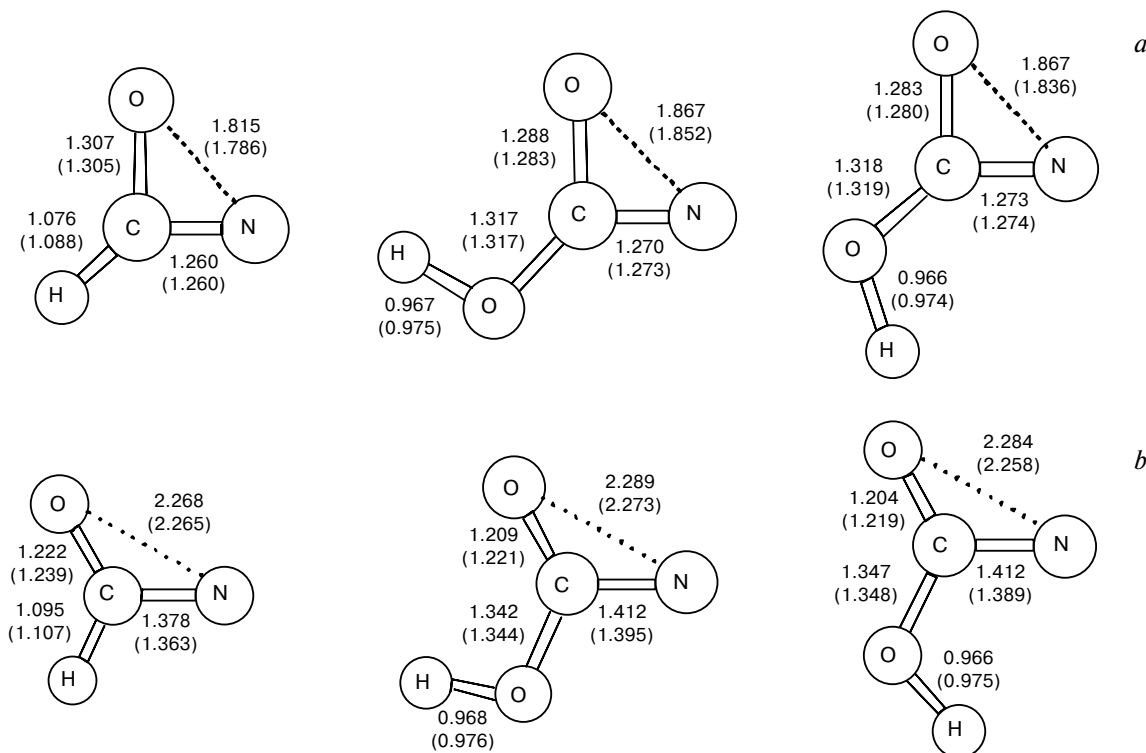
### Quantum chemical calculations of the singlet-triplet splitting

Most of the calculations originally available in the literature concerned the simplest acyl azide and acylnitrene, that is, formyl azide and formylnitrene, respectively.<sup>44–49</sup> Until recently,<sup>20,50–52</sup> all theoretical studies on acylnitrenes were based on low-level *ab initio* calculations<sup>44–49</sup> which gave inconsistent results. As mentioned above, B3LYP/6-31G(d) calculations<sup>20</sup> of molecules **2**, **3**, and **5** in the lowest singlet state showed that their CON fragments resemble that of a cyclic oxazirane, although the calculated N–O distance ( $\sim 1.76$  Å) is much longer than a normal N–O single bond.

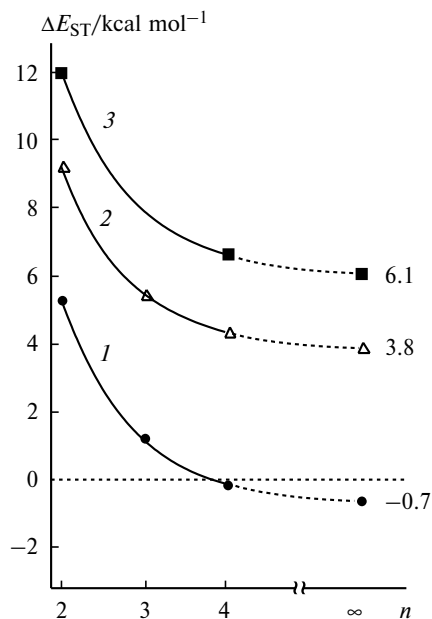
Recently,<sup>50,51</sup> high-level calculations of the structure and energy of triplet formylnitrene and "cyclic" singlet species were performed. The MP2/6-31G(d) calculated geometries of these intermediates are very similar to those optimized using the B3LYP/6-31G(d) procedure.<sup>20</sup> The  $\Delta E_{ST}$  values calculated at the CASPT2/cc-pVTZ, QCISD(T)/cc-pVTZ, and G2 levels of theory are 3.5, 0.6, and  $-2.9$  kcal mol<sup>-1</sup>, respectively.<sup>50,51</sup>

