Photoelectron spectroscopic and theoretical study of ketene imine, CH2:C:NH, and ketene-N-methylimine, CH2:C:NCH3

6 AUTHORS, INCLUDING:

Harold Kroto
Florida State University
509 PUBLICATIONS **21,921** CITATIONS

SEE PROFILE

Magnus Rittby
Texas Christian University
86 PUBLICATIONS **2,443** CITATIONS

SEE PROFILE

Rodney J. Bartlett
University of Florida
664 PUBLICATIONS **40,929** CITATIONS

SEE PROFILE

Photoelectron Spectroscopic and Theoretical Study of Ketene Imine, $CH_2=C=NH$, and Ketene N-Methylimine, $CH_2=C=NCH_3$

Harold W. Kroto,[†] **George Y. Matti,**[†] **Roger J. Suffolk,**[†] **John D. Watts,**[‡] **Magnus Rittby,**[‡] **and Rodney J. Bartlett***,[‡]

Contribution from the School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ United Kingdom, and Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611. Received April 3, 1989

Abstract: The organic transient molecule ketene imine, $CH_2=C=NH$, which may be important to the chemistry of the interstellar medium, has been produced by thermolysis of 3-hydroxypropionitrile, $HOCH_2CH_2CN$, and its He I photoelectron spectrum obtained for the first time. The interpretation of the spectrum is assisted by the calculation of the lowest four vertical ionization energies by a recently developed ab initio multireference coupled-cluster method (MRCC) and the SCF calculation of the vibrational frequencies of the lowest two cationic states. The lowest three observed ionization energies are 9.28, 11.91, and 13.04 eV. A fourth ionization is observed in the range 15–16 eV, but precise measurement is not possible because of contamination of this region of the spectrum by formaldehyde. The MRCC calculations predict ionization energies of 9.18 (a'), 12.03 (a''), 13.17 (a'), and 15.68 (a'') eV. Additional experimental and MRCC results for ketene N-methylimine, $CH_2=C=NCH_3$, provide further confirmation of the assignments for ketene imine.

The existence of ketene imine, $H_2C=C=NH$, was first suggested early this century,[1] but it was not until more than 40 years had passed that spectroscopic evidence for its existence was obtained.[2] The molecule was produced by the reaction of NH radicals with acetylene and condensed as a matrix with argon at 4 K. Following this pioneering work, ketene imine was produced by the reaction of methyl cyanide in the presence of argon atoms excited by a low-power microwave discharge.[3] The products were trapped at 77 K, and the infrared and ultraviolet spectra were obtained. From the C=N stretching frequency measured in this work, ketene imine was shown to be present in the thermolysis products of 9,10-dihydro-9,10-bis(iminoethylene)anthracene.[4] The first microwave observation of ketene imine was published in 1984,[5] when it was generated by the thermolysis of 3-hydroxypropionitrile, and its lifetime was estimated to be less than 1 s. In 1986 further microwave measurements were made,[6] the molecule this time having been produced by gas-phase elimination of dinitrogen from 1,2,3-triazole, $\overline{HC=CHN=NNH}$, and from this route, analyses of the Fourier transform infrared spectra of ketene imine have recently been published.[7,8]

There are several theoretical studies of ketene imine in the literature.[6,9–12] Three studies of the relative energies of several C_2H_3N isomers[9,11,12] each predict that ketene imine is the third most stable isomer after methyl cyanide, CH_3CN, and methyl isocyanide, CH_3NC. Third-order many-body perturbation theory (MBPT(3)) calculations with a near double-ζ plus polarization basis set by Brown et al.[12] predict ketene imine to be 32 kcal mol^{-1} less stable than methyl cyanide and 7 kcal mol^{-1} less stable than methyl isocyanide but 16 kcal mol^{-1} more stable than ethynamine, $HC\equiv CNH_2$. SCF calculations by Hopkinson et al.[9] and by Ha and Nguyen[11] indicate that ketene imine is also considerably more stable than the two cyclic isomers 1H-azirine, $\overline{HC=CHNH}$, and 2H-azirine, $\overline{H_2CCH=N}$. Of the C_2H_3N isomers, ethynamine and 1H-azirine are as yet uncharacterized, despite a detailed theoretical investigation of the former.[13]

It has been suggested that isomers of formula C_2H_3N play an important role in the chemistry of the interstellar medium,[14] and ketene imines have been implicated in chemical evolution studies to explain prebiological protein formation.[15] Methyl cyanide is an important interstellar molecule, and a tentative report of ketene imine in the interstellar medium has been made.[16]

Ketene imines are tautomers of aliphatic nitriles and, as such, are believed to be intermediates in a number of chemical reactions.[17] Usually transient, they may be stabilized by appropriate substitution, and stable ketene imines are of value in organic synthesis.[17] Like the isoelectronic allenes, ketene imines have the potential for optical isomerism, but a low-energy inversion pathway renders them configurationally unstable.[6,10,17,18]

In this paper, we report the production of ketene imine by the thermolysis of 3-hydroxypropionitrile and, for the first time, its He I photoelectron spectrum. The spectrum is interpreted with the aid of ab initio calculations of (i) the vertical ionization energies by the multireference coupled-cluster approach and (ii) the harmonic vibrational frequencies of the two lowest lying electronic states of the ketene imine monocation at the SCF MO level.

