Electronic Structure of Carbonyl Nitrenes. Mechanism of Insertion and Abstraction Reactions[1]

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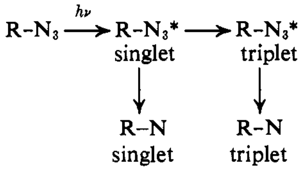
Abstract: The electronic configuration of several carbonyl nitrenes has been determined by nonempirical molecular orbital studies. The computations suggest that alkanoylnitrenes, RC(O)N, are ground state triplets while carbalkoxynitrenes, ROC(O)N, may have singlet ground states. The lowest energy transition is $\sigma^* \leftarrow \pi$. The heat of formation of amides from reaction of an alkanoylnitrene with hydrogen is estimated to be −111 kcal/mol and with methane −86 kcal/mol. The experimentally observed selectivity and stereochemistry of carbonylnitrene insertions into bonds is explained in terms of "forbiddenness," concertedness, activation energy, and the development of singlet diradical character in the transition state.

Nitrenes are members of a class of compounds which contain first row atoms that, formally, have six electrons in their valence shells. The chemistry and structure of such electron deficient species is a fascinating and active area of study both to the experimental and theoretical chemist. With rare exceptions such species are unstable under ordinary laboratory conditions. Their physical properties can sometimes be observed spectroscopically or deduced, along with their chemical properties, from observed products of reactions in which their intermediacy is postulated. A vast literature now exists on the compounds of boron. The unusual bonding has been elucidated by means of molecular orbital calculations.[2] Perhaps even more thoroughly studied are carbonium ions.[3] However, after numerous theoretical[5] and experimental[6] investigations, considerable doubt remains as to the structures of all but the parent methyl carbonium[3] ion, $^+CH_3$. Over the past 20 years, the chemistry of carbenes $(-\ddot{C}-)$ has come to play an important role in synthetic organic chemistry.[7] The electronic structure[8] and some reactions[9,10] of carbenes have been investigated by theoretical means and will be discussed in later sections. Very recently, some molecular orbital calculations have been performed on nitrenium[11] ions $(-\ddot{N}^+-)$, but there are no reports of computations on oxenium ions $(-\underset{..}{O}{:}\,^+)$. With the exception of the parent nitrene, H–N,[12] there is a paucity of computed data on the electronic structure of nitrenes $(-\underset{..}{\ddot{N}})$[13–15] although a large body of experimental evidence,[16] designed to shed light on the electronic structure and mode of reaction of nitrenes, has accumulated over the last 10 years. Further, to the last class of compounds, we present herein the results of molecular orbital studies on several carbonyl nitrenes and investigate the mechanism of insertion and abstraction reactions with bonds to hydrogen.

Skell's hypothesis[17] that singlet insertions (into double bonds) should occur stereospecifically and that triplet insertions should occur in a nonconcerted, nonstereospecific manner has been thoroughly tested for carbenes[18] and appears to be valid for nitrenes as well. By spin conservation, thermolysis of organic azides leads to nitrenes exclusively in the singlet state as does α elimination of benzenesulfonic acids from compounds such as $Ar-SO_2O-NH-COOR$. On the other hand, the photolytic decomposition of azides can produce nitrenes of both multiplicities, perhaps through an intermediate excited singlet state of the azide moiety



$$\begin{tikzcd}[column sep=small] R\text{-}N_3 \arrow[r, "h\nu"] & \underset{\text{singlet}}{R\text{-}N_3^*} \arrow[r] \arrow[d] & \underset{\text{triplet}}{R\text{-}N_3^*} \arrow[d] \\ & \underset{\text{singlet}}{R\text{-}N} & \underset{\text{triplet}}{R\text{-}N} \end{tikzcd}$$

which may undergo intersystem crossing to an excited triplet state before decomposing to the nitrene.[19] Thus,

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[1] This work was supported by the National Research Council of Canada.

[2] See, for example, the following papers and references therein: (a) D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 1748 (1972); (b) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *ibid.*, **94**, 4461, 4467 (1972); (c) D. S. Marynick and W. N. Lipscomb, *ibid.*, **94**, 8692, 8699 (1972).

[3] It has been suggested that these should properly be called carbenium ions.[4]

[4] G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

[5] See, for example, (a) L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **94**, 5395 (1972); (b) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **94**, 311 (1972); (c) N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5303 (1972).

[6] See, for example, G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions," Vol. I, Wiley-Interscience, New York, N. Y., 1968.

[7] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

[8] J. F. Harrison, ref 7, p 159.

[9] (a) R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Amer. Chem. Soc.*, **92**, 1460 (1970); (b) R. Hoffmann, *ibid.*, **90**, 1475 (1968); (c) R. C. Dobson, D. M. Hayes, and R. Hoffmann, *ibid.*, **93**, 6188 (1971); (d) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *ibid.*, **90**, 1485 (1968).

[10] (a) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, **94**, 9095 (1972); (b) N. Bodor and M. J. S. Dewar, *ibid.*, **94**, 9103 (1972).

[11] (a) S. T. Lee and K. Morokuma, *ibid.*, **93**, 6863 (1971); (b) S. Y. Chu, A. K. Q. Siu, and E. F. Hayes, *ibid.*, **94**, 2969 (1972).

[12] (a) P. E. Cade and W. Huo, *J. Chem. Phys.*, 47, 614 (1967), and references therein; (b) W. J. Stevens, *ibid.*, **58**, 1264 (1973), and references therein.

[13] (a) L. J. Hayes, F. P. Billingsley II, and C. Trindle, *J. Org. Chem.*, **37**, 3924 (1972); (b) V. Ya. Bespalov, L. A. Kartsova, V. I. Baranovskii, and B. V. Ioffe, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **200**, 99 (1971); (c) C. Wentrup, C. Thetaz, and R. Gleiter, *Helv. Chem. Acta*, **55**, 2633 (1972); (d) C. Thomson, *J. Chem. Phys.*, **58**, 841 (1973); (e) J. Peslak, Jr., D. S. Klett, and C. W. David, *J. Amer. Chem. Soc.*, **93**, 5001 (1971).

[14] R. Gleiter and R. Hoffmann, *Tetrahedron*, 24, 5899 (1968).

[15] J. A. R. Coope, J. B. Farmer, C. L. Gardner, and C. A. McDowell, *J. Chem. Phys.*, 42, 54 (1965).

[16] W. Lwowski, Ed., "Nitrenes," Wiley-Interscience, New York, N. Y., 1970.

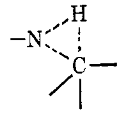
[17] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).

[18] P. P. Gaspar and G. S. Hammond, "Carbene Chemistry," 1st ed, Academic Press, New York, N. Y., 1964, p 235.

[19] Experimental data pertaining to this point are inconclusive. See, for example, F. D. Lewis and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **90**, 7031, 7033 (1968).

although hydrazoic acid,[20] HN_3, and cyanogen azide,[21] N_3CN, yield only singlet nitrenes upon photolysis, phenyl azide yields 12–13% of triplet phenylnitrene[22] and ethyl azidoformate yields a mixture of singlet and triplet carbethoxynitrenes[23] in the approximate ratio 2:1. Unlike carbenes, all nitrenes that have been observed by physical methods appear to have triplet ground states, at least under the conditions of observation[24] (matrix isolation, esr). Thus the singlet nitrene produced thermochemically or by photolysis may react directly as the singlet or may undergo collision- or heavy-atom-induced intersystem crossing to its triplet ground state.