To analyze the influence of the basis set and the level of treatment of electron correlation on the calculated  $\Delta E_{ST}$  values, we computed the geometries and energies of the lowest singlet and triplet states of formylnitrene and two (*syn*- and *anti*-) rotamers of carboxynitrene at the CCSD and CCSD(T) levels, increasing the size of the basis set from double- to quadruple-zeta quality. Figure 1 shows that the geometries optimized by the CCSD(T)/cc-pVTZ procedure agree very well with those found by the B3LYP/6-31G(d) method, which therefore appears to provide adequate geometries of the lowest singlet and triplet states of acylnitrenes.

In the case of formylnitrene B3LYP and CCSD calculations provide strongly positive  $\Delta E_{ST}$  values of 8.1 and 14.1 kcal mol<sup>-1</sup>, respectively if 6-31G(d) basis is used (*i.e.*, they predict triplet ground states). The splitting is slightly reduced on going to larger basis sets; extrapolation to a complete basis set gives 6.6 (B3LYP) and 9.4 kcal mol<sup>-1</sup> (CCSD). However,  $\Delta E_{ST}$  decreases dramatically on perturbative inclusion of triple excitations in



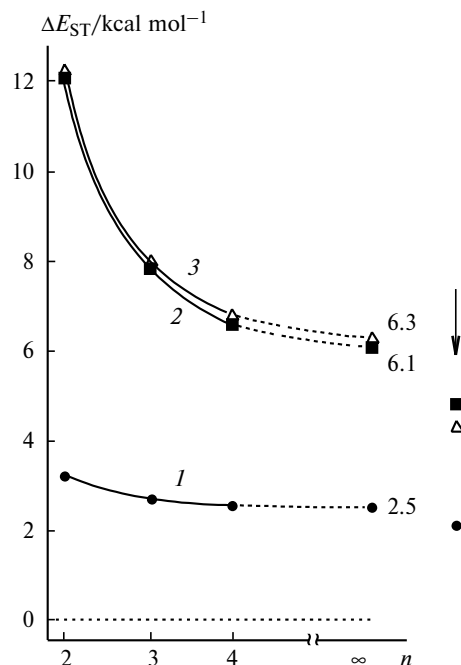
**Fig. 1.** Bond lengths (Å) in the formylnitrene **5** and in the *syn*- and *anti*-rotamers of carboxynitrene **6** obtained from CCSD(T)/cc-pVTZ and B3LYP/6-31G(d) (in parentheses) calculations for the <sup>1</sup>A' (a) and <sup>3</sup>A'' (b) states.



**Fig. 2.** The values of the singlet–triplet splitting ( $\Delta E_{ST}$ ) for formyl nitrene **5** (*1*) and for the *anti*- (*2*) and *syn*-rotamers (*3*) of carboxynitrene **6** evaluated at the CCSD(T) level of theory with Dunning's correlation-consistent basis sets ranging from double ( $n = 2$ ) to quadruple-zeta ( $n = 4$ ) quality, by extrapolation to a complete basis set using the Dunning–Feller formula,<sup>32–34</sup> and at the G2 level (arrowed). The CCSD(T)/cc-pVTZ and B3LYP/6-31G(d) calculated geometries were used in the coupled cluster calculations of formyl nitrene and carboxynitrene, respectively.