As noted by Rodler et al.[5] since ketene imine rapidly tautomerizes to methyl cyanide, it is not easy to generate sufficient quantities for spectroscopic studies. Perhaps because of this,

(1) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919,** *2,* 619.
(2) Jacox, M. E.; Milligan, D. E. *J. Am. Chem. Soc.* **1963,** *85,* 278.
(3) Jacox, M. E. *Chem. Phys.* **1979,** *43,* 157.
(4) Guillemin, J.-C.; Denis, J.-M.; Lasne, M.-C.; Ripoll, J.-L. *J. Chem. Soc., Chem. Commun.* **1983,** 238.
(5) Rodler, M.; Brown, R. D.; Godfrey, P. D.; Tack, L. M. *Chem. Phys. Lett.* **1984,** *110,* 447.
(6) Rodler, M.; Brown, R. D.; Godfrey, P. D.; Kleibomer, B. *J. Mol. Spectrosc.* **1986,** *118,* 267.
(7) (a) August, J.; Kroto, H. W.; Walton, D. R. M. to be published. (b) August, J. Ph.D. Thesis, University of Sussex, 1985.
(8) Amatatsu, Y.; Namada, Y.; Tsuboi, M. *J. Mol. Spectrosc.* **1987,** *123,* 476.
(9) Hopkinson, A. C.; Lien, M. H.; Yates, K.; Csizmadia, I. G. *Int. J. Quantum Chem.* **1977,** *12,* 355.
(10) Kaneti, J.; Nguyen, M.-T. *J. Mol. Struct.* **1982,** *87,* 205.
(11) Ha, T.-K.; Nguyen, M.-T. *J. Mol. Struct.* **1982,** *87,* 355.
(12) Brown, R. D.; Rice, E. H. N.; Rodler, M. *Chem. Phys.* **1985,** *99,* 347.
(13) Saebo, S.; Farnell, L.; Riggs, N. V.; Radom, L. *J. Am. Chem. Soc.* **1984,** *106,* 5047.
(14) Green, S.; Herbst, E. *Astrophys. J.* **1979,** *229,* 121.
(15) Kliss, R. M.; Mathews, G. N. *Proc. Natl. Acad. Sci. U.S.A.* **1962,** *48,* 1300.
(16) Brown, R. D. 9th Colloquium on High Resolution Spectroscopy; Riccione, 1985.
(17) (a) Barker, M. W.; McHenry, W. E. In *The Chemistry of Ketenes, Allenes, and Related Compounds;* Patai, S., Ed.; Wiley-Interscience: New York, 1980. (b) McCarthy, D. G.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1980,** 579.
(18) Jochims, J. C.; Herzberger, S.; Gambke, B.; Anet, F. A. K. *Tetrahedron Lett.* **1977,** 2255.

[†] University of Sussex.
[‡] University of Florida.

3780 *J. Am. Chem. Soc., Vol. 112, No. 10, 1990*

Kroto et al.

microwave[19] and infrared[20] studies of the pyrolysis products of aliphatic amines did not detect ketene imine. In the present study a photoelectron spectrometer designed for the study of transient molecules is used. Nevertheless, as we show below, the photoelectron spectrum is contaminated by methyl cyanide and formaldehyde, and in order to assign it with any confidence, it is extremely useful, probably essential in fact, to have accurate theoretical estimates (within about 0.2 eV of experiment) of the valence ionization energies of ketene imine. In this work, these are provided by a recently developed multireference coupled-cluster approach.[21]

Rather few other quantum chemical methods[22,23] could be used for this purpose, because of either the inherent inaccuracy or the inability to obtain the energies of more than one electronic state of a given symmetry type. In particular, the theoretical technique must account for electron correlation in order to be accurate enough, yet any technique that requires separate calculations on the neutral molecule and cationic states to determine the ionization energies is probably able to determine only the lowest two ionization energies of ketene imine because of the likelihood of variational collapse in the initial SCF procedure (ketene imine has C_s symmetry).

This paper illustrates the effective combination of forefront theory and experiment in resolving the photoelectron spectrum of the interesting transient molecule ketene imine.

Experimental Section

Ketene imine was produced by thermolysis of 3-hydroxypropionitrile (Aldrich). This precursor, which was used without any further purification, was held in a Rotaflo ampule connected to the thermolysis apparatus and was heated to 1050 °C. The thermolysis products were rapidly pumped into the ionization region of the photoelectron spectrometer. No form of selective trapping was employed. The photoelectron spectrometer has been designed for the study of short-lived molecules and is described elsewhere.[24] The spectra, produced with He I photons, were calibrated with argon and methyl iodide and were obtained with a typical resolution of 25 meV.

Computational Details

In order to facilitate the interpretation of the photoelectron spectra, we have performed some ab initio calculations on ketene imine and its monocations, as well as a calculation on ketene N-methylimine. All of the calculations were performed with the ACES program system.[25]

First, we have computed the vertical valence ionization energies of ketene imine and ketene N-methylimine using the multireference coupled-cluster approach.[21] This method is a highly efficient and accurate approach to the calculation of molecular ionization energies. From the principle of valence universality, the wave functions of several cationic states are constructed from the neutral molecule wave function and a small number of correction terms. Ionization energies are determined directly (i.e. not as the difference of two separately calculated energies),

Table I. Experimental and Calculated IE's for 3-Hydroxypropionitrile, $HOCH_2CH_2CN$

expt[a]	calcd[b]	assgnt
11.29	12.46	n_O
12.36	12.71 ⎫	$\pi_{C=N}$
12.59	12.81 ⎭	
13.14	14.02	n_O
14.91	15.06	$\sigma_{C=N}$
15.36	15.95	σ_{CH_2}
16.45	17.07	σ_{CO}
18.11	17.93	σ_{OH}

[a] Experimental values are estimated to have an accuracy of ±0.05 eV. [b] The IE's were calculated with Koopmans' theorem and the 4-31G basis set.

and several may be determined in a single calculation. On the basis of the results of several studies,[21,26] with a reasonable basis set, we anticipate an agreement with experiment of better than 0.2 eV, which is competitive with other more expensive techniques such as CCSDT-1.[26,27] We include both one- and two-body cluster operators and hereafter denote the method MR-CCSD. Certain higher order effects that are neglected in the MR-CCSD model are in some cases important,[28] but for ketene imine seem not to be (see below).