Insertion reactions of nitrenes have been reviewed[16,25] recently. Both carbalkoxynitrenes and alkanoylnitrenes appear to react by insertion only in their singlet states. Although stereochemical data are lacking for the latter compounds, the former react with 100% retention of configuration. Incidents of insertion by triplet nitrenes into C–H bonds are scarce and concomitant with loss of stereospecificity. Compared with the isoelectronic carbenes, nitrenes show much greater selectivity[25] in insertion reactions with C–H bonds. Invariably, the order of reactivity is 3° > 2° > 1°. The selectivity ratios 3°:2°:1° for insertion of several nitrenes into the C–H bonds on 2-methylbutane are as follows:[26] carbethoxynitrene 34:10:1; pivaloylnitrene 160 ± 40:9 ± 1:1; phenylnitrene 140–280: >7:1. The kinetic isotope effect for insertion of phenylnitrene into the 3° C–H bond of isobutane is $k_H/k_D = 4.1$,[27] which is consistent with other data that suggest this nitrene reacts in its triplet state by abstraction–recombination.[27] A much smaller value was obtained[28] for insertion of carbethoxynitrene into c-C_6H_{12} and c-C_6D_{12}, $k_H/k_D = 1.5$. The latter value is consistent with direct insertion *via* the often postulated symmetrical three-center transition state.



In this work we attempt to explain the origin of the relatively high barrier to insertion–abstraction reactions of nitrenes and the observed selectivity. We will show that, although the transition state to insertion may resemble that shown above, the approach of the nitrene to the C–H bond is highly nonlinear.

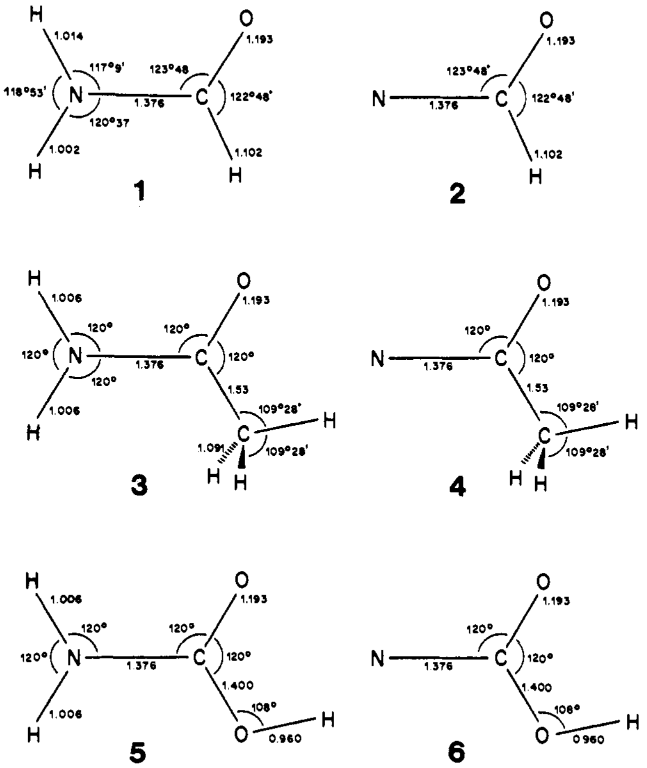


Figure 1. Structural data on the nitrenes and amides studied.

Method

Nonempirical Studies. Restricted Hartree–Fock–Roothaan LCAO-MO-SCF[29] calculations were performed on the following compounds: formamide (**1**), formylnitrene (**2**), acetamide (**3**), acetylnitrene (**4**), carbamide (**5**), and carbhydroxynitrene (**6**). All one- and two-center integrals are computed over a minimal basis set of exponential-type functions (STO). All three- and four-center integrals are computed using Pople's[30] STO-3G Gaussian expansion of the STO's. It was anticipated that approximation of the smaller three- and four-center integrals in this fashion would not lead to anomalous results in the electronic structure.[31] The geometries of the compounds are shown in Figure 1. Idealized angles of 120° were used about the amide functional group except in the case of formamide (**1**). Here the geometry is that used by Robb and Csizmadia[32] in their study of isomerism in the formamide system, in order to facilitate evaluation of the quality of the calculation. In all cases, the nitrene has the same geometry as the amide except for the absence of the two hydrogen atoms. Slater exponents[33] were employed for all atoms except hydrogen, where an exponent of 1.2 was chosen. The energies of hydrogen (−1.128 hartree), methane (−40.113 hartree), and (*E*)-*N*-methylformamide (−207.272 hartree) were also computed for determination of heats of reaction (see below).

Semiempirical Studies. All semiempirical results were obtained using the CNDO/2 method.[34,35] The

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[20] (a) K. H. Welge, *J. Chem. Phys.*, **45**, 4373 (1966); (b) H. Okabe, *ibid.*, **49**, 2726 (1968).

[21] (a) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **89**, 3184 (1967); (b) H. W. Kroto, *J. Chem. Phys.*, **44**, 831 (1966).

[22] A. Rieser and L. J. Leyshon, *J. Amer. Chem. Soc.*, **93**, 4051 (1971).

[23] W. Lwowski, *Angew. Chem., Int. Ed. Engl.*, **6**, 897 (1967).

[24] E. Wasserman, *Progr. Phys. Org. Chem.*, **8**, 319 (1971).

[25] M. Takebayashi and T. Shingaki, *Kagaku* (*Kyoto*), **26**, 602 (1971).

[26] Reference 16, p 201.

[27] J. H. Hall, J. W. Hill, and J. M. Fargher, *J. Amer. Chem. Soc.*, **90**, 5313 (1968).

[28] W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965).

[29] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[30] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

[31] All of the results for compounds **1** and **2** were also computed using the STO-4G Gaussian expansion. None of the results differ significantly from those reported and the conclusions are unaffected.

[32] (a) M. A. Robb and I. G. Csizmadia, *J. Chem. Phys.*, **50**, 1819 1969); (b) M. A. Robb and I. G. Csizmadia, *Theor. Chim. Acta*, **10**, 269 (1968).

[33] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[34] A modified version of the program CNINDO (P. A. Dobosh) received from the Quantum Chemistry Program Exchange (QCPE), Bloomington, Ind., was used.

[35] (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); (c) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

nitrogen orbital electronegativities, χ_{2s} and χ_{2p}, were adjusted slightly to reproduce *ab initio* results for the heat of reaction of formylnitrene (**2**) with hydrogen to give formamide (**1**) (Table IV). The parameters obtained are $\chi_{2s} = 25.056$ and $\chi_{2p} = 5.1133$.[36] The reparametrization did not appreciably affect the agreement between calculated and experimental[37] N–C and N–H bond lengths: N–C calcd 1.42 Å, exptl 1.44 Å; N–H calcd 1.08 Å, exptl 1.02 Å.

Semiempirical computations were used only in the last section for the examination of potential surfaces.

Results and Discussion

Electronic Structure of Carbonyl Nitrenes. The total energy and molecular orbital energies for compounds **1–6** are shown in Tables I–III. The orbitals are classified as transforming as one or the other of the irreducible representations of the point group C_s. In the case of formamide (**1**) where a slightly nonplanar geometry was employed, the classification is approximate. In each column of the three tables, the last two orbitals are the two lowest unoccupied orbitals. The valence molecular orbitals of **1–6** are presented as linear combinations of hybridized atomic orbitals in Figures 2–4. The depicted magnitude of each AO is directly proportional to the absolute magnitude of its coefficient in the LCAO expansion of the MO.

Table I. Total and MO Energies for **1** and **2**

	Formamide (**1**)		Formylnitrene (**2**)	
	Energy,[a] hartree	C_s[b] symmetry	Energy,[a] hartree	C_s symmetry
Total	−168.32814		−167.01912	
MO 1	−20.5057	1a′	−20.5455	1a′
MO 2	−15.5620	2a′	−15.6218	2a′
MO 3	−11.3839	3a′	−11.4120	3a′
MO 4	−1.3558	4a′	−1.3875	4a′
MO 5	−1.1426	5a′	−1.1131	5a′
MO 6	−0.7921	6a′	−0.7686	6a′
MO 7	−0.6879	7a′	−0.6067	7a′
MO 8	−0.6100	8a′	−0.5579	1a″
MO 9	−0.5278	9a′	−0.5440	8a′
MO 10	−0.5212	1a″	−0.3670	9a′
MO 11	−0.3530	10a′	−0.3466	2a″
MO 12	−0.3259	2a″	0.1374	10a′
MO 13	0.3093	3a″	0.2771	3a″
MO 14	0.5426	11a′		

[a] 1 hartree = 627.7 kcal/mol. [b] The formamide is treated as approximately planar.