the coupled cluster scheme. The  $\Delta E_{ST}$  values obtained for formyl nitrene from CCSD(T) calculations with different basis sets are shown in Fig. 2. These values further decrease with an increase in the size of the basis set. Extrapolation to a complete basis set leads to  $\Delta E_{ST} = -0.7$  kcal mol<sup>-1</sup>. However, on adding the zero-point vibrational energy difference between the two states,  $\Delta E_{ST}$  goes back to nearly zero. At the G2 level of theory,  $\Delta E_{ST}$  was calculated to be  $-2.9$  kcal mol<sup>-1</sup>. Therefore, we can conclude that the two spin states of molecule **5** must lie very close in energy and that the B3LYP/6-31G(d) method overestimates  $\Delta E_{ST}$  for formyl nitrene by about 9 kcal mol<sup>-1</sup> compared to the most accurate calculations (extrapolation of CCSD(T) results to a complete basis set).

However, prediction of a singlet ground state should be valid for aroylnitrenes. A  $\Delta E_{ST}$  value of about 5 kcal mol<sup>-1</sup> was calculated for benzoylnitrene and 2-naphthoynitrene by B3LYP/6-31G(d) method,<sup>20</sup> but the high-level calculations mentioned above show that it overestimates  $\Delta E_{ST}$  for formyl nitrene by about 9 kcal mol<sup>-1</sup>. Assuming that a similar error carries over to benzoylnitrene and 2-naphthoynitrene, the B3LYP calculated  $\Delta E_{ST}$  values for these two nitrenes suggest that they have singlet ground states ( $\Delta E_{ST} \approx -4$  kcal mol<sup>-1</sup>).



**Fig. 3.** Relative electronic energies of the triplet state of the *anti*-rotamer of carboxynitrene **6** (*1*) and of the singlet states of the *syn*- (*2*) and *anti*-rotamers (*3*) of molecule **6** obtained from CCSD(T) calculations with Dunning's correlation-consistent basis sets ranging from double ( $n = 2$ ) to quadruple-zeta ( $n = 4$ ) quality using the B3LYP/6-31G(d) calculated geometries, by extrapolation to a complete basis set, and at the G2 level (arrowed). The energy of the triplet state of the *syn*-rotamer of molecule **6** was chosen as a reference and set to zero.

The  $\Delta E_{ST}$  values obtained from B3LYP/6-31G(d) calculations of the *syn*- and *anti*-rotamers of HOC(O)N were found to be 13.1 and 11.0 kcal mol<sup>-1</sup>, respectively (13.2 and 11.5 kcal mol<sup>-1</sup>, respectively, with inclusion of zero-point vibrational energy correction). The energies of the structures were recalculated at the CCSD(T) level with the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. Figure 3 shows that at all levels of theory the *syn*- and *anti*-rotamers of singlet carboxynitrene are very close in energy and that the triplet state of the *anti*-rotamer is higher in energy than that of the *syn*-rotamer (Fig. 3). The  $\Delta E_{ST}$  values for two rotamers of HOC(O)N, derived from the relative energies plotted in Fig. 3, are presented in Fig. 2. Extrapolation to a complete basis set leads to  $\Delta E_{ST} = 6.1$  and 3.8 kcal mol<sup>-1</sup>, respectively, for the *syn*- and the *anti*-rotamer, thus providing strong evidence for a triplet ground state of carboxynitrene. We also conclude that the B3LYP/6-31G(d) method overestimates  $\Delta E_{ST}$  by about 7 kcal mol<sup>-1</sup> in the case of HOC(O)N. Note that the G2 theory also leads to the positive values of  $\Delta E_{ST}$  (4.8 kcal mol<sup>-1</sup> for the *syn*- and 2.2 kcal mol<sup>-1</sup> for the *anti*-rotamer) of carboxynitrene (see Fig. 2).

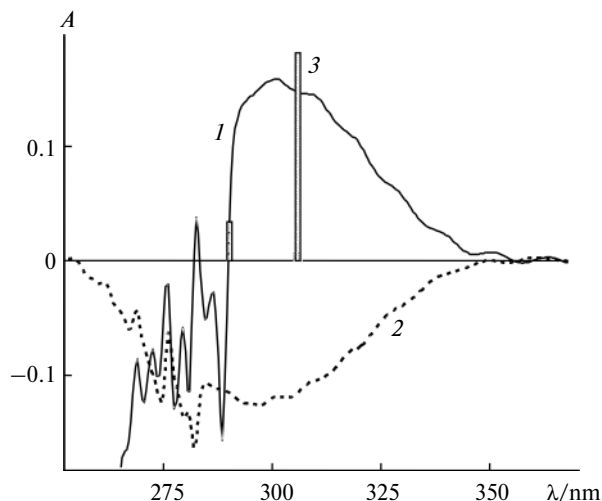
The difference in  $\Delta E_{ST}$  between carboxynitrene and formyl nitrene can be attributed to a weaker bonding in-