As the MR-CCSD model is still relatively new, as a further calibration of this model, we have determined the first two vertical ionization energies of ketene imine with the CCSDT-1 method[27] based upon a UHF reference function for the open-shell ion states. This method is correct through fourth-order of perturbation theory and iteratively includes the effects of triple excitations (relative to a single reference function). This required separate CCSDT-1 calculations on the neutral molecule and the two lowest cationic states and taking the difference between large numbers.

To underscore the value of the MR-CCSD approach, we note that the computation time required to obtain the lowest four ionization energies using this method was less than that required to do a single CCSDT-1 calculation. In addition, as the CCSDT-1 calculations used Hartree–Fock orbitals for each state investigated, only two ionization energies could be obtained by this method. Of course, the QRHF-CCSDT-1 method could have been used to obtain more valence ionization energies[23] but, as presently implemented (see remarks in ref 26), would still require taking the difference between large numbers. As a byproduct of the CCSDT-1 calculations, finite-order perturbation theory results through the full fourth-order model (MBPT(4)) were obtained, which we include along with ΔSCF and Koopmans' theorem results for comparison.

The MR-CCSD and CCSDT-1 calculations on ketene imine were performed at the geometry determined by Rodler et al.[6] using third-order perturbation theory. This geometry should be close to the experimental one.[29] We assumed ketene N-methylimine to be of C_s symmetry. We used the same geometry as ketene imine with, in addition, a N–C single bond length of 1.475 Å and a "standard" geometry[30] for the methyl group. Both orientations of the methyl group consistent with C_s symmetry were considered, and the one having the lowest SCF energy was used in the MR-CCSD calculation.

We used a standard Huzinaga–Dunning[31] double-ζ plus polarization (DZP) basis set in the MR-CCSD and CCSDT-1 calculations. The polarization exponents were 0.75, 0.8, and 1.0 for C, N, and H, respectively.[32]

Second, we determined the geometries and harmonic vibrational frequencies of ketene imine and its two lowest cationic states at the SCF level using standard analytic gradient and analytic Hessian techniques.[33] These calculations were not carried out with the intention of obtaining highly accurate geometries and vibrational frequencies, for which cor-

(19) Lovas, F. J.; Clark, F. O.; Tiemann, E. *J. Chem. Phys.* **1975**, *62*, 1925.

(20) Hamada, Y.; Hashiguchi, K.; Tsuboi, M.; Koga, Y.; Kondo, S. *J. Mol. Spectrosc.* **1984**, *105*, 93.

(21) (a) Pal, S.; Rittby, M.; Bartlett, R. J.; Sinha, D.; Mukherjee, D. *Chem. Phys. Lett.* **1987**, *137*, 273. (b) Pal, S.; Rittby, M.; Bartlett, R. J.; Sinha, D.; Mukherjee, D. *Ibid.* **1987**, *142*, 575. (c) Pal, S.; Rittby, M.; Bartlett, R. J.; Sinha, D.; Mukherjee, D. *J. Chem. Phys.* **1988**, *88*, 4357. (d) Rittby, M.; Pal, S.; Bartlett, R. J. *Ibid.* **1989**, *90*, 3214.

(22) (a) von Niessen, W.; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57. (b) Cederbaum, L. S.; Domcke, W.; Schirmer, J.; von Niessen, W. *Adv. Chem. Phys.* **1986**, *65*, 115. (c) Graham, R. L.; Golab, J. T.; Yeager, D. L. *J. Chem. Phys.* **1988**, *88*, 2572.

(23) Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1988**, *92*, 3033.

(24) Dyke, J. M.; Jonathan, N.; Morris, A. *Electron Spectroscopy: Theories, Techniques, and Applications*; Academic Press: New York, 1979; Vol. 3.

(25) ACES (advanced concepts in electronic structure) ab initio program system: Bartlett, R. J.; Purvis, G. D.; Fitzgerald, G. B.; Harrison, R. J.; Lee, Y. S.; Laidig, W. D.; Cole, S. J.; Magers, D. H.; Salter, E. A.; Trucks, G. W.; Sosa, C.; Rittby, M.; Pal, S.; Watts, J. D.; Stanton, J. F.; Bernholdt, D. E. This is a general program system capable of carrying out molecular SCF, MBPT, and CC calculations; evaluating analytic first derivatives at the SCF, MBPT, and CC levels; evaluating analytic second derivatives at the SCF and MBPT(2) levels; and studying excitation and ionization processes with MR-CC theory. The program uses the integral packages of J. Almlöf (MOLECULE) and R. Pitzer (SOINTS) and parts of the GRNFNC system developed by G. D. Purvis for the SCF and integral transformation steps.

(26) Watts, J. D.; Rittby, M.; Bartlett, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 4155.

(27) Lee, Y. S.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1984**, *81*, 5906.

(28) Pal, S.; Rittby, M.; Bartlett, R. J. *Chem. Phys. Lett.* **1989**, *160*, 212.

(29) DeFrees, D. J.; Raghavachari, K.; Schlegel, H. B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5576.

(30) Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* **1967**, *89*, 4253.

(31) (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H. *Ibid.* **1970**, *53*, 2823.

(32) Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977.

(33) (a) Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977. (b) Carsky, P.; Urban, M. *Ab Initio Calculations: Methods and Applications in Chemistry*; Springer-Verlag: Berlin, 1980. (c) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 225.