Table II. Total and MO Energies for **3** and **4**

	Acetamide (**3**)		Acetylnitrene (**4**)	
	Energy,[a] hartree	C_s symmetry	Energy,[a] hartree	C_s symmetry
Total	−207.29610		−205.98876	
MO 1	−20.4807	1a′	−20.5233	1a′
MO 2	−15.5543	2a′	−15.6124	2a′
MO 3	−11.3801	3a′	−11.4058	3a′
MO 4	−11.2896	4a′	−11.3163	4a′
MO 5	−1.3504	5a′	−1.3841	5a′
MO 6	−1.1360	6a′	−1.1094	6a′
MO 7	−0.9706	7a′	−0.9828	7a′
MO 8	−0.7374	8a′	−0.6874	8a′
MO 9	−0.6648	9a′	−0.6187	1a″
MO 10	−0.6147	10a′	−0.6024	9a′
MO 11	−0.5931	1a″	−0.5801	10a′
MO 12	−0.5424	11a′	−0.5135	2a″
MO 13	−0.4989	12a′	−0.5119	11a′
MO 14	−0.4855	2a″	−0.3508	12a′
MO 15	−0.3366	13a′	−0.3394	3a″
MO 16	−0.3169	3a″	0.1424	13a′
MO 17	0.3192	4a″	0.2863	4a″
MO 18	0.5176	14a′		

[a] 1 hartree = 627.7 kcal/mol.

Table III. Total and MO Energies of **5** and **6**

	Carbamide (**5**)		Carbhydroxynitrene (**6**)	
	Energy,[a] hartree	C_s symmetry	Energy,[a] hartree	C_s symmetry
Total	−242.90375		−241.59118	
MO 1	−20.5387	1a′	−20.5706	1a′
MO 2	−20.4538	2a′	−20.5075	2a′
MO 3	−15.5659	3a′	−15.6328	3a′
MO 4	−11.4221	4a′	−11.4563	4a′
MO 5	−1.4003	5a′	−1.4354	5a′
MO 6	−1.2867	6a′	−1.3215	6a′
MO 7	−1.1411	7a′	−1.1156	7a′
MO 8	−0.7762	8a′	−0.7459	8a′
MO 9	−0.6803	9a′	−0.6169	1a″
MO 10	−0.6206	10a′	−0.6143	9a′
MO 11	−0.5807	1a″	−0.5945	10a′
MO 12	−0.5729	11a′	−0.4809	11a′
MO 13	−0.4635	12a′	−0.4232	2a″
MO 14	−0.3977	2a″	−0.3667	12a′
MO 15	−0.3412	13a′	−0.3490	3a″
MO 16	−0.3158	3a″	0.1257	13a′
MO 17	0.3414	4a″	0.3011	4a″
MO 18	0.4849	14a′		

[a] 1 hartree = 627.7 kcal/mol.

For each of the amides **1**, **3**, and **5**, the highest occupied molecular orbital may be regarded as the lone pair on the nitrogen, although it is somewhat delocalized over the carbonyl group. The lowest unoccupied molecular orbital (LUMO) is also a π orbital but is largely localized to the carbonyl fragment and is antibonding.

For each of the nitrenes **2**, **4**, and **6**, the HOMO is again a π orbital with approximately the same electron distribution as that of the HOMO in the corresponding amide. However, the LUMO of the nitrene is a very highly localized 2p-like orbital on nitrogen which lies in the plane of the molecule, in sharp contrast to the LUMO of the corresponding amide. Particular note is taken of MO 7 and MO 9 of **2** (Figure 2), MO 10 and MO 13 of **4** (Figure 3), and MO 11 of **6** (Figure 4), which place a large amount of electron density in the bonding region of the corresponding amide.

Heats of Reaction. The standard heat of reaction $\Delta H°_T$ at temperature T for a gas-phase reaction of the type

$$R^1\text{-H} + \text{N-R} = R^1\text{-NH-R}$$

is given[38] by

$$\Delta H°_T = \Delta(E_{HF} + E_{corr} + E_{vib} + E_{rot} + E_{trans}) - RT$$

where E_{HF} is the exact Hartree–Fock energy, E_{corr} is the correlation energy,[39] and E_{vib}, E_{rot}, and E_{trans} are the vibrational, rotational, and translational energies. It has previously been found that correlation energy[39] is

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[36] The rationale for this procedure is given in A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 6507 (1971).

[37] L. E. Sutton, Ed., *Chem. Soc. Spec. Publ.*, **No. 11** (1958); **No. 18** (1965).

[38] L. C. Snyder, *J. Chem. Phys.*, **46**, 3602 (1967).

[39] Correlation energy is here defined as the difference between the exact energy of a system and the lowest energy attainable within the Hartree–Fock approximation.

