A Theoretical Study of the CHNO Isomers

Dieter Poppinger,[*1a,b] **Leo Radom,**[*1a] **and John A. Pople**[1c]

Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T., 2600, Australia, and the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received November 15, 1976*

Abstract: A detailed exploration of the singlet potential surface for the system CHNO has been carried out with the aid of ab initio molecular orbital theory with minimal, split-valence, and split-valence + polarization basis sets. Direct search procedures are used to locate minima and transition states within the surface. The most stable isomer of CHNO is predicted to be isocyanic acid (HNCO) followed by cyanic acid (HOCN), formonitrile oxide (HCNO), and carboxime (HONC). Each of these isomers is predicted to be quite stable with respect to intramolecular rearrangement. HCNO is found to have a linear equilibrium geometry while HNCO, HOCN, and HONC are each predicted to have trans bent structures. It is shown that singlet formyl nitrene and the cyclic isomers of CHNO are unlikely to be observable species. The rearrangement of HCNO to HNCO proceeds via structures resembling oxazirine and formylnitrene; however, neither of these species is predicted to be an intermediate on the reaction path.

One of the simplest typical "organic" molecules—containing the typical "organic" elements carbon, hydrogen, nitrogen, and oxygen—is the molecule with the empirical formula CHNO. Although reasonable valence structures may be drawn for at least seven CHNO isomers (Table I), relatively little is known experimentally about these compounds. Only two isomers, HNCO[2] and HCNO,[3] have been isolated in pure form and subjected to detailed spectroscopic examination. The substituted isomers RNCO,[4] RCNO,[5] and ROCN[4] are more common, and substituted formylnitrenes RC(O)N have frequently been invoked as reactive intermediates.[6] Theoretical information on the CHNO isomers is equally scarce. Half a century ago, Pauling and Hendricks[7] used a simple electrostatic model to predict the relative energies of HCNO and HONC. Since then, theoretical investigations have been limited to selected isomers and ab initio calculations have been reported for isocyanic acid,[8-10] formonitrile oxide,[11] two cyclic CHNO isomers,[12] and formylnitrene.[13,14]

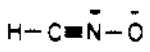
In the present work, we use ab initio molecular orbital theory to systematically examine the various CHNO isomers, their geometries, their electronic structures, their energetic relationships, and the reaction pathways which interconvert them. Among the 38 possible, topologically different, bound CHNO isomers we focus our attention on the 12 potentially stable species **1–12** and various bridged structures (see below) which may serve as transition states in intramolecular rearrangements. Our aim is to treat all stable isomers and transition states at uniform levels of sophistication rather than to generate high-quality wave functions for a few selected species. We hope that our study will facilitate subsequent applications of more sophisticated techniques to specific regions of interest.

$O{=}C{=}N{-}H$

1

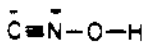
$H{-}O{-}C{\equiv}N$

2



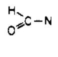
$H{-}C{\equiv}\bar{N}{-}\bar{O}$

3

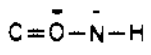


$\bar{C}{\equiv}\bar{N}{-}O{-}H$

4

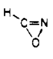


5

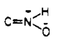


$C{=}\bar{O}{-}\bar{N}{-}H$

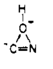
6



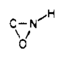
7



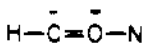
8



9

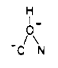


10



$H{-}\bar{C}{=}\bar{O}{-}N$

11



12

Computational Methods. For all molecules considered in this paper, the wave function of the lowest singlet state was approximated by a single determinant of 11 real, doubly occupied molecular orbitals. The spatial form of these orbitals was optimized by the LCAO-MO-SCF technique introduced by Roothaan.[15] It is well known that single determinant SCF-MO theory is a reliable tool for the prediction of equilibrium geometries,[16-19] and that heats of reactions can often be reproduced quite well at this level of sophistication.[20-24] On the other hand, single determinant SCF-MO theory is known to fail seriously in cases where the gap between occupied and unoccupied orbitals is small, such as for H_2 at large internuclear distances[25] or for biradicals.[26] Configuration interaction is the most general method to correct these deficiencies. In this paper, however, we have used exclusively the single determinant approach, a limitation which was imposed by the large number of individual calculations which were needed to map out the energy hypersurface. In the discussion, we shall note which of our conclusions are likely to be seriously affected by this restriction.