Table II. Experimental and Calculated Ionization Energies for Ketene Imine, H_2C=C=NH

	calcd (eV)[b]								assignment
exptl (eV)[a]	MR-CCSD	CCSDT-1	MBPT(4)	SDQ-MBPT(4)	MBPT(2)	SCF	Koopmans' theorem		
9.28[c]	9.18	9.18	9.38	9.32	9.47	8.38	9.71	a'	antibonding combination of C=C π and N lone-pair orbitals
11.91[d]	12.03	12.00	12.20	12.08	12.43	10.70	12.66	a''	C=N π-bonding orbital
13.04[e]	13.17						15.07	a'	bonding combination of C=C π and N lone pair; appears to have C=N "π" character although it is formally of a' symmetry
15-16	15.68						16.98	a'	mainly C—H with some C—C σ-bonding character

[a] The experimental values are estimated to have an accuracy of ±0.01 eV. [b] DZP basis set. [c] Vibrational progressions in ν_5 and ν_6. [d] Vibrational progressions in ν_5 and ν_3. [e] Vibrational progressions in ν_7.

related methods are needed.[34] Rather, their purpose was to obtain reasonably accurate results in order to assist in understanding the vibrational fine structure of the photoelectron bands and the structural changes on ionization. The geometries were determined with the 6-31G and 6-31G** basis sets,[35] which are of approximately DZ and DZP quality, and the vibrational frequencies were determined only with the 6-31G set. A large body of data shows that geometries calculated at this level are accurate to within 0.01-0.03 Å for bond lengths (usually shorter than experiment) and a few degrees for bond angles, while vibrational frequencies calculated at this level are usually 10-15% higher than experiment.[36]

Third, to understand better the electronic structure of ketene imine, we plotted MOs of this molecule using the QUIPU package of Purvis,[37] which incorporates parts of ACES. A density of 0.1 e/Å³ was used.

Finally, an SCF calculation on the precursor 3-hydroxypropionitrile was performed to estimate the ionization energies of this molecule by Koopmans' theorem. This calculation used the 4-31G basis set[35a] and the GAUSSIAN 82 program.[38] Ionization energies obtained in this way are usually about 10% higher than those determined experimentally.[39]

Results and Discussion

Although conditions for the production of ketene imine during the experiments were optimized, previously published work with infrared spectroscopy[7] gave a starting point. It was necessary to heat the 3-hydroxypropionitrile to ca. 60 °C in order to produce sufficient vapor pressure under the fast-pumping conditions. The photoelectron spectrum of 3-hydroxypropionitrile is shown in Figure 1a. The ionization energies are given in Table I together with those obtained from an ab initio SCF calculation. If a comparison is made between this spectrum and that of propionitrile,[40] it is clear that two changes have occurred. A new band associated with the -OH group has appeared (11.29 eV), and a general shift of the bands to higher energies has occurred, caused by the -I electron-withdrawing effect of the -OH group.

The thermolysis of 3-hydroxypropionitrile is expected to produce formaldehyde and methyl cyanide in addition to ketene imine, viz.:
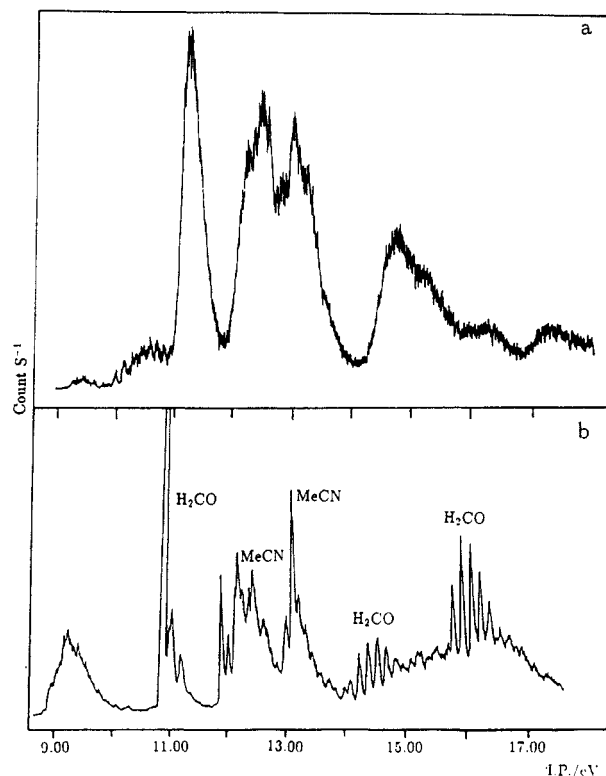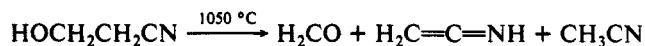
$$HOCH_2CH_2CN \xrightarrow{1050\ °C} H_2CO + H_2C=C=NH + CH_3CN$$

(34) See, for example: (a) Bartlett, R. J.; Cole, S. J.; Purvis, G. D.; Ermler, W. C.; Hsieh, H. C.; Shavitt, I. *J. Chem. Phys.* **1987**, *87*, 6579. (b) Scuseria, G. E.; Schaefer, H. F. *Chem. Phys. Lett.* **1988**, *146*, 23. (c) Scuseria, G. E.; Schaefer, H. F. *Ibid.* **1988**, *152*, 382. (d) Trucks, G. W.; Watts, J. D.; Salter, E. A.; Bartlett, R. J. *Ibid.* **1988**, *153*, 490.

(35) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *Ibid.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(36) (a) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 269. (b) Hehre, W. J.; Radom, L.; Schleyer, P. von R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(37) Purvis, G. D. *QUIPU (Quantum Chemical Interactive Program Utility)*, Version 3.6; Quantum Theory Project, University of Florida: Gainsville, FL, 1987.

(38) Binkley, J. S.; Frisch, M. J.; Raghavachari, K.; DeFrees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, G.; Seeger, R.; Pople, J. A. *GAUSSIAN 82*, Release A; Carnegie-Mellon University: Pittsburgh, 1982.

(39) Schwarz, M. E. In *Applications of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977.

(40) Lake, R. F.; Thompson, H. *Proc. R. Soc. London* **1970**, *A317*, 187.

Figure 1. PES of (a) 3-hydroxypropionitrile and (b) the thermolysis products of 3-hydroxypropionitrile.