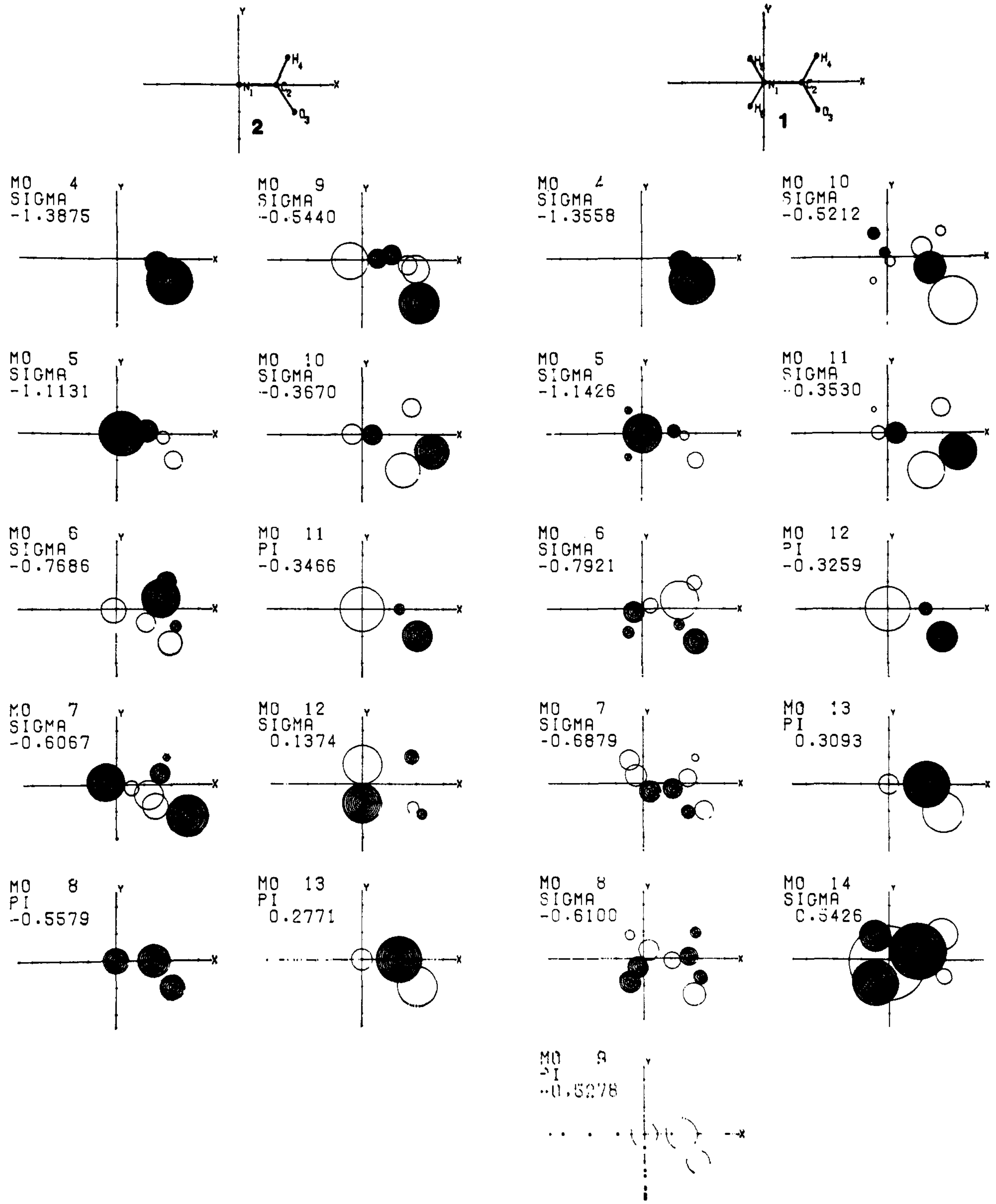

Figure 2. The valence molecular orbitals of formylnitrene (2) and formamide (1) are displayed as linear combinations of hybridized atomic orbitals. The magnitude of each atomic orbital is directly proportional to the magnitude of its coefficient in the LCAO expansion of the MO. Only the top lobes of each PI(a'') orbital are shown. The MO energy is in hartree units (1 hartree = 627.7 kcal/mol).

conserved to a reasonable approximation in reactions involving closed shell species.[39,40] Thus $\Delta E_{corr} \simeq 0$. The classical values for E_{rot} of (3/2)RT for nonlinear molecules and RT for linear molecules and E_{trans} = (3/2)RT are assumed. Since vibrational frequencies for the nitrenes are not known, we must neglect ΔE_{vib}. ΔE_{HF} should be closely approximated by ΔE_{SCF}, which is calculated from the total energies given in Tables I-III and (H_2) −1.128 hartree, (CH_4) −40.113 hartree, and (CH_3NHCHO) −207.272 hartree. The calculated $\Delta H°_{298}$ values are collected in Table IV. The heat of reaction for the formation of ammonia from H_2 and

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(40) A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, 52, 4133 (1970).

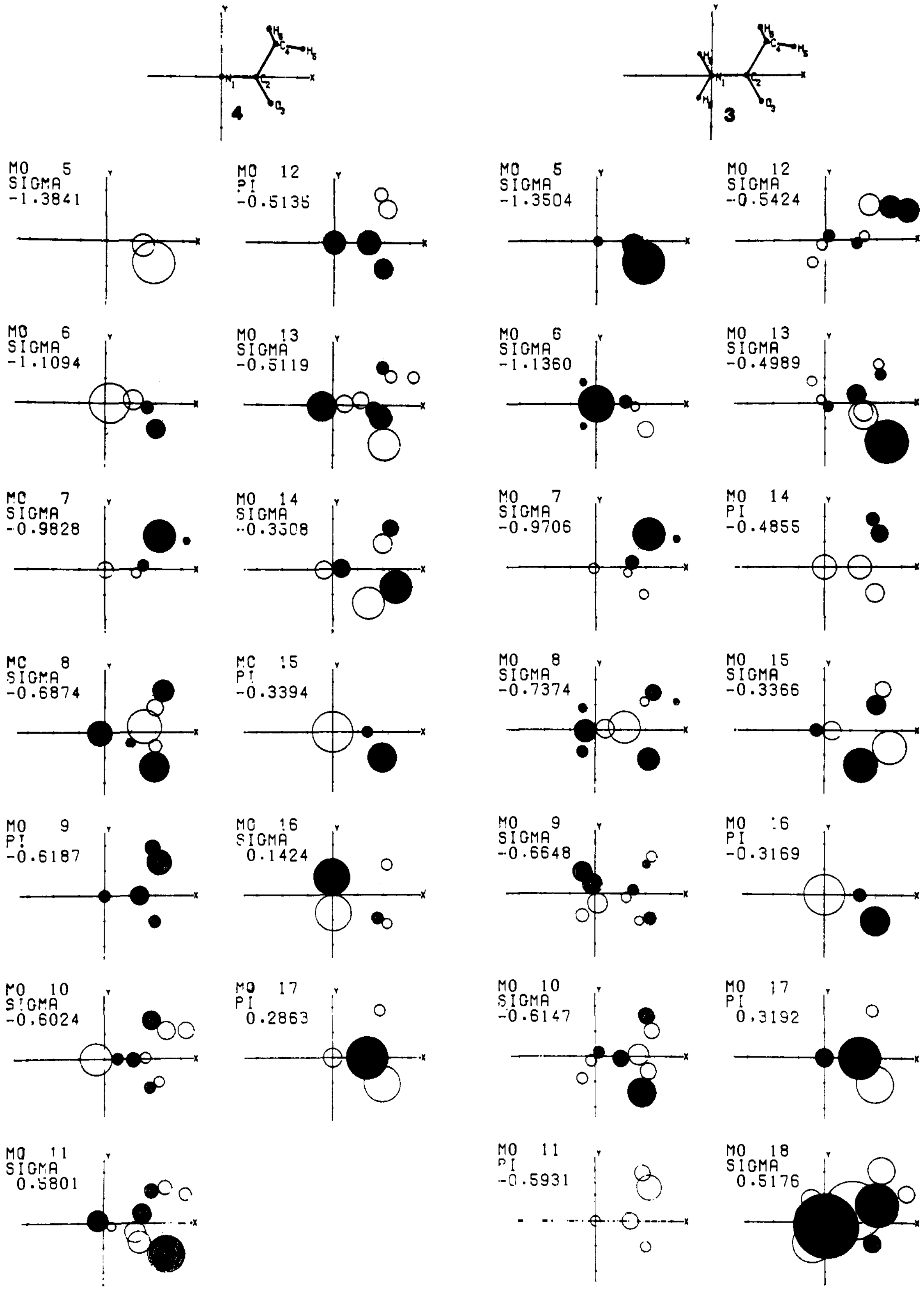

Figure 3. The valence molecular orbitals of acetylnitrene (**4**) and acetamide (**3**) are displayed as linear combinations of hybridized atomic orbitals. The magnitude of each atomic orbital is directly proportional to the magnitude of its coefficient in the LCAO expansion of the MO. Only the top lobes of each PI(a″) orbital are shown. The MO energy is in hartree units (1 hartree = 627.7 kcal/mol).

nitrene (H–N) has been estimated spectroscopically, $\Delta H°_{298}$ = 90 kcal/mol.[41] Crude estimates for the energy changes taking place in the reaction of Table IV can be made from bond dissociation energies. These are included in the last column of Table IV. The value $\Delta H_{298} = -86$ kcal/mol for insertion of singlet formylnitrene (**2**) into the C–H bond of methane is

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[41] Reference 16, p 23.