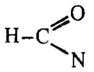
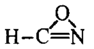
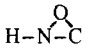
The basis sets used in this work (STO-3G,[27] 4-31G,[28] and 6-31G*[22]) have been thoroughly tested for geometry predictions[16-19] and calculations of relative energies.[20-24] The procedures used to calculate equilibrium geometries and transition states have been described previously.[29,30] Computations were carried out with a modified version of Gaussian 70.[31]

Presentation of Results. Total energies for all the stationary points that we have been able to locate on the STO-3G and 4-31G hypersurfaces are shown in Tables II and IV. Energies are presented at four different levels: STO-3G at optimum STO-3G geometry, 4-31G at optimum STO-3G geometry, 4-31G at optimum 4-31G geometry, and 6-31G* at optimum 4-31G geometry. In the following we denote these levels by "(energy)/(geometry)", e.g., 4-31G/STO-3G. We have also generated contour surfaces at the STO-3G and 4-31G levels which contain all minima and transition states and which show reaction paths more clearly. Partially optimized (STO-3G) geometries and energies (STO-3G and 4-31G) for the 274 points which we have used to construct the contour plots are listed in Table V (microfilm edition). Atomic net charges were obtained from the STO-3G wave functions by a Mulliken population analysis[32] and are displayed (in units of −0.01 e), together with the STO-3G dipole moments, in the text. Structural data shown with the formulas are the result of complete geometry searches at the STO-3G and 4-31G levels. Values in parentheses are experimental data. All bond lengths in the paper are in angstroms and bond angles in degrees.

Discussion

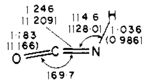
Minima. On the STO-3G surface, we have been able to locate nine minima. Only seven minima appear to exist at the 4-31G level. We begin our discussion by examining these theoretical structures, comparing our results with experimental data when available.

Table I. Structures and Names of CHNO Isomers

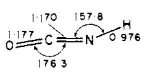
Molecule	Structure	Name
HN=C=O	**1**	Isocyanic acid
HOC≡N	**2**	Cyanic acid
$HC\equiv\overset{+}{N}-\bar{O}$	**3**	Formonitrile oxide
HON=C	**4**	Carboxime[a]
	**5**	Formylnitrene
	7	Oxazirine
	**10**	Oxaziridinylidene

[a] According to the IUPAC rules (IUPAC, "Nomenclature of Organic Chemistry," Butterworths, London, 1969) compounds RONC are "fulminates" and hence HONC should be termed "fulminic acid". However, we prefer to name the parent compound HONC as an oxime of carbon monoxide to avoid confusion with HCNO, for which the historical trivial name "fulminic acid" is still frequently used.

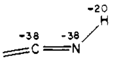
Isocyanic Acid (1). According to our best (4-31G, 6-31G*) calculations, isocyanic acid (HNCO) is the most stable CHNO isomer. This result seems to conform with available experimental evidence: isocyanates are often the final products in attempts to generate other CRNO isomers. Previous ab initio calculations on isocyanic acid have been carried out at experimental or model geometries using minimal[8] or extended[9,10] basis sets. The best experimental structures[33,34] for HNCO have, in turn, been derived from microwave spectral data assuming a linear NCO chain. Our calculations suggest, however, that the NCO group is nonlinear. Both the STO-3G and



1a
(θ=29, ϕ=355)
(STO-3G; C_s)



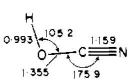
1b
(θ=10, ϕ=358)
(4-31G; C_s)



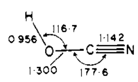
1c
(μ=1·48D;
cf. exptl 2·07D[34])

4-31G calculations support earlier CNDO/2 results[35] in predicting a trans bent equilibrium structure for HNCO.[36] From studies of small triatomic hydrides,[22] it is well known that the 4-31G basis set is biased in favor of linear as opposed to angular structures. That we find, even at the 4-31G level, a trans bent equilibrium geometry therefore strongly indicates that the NCO group in HNCO is in fact bent. Experimental verification of this result would be highly desirable.