teraction between the nitrogen and oxygen atoms in the 1A' state of the former molecule, which manifests itself in lengthening of the N—O bond (Fig. 1). As there is no apparent reason why the presence of the hydroxyl O atom should interfere with the  $\sigma$ -bonding between the N and O atoms of the acylnitrene, we believe that it is the extension of the  $\pi$ -system, which leads to a weakening of the  $\pi$ -bond between these two atoms.

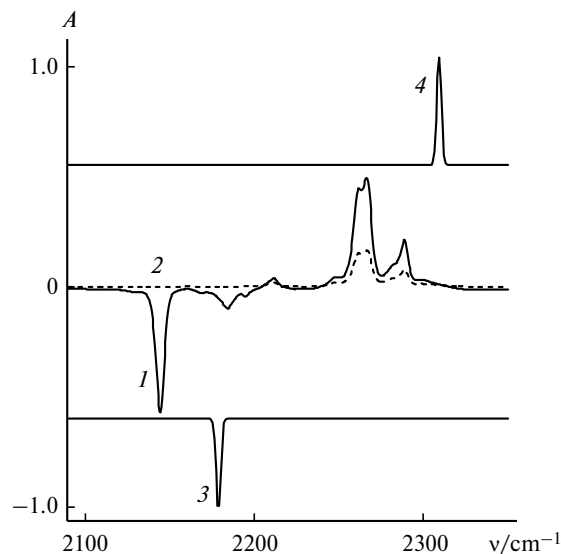
We also performed the B3LYP/6-31G(d) calculations of  $\Delta E_{ST}$  values for the *syn*- and *anti*-rotamers of phenoxycarbonylnitrene, which were found to be 12.3 and 9.5 kcal mol<sup>-1</sup>, respectively (12.6 and 10.1 kcal mol<sup>-1</sup>, respectively, with inclusion of zero-point vibrational energy correction). Taking into account that the B3LYP/6-31G(d) method overestimates  $\Delta E_{ST}$  for HOC(O)N by about 7 kcal mol<sup>-1</sup>, we may assume that  $\Delta E_{ST}$  is about 5 kcal mol<sup>-1</sup> for the *syn*- and 2.5 kcal mol<sup>-1</sup> for the *anti*-rotamer of phenoxycarbonylnitrene. This is in good agreement with the estimation<sup>12</sup> for 4-acetylphenoxycarbonylnitrene ( $0 < \Delta E_{ST} < 5$  kcal mol<sup>-1</sup>).

#### Photolysis of benzoyl azide in argon matrices

In order to determine the ground-state multiplicity and structure of benzoylnitrene experimentally, the photochemistry of benzoyl azide was studied in an Ar matrix at 12 K. After two minutes of photolysis in Ar at 254 nm, the optical spectrum of benzoyl azide was replaced by a new band with a maximum around 300 nm (Fig. 4, curve 1). Simultaneously, the IR bands of benzoyl azide, in particular, the strong stretching band of the N<sub>3</sub> group at 2145 cm<sup>-1</sup> (Fig. 5, curve 1, negative peaks), disappeared almost completely and gave rise to a set of new peaks,



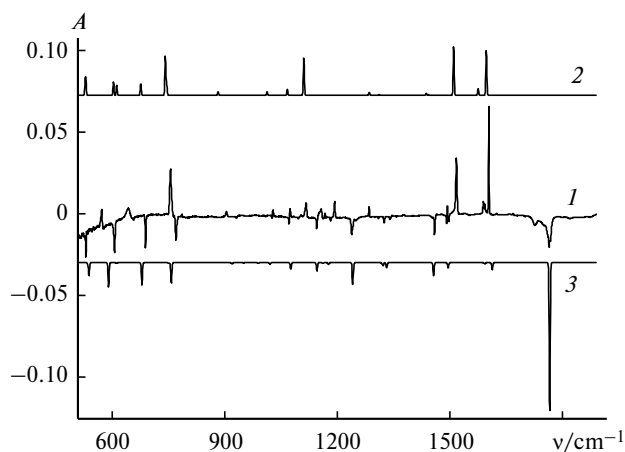
**Fig. 4.** Changes in the optical spectrum of benzoyl azide **1** on 254 nm photolysis in an Ar matrix for 2 min at 12 K (1) and changes in the spectrum 1 upon subsequent irradiation at 313 nm for 8 min (2). Positions and relative oscillator strengths of the absorption bands of the singlet benzoylnitrene **2** calculated by the CASSCF/CASPT2 method are depicted as solid bars (3).



