CASSCF and CASPT2 Ab Initio Electronic Structure Calculations Find Singlet Methylnitrene Is an Energy Minimum

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Abstract: (12/11)CASSCF and (12/11)CASPT2 ab initio electronic structure calculations with both the cc-pVDZ and cc-pVTZ basis sets find that there is a barrier to the very exothermic hydrogen shift that converts singlet methylnitrene, CH_3N, to methyleneimine, $H_2C{=}NH$. These two energy minima are connected by a transition structure of C_s symmetry, which is computed to lie 3.8 kcal/mol above the reactant at the (12/11)CASPT2/cc-pVTZ//(12/11)CASSCF/cc-pVTZ level of theory. The (12/11)CASSCF/cc-pVTZ value for the lowest frequency vibration in the transition structure is 854 cm^{-1}, and CASPT2 calculations concur that this a″ vibration does indeed have a positive force constant. Thus, there is no evidence that this geometry is actually a mountain top, rather than a transition structure, on the global potential energy surface or that a C_1 pathway of lower energy connects the reactant to the product. Therefore, our computational results indicate that the bands seen for singlet methylnitrene in the negative ion photoelectron spectrum of CH_3N^- are due to singlet methylnitrene being an energy minimum, rather than a transition state. Our results also lead us to predict that, at least in principle, singlet methylnitrene should be an observable intermediate in the formation of methyleneimine.

Nitrenes are reactive intermediates that have found uses in synthesis, photoaffinity labeling, and photoresist technology.[1] One of the best studied of these species is phenylnitrene, which in its lowest singlet state undergoes ring expansion to give azacycloheptatetraene.[2] The same type of ring-expansion reaction has been observed in a variety of other aromatic nitrenes.[3] Recent computational studies have led to an understanding of several puzzling aspects of this reaction.[4]

A much simpler nitrene rearrangement is that of singlet methylnitrene to methyleneimine, $CH_3{-}N \rightarrow CH_2{=}NH$. Although the triplet ($^3A_2$) ground state of methylnitrene[5] has been the subject of several experimental studies,[6] singlet methylnitrene rearranges so quickly that it has not been chemically trapped; and even attempts to detect it by femtosecond flash photolysis have failed.[7] Nevertheless, the negative ion photoelectron spectrum of CH_3N^- contains features which were assigned to the lowest singlet state of methylnitrene, and the singlet−triplet splitting was measured to be $\Delta E_{ST} = 1.352 \pm 0.011$ eV.[8]

On the basis of the results of CISD calculations with a two-configuration (TC) reference wave function, Schaefer and coworkers suggested that singlet methylnitrene rearranges to methyleneimine without a barrier.[9] Were this the case, the features assigned to this state in the photoelectron spectrum of CH_3N^- would have to be interpreted as belonging to a resonance, rather than to a true minimum on the singlet CH_3N potential energy surface.[8]

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(1) (a) *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: New York, 1984. (b) Kotzyba-Hibert, F.; Kapfer, I.; Goeldner, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1296. (c) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900.

(2) (a) Huisgen, R.; Vossius, D.; Appl, M. *Chem. Ber.* **1958**, *91*, 1. (b) Huisgen, R.; Appl, M. *Chem. Ber.* **1958**, *91*, 12. (c) Doering, W. v. E.; Odum, R. A. *Tetrahedron* **1966**, *22*, 81. (d) Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282.

(3) Reviews of arylnitrene chemistry: (a) Smith, P. A. S. In *Nitrenes*; Lwowski, W., Ed.; Wiley-Interscience: New York, 1970; Chapter 4. (b) Scriven, E. F. V. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Vol. 2, Chapter 1. (c) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984; Chapter 4. (d) Platz, M. S. In *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: New York, 1984; Chapter 7. (e) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; pp 303−320. (f) Platz, M. S.; Leyva, E.; Haider, K. *Org. Photochem.* **1991**, *11*, 367. (g) Schuster, G. B.; Platz, M. S. *Adv. Photochem.* **1992**, *17*, 69. (h) Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.