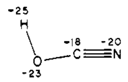
Cyanic Acid (2). We find cyanic acid (HOCN) to lie 21 kcal mol^{-1} (6-31G*/4-31G) above HNCO (**1**). As in the case of isocyanic acid, the optimum structure is calculated to be trans bent. The optimum STO-3G and 4-31G C-N bond lengths are slightly longer than in HCN (STO-3G, 1.153 Å;[18] 4-31G,



2a
(θ=153, ϕ=358)
(STD-3G; C_s)



2b
(θ=156, ϕ=359)
(4-31G; C_s)



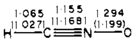
2c
(μ=2·89D)

1.140 Å[28]) while the C-O lengths are somewhat shorter than normal C-O single bonds. These results may be rationalized using simple resonance arguments (**2d**).

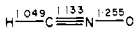
2d

computed N-O bond length in hydroxylamine is 1.42 Å,[18] 0.04 Å shorter than the experimental value.[40] The large difference between the C-H bond lengths observed experimentally in HCN (1.063 Å[41]) and HCNO (1.027 Å[38]) is also not reproduced by the calculations. The very short C-H internuclear distance in HCNO has recently been interpreted as the projection of a C-H bond length of 1.061 Å upon the heavy-atom

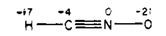
Formonitrile Oxide (3). This molecule is computed to be 80 kcal mol^{-1} (6-31G*/4-31G) less stable than the most stable isomer isocyanic acid (**1**). Compared with the r_s structure derived from microwave spectra,[38] the computed N-O and C-H bond lengths are too large. Minimal and double ζ basis set calculations also overestimate the length of the dative N-O



3a
(θ=180, ϕ=180)
(STO-3G, $C_{\infty v}$)



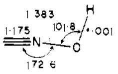
3b
(θ=180, ϕ=180)
(4-31G, $C_{\infty v}$)



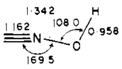
3c
(μ=3·62D;
cf. exptl 3·06D[38])

bond in amine oxides.[18,39] Normal N-O bonds, however, appear to be described quite well by the STO-3G basis: the axis of a *quasi-linear* molecule.[42] This model leads to an HCN angle of approximately 165° and an inversion barrier of about 0.1 kcal mol^{-1}. Our theoretical results do not support this conclusion. Constraining the HCN angle in HCNO at 165° but optimizing all other bond lengths and angles leads to an energy *increase* of 0.85 kcal mol^{-1} (STO-3G). Thus, the theoretical equilibrium structure of HCNO is $C_{\infty v}$.

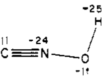
Carboxime (4). We predict that this molecule is less stable than its tautomer formonitrile oxide (**3**) by 2 kcal mol^{-1} (6-31G*/4-31G). As in the case of HNCO and HOCN, the optimum structure is trans bent and planar. The theoretical C-N



4a
(θ=15, ϕ=187)
(STO-3G; C_s)



4b
(θ=11, ϕ=190)
(4-31G; C_s)

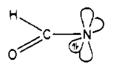


4c
(μ=2·66D)

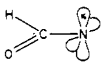
bond length is essentially the same as in HNC (STO-3G, 1.170 Å;[18] 4-31G, 1.162 Å) and indicative of a C-N triple bond (1.153 Å, STO-3G in HCN[18]) rather than a C-N double bond (1.237 Å, STO-3G in CH_2NH[18]). In valence bond terms, this would be consistent with a large weight of the polar structure shown in **4d**.

4d

Formylnitrene (5). Formylnitrene has attracted the attention of theoretical chemists as the simplest carbonyl nitrene. Configuration interaction calculations using minimal (STO-3G) and extended basis sets were reported by Harrison and Shalhoub.[13] They find a triplet ($^3A''$) ground state and a singlet ($^1A'$) first excited state, closely followed by another singlet ($^1A''$) state. Their wave function for the $^1A'$ state contains, amongst others, the "4π electron" configuration **5a** and the



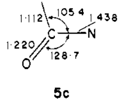
5a



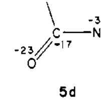
5b

"2π electron" configuration **5b**, the former predominating. Minimal basis set SCF calculatons for formylnitrene were also reported by Alewood, Kazmaier, and Rauk.[14]

Our SCF calculations, which were carried out for the singlet configuration of lowest energy (**5a**), place formylnitrene 88 kcal mol^{-1} (4-31G/STO-3G) above HNCO. Our STO-3G optimized C-O and C-N bond lengths are smaller by ap-



5c
(θ=105, ϕ=337)
(STO-3G; C_s)