The ketene imine and formaldehyde are produced by a cyclic rearrangement and elimination, i.e.
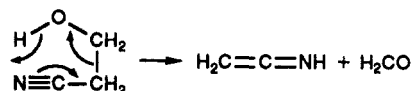
Ketene imine then rapidly tautomerizes, giving methyl cyanide.

When 3-hydroxypropionitrile was passed through the quartz tube heated to 1050 °C, the spectrum shown in Figure 1b was obtained. This shows that the precursor has been completely destroyed and many new features have been produced. As predicted, strong bands due to formaldehyde are observed at 10.88, 14.5, and 16.0 eV.[41] It proved impossible to remove these bands by selective trapping, while maintaining the peaks of interest. In addition to the H_2CO bands, there are peaks assignable to methyl cyanide at 12.21 and 13.14 eV.[42] There is a new structured band, well removed from the positions of the bands of H_2CO and CH_3CN and clear of the precursor bands, having a vertical ionization energy of 9.28 eV, which we assign to ketene imine. This

(41) Brundle, C. R.; Robin, M. B.; Kuebler, N. A.; Basch, H. *J. Am. Chem. Soc.* **1972**, *94*, 1451.

(42) Frost, D. C.; Herring, F. G.; McDowell, C. A.; Stenhouse, I. A. *Chem. Phys. Lett.* **1970**, *4*, 533.
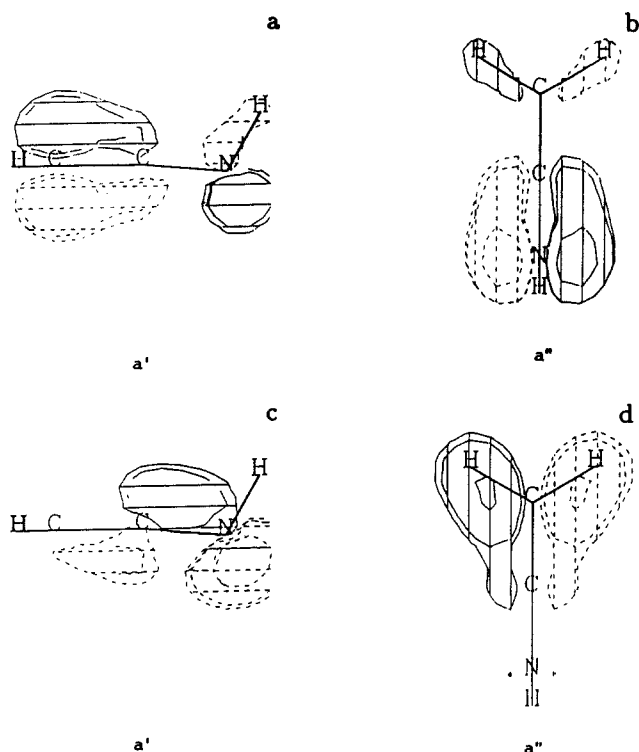
3782   *J. Am. Chem. Soc., Vol. 112, No. 10, 1990*

Kroto et al.

a

b

a'

a"

c

d

a'

a"

Figure 2. Electron density plots of the first four occupied molecular orbitals of ketene imine. The HOMO is 2a.

assignment is confirmed by our calculations (Table II). Thus, the MR-CCSD and CCSDT-1 predictions for the first ionization energy of ketene imine are in very good agreement with the energy of this band. In other studies on H_2CO, N_2, CO, CH_2CO, CH_2N_2,[21] H_2CNH, and H_2CPH[26] for similar levels of approximation the average deviations from the experimental ionization energies have been less than 0.2 eV. The fact that the MR-CCSD and CCSDT-1 results are identical indicates that the higher order effects not considered in the MR-CCSD model are comparatively unimportant, at least for this band. Although the SDQ-MBPT(4) model gives the best results for this band, this is fortuitous since more complete models lead to slightly larger deviations from experiment. The inaccuracies of the uncorrelated Koopmans' theorem and ΔSCF ionization energies are apparent.

If we compare the value of the first ionization energy of ketene imine with those of methylenimine, 10.50–10.70,[43] and ethylene, 10.51,[44] we notice a considerable shift in energy. This shift can be rationalized on the basis of the interaction between the nitrogen lone-pair orbital and the ethylenic π system. The out-of-phase ("antibonding") combination leads to a destabilization (a lower ionization energy) and the in-phase ("bonding") combination to a stabilization (a higher ionization energy) relative to the HOMOs of methylenimine and ethylene. A plot of the HOMO of ketene imine is shown in Figure 2a. This shows that this orbital is indeed the out-of-phase combination of the fragment HOMOs and has significant contributions from both the nitrogen lone pair and the C=C π system.

Examination of the first band of ketene imine under higher resolution (Figure 3) suggests that it is composed of two vibrational progressions of the >C=C=N- stretching fundamental, ν_5, separated by 1 quantum of the CNH bend, ν_6. The values of ν_5 and ν_6 for the ion obtained from the spectrum are 1040 and 550 cm⁻¹, compared with 1127 and 1004 cm⁻¹ in the neutral molecule.[7] The values obtained from our SCF calculations on the lowest ²A′

(43) (a) Peel, J. B.; Willett, G. D. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1799. (b) Bock, H.; Dammel, R.; Horner, L. *Chem. Ber.* **1981**, *114*, 220. (c) Schulz, R.; Schweig, A. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *28*, 33.