(4) (a) Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 1378. (b) Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 3347. (c) Kemnitz, C. R.; Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc*. **1998**, *120*, 3499.

(5) Wasserman, E. Electron Spin Resonance of Nitrenes. In *Progress in Physical Organic Chemistry*; Streitwieser, A., Taft, R. W., Eds.; Wiley-Interscience: New York, 1971; Vol. 8; p 319.

(6) (a) Carrick, P. G.; Engelking, P. C. *J. Chem. Phys.* **1984**, *81*, 1661. (b) Carrick, P. G.; Brazier, C. R.; Bernath, P. F.; Engelking, P. C., *J. Am. Chem. Soc.* **1987**, *109*, 5100. (c) Chappell, E. L.; Engelking, P. C. *J. Chem. Phys.* **1988**, *89*, 6007. (d) Brazier, C. R.; Carrick, P. G.; Bernath, P. F. *J. Chem. Phys.* **1992**, *96*, 919.

(7) Glowina, J. H.; Misewich, J.; Sorokin, P. P. Utilization of UV and IR Supercontinua in Gas-Phase Subpicosecond Kinetic Spectroscopy. In *Supercontinuum Laser Sources*; Alfano, R. R., Ed. Springer-Verlag: New York, 1989; Vol. p 337.

(8) Travers, M. J.; Cowles, D. C.; Clifford, E. P.; Ellison, G. B.; Engelking, P. C. *J. Phys. Chem.* **1999**, *111*, 5349.

(9) Richards, C., Jr.; Meredith, C.; Kim, S.-J.; Quelch, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1994**, *100*, 481.

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However, the closely related rearrangement of singlet methylcarbene to ethylene is computed to have a small but finite energy barrier,[10] and methylcarbene-d_3 has, in fact, been trapped chemically.[11] Since the rearrangement of singlet methylcarbene to ethylene does have a barrier, it is not obvious why the rearrangement of singlet methylnitrene to methyleneimine should not.[12]

To investigate the possibility that an energy barrier separates singlet methylnitrene from methyleneimine, we have undertaken CASSCF and CASPT2 calculations, the results of which are reported here. The calculations find that singlet methylnitrene is indeed an energy minimum, rather than a transition state. Thus, we predict that, at least in principle, methylnitrene should be an observable intermediate.

(12/11)CASSCF calculations were performed in which all 12 valence electrons and all 11 valence orbitals were included in the active space. Geometry optimizations and vibrational analyses were performed at this level of theory. To include the effects of electron correlation that involve excitations of the valence electrons into orbitals outside the active space, we applied second-order Möller−Plesset perturbation theory to the (12/11)CASSCF wave functions, using the CASPT2 method.[13] The CASSCF wave function had a reference weight of 93−95% in each of the CASPT2 calculations.

The (12/11)CASSCF geometry optimizations and the CASPT2 single-point calculations were carried out with Dunning's cc-pVDZ and cc-pVTZ correlation-consistent basis sets.[14] The former was used for vibrational analyses, performed at (12/11)-CASSCF/cc-pVDZ optimized geometries. The latter is a valence triple-ζ basis set with two sets of d and one set of f polarization functions on C and N and two sets of p and one set of d polarization functions on H. It is equivalent to the largest basis set used by Schaefer and co-workers.[9] All calculations were performed with the MOLCAS-4 suite of electronic structure programs.[15]

The (12/11)CASSCF/cc-pVTZ optimized geometries for the lowest singlet state of methylnitrene, methyleneimine, and the transition state that connects these two energy minima are shown in Figure 1. Their (12/11)CASSCF and CASPT2 energies are given in Table 1. Optimized geometries for all other species whose energies are given in Table 1 are available as Supporting Information, as are the unscaled (12/11)CASSCF vibrational frequencies that were computed at these geometries.