**Fig. 5.** Changes in a characteristic region of the IR spectrum of benzoyl azide **1** obtained upon 254 nm photolysis in an Ar matrix for 2 min at 12 K (curve 1) and subsequent 313 nm photolysis for 8 min (curve 2). Positions and relative oscillator strengths of the N<sub>2</sub> stretching bands in molecule **1** (3) and NCO stretching bands in phenyl isocyanate **7** (4) obtained from B3LYP/6-31G(d) calculations and scaled by 0.97.

notably a strong group around 2270 cm<sup>-1</sup> (Fig. 5, curve 1, positive peaks).

Subsequent irradiation at 313 nm led to the disappearance of the newly formed UV band (Fig. 4, curve 2). Concomitantly, some of the newly formed IR peaks diminished strongly (Fig. 6, curve 1, negative peaks), whereas some other peaks, notably the intense group



**Fig. 6.** Changes in IR spectrum after subsequent 313 nm photolysis (performed after 2 min of 254-nm irradiation) of benzoyl azide **1** in an Ar matrix for 8 min at 12 K (curve 1). Positions and relative oscillator strengths of phenyl isocyanate **7** (2) and singlet benzoylnitrene **2** (3) calculated by the B3LYP/6-31G(d) and scaled by 0.97.

around 2270  $\text{cm}^{-1}$ , continued to grow (Fig. 5, curve 2; Fig. 6, curve 1, positive peaks).

Thus, this experiment indicates very clearly the formation of at least two products on the 254 nm photolysis of benzoyl azide. The first of these products has an absorption maximum at  $\sim 300$  nm and rearranges to the other primary product on exposure to 313 nm light.

The formation of phenyl isocyanate (**7**), along with products derived from singlet benzoylnitrene, is well known to occur upon photolysis of benzoyl azide at room temperature.<sup>2,6–10</sup> Therefore, we assumed that the products of the benzoyl azide photolysis at 12 K are phenyl isocyanate and benzoylnitrene, the latter in turn being converted to compound **7** on subsequent photolysis.

Next to the very intense doublet at 2266/2289  $\text{cm}^{-1}$ , the IR spectrum of the final product of photolysis (Fig. 6, curve 1, positive peaks) exhibits many less intense peaks in the range of 500–1800  $\text{cm}^{-1}$  (570, 642, 755, 904, 1028, 1074, 1117, 1285, 1517, and 1604  $\text{cm}^{-1}$ ). All of them correlate well with the IR spectrum calculated for phenyl isocyanate (Fig. 6, curve 2).

The absorption band at  $\sim 300$  nm (Fig. 4) belongs presumably to the singlet benzoylnitrene, which has a structure intermediate between that of a nitrene and an oxazirene. Indeed, the two most intense transitions in the spectrum of this species calculated by the CASSCF/CASPT2 procedure are at 306 and 290 nm, respectively (solid bars in Fig. 4). In addition, a very weak transition to the first excited state is predicted at 513 nm. It consists mainly of electron promotion from an allylic type  $\pi$ -orbital to the low-lying  $\sigma^*$ -orbital of the very weak N—O bond.

The experimental IR spectrum (529, 606, 689, 770, 1071, 1145, 1238, 1325, 1341, 1459, and 1765  $\text{cm}^{-1}$ ) of a transient species with an absorption maximum at 300 nm (Fig. 6, curve 1, negative peaks) is also in very good agreement with the calculated IR spectrum of singlet benzoylnitrene (Fig. 6, curve 3).