(44) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Halsted Press: New York, 1981.
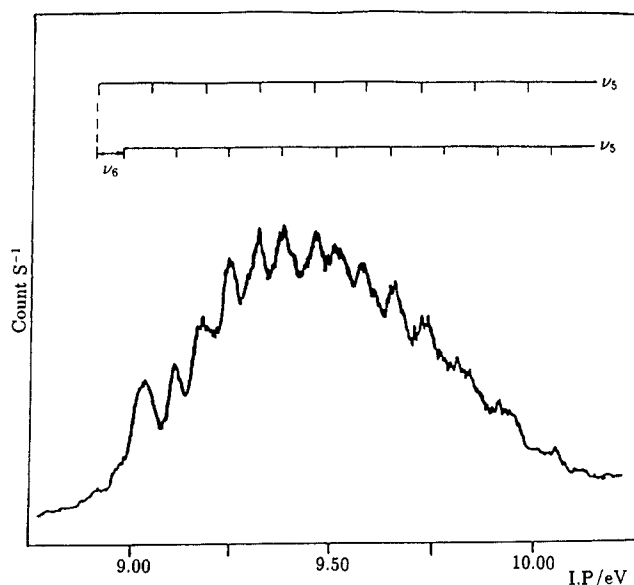

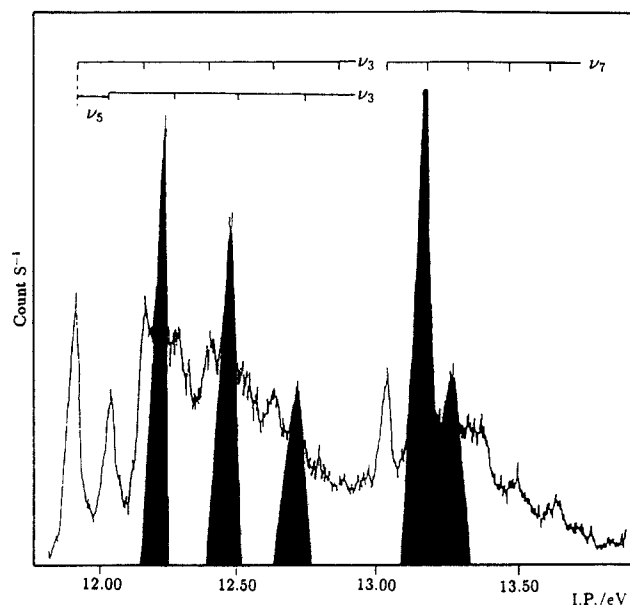**Figure 3.** High-resolution PES of the first band of ketene imine.

Figure 4. High-resolution PES of the 11.8–13.9-eV region of ketene imine.

state of the cation are 1078 and 618 cm⁻¹. There is a strong feature on the first band at 9.02 eV, which is due to the He I "shadow" of the intense band of H_2CO at 10.88 eV. This obviously masks one of the vibrational components in the first vibrational series.

The lowest ²A′ cation of ketene imine, i.e., that which arises from ionization of the HOMO, has a structure rather different from that of the neutral molecule. It actually is planar and the >C=C=NH unit is linear, so that the ion has C_{2v} symmetry. In C_{2v} the electronic state is ²B₁; that is, the SOMO is perpendicular to the molecular plane. A large increase in CNH bond angle is to be expected following ionization of an orbital having significant nitrogen lone-pair character. This has been observed also in calculations on methylenimine.[43c] Again as expected from the nature of the HOMO of the neutral molecule, the C=C bond length in the cation is significantly longer than in the neutral molecule, namely about 0.1 Å according to our 6-31G** calculations. The other geometrical parameters are not greatly changed relative to their values in the neutral molecule. The structure of the cation is further evidence for the excitation of the >C=C=N- stretching and CNH bending modes.

The second region of interest in Figure 1b, shown in more detail in Figure 4, is from approximately 12 to 14 eV. After allowing for the presence of methyl cyanide and guided by our MR-CCSD

Table III. Experimental and Calculated Ionization Energies for Ketene *N*-Methylimine, $H_2C=C=NCH_3$

exptl (eV)	calcd (eV^a)			assignment
	MR-CCSD	Koopmans' theorem		
8.60	8.90	9.55	a′	antibonding combination of C=C π and N lone-pair orbitals
	11.13	11.74	a″	C=N π-bonding orbital
12.20	11.92	13.40	a′	bonding combination of C=C π and N lone-pair orbitals
	14.99	16.15	a″ ⎫	
	15.19	16.66	a′ ⎪	predominantly C—H bonding with also some contribution
	15.74	17.12	a″ ⎬	from C—N and C—C σ bonding
	15.86	17.59	a′ ⎭	

^{a} DZP basis set.

calculations, there appear to be two bands in this region belonging to ketene imine.

The first of these, which is the second band of the molecule, has a vertical ionization energy of 11.91 eV and extensive vibrational structure. This band is expected to arise from ionization of a C=N π-bonding orbital. This orbital is somewhat destabilized relative to the corresponding orbital in methylenimine[43] and is shown in Figure 2b. The MR-CCSD and CCSDT-1 calculated ionization energies are again in excellent agreement with the experimental value (Table II) and are clearly superior to the finite-order perturbation theory and uncorrelated ΔSCF and Koopmans' theorem results. As observed for the first band, the close agreement of the MR-CCSD and CCSDT-1 results indicates that the higher order effects neglected in the MR-CCSD model are also not of significance for this ionization.

The most likely explanation of the vibrational fine structure is two series in ν_3, the >C=C=N- asymmetric stretching fundamental separated by 1 quantum of ν_5. The vibrational frequencies obtained from this band are 1900 and 860 cm^{-1} for ν_3 and ν_5, respectively. Our SCF calculations on the lowest $^2A''$ state of the cation predict these frequencies to be 1989 and 1012 cm^{-1}, compared with 2037 and 1127 cm^{-1} in the neutral molecule.

The structure of the lowest $^2A''$ cation differs mainly from that of the neutral molecule in having a longer C=N bond length, about 0.12 Å longer from 6-31G** calculations. Apart from the C=C bond length, which decreases by almost 0.04 Å, the other geometrical parameters do not alter significantly on ionization. These observations are consistent with the assignment of the a″ orbital.