5d
(μ=1·55D)

proximately 0.04 Å than the values reported by Harrison and Shalhoub.[13] Variation of all bond lengths and bond angles at

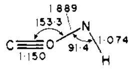
Table II. Total Energies of Minima and Fragmentation Products

Molecule	Total energy, hartrees			
	STO-3G/STO-3G	4-31G/STO-3G	4-31G/4-31G	6-31G*/4-31G[a]
1	−165.502 92	−167.484 70	−167.497 27	−167.754 17
2	−165.511 98	−167.457 39	−167.464 29	−167.720 51
3	−165.392.21	−167.367 59	−167.370 12	−167.627 20
4	−165.441 45	−167.365 45	−167.369 28	−167.624 68
5	−165.391 46	−167.345 19	*b*	*c*
6	−165.369 19	−167.325 79	−167.334 91	*c*
7	−165.406 29[d]	−167.312 03[d]	*b*	*c*
8	*b*	*b*	−167.307 05	*c*
9	−165.391 58	−167.296 10	*b*	*c*
10	−165.404 06[d]	−167.279 46[d]	−167.288 68	*c*
NH + CO[e]	−165.361 36	−167.327 00	−167.329 54	*c*
HCN + O[f]	−165.337 03	−165.311 43	−165.312 16	*c*
HNC + O[g]	−165.306 26	−167.295 83	−167.297 01	*c*

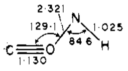
[a] At optimum 4-31G geometry with linear heavy atom chain. [b] Not a minimum at this level. [c] Not examined at this level. [d] From ref 12. [e] Optimum STO-3G (4-31G) bond lengths are, in Å: r(N-H) = 1.079 (1.028); r(C-O) = 1.146 (1.128). [f] r(C-H) = 1.070 (1.051); r(C-N) = 1.153 (1.140). [g] r(N-H) = 1.011 (0.979); r(N-C) = 1.170 (1.162).

the 4-31G level led to spontaneous relaxation to isocyanic acid, without any indication of an activation barrier being passed. Thus, at the single determinant 4-31G level, singlet formylnitrene is not a discrete molecule. We shall return to this point later.

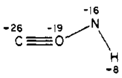
CO···NH (6). With a very short C-O bond and an exceptionally long N-O bond, this species resembles a weak complex of carbon monoxide and imidogen NH. The theoretical binding energy is low (4-31G/4-31G: 3 kcal mol^{-1}) but possibly not meaningful at this level of calculation.



6a
(θ = 18, ϕ = 10)
(STO-3G; C_s)

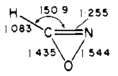


6b
(θ = 17, ϕ = 16)
(4-31G; C_s)

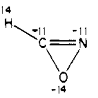


6c
(μ = 1.44D)

Oxazirine (7). Oxazirine is isoelectronic with the antiaromatic cyclopropenyl anion and might therefore be expected to distort to a nonplanar structure or to decrease its antiaromaticity by lengthening one or several bonds. Using the STO-3G basis set, one finds a planar structure (**7a**) with a rather long N-O bond.[12] The relative energy of this species is 108 kcal mol^{-1} (4-31G/STO-3G). An attempted optimization of **7** at the 4-31G level led into the HNCO minimum **1**.

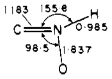


7a
(θ = 151, ϕ = 299)
(STO-3G; C_s)



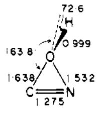
7b
(μ = 2.68D)

Nitronylidene (8). This is the parent compound of the experimentally unknown class of nitrone carbenes. According to our 4-31G calculations, nitronylidene (**8a**) resembles a weak complex of hydrogen isocyanide and oxygen and is bound with respect to these fragments by just 6 kcal mol^{-1} (4-31G/4-31G). As for **6**, it would be desirable to redetermine the structure and relative energy of this loosely bound species **8** using more sophisticated techniques, possibly incorporating electron correlation.

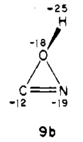


8a
(θ = 11, ϕ = 261)
(4-31G; C_s)

HOCN (9). This species may formally be derived from the oxazirinyl anion by protonation of the oxygen atom. A planar molecule of this type would be antiaromatic. At the STO-3G level, the N-O and C-O bonds are exceptionally long and the O-H bond is bent out of the ring plane by 73°. Presumably both distortions are needed to reduce the antiaromatic character of **9**. As in the case of oxazirine (**7**), we were unable to find a stable 4-31G structure for this molecule.