Hence, two products, phenyl isocyanate **7** and a singlet species **2** with a structure intermediate between those of a nitrene and an oxazirene, are produced on photolysis of benzoyl azide **1** (Scheme 1). According to the IR spec-

tral data, about 75% of phenyl isocyanate is formed after complete decomposition of benzoyl azide (2 min of photolysis at 254 nm). Using the initial slope of the kinetic curves of the formation of the products **7** and **2** on 254-nm irradiation, we can estimate the **7** : **2** yield ratio in the primary process at 64 : 36.

A positive answer can now be given to the question "Are aroylnitrenes ground-state singlets?"<sup>11</sup> Calculations and experiments now agree that aroylnitrenes are indeed ground-state singlets, but calculations show that these species have electronic structures and geometries that are intermediate between those of nitrenes and oxazirenes. Therefore, a new question arises — do these species undergo reactions that are typical of singlet nitrenes?

Recently,<sup>27</sup> the photochemistry of benzoyl azide in solution at ambient temperatures was studied by nanosecond time-resolved IR spectroscopy. It was found that photolysis of **1** produces two primary species, namely, singlet benzoylnitrene (**2**) and phenyl isocyanate (**7**). The singlet nitrene **2** undergoes an insertion into solvent C—H bonds to give amides (cyclohexane,  $\tau = 0.9$   $\mu\text{s}$ ) and adds to acetonitrile to give an ylide ( $\text{CD}_3\text{CN}$ ,  $\tau = 0.3$   $\mu\text{s}$ ).<sup>27</sup> The lifetime of **2** was 6  $\mu\text{s}$  in the most inert solvent  $\text{CH}_2\text{Cl}_2$ .<sup>27</sup>

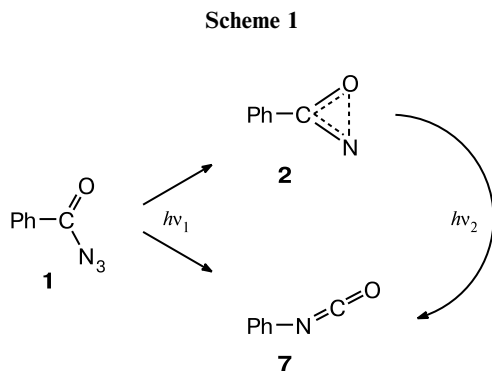
Stereospecific formation of aziridines in reactions with olefins is traditionally considered to be a characteristic reaction of singlet nitrenes.<sup>16</sup> To understand how the singlet acylnitrenes with their unusual electronic structure add to olefins, we modeled the reactions of singlet acylnitrenes with ethylene.

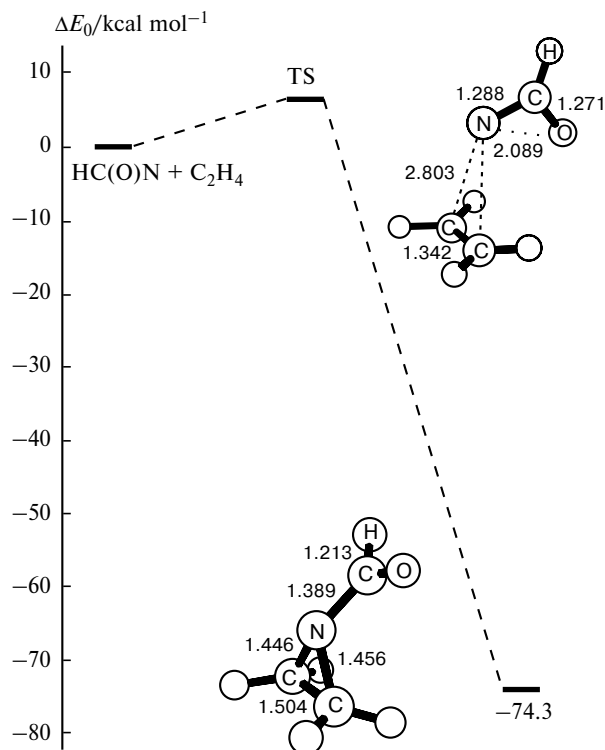
#### *Calculations of barriers to reactions of singlet acylnitrenes with ethylene*

It is known<sup>2</sup> that addition of both singlet and triplet acylnitrenes to the C=C bonds results in aziridines, but proceeds by drastically different reaction mechanisms. Singlet nitrenes react in a single step, and the addition is stereospecific. Conversely, triplet nitrenes undergo a two-step reaction *via* a 1,3-diradical and, as a result, the addition is not stereospecific.

