TOWARDS THE LIF SPECTRUM OF PHENYLNITRENE: YET ANOTHER PRECURSOR THAT YIELDS SOMETHING ELSE

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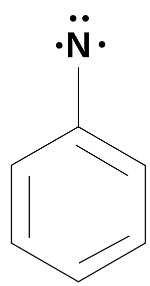
The excimer photolysis of C_6H_5-N=S=O was expected to lead to scission of the N-S bond to yield triplet SO and triplet phenyl nitrene, **1**. We observed SO following KrF excimer photolysis of the precursor in a free jet expansion by probing its $\tilde{B}\ ^3\Sigma^- \leftrightarrow \tilde{X}\ ^3\Sigma^-$ transition. A rich LIF spectrum beginning at 19,500 cm^{-1} and extending beyond 20,500 cm^{-1} was also observed. The origin of the spectrum and two additional bands have been rotationally resolved. The rotational constants of 0.945 GHz (B) and 0.943 GHz (C) are irreconcilable with the carrier of the spectrum being phenyl nitrene. Rotational constants for the deuterated molecule have also been obtained and support this argument.
To aid in the identification of the photoproduct, we have performed *ab initio* calculations on phenyl nitrene and several other possible molecules that have been observed in solution and matrix studies of phenylnitrene (see figures, below). Of the calculated rotational constants and vibrational frequencies, only those for the carbene **3** are consistent with the experimental data.



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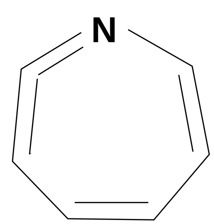

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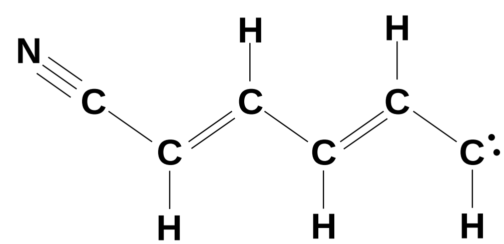

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