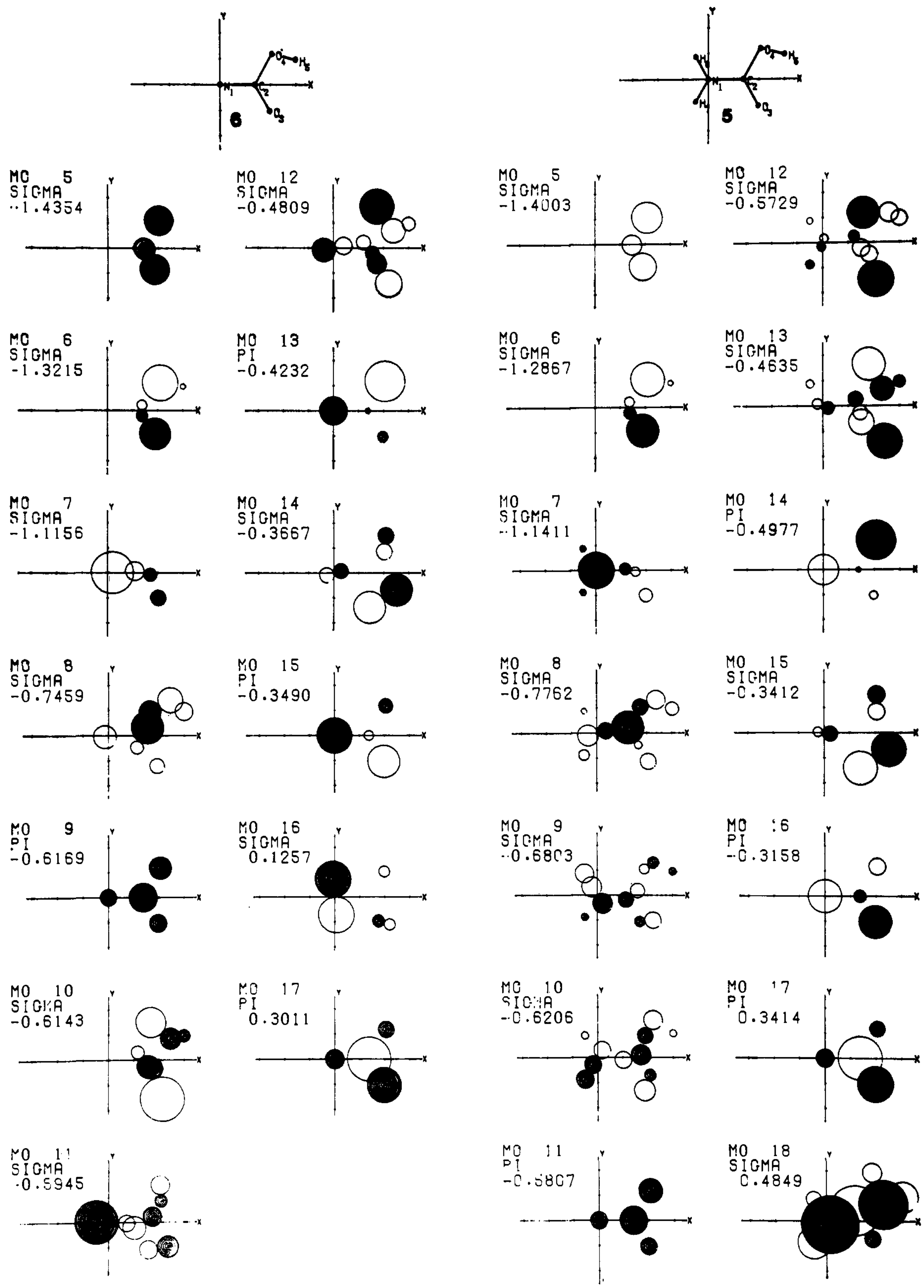

Figure 4. The valence molecular orbitals of carbhydroxynitrene (**6**) and carbamide (**5**) are displayed as linear combinations of hybridized atomic orbitals. The magnitude of each orbital is directly proportional to the magnitude of its coefficient in the LCAO expansion of the MO. Only the top lobes of each PI(a'') orbital are shown. The MO energy is in hartree units (1 hartree = 627.7 kcal/mol).

somewhat lower than that computed for insertion of singlet carbene, CH_2, into the C–H bond of methane, $\Delta H = -100$ kcal/mol.[10a]

Spin State of Carbonyl Nitrenes. In Table V are shown singlet and triplet excitation energies for nitrenes **2**, **4**, and **6** and amides **1**, **3**, and **5**, as calculated by the virtual orbital approximation.[29] For the amides the calculated lowest energy excitation is a $\pi^* \leftarrow n$ as has

Table IV. Standard Heats of Reaction

Reaction	ΔE^1_{SCF},[a] kcal	ΔE^3_{SCF}[b]	ΔH_{298}, kcal Calcd[c]	Est[d]
1. $H_2 + NCHO = H_2NCHO$	−113	−98	−111	−83
2. $H_2 + NCOCH_3 = H_2NCOCH_3$	−112	−100	−100	−83
3. $H_2 + NCOOH = H_2NCOOH$	−116	−116	−114	−83
4. $CH_4 + NCHO = CH_3NH\text{-}CHO$	−88	−73	−86	−64

[a] Calculated for all reactants in their lowest singlet states. [b] Calculated for all reactants in their lowest electronic states. [c] $\Delta H_{298} = \Delta E^1_{SCF} + \Delta E_{rot} + \Delta E_{trans} - R(298°)$. [d] Estimated from bond dissociation energies: L. Pauling "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 85.

Table V. Singlet and Triplet Excitation Energies

Compound	$i \leftarrow j$	Excited state	$\epsilon_i - \epsilon_j$	J_{ij}	K_{ij}	ΔE_T	ΔE_s
Nitrenes							
2	12 ← 11	A''	0.4840	0.5081	0.0252	−0.0241	0.0263
	12 ← 10	A'	0.5044	0.3405	0.0150	0.1639	0.1939
	13 ← 11	A'	0.6237	0.4245	0.1241	0.1992	0.4474
	13 ← 10	A''	0.6341	0.4721	0.0161	0.1620	0.1942
4	16 ← 15	A''	0.4819	0.5004	0.0244	−0.0185	0.0303
	16 ← 14	A'	0.4933	0.3303	0.0161	0.1630	0.1952
	17 ← 15	A'	0.6258	0.4152	0.1184	0.2106	0.4474
	17 ← 14	A''	0.6372	0.4539	0.0156	0.1833	0.2145
6	16 ← 15	A''	0.4748	0.4387	0.0187	0.0361	0.0735
	16 ← 14	A'	0.4926	0.3166	0.0218	0.1760	0.2196
	17 ← 15	A'	0.6502	0.4337	0.1258	0.2165	0.4681
	17 ← 14	A''	0.6680	0.4530	0.0134	0.2150	0.2418
Amides							
1	13 ← 12	A'	0.6352	0.4245	0.1191	0.2107	0.4489
	13 ← 11	A''	0.6624	0.4918	0.0195	0.1706	0.2096
	14 ← 12	A''	0.8686	0.4057	0.0353	0.4629	0.5335
	14 ← 11	A'	0.8958	0.2690	0.0138	0.6268	0.6544
3	17 ← 16	A'	0.6361	0.4172	0.1183	0.2189	0.4555
	17 ← 15	A''	0.6558	0.4758	0.0172	0.1800	0.2144
	18 ← 16	A''	0.8345	0.3636	0.0259	0.4709	0.5227
	18 ← 15	A'	0.8542	0.2822	0.0183	0.5720	0.6086
5	17 ← 16	A'	0.6574	0.4419	0.1307	0.2155	0.4769
	17 ← 15	A''	0.6827	0.4726	0.0148	0.2071	0.2367
	18 ← 16	A''	0.8009	0.3253	0.0169	0.4756	0.5094
	18 ← 15	A'	0.8262	0.2914	0.0171	0.5348	0.5690

been found previously in the case of **1**.[32] For each of the nitrenes, the lowest calculated singlet–triplet separation corresponds to n ← π. The lowest singlet configurations (S_0) of the three nitrenes are: **2**, ... $(9a')^2(2a'')^2$; **4**, ... $(12a')^2(3a'')^2$; and **6**, ... $(12a')^2(3a'')^2$. The lowest triplet configurations (T_1) are: **2**, ... $(9a')^2(2a'')^1(10a')^1$; **4**, ... $(12a')^2(3a'')(13a')^1$; and **6**, ... $(12a')^2(3a'')^1(13a')^1$. In the case of **2** and **4**, which are models for alkanoylnitrenes, the triplet state, T_1, is computed to be more stable than the singlet state, S_0, by 15 and 12 kcal/mol, respectively. By contrast, the singlet state of **6**, a model for carbalkoxynitrenes, is determined to be more stable than the triplet by 23 kcal/mol.