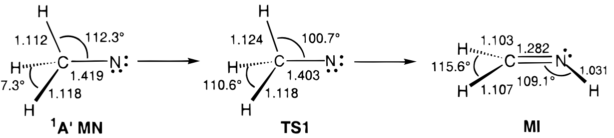

Figure 1. (12/11)CASSCF/cc-pVTZ geometries (bond lengths in Å, bond angles in degrees) of the stationary points along the lowest energy pathway for the rearrangement of the lowest singlet state of methylnitrene (**^{1}A′ MN**) to methyleneimine (**MI**).

Table 1. Relative (12/11)CASSCF Zero-Point Energies (ZPEs) and (12/11)CASSCF and (12/11)CASPT2 ZPE-Corrected Electronic Energies (kcal/mol) of ^{1}A′ and $^3A_2$ Methylnitrene (**MN**), Methyleneimine (**MI**), and of the Transition Structures Connecting ^{1}A′ **MN** to **MI** (**TS1**) and for Nitrogen Inversion in Methyleneimine (**TS2**), Computed with cc-pVDZ and cc-pVTZ Basis Sets

	ZPE	*E* (CASSCF/ cc-pVDZ)	*E* (CASPT2/ cc-pVDZ)	*E* (CASSCF/ cc-pVTZ)	*E* (CASPT2/ cc-pVTZ)
1A′ **MN**	0	0	0	0	0
$^3A_2$ **MN**	1.8	−41.1	−35.9	−39.7	−32.0
TS1	0.1	0.4	2.8	0.5	3.8
TS2	1.3	−59.4	−51.6	−62.2	−54.9
MI	3.2	−91.7	−83.1	−92.0	−82.9

In C_{3v} methylnitrene two electrons must be distributed between a degenerate pair of e MOs, which are largely comprised of the two 2p orbitals on N. The lowest-energy states that result are a triplet ($^3A_2$) and a degenerate pair of singlets (^{1}E). According to the Jahn−Teller theorem,[16] the latter should undergo Jahn−Teller distortions, giving rise to ^{1}A′ and ^{1}A″ states in C_s symmetry.

As shown in Figure 1, the ^{1}A′ state has one short and two long C−H bonds. The ^{1}A″ state distorts from C_{3v} symmetry in the opposite sense. However, the distortions from C_{3v} symmetry of both components of ^{1}E are quite small; and at their C_s optimized geometries, the ^{1}A′ and ^{1}A″ states differ in energy by less than 0.01 kcal/mol at the (12/11)CASSCF level of theory with both basis sets. As found by Schaefer and co-workers,[9,17] the C−N bond lengths in the two singlets are nearly the same, and both are slightly shorter than the C−N bond length in the lowest triplet state.

It is in the ^{1}A′ state that migration of the unique hydrogen can most easily occur.[9] In fact, the lowest frequency vibrational mode of 564 cm^{-1} in this state of methylnitrene corresponds to an a′ motion that moves this hydrogen toward the nitrogen.

The zeroth-order wave function for ^{1}A′ has the form $^1A' = c_1|\cdots 7a'^2\rangle - c_2|\cdots 2a''^2\rangle$. The 7a′ MO is largely comprised of the 2p$_y$ AO on nitrogen, interacting in an antibonding fashion with the unique hydrogen; and 2a″ is largely the 2p$_x$ orbital on nitrogen, interacting with the remaining two hydrogens, also in an antibonding fashion. In the reactant $c_1 \approx c_2$, so that the 7a′ and 2a″ nonbonding (NB)MOs are each occupied by an average of about one electron.

However, as hydrogen migration from carbon to nitrogen occurs, the electrons that form the unique C−H bond in the reactant are delocalized toward nitrogen. Concomitantly, c_1 decreases and c_2 increases, so that the pair of electrons that are initially distributed nearly equally between 2p$_x$ and 2p$_y$ on nitrogen become increasingly localized in 2p$_x$. Completion of the formation of methyleneimine can be thought of as requiring rotation about the C−N bond, so that this pair of electrons in 2p$_x$ on nitrogen can delocalize into the now largely empty 2p$_y$ orbital on carbon, thus forming the C−N π bond.