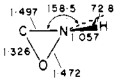


9a
(θ = 67, ϕ = 71)
(STO-3G)

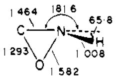


9b
(μ = 2.08D)

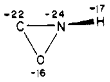
Oxaziridinylidene (10). This is the second three-membered ring in the CHNO series which can be written as a classical valence structure without formal charges. STO-3G/STO-3G and 4-31G/STO-3G results have been published previously.[12] Using data published by Lathan et al.[12] we estimate that oxaziridinylidene is 131 kcal mol^{-1} (4-31G/STO-3G) less stable than isocyanic acid. Oxaziridinylidene is the only cyclic CHNO isomer for which we were able to find a minimum on the 4-31G energy hypersurface. The optimum out of plane angle of the N-H bond (66°) is slightly less than at the STO-3G level (73°),[12] but the N-O bond is considerably longer.



10a
(θ = 30, ϕ = 307)
(STO-3G)



10b
(θ = 26, ϕ = 50)
(4-31G)



10c
(μ = 1.47D)

Isomers 11 and 12. These species were examined at the STO-3G level only. **11** was found to collapse without activation to oxazirine (**7**), whereas **12** closed the ring to structure **9**. We suspect that, at the 4-31G level, **11** and **12** will collapse to isocyanic acid and carboxime or cyanic acid, respectively. We have not, however, verified this point computationally.

Relative Energies of CHNO Isomers. We conclude this section by summarizing the relative energies of structures found to be minima in one or other of our potential energy surfaces, i.e., structures which are potentially stable isomers of CHNO. These are displayed in Table III. Our most reliable calculations are consistent with the order of stabilities **1** > **2** > **3** > **4** > **6** > **8** > **10**. 4-31G geometry optimization (4-31G/4-31G) does not affect the qualitative ordering of energies obtained at the simpler 4-31G/STO-3G level.

Potential Energy Surfaces. The structure of the CHNO

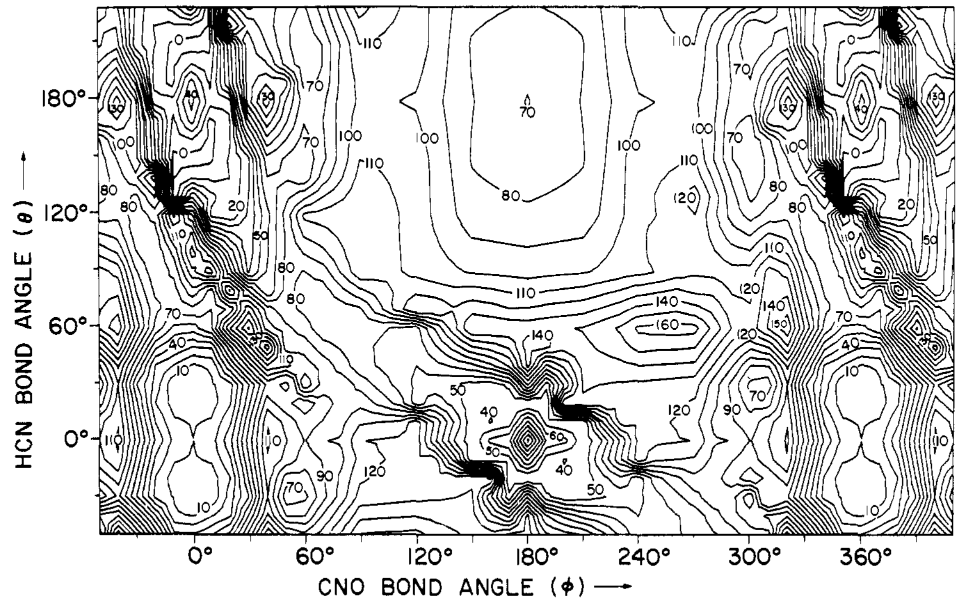
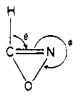
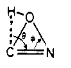


Figure 1. STO-3G potential energy surface for CHNO. Contour labels are in kcal mol^{-1} relative to the energy of the fully optimized HOCN structure (**2a**), the lowest point on the STO-3G surface.