Esr measurements suggest the ground states of analogous nitrenes are triplets[24] (by virtue of the fact that they have an esr signal). An SCF calculation for the triplet state of the nitrenes, accompanied by geometry optimization, should lead to relatively lower energies than those estimated in Table V and thus would *increase* the computed singlet–triplet separation of nitrenes **2** and **4**, but *decrease* the separation of nitrene **6**.[42] With these considerations, the data in Table V suggest that singlet–triplet separations in carbalkoxynitrenes may be much smaller than for alkanoylnitrenes. This may manifest itself (if singlet and triplet geometries are significantly different) in a reduced tendency of carbalkoxynitrenes to undergo intersystem crossing and/or in the existence of both singlet and triplet states in thermal equilibrium. Although direct evidence for the latter is lacking, two recent reports[43,44] lend support to the former possibility. Theoretical studies have shown that the singlet state in electron deficient species may be stabilized by electron-rich three-center bonding.[14] In accord with the theory, methylene chloride has been shown to markedly increase the yield of (singlet) C–H insertion products of several alkanoylnitrenes.[43] However, carbethoxynitrene is remarkably insensitive to the presence or absence of methylene chloride.[45] The effect of hexafluorobenzene on the C–H insertion reactions of several carbalkoxynitrenes[44] seems ambivalent in this context. Yields of insertion products are high and not dramatically decreased by successive dilution with hexafluorobenzene. However, a maximum in the yield *vs.* [C_6F_6] curve is observed. The ambivalence is in part removed if, as the authors[44] suggest, the hexafluorobenzene is acting as a radical trap.

Mechanism of Amide Formation. Naive considerations would lead one to expect that the two bonding orbitals corresponding to the $-NH_2$ fragment of the amide should be as shown on the right-hand side of

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(42) This will be cancelled in part by the presence of greater correlation energy in the singlet than the triplet. The magnitude of this effect is something only a more detailed study can reveal.

(43) G. R. Felt, S. Linke, and W. Lwowski, *Tetrahedron Lett.*, 2037 (1972).

(44) D. S. Breslow and E. I. Edwards, *ibid.*, 2041 (1972).

(45) W. Lwowski and F. P. Woerner, *J. Amer. Chem. Soc.*, **87**, 5491 (1965).

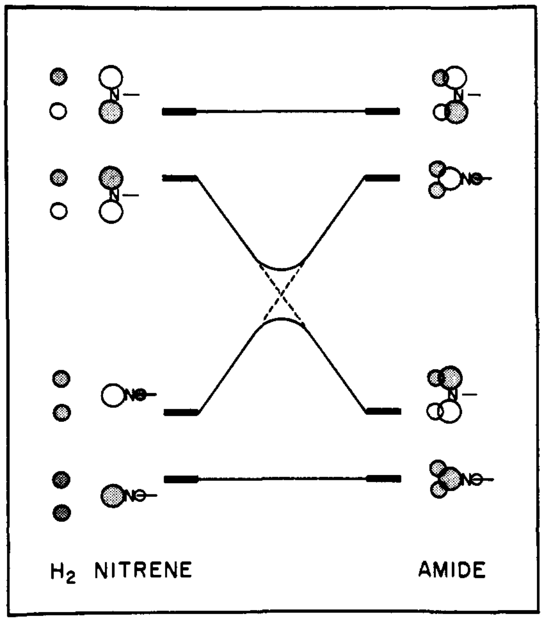

Figure 5. A schematic correlation diagram connecting amide $-NH_2$ bonding and antibonding orbitals to orbitals of the nitrene/H_2 system.

Figure 5. The lower energy orbital is derived from the appropriate combination of the bonding H_2 orbital and a nonbonded orbital on the nitrene, both of which are occupied. The other, however, arises from the antibonding orbital of H_2 and another nonbonded orbital on the nitrene, neither of which are occupied. Inspection of the computed molecular orbitals of the amides reveals that the above speculation is qualitatively correct but must be modified somewhat in detail due to the lack of an element of symmetry bisecting the H–H bond. Although the nitrene orbital fragments shown in Figure 5 are clearly discernible in the SCF orbitals of the nitrenes (**2**, MO 7 or MO 9 and MO 12 in Figure 2; **4**, MO 10 or MO 13 and MO 16 in Figure 3; and **6**, MO 11 and MO 16 in Figure 4), the computed orbitals of the amides which are principally responsible for N–H bonding (**1**, MO 7 and MO 8 in Figure 2; **3**, MO 8, MO 9 and MO 10 in Figure 3; **5**, MO 9 and MO 10 in Figure 4) can be regarded as arising from linear combinations of the bonding orbitals of Figure 5.

Computed MO energies for some points along an approximate reaction coordinate for the reaction

$$HC(O)N + H_2 = HC(O)NH_2$$

are shown in Figure 6. The points on the left-hand side of Figure 6 represent the MO energy levels for separate computations on formylnitrene (**2**) and hydrogen molecule. The hydrogen MO's are designated σ and σ^*. The set of points on the extreme right are the MO energies of formamide. The other two sets of points on the right are computed for stepwise contraction of the H–H separation and simultaneous withdrawal of the nitrene fragment from its position in formamide by increments of 0.25 and 0.26 Å, respectively. For clarity, the noncrossing rule is ignored and the intended correlations are shown. The 8a′ level of formamide is rapidly destabilized by withdrawal of the nitrogen[46] and its intended correlation is with the unoccupied 10a′ level of the nitrene **2**. Similarly, the intended correlation of the σ (or 7a′) level of the nitrene/H_2 system is with the 11a′ level of formamide. It is clear that direct insertion of the singlet nitrene into the H–H bond is a thermally forbidden process in the Woodward–Hoffmann[49] sense.[50]

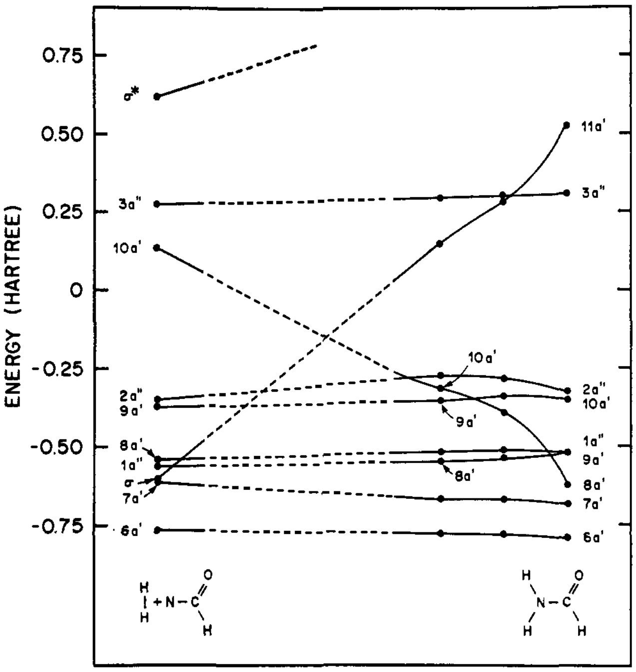

Figure 6. A correlation diagram connecting the higher valence MO's of the formylnitrene/H_2 system and the valence MO's of formamide. The intended correlations are shown. The H_2 MO's are designated σ and σ^*.

Two factors, however, favor concertedness in the insertion of carbonyl nitrenes into bonds despite the above considerations, namely (1) the lack of a strong symmetry requirement due to the low molecular symmetry and (2) the very large thermodynamic driving force of about 80 kcal/mol[51–53] (Table IV). With regard to the former, it will be seen that the symmetry requirement is further reduced by adoption of a highly unsymmetrical reaction coordinate. However, the "forbiddenness" is apparent in an increased energy of activation which is responsible for the lower reactivity of nitrenes (relative to carbenes) in insertion and abstraction reactions.

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(46) It was not possible to follow the reaction all of the way along the reaction coordinate because of convergence problems with the SCF procedure. It is well known that in cases such as the present, where orbital correlations are between bonding and antibonding orbitals, one requires at least a two-configuration CI procedure to account for the electronic distribution in the transition state region and to give a smooth variation of the energy along the reaction coordinate.[47,48]

(47) (a) A. R. Gregory and M. W. Paddon-Row, *Chem. Phys. Lett.*, **12**, 552 (1972); (b) S. Shih, R. J. Buenker, S. Peyerimhoff, and C. J. Michejda, *J. Amer. Chem. Soc.*, **94**, 7620 (1972).