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(10) (a) Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 9148. (b) Ma, B.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1994**, *116*, 3539.

(11) (a) Kramer, K. A.; Wright, A. N. *Tetrahedron Lett.* **1962**, 1095. (b) Frey, H. M. *J. Chem. Soc.* **1962**, 2293. (c) Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183. (d) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 470.

(12) Phenylnitrene does have a significantly lower barrier to ring expansion than phenylcarbene,[3h] but this difference is now understood to be caused by the difference between the nature of the lowest singlet state of the nitrene (open-shell, with one σ and one π electron) and the carbene (closed-shell, with both nonbonding electrons largely localized in the σ orbital at the carbenic center).[4a] However, the reactive singlet states of methylnitrene and methylcarbene have wave functions that are much more similar, especially after hydrogen migration begins in CH_3N, so that the occupation number of the 2a″ MO becomes much greater than that of the 7a′ MO.

(13) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(14) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796. (c) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys* **1993**, *98*, 1358. (d) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410. (e) Wilson, A.; van Mourik, T.; Dunning, T. H., Jr. *THEOCHEM* **1997**, *388*, 339.

(15) MOLCAS version 4. K. Andersson, M. R.A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P.-Å. Malmqvist, P. Neogrády, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schütz, L. Seijo, L. Serrano-Andrés, P. E. M. Siegbahn, and P.-O. Widmark, Lund University, Sweden 1997.

(16) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937**, *161*, 220.

(17) Xie, Y.; Scuseria, G. E.; Yates, B. F.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1989**, *111*, 5181.

Product formation requires loss of the plane of symmetry that exists in the reactant. Therefore, to establish the existence of an energy barrier to product formation, it is insufficient simply to find an energy maximum along a reaction pathway that preserves this symmetry plane. For a C_s energy maximum to be a true transition structure, rather than a mountain top, on the potential energy surface for rearrangement of singlet methylnitrene to singlet methyleneimine, the force constant for rotation about the C−N bond at the C_s energy maximum must also be positive.

Schaefer and co-workers did, in fact, find a C_s energy maximum.[9] At the TC−CISD level of theory, with the largest basis set that they used and with addition of the Davidson correction for quadruple excitations, this maximum was computed to be 0.9 kcal/mol higher in energy than the reactant. However, Schaefer and co-workers apparently found that the energy of this C_s maximum decreases upon an asymmetric distortion of the geometry, because they concluded, “If there is a $^1A'$ transition state at this level of theory, it occurs in C_1 symmetry.”

The (12/11)CASSCF/cc-pVTZ geometry of the C_s energy maximum that we located is given in Figure 1 and is similar to the TC−CISD geometry for this species found by Schaefer and co-workers.[9] Table 1 shows that with both the cc-pVDZ and cc-pVTZ basis sets the (12/11)CASSCF energy of this species is 0.3−0.4 kcal/mol above that of the reactant, and this energy difference increases by 0.1 kcal/mol with inclusion of the correction for differences in zero-point vibrational energies. However, excitations outside the valence space apparently provide more stabilization for the reactant than for the transition state, because at the CASPT2 level of theory the C_s energy barrier increases to 2.8 kcal/mol with the smaller of the two basis sets and to 3.8 kcal/mol with the larger.

Because CASPT2 uses second-order perturbation theory,[13] it is likely to overestimate the effect of including electron correlation due to excitations outside the valence space. Without correction for differences between the heat capacities of the reactant and transition state, the actual height of the barrier to passage over the C_s energy maximum is likely to be lower than the (12/11)CASPT2/cc-pVTZ//(12/11)CASSCF/cc-pVTZ value of 3.8 kcal/mol, but closer to it than to the (12/11)CASSCF/cc-pVTZ value of 0.5 kcal/mol. A barrier height in the range of 2.5 ± 1.0 kcal/mol seems likely.