isomers **1–10** may be conveniently described in terms of two bond angles, θ(H–C–N) and φ(C–N–O) (see **13**). Assuming that, for each point on the surface $E = E(\theta, \phi)$, the molecular energy E has been minimized with respect to the remaining four geometrical variables (and provided that E has no double minima with respect to these variables),[43] each isomer is uniquely defined as a point (θ, φ) on the surface $E(\theta, \phi)$. For example, formonitrile oxide $HC{\equiv}N^{+}{-}O^{-}$ corresponds to θ = 180°, φ = 180°, and linear isocyanic acid HN=C=O would be defined by θ = 0°, φ = 0°. To be able to distinguish between structures such as **13** and **14**, we use the additional convention that the C–N bond be always written from the left to the right, and that φ(C–N–O) and the projection of θ(H–C–N) on the CNO plane be measured clockwise. Thus, we have for **13** θ = 90°, φ = 300°, whereas **14** is defined by θ = 90°, φ = 60°.


13


14

The STO-3G potential energy surface is shown in Figure 1. This contour plot[44] is based on 274 distinct values of $E(\theta, \phi)$, each of which is a minimum with respect to the four remaining variables r(C–N), r(N–O), r(C–H), and Ω(H–C, N–O).[45] The 4-31G surface (Figure 2) is based on 274 single extended basis set calculations at these partially optimized STO-3G geometries (cf. Table V). Note that the energies of the minima which can be extracted from the 4-31G surface do not exactly correspond to either the 4-31G/STO-3G or the 4-31G/4-31G levels. It is only if STO-3G and 4-31G predictions for r(C–H), r(C–N), r(N–O), and Ω(H–C, N–O) were identical that the energies of the minima would agree precisely with the values shown in Table II.

On the STO-3G surface (Figure 1) there are six rather deep minima corresponding to isocyanic acid (**1**) (θ ≃ 30°, φ ≃ 0°), cyanic acid (**2**) (θ ≃ 150°, φ ≃ 0°), formonitrile oxide (**3**) (θ ≃ 180°, φ ≃ 180°), carboxime (**4**) (θ ≃ 20°, φ ≃ 170°), oxazirine (**7**) (θ ≃ 150°, φ ≃ 300°), and oxaziridinylidene (**10**) (θ ≃ 30°, φ ≃ 305°). The minima corresponding to **9** (θ ≃ 70°, φ ≃ 70°) and **5** (θ ≃ 105°, φ ≃ 335°) are less than 10 kcal mol^{-1} deep and therefore not visible on the contour plot. There are only four significant minima (**1–4**) on the 4-31G surface (Figure 2). The nitronylidene minimum **8** (θ ≃ 10°, φ ≃ 260°) is only just visible on the contour plot, while the 10 kcal mol^{-1} spacing of our contour lines gives no indication of the oxaziridinylidene minimum (**10**) which had been found with full 4-31G optimization. This suggests that the 4-31G/4-31G minimum lies in a very shallow (and therefore chemically insignificant) potential well. Neither formylnitrene (**5**) nor the cyclic isomers **7** and **9** seem to correspond to stable structures.

Table III. Relative Energies of CHNO Isomers

Molecule	Rel energy, kcal mol^{-1}	Level
1	0.0	6-31G*/4-31G
2	21.1	6-31G*/4-31G
3	79.7	6-31G*/4-31G
4	81.3	6-31G*/4-31G
5	87.5	4-31G/STO-3G
6	101.9	4-31G/4-31G
7	108.4	4-31G/STO-3G
8	119.4	4-31G/4-31G
9	118.3	4-31G/STO-3G
10	130.9	4-31G/4-31G
NH + CO	105.3	4-31G/4-31G
HCN + O	116.2	4-31G/4-31G
HNC + O	125.7	4-31G/4-31G

Whereas the contour surfaces show several saddle points quite clearly, there are unfortunately also regions in which they are of little help in establishing reaction paths. In these regions the total optimized energy is very sensitive to rather small changes in θ or φ, and this manifests itself in apparent ridges or cliffs on the $E(\theta, \phi)$ surface. Near such cliffs (e.g., between θ ≃ 180°, φ ≃ 330° and θ ≃ 40°, φ ≃ 40°, near θ ≃ 180°, φ ≃ 30°, and near θ ≃ 30°, φ ≃ 320°) it is difficult to determine from the contour surface, geometries and energies of possible transition states with any reliability. In the light of this consideration, we have employed a direct method for locating saddle points[30] to examine such critical regions of the potential energy surfaces and we have also used this procedure to refine geometries of transition states which we had located only approximately on our contour plots. All structural data for transition states which we report in the following have been