(48) R. C. Bingham and M. J. S. Dewar, *ibid.*, **94**, 9107 (1972).

(49) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(50) It has previously been pointed out that direct insertion of a singlet carbene into an ethylenic π bond is a thermally forbidden process.[9b] Semiempirical computations,[9b,10a] yield a very low activation energy for the process.

(51) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Accounts Chem. Res.*, **5**, 402 (1972).

(52) Reference 48, p 174.

(53) See also (a) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94** 8918 (1972); (b) J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972); (c) N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924 (1972); (d) W. Schmidt, *Tetrahedron Lett.*, 581 (1972); (e) R. C. Dougherty, *J. Amer. Chem. Soc.* **93**, 7187 (1971); (f) T. F. George and J. Ross, *J. Chem. Phys.*, **55**, 3851 (1971).

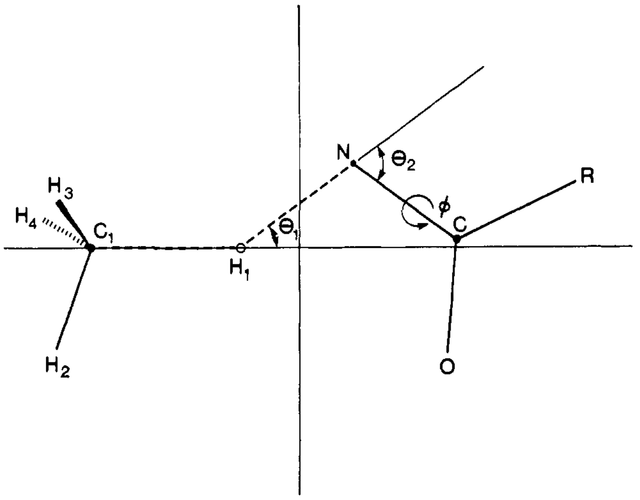

Figure 7. Definition of the geometry and variables used in the semiempirical calculations: C_1–H_1 = 1.6 Å and N–H_1 = 1.5 Å.

Orbital symmetry considerations also yield an explanation for the observed selectivity of singlet C–H insertion reactions: 3° > 2° > 1°.[26] In order to describe adequately the electronic configuration of the transition state implied by correlation diagrams such as in Figures 5 and 6, one needs to use two configurations.[47,48] Specifically, for the reaction shown in Figure 6, one requires

$$C_1[\ldots(10a')^2(11a')^0] + C_2[\ldots(10a')^0(11a')^2]$$

For the noninteracting nitrene + $H_2(\sigma \equiv a')$, or for formamide, the first configuration is sufficient ($C_1 \gg C_2$). However, at the transition state both configurations are of comparable importance ($C_1 \simeq C_2$). We have, in effect, a situation where the distribution of the two highest valence electrons is described by a superposition of two degenerate orthogonal distributions. Correlation of the electronic motions (due to mutual repulsion) leads to the conclusion that at least part of the time one electron occupies the 10a′ orbital while the other occupies the 11a′ orbital.[54] Thus appreciable diradical character may develop in the transition state of a concerted insertion of singlet nitrene into H–H bond. The same reasoning applies equally well for insertion into C–H bonds and for direct insertion into ethylenic π bonds. Since, on the nitrene side of the reaction, the 10a′ orbital of the transition state evolves from the σ bonding orbital of the substrate, effectiveness of radical stabilization by the substrate should have direct consequences on the selectivity of the reaction. The development of radical character in the transition state has often been invoked to explain the observed selectivity of nitrenes in concerted C–H insertion reactions.[16,25]

An examination of the potential surfaces for reaction of a singlet and triplet nitrene with a C–H bond in the vicinity of the transition state was carried out by means of semiempirical (CNDO/2) computations. The geometries of the systems (CH_4/**4** and CH_4/**6**) for which computations were carried out are illustrated in Figure 7. The C_1–H_1 bond was assumed stretched by 0.5 Å and the N–H_1 distance was kept fixed at the value 1.5 Å, which corresponds to a stretch of 0.5 Å from the experimental N–H distance in amides.[37] Angles at C_1 are 109°28′ and angles at the carbonyl carbon are 120°. All bond lengths except C_1–H_1 and N–H_1 are the same as shown in Figure 1. Computations were carried out at θ_1 = 0, 45, and 90°, θ_2 = 0, 45, or 63,[55] and 90°, and ϕ = 0, 90, and 180° for each of R = CH_3 and OH. For each orientation, the excitation energy to the lowest triplet was calculated by the virtual orbital approximation.[29]

The CNDO/2 ordering of the MO levels for each of the nitrenes **2**, **4**, and **6** is the same as given in Tables I–III and Figures 2–4 with the exception that the highest two molecular orbitals are reversed; *i.e.*, the CNDO/2 S_0 configuration is . . . $(na'')^2(ma')^2$. However, the configuration of the lowest triplet T_1 involved the same two orbitals as in the *ab initio* study . . . $(na'')^1(ma')^2((m + 1)a')^1$. The triplet state T_1 of each of the three nitrenes **2**, **4**, and **6** is computed by the CNDO/2 procedure to be ~100 kcal less stable than the singlet S_0. While this disagreement with the *ab initio* results of Table V appears to be an artifact of the semiempirical method,[56] we do not believe that it will alter the discussion of *changes* of triplet energy that follow. However, we recognize that the method is not sensitive enough to distinguish between nitrenes **4** and **6**. We therefore report the results only for **4**.

The range of variables allows a limited mapping of the potential surface of the singlet and triplet states in the region of interaction of the nitrene with the C–H bond. The results are displayed in Figures 8 and 9, respectively. Several conclusions can be drawn.

(1) A planar geometry of interaction (ϕ = 0 or 180°) is energetically favored for all values of θ_1 and θ_2 for the nitrene in both singlet and triplet states.

(2) For the singlet state (Figure 8) all considered angles of approach (θ_1) lead to a minimum at θ_2 = 90°. This corresponds to a geometry in which the LUMO of the nitrene (**4**, MO 16 in Figure 3) is directed toward the hydrogen. A considerable effect is seen as the nitrogen approaches a region where direct insertion becomes possible ($\theta_1 = \theta_2$ = 90°). Recent semiempirical computations (MINDO/2,[10a] EHMO[9c]) of the potential surface for insertion of the isoelectronic singlet carbene into a C–H bond showed some of the same features.

(3) The triplet potential surface (Figure 9) is somewhat flatter and has areas of relative stability when $\theta_1 = \theta_2$ = 0° and θ_1 = 0°, θ_2 = 90°, clearly favoring the abstraction mode. The former channel, if pursued, would lead to an energetically disfavored linear nitrogen radical. On the other hand, the second (θ_1 = 0°, θ_2 = 90°) would lead to a geometry of the nitrogen radical that is closer to equilibrium geometry (CNH = 117°). The highest (singly) occupied orbital of the triplet species is shown in Figure 10. It is apparent

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[54] We are aware of the difficulties involved in the physical interpretation of configuration interaction wave functions and are not suggesting that the wave function $[\phi_n(1)\phi_n(2) + \phi_{n+1}(1)\phi_{n+1}(2)]s$ (where s is the singlet spin function $\alpha(1)\beta(2) - \alpha(2)\beta(1)$ and ϕ_n = 10a′, ϕ_{n+1} = 11a′) is equivalent to the S_1 (first excited singlet) wave function $[\phi_n(1)\phi_{n+1}(2) + \phi_{n+1}(1)\phi_n(2)]s$.

[55] The value θ_2 = 63°, used when θ_1 = 0°, corresponds to an H_1–N–C angle of 117° which was found to be the equilibrium value for the HṄCHO radical.