(12/11)CASSCF vibrational analyses with both the cc-pVDZ and cc-pVTZ basis sets found the C_s energy maximum to be a true transition state for rearrangement of singlet methylnitrene to methyleneimine. Except for the imaginary frequency for the a′, symmetry-preserving vibration that corresponds to hydrogen migration, all the other frequencies were computed to be real.[18] The lowest of these does correspond to a symmetry-breaking a″ vibration, but this mode is computed at (12/11)CASSCF/cc-pVTZ level to have a frequency of 854 cm^{-1}.

CASPT2 calculations along this a″ vibrational coordinate also found its force constant to be positive. Therefore, at both the (12/11)CASSCF and CASPT2 levels of theory the C_s energy maximum does, in fact, appear to be a true transition state on the potential energy surface for rearrangement of singlet methylnitrene to methyleneimine.

The finding that rotation about the C−N bond is unfavorable in the transition structure is not really surprising. The tremendous exothermicity of the rearrangement of singlet methylnitrene to methyleneimine, amounting to 83 kcal/mol at CASPT2, results in the C_s energy maximum occurring very early along the reaction coordinate, before much migration of the hydrogen from carbon to nitrogen has occurred. As shown in Figure 1, in this C_s transition structure (**TS1**) the unique C−H bond has lengthened by only 0.01 Å, and the C−N distance has decreased from that in the reactant by only 0.016 Å. Nevertheless, the occupation of the 7a′ NBMO does fall from 1.07 electrons in the reactant to 0.35 electrons in the transition structure.

Continuing along the C_s coordinate, past this transition structure for hydrogen transfer, the (12/11)CASSCF energy decreased monotonically, and our calculations found no other stationary points, until a C_{2v} geometry was reached. A vibrational analysis showed only one imaginary frequency at this geometry, corresponding to the contraction of the H−N−C angle which maintains the C_{2v} symmetry plane that is orthogonal to the plane in which hydrogen migration occurs. At the C_{2v} transition structure (**TS2**) the force constant for hydrogen motion that destroys the original C_s symmetry plane is obviously negative; therefore, somewhere between the C_s and C_{2v} transition structures, the force constant for a symmetry-breaking a″ mode, involving this hydrogen, apparently changes sign.

This C_{2v} geometry is the transition structure for nitrogen inversion in methyleneimine, for which our calculations predict a barrier height of 28.0 kcal/mol.[19] The C−N and the C−H bond lengths in this transition structure are both ∼0.04 Å shorter than those shown in Figure 1 for methyleneimine,[20,21] reflecting the change in hybridization of nitrogen from sp^2 in the methyleneimine to sp in the transition structure. Since we were unable to locate a stationary point of C_s symmetry that could correspond to the transition structure for C−N bond rotation, our (12/11)CASSCF calculations find that *syn*−*anti* isomerization in methyleneimine takes place via nitrogen inversion, rather than by rotation, which requires breaking the C−N π bond.[22]

Evidence for the reliability of our calculations comes from comparison of our calculated value for the singlet−triplet energy difference in methylnitrene with that obtained from the negative ion photoelectron spectrum of CH_3N^-.[8] As shown in Table 1, our (12/11)CASPT2/cc-pVTZ value of $\Delta E_{ST} = 32.0$ kcal/mol is in excellent agreement with the experimental value of $\Delta E_{ST} = 31.2 \pm 0.2$ kcal/mol. In addition, even without scaling to correct for anharmoncity and other effects, the vibrational frequencies that we calculate for the triplet (available as Supporting Information) agree well with those measured by Chappell and Engelking.[6c] Finally, the frequency of 1057 cm^{-1} that we compute for the C−N stretch in the singlet is within experimental error of the dominant progression seen in the bands assigned to this state in the negative ion photoelectron spectrum of CH_3N^-.[8]