The second band in the 12–14-eV region, which is also the third band of ketene imine, has an adiabatic ionization energy of 13.04 eV, which may also be the vertical ionization energy. Again, the MR-CCSD estimate is in excellent agreement with this value (Table II). The second component of this band is hidden under the strong methyl cyanide peak. This band shows a vibrational series of at least five members with a value of 600 cm^{-1} and is probably due to excitation of ν_7, the CH$_2$ wag (690 cm^{-1} in the neutral molecule).

The third orbital of ketene imine is shown in Figure 2c and can be considered to arise from the bonding combination of the nitrogen lone pair and the C=C π system, although this is an oversimplification as there appears also to be significant electron density in the C=N internuclear region.

Our calculations also predict a fourth band at 15.68 eV, and there is certainly a broad band with some vibrational structure in the region 15–16 eV. Due to the overlapping bands of H$_2$CO in this region, a positive assignment is not possible. The fourth orbital of ketene imine is predicted to be largely an antisymmetric combination of C–H bonding orbitals, along with some CC σ-bonding character, and is shown in Figure 2d.

As further proof of the assignments given above for ketene imine, we have attempted to produce and observe ketene *N*-methylimine, H₂C=C=NCH₃, from the thermolysis of 3-methyl-4-[(methylamino)methylidene]isoxazol-5(4H)-one (hereafter referred to as I). This precursor is known to produce ketene *N*-methylimine,[45] and accordingly a search of the region of the

photoelectron spectrum in which the ionization energies of this molecule are expected to lie was carried out. The spectra were very weak, but new bands were observed at approximately 8.60, 12.20, and 13.82 eV. With the aid of our MR-CCSD calculations on ketene *N*-methylimine, we now attempt to assign these bands. The DZP basis for ketene *N*-methylimine comprises 84 functions. Of these, the four 1s core orbitals are not correlated.

In Table III we show the first seven ionization energies of ketene *N*-methylimine calculated by the MR-CCSD method and by Koopmans' theorem. We give also a brief description of the nature of the ionized orbital in each case.

Intuitively, one expects a methyl group to stabilize a cation better than a hydrogen atom. Consequently, the ionization energies of ketene *N*-methylimine are expected to be smaller than the corresponding energies of ketene imine. When the calculated data in Tables II and III are compared, this prediction is seen to be confirmed.

We now compare the energies of the new bands in the photoelectron spectrum of the products of the thermolysis of I, namely 8.60, 12.20, and 13.82 eV, with the MR-CCSD ionization energies of ketene *N*-methylimine (Table III).

The good agreement between the calculated energy of the first band of ketene *N*-methylimine and the energy of the first new band in the spectrum strongly suggests that the first new band is due to ionization of the HOMO of ketene *N*-methylimine. The agreement between theory and experiment for this band is not quite as good as for ketene imine. Part of reason for this is that the geometry for ketene *N*-methylimine is less accurate than that of ketene imine. The alternative of using the uncorrelated Koopmans' theorem values for the assignment would clearly not be possible.

Since the energy of the second new band is quite close to the MR-CCSD calculated energy of the third band of ketene *N*-methylimine, we believe this band arises from ionization of the third highest occupied orbital of ketene *N*-methylimine, rather than the second highest occupied orbital. Were it to arise from ionization of the second highest occupied orbital, it would follow that the MR-CCSD estimate of the energy is in error by over 1 eV. Such a large error for this method is unprecedented.

Using the same reasoning, since none of the MR-CCSD ionization energies are within 1 eV of the energy of the third new band (13.82 eV), we do not believe this band is due to any of the principal ionizations of ketene *N*-methylimine.

The second band of ketene *N*-methylimine is predicted by the MR-CCSD method to have an energy of 11.13 eV. This band is not observed, probably because the spectrum is in any case weak and also because this band may be marked by I.

We believe, then, that the first two new bands in the spectrum of the products of thermolysis of I are due to ionization of the two highest occupied a′ orbitals of ketene *N*-methylimine. The energies of these bands are 8.60 and 12.20 eV, which may be compared with 9.28 and 13.04 eV for the corresponding bands of ketene imine. The decrease in ionization energy following methyl substitution is in line with our theoretical findings (see above). The magnitudes of the shifts in energy of the two bands are, however, not quantitatively reproduced even by the MR-CCSD method. Again, this is due in part to the use of a less accurate geometry for ketene *N*-methylimine. So although the experimental data for ketene *N*-methylimine are incomplete, the

(45) August, J.; Klemm, K.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. II* **1989**, 1841.

assignments for this molecule are consistent with those for ketene imine, thus providing further evidence for the assignments we have made for ketene imine.

Acknowledgment. G.Y.M. thanks the Iraqi Government for a scholarship, and Dr J. August is gratefully thanked for outlining the subtleties of the preparation of ketene imine. The work carried out at the University of Florida was supported by the U.S. Air Force Office of Scientific Research, Division of Chemistry and Atmospheric Sciences, under Contract No. AFOSR-89-0207.

Note Added in Proof. Wentrup et al.[46] have recently detected the elusive ethynamines $HC\equiv CNH_2$ and $PhC\equiv CNH_2$.

(46) Wentrup, C.; Briehl, H.; Lorenčak, P.; Vogelbacher, U. J.; Winter, H.-W.; Maquestiau, A.; Flammung, R. J. Am. Chem. Soc. 1988, 110, 1337.

A Helical Face-Sharing Tetrahedron Chain with Irrational Twist, Stella Quadrangula, and Related Matters

Chong Zheng,[†] Roald Hoffmann,*,[†] and David R. Nelson[‡]

Contribution from the Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853, and the Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138. Received May 19, 1989

Abstract: Aggregates in which tetrahedra share faces are rare; this paper describes the electronic structure of some one-dimensional chains of this type. The archetype is gracefully winding triple helix with irrational twist, also described by R. Buckminster Fuller as a tetrahelix. We examine some realizations of this structure exemplified by stoichiometries such as BR, PtCO, CuI, and TaI. Optimum electron counts for approaching stability in this structural type are given. A related tetracapped tetrahedral building block, the stella quadrangula or tetraederstern, is also the subject of calculations. Undeformed, it cannot propagate in space, but a relatively small distortion of all tetrahedra leads to a reasonably common stacking unit.