Here we only examine the addition of singlet acylnitrenes  $\text{RC(O)N}$  ( $\text{R} = \text{H}, \text{OH}, \text{Ph}$ ) to ethylene. The geometries of the aziridines and the transition states (TS) leading there were optimized by the B3LYP/6-31G(d) method. The TS structure for the addition of formylnitrene to ethylene and the structure of the resulting aziridine are shown in Figure 7. It is seen that the TS apparently occurs very early along the reaction coordinate, as the lengths of the forming C—N bonds are very long ( $\sim 2.8$  Å, Fig. 7). The height of the barrier to this reaction was found to be only 6.7  $\text{kcal mol}^{-1}$ .

We also calculated the TS structures of the reactions of the singlet molecules **2** and **6** with ethylene (Table 1). Once more we found very early transition states with long





**Fig. 7.** Energy diagram for the addition of singlet formyl nitrene **5** to ethylene  $C_2H_4$ . The relative electronic energies ( $\Delta E_0/kcal\ mol^{-1}$ ) were calculated by the B3LYP/6-31G(d) method with inclusion of ZPE corrections. The sum of the energies of the singlet **5** and  $C_2H_4$  was set to zero. Shown are the transition-state and the reaction product (aziridine) structures optimized by the same method.

**Table 1.** Bond lengths of the forming C—N bonds ( $r$ , Å) and imaginary frequencies ( $\omega_{imag}/cm^{-1}$ ) in the transition states of the reactions of singlet acylnitrenes  $RC(O)N$  with ethylene; values of the barriers ( $\Delta E_0^\ddagger$ ) to reactions and the enthalpies ( $\Delta E_0^{react}$ ) of these reactions calculated for 0 K; and the activation enthalpies ( $\Delta H^\ddagger$ ) and enthalpies ( $\Delta H^{react}$ ) of these reactions calculated for 298 K by the B3LYP/6-31G(d) method

R	$r/\text{Å}$	$-\omega_{imag}/cm^{-1}$	$kcal\ mol^{-1}$			
			$\Delta E_0^\ddagger$	$-\Delta E_0^{react}$	$\Delta H^\ddagger$	$-\Delta H^{react}$
H	2.803	292i	6.7	74.3	6.6	75.7
Ph	2.702	231i	9.6	68.6	9.5	69.9
OH <sup>a</sup>	2.875	155i	3.3	78.9	3.3	80.3
OH <sup>b</sup>	2.844	172i	4.0	76.3	4.0	77.6

<sup>a</sup> *syn*-Rotamer.

<sup>b</sup> *anti*-Rotamer.

incipient C—N bonds ( $\sim 2.8$  Å). The barrier to the reaction **2** +  $C_2H_4$  was calculated to be about 3  $kcal\ mol^{-1}$  higher than in the case of formyl nitrene (**5** +  $C_2H_4$ ). Unfortunately, no kinetic data on the former reaction are

available in the literature, but this value is consistent with the high yield of aziridines on photolysis of benzoyl azide in the presence of olefin traps.<sup>2,8–10</sup>

Analysis of the results obtained in a study<sup>26</sup> of the reaction of singlet ethoxycarbonylnitrene **4** with TME allows the rate constant for this addition reaction to be estimated at  $(1-5) \cdot 10^9\ L\ mol^{-1}\ s^{-1}$  at ambient temperature. According to our calculations, the barrier to the reaction of singlet molecule **6** (which could serve as a model of molecule **4**) with ethylene is much lower than the barriers to reactions of ethylene with molecules **2** and **5** (Table 1). The very rough estimation of the rate constant for the addition of singlet molecule **6** to ethylene as

$$k \approx 5 \cdot 10^{11} \cdot \exp[-\Delta H^\ddagger/(RT)]$$

for  $T = 298\ K$  leads to a  $k$  value of about  $1.3 \cdot 10^9\ L\ mol^{-1}\ s^{-1}$ , which reasonably agrees with the published data.<sup>26</sup>

Thus, although the singlet intermediates are structurally similar to cyclic oxazirene, their reactivities are typical of singlet nitrenes.

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