As pointed out by Ellison and co-workers, a band in this spectrum, found at 0.12 eV above the triplet origin, is apparently absent from the bands assigned to the singlet.This band in the

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[18] (10/8)CASSCF/6-31G* calculations on the rearrangement of methylnitrene to methyleneimine, which were published after this manuscript had been submitted, also found the C_s energy maximum to be a transition structure on the global potential energy surface. Arenas, J. F.; Marcos, J. I.; Otero, J. C.; Sánchez-Gálvez, A.; Soto, J. *J. Chem. Phys.* **1999**, *111*, 551.

[19] For a previous study of the CH_3N potential energy surface, see: Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Binckley, J. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 6389.

[20] Our calculated geometry agrees well with the microwave structure reported by Pearson, R.; Lovas, F. T. *J. Chem. Phys.* **1977**, *66*, 4149.

[21] If a scaling factor of 0.988 for anharmonicity is applied to our (12/11)CASSCF/cc-VDZ frequencies (listed in the Supporting Information), the calculated frequencies for methyleneimine deviate by an average of less than 14 cm^{-1} from those measured in the gas phase by (a) Hamada, Y.; Hashiguchi, K.; Tsuboi, M.; Koga, Y.; Kondo, S. *J. Mol. Spectrosc.* **1984**, *105*, 70. (b) Halonen, L.; Duxbury, G. *Chem. Phys. Lett.* **1985**, *118*, 246. (c) Halonen, L.; Duxbury, G. *J. Chem. Phys.* **1985**, *83*, 2091.

[22] Apparently first noted by Lehn, J. M.; Munsch, B. *Theor. Chim. Acta* **1968**, *12*, 91.

triplet region of the spectrum has been assigned to ν_6, the degenerate C−H rocking motion. It has been observed at 903 cm^{-1} in the optical spectrum of the $^3A_2$ state of CH_3N;[6c] and, without scaling, we compute its frequency to be 986 cm^{-1}.

The absence of this band from the singlet region of the negative ion photoelectron spectrum of CH_3N^- provides the only experimental evidence that singlet methylnitrene is a transition structure; for one component of the ν_6 vibration leads toward migration of a hydrogen from carbon to nitrogen. We calculate the harmonic frequency of this vibration in the singlet to be 564 cm^{-1}. However, there is no peak apparent in this energy region above the singlet origin.

Among the many possible reasons for the absence of this band, two seem most plausible. One is that the first excited level of the ν_6 C−H rocking vibration is above the barrier for the rearrangement that this mode promotes. This would place an upper limit on the barrier to rearrangement of 564 cm^{-1} = 1.6 kcal/mol.

Alternatively, because this mode is likely to be very anharmonic in the singlet, the first excited level of ν_6 in this state may actually be at a frequency which is somewhat lower than that computed under the harmonic approximation. The band for the first excited level of the C−H rocking vibration could easily be at a low enough frequency that it might not be resolved from the (0,0) band of the singlet. In fact, ν_6 could be responsible for what appears to be an unresolved shoulder on the high energy side of the rather broad peak for the (0,0) band of the singlet in the negative ion photoelectron spectrum of CH_3N^-.[8]

Despite the absence of a well-resolved peak for the C−H rocking mode from the singlet region of the photoelectron spectrum, our calculations unequivocally predict that singlet methylnitrene is an energy minimum with a barrier to rearrangement to methylenimine that we estimate to be in the range of 2.5 ± 1.0 kcal/mol. We hope that this computational finding will stimuate attempts to observe singlet CD_3N spectroscopically and/or to trap it chemically.

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Supporting Information Available: Tables of (12/11)-CASSCF/cc-pVDZ and cc-pVTZ geometries and vibrational frequencies for singlet and triplet methylnitrene, methyleneimine, the transition state connecting the lowest singlet state of methylnitrene to methyleneimine, and the transition state for nitrogen inversion in methyleneimine (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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