Tetrahedra are a ubiquitous building brick of extended one-dimensional structures.[1] Corner-sharing tetrahedral chains of type AX_3, **1**, are found in many silicates such as enstatite, jadeite,


1　　　　　　　　　　**2**
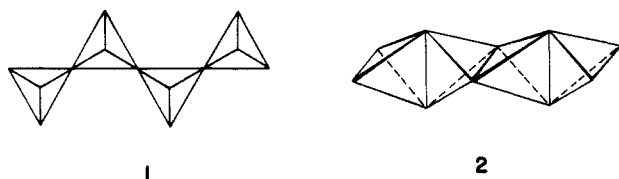
and spodumene.[2] The chain can be linear or helical (e.g. $NaPO_3$).[3] A transition-metal analogue includes K_2CuCl_3.[4] Examples of edge-sharing chains, **2**, are $KFeS_2$[5] and K_2PtS_2.[6] Still other types of tetrahedral chains include the corner-connected Rh_4 or Ru_4 tetrahedra in the ternary superconducting borides REM_4B_4.[7]

Face-sharing tetrahedral chains, however, are rare. The isolated $Cu_3I_4^-$ chain in RCu_3I_4 (R = organic counterion) contains a building block made up of three face-sharing tetrahedra. But these blocks are connected by sharing a tetrahedral edge, **3**.[8] The basic structural component in RCu_2I_3 is an isolated $Cu_2I_3^-$ unit of two face-sharing tetrahedra, **4**.[8,9a] In $[(CoCp_2)(CuI_2)]_3$ there are units consisting of three face-sharing CuI_4 tetrahedra.[9b] Recently, there have been reports of $[Cu_5I_7]^{2-}$ and $[Cu_5Br_7]^{2-}$ chains, in which there are no less than five face-sharing tetrahedra.

3　　　　　　　　　　**4**
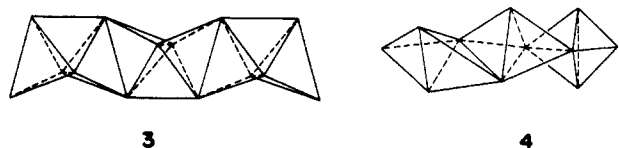
Still another set of molecules with face-sharing tetrahedra as units is to be found in the cluster carbonyls. $Os_5(CO)_{16}$,[10] **5**, can

be viewed as two tetrahedra sharing a face, and $Os_6(CO)_{18}$,[11] **6**, is a bicapped tetrahedron, or a "chain" of three tetrahedra sharing faces. These tetrahedra are not centered by a metal atom.

$Os_5(CO)_{16}$

5　　　　　　　　　　**6**
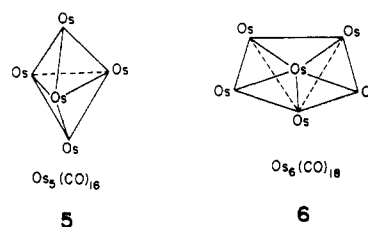
(1) Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon Press: Oxford, 1975; p 161.
(2) Reference 1, p 817.
(3) Jost, K. H. *Acta Crystallogr.* **1961**, *14*, 844.
(4) Brink, C.; Kroese, H. A. S. *Acta Crystallogr.* **1952**, *5*, 433. Brink, C.; van Arkel, A. E. *Acta Crystallogr.* **1952**, *5*, 506.
(5) (a) Boon, J. W.; MacGillavry, C. H. *Recl. Trav. Chim. Pays-Bas* **1942**, *61*, 910. (b) Bronger, W.; Müller, P. *J. Less-Common Met.* **1984**, *100*, 241.
(6) Bronger, W.; Günther, O. *J. Less-Common Met.* **1972**, *27*, 73.
(7) (a) Matthias, B. T.; Corenzwit, E.; Vandenberg, J. M.; Barz, H. E. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 1334. (b) Vandenberg, J. M.; Matthias, B. T. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 1336. (c) Woolf, L. D.; Johnston, D. C.; Mackay, H. B.; McCallum, R. W.; Maple, M. B. *J. Low Temp. Phys.* **1979**, *35*, 651. (d) Hornig, H. E.; Shelton, R. N. In *Ternary Superconductors*; Shenoy, G. K., Dunlap, B. D., Fradin, F. Y., Eds.; North-Holland: New York, 1981; p 213.
(8) Hartl, H.; Mahdjour-Hassan-Abadi, F. *Z. Naturforsch.* **1984**, *39B*, 149; *Angew. Chem.* **1981**, *93*, 804.
(9) (a) Andersson, S.; Jagner, S. *Acta. Chem. Scand.* **1985**, *A39*, 181. (b) Hartl, H. *Angew. Chem.* **1987**, *99*, 925. (c) Hartl, H.; Mahdjour-Hassan-Abadi, F. *Angew. Chem.* **1984**, *96*, 359. Andersson, S.; Jagner, S. *J. Crystallogr. Spectroscop. Res.* **1988**, *18*, 601.
(10) (a) Johnson, B. F. G.; Eady, C. R.; Lewis, J.; Reichert, B. E.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1976**, 271. (b) Reichert, B. E.; Guy, J. J.; Sheldrick, G. M. *Acta Crystallogr.* **1977**, *B33*, 173.
(11) (a) Mason, R.; Thomas, K. M.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802. (b) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton* **1975**, 2606.

†Cornell University.
‡Harvard University.