[56] At a variety of points, separate calculations of the triplet energy were performed using the open shell feature of the CNINDO program.[34] In every case, the SCF computed energy agreed very closely with that obtained directly from the closed shell calculation by the virtual orbital approximation.[29] As a result, separate open shell computations were deemed unnecessary.

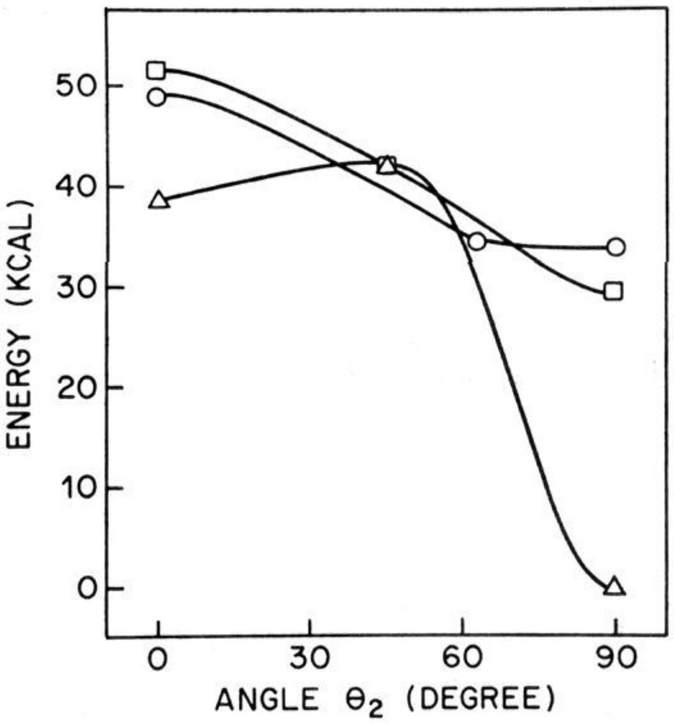

Figure 8. Cross sections of the potential surface for the reaction of singlet nitrene **4** with methane in terms of variables defined in Figure 7. $\phi = 0°$: (⊙) $\theta_1 = 0°$; (⊡) $\theta_1 = 45°$; (△) $\theta_1 = 90°$.

that the odd electron is highly delocalized over both carbon and nitrogen. The C–H bond is broken while positive overlap exists between the nitrogen and the hydrogen. The other odd electron is in a π orbital that is highly localized to the nitrene fragment.

Conclusions

The electronic configuration of the lowest singlet state of carbonyl nitrenes has been calculated to be . . . $(m\sigma)^2(n\pi)^2$. Except for two low-lying σ orbitals which correspond to missing bonds to nitrogen, the lowest singlet configurations of the carbonyl nitrenes are very similar to the ground state configurations of amides. The electronic configuration of the lowest triplet state . . . $(m\sigma)^2(n\pi)^1((m+1)\sigma)^1$, however, differs radically from the amide triplet configuration, the lowest transition being n ← π rather than π^* ← n. *Ab initio* calculations suggest that carbalkoxynitrenes may have singlet ground states. The estimated heat of formation of *N*-methylformamide from formylnitrene and methane is −86 kcal/mol, which is approximately 15 kcal/mol less than that calculated for the reaction of methylene with methane. It was shown by orbital correlation diagrams that direct insertion of the lowest singlet nitrene into σ bonds is a forbidden process in the Woodward–Hoffmann sense. However, we conclude that the reaction does proceed in a concerted manner. An energetically favorable insertion pathway occurs when the nitrene approaches the σ bond in an orientation which aligns its lowest unoccupied orbital with one end of the bond, thus avoiding the symmetry restrictions. A large amount of singlet diradical character can develop in the transition state. These results explain the high degree of selectivity and stereospecificity observed in nitrene insertion reactions.

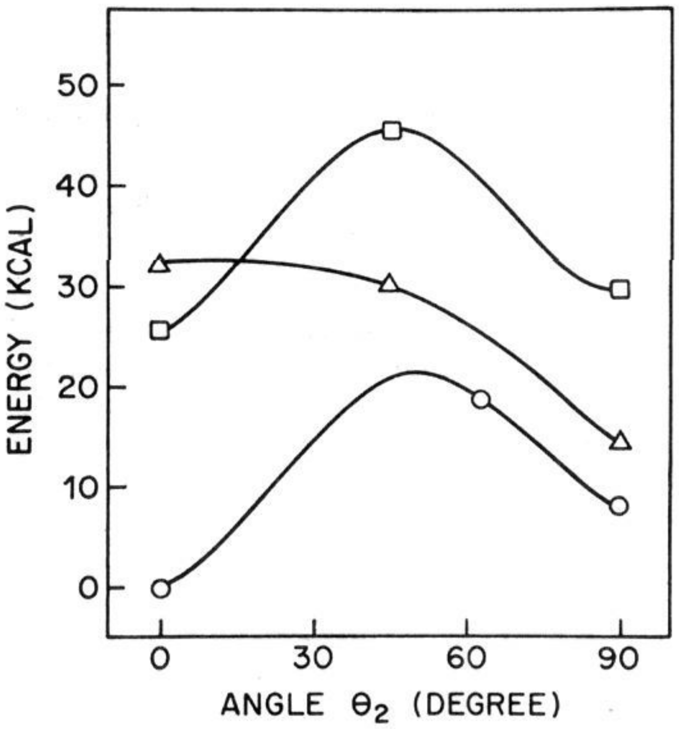

Figure 9. Cross sections of the potential surface for the reaction of triplet nitrene **4** with methane in terms of variables defined in Figure 7. $\phi = 0°$: (⊙) $\theta_1 = 0°$; (⊡) $\theta_1 = 45°$; (△) $\theta_1 = 90°$.

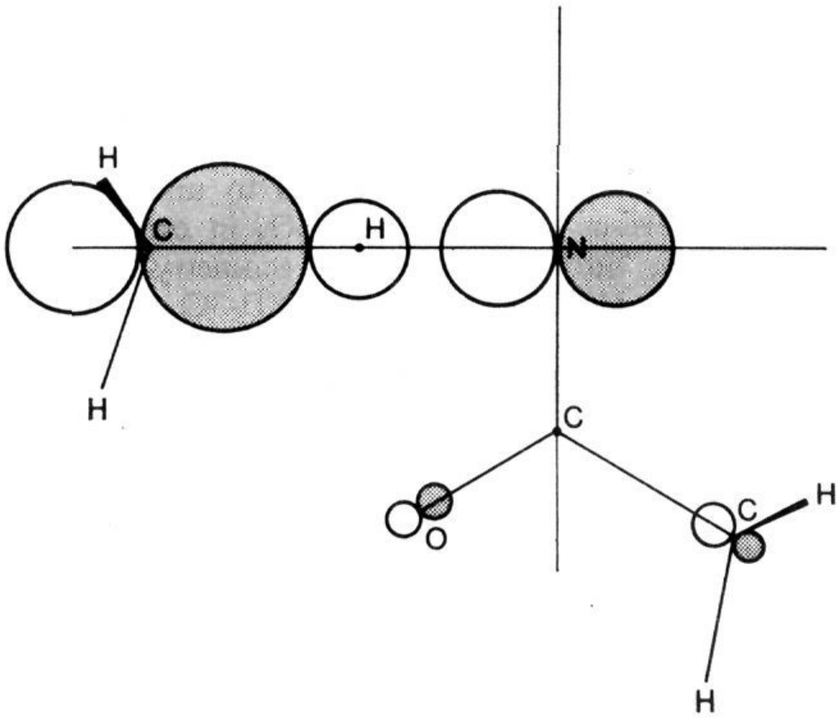

Figure 10. The highest (singly) occupied MO of the triplet acetylnitrene/methane system at $\theta_1 = 0°$, $\theta_2 = 90°$, $\phi = 0°$.

Acknowledgments. We thank Professor M. H. Benn for many stimulating discussions. Figures 2–4 were generated by a plotting program developed under an IBM Fellowship Grant.