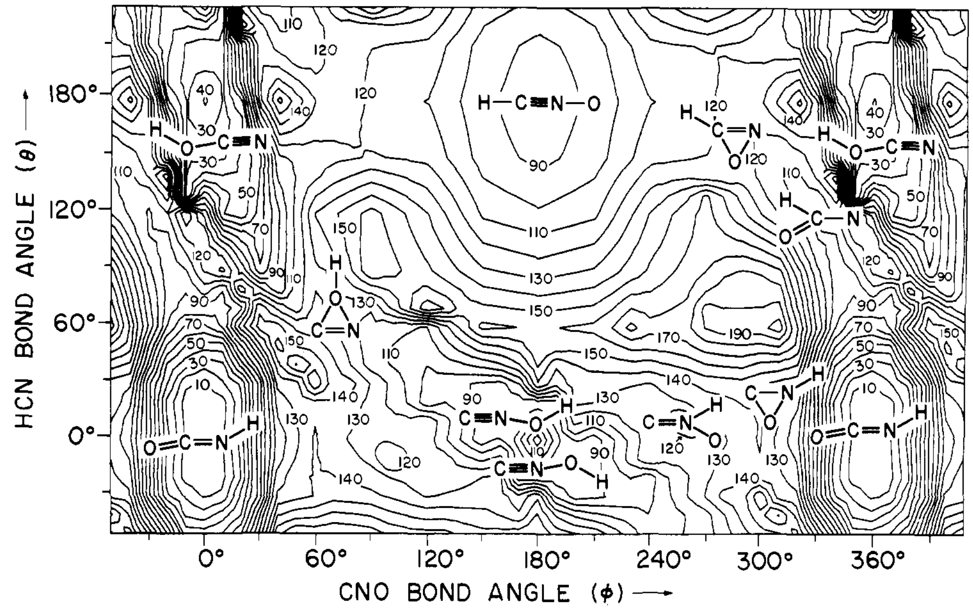


Figure 2. 4-31G potential energy surface for CHNO. Contour labels are in kcal mol^{-1} relative to $E(0,0)$, the lowest calculated point on the 4-31G/STO-3G contour surface. The more important structures are superimposed on the surface.

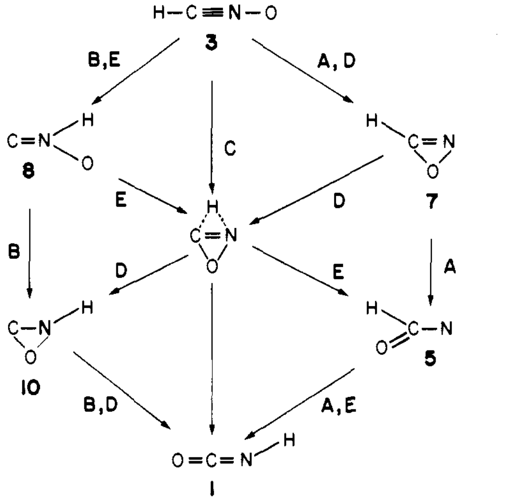


Figure 3. Five hypothetical routes from formonitrile oxide HCNO (3) to isocyanic acid HNCO (1).

Table IV. Total Energies of Transition States

	Total energy, hartrees		
Molecule	STO-3G/STO-3G	4-31G/STO-3G	4-31G/4-31G
15	−165.341 01	−167.317 47	−167.318 03
17	−165.369 01	−167.327 01	*a*
18	−165.385 03	−167.352 82	*a*
19	−165.279 56	−167.250 92	−167.252 78
20	−165.299 66	−167.180 35	*b*
25	−165.387 48	−167.312 43	*a*
26	−165.370 34	−167.305 83	−167.307 52
27	−165.302 45	−167.220 03	*b*
28	*b*	*b*	−167.304 36
29	−165.319 09	−167.226 09	*a*
30	*a*	*a*	−167.286 00
33	−165.324 66	−167.293 91	*b*

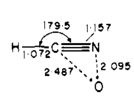
[a] Not a saddle point at this level. [b] Not examined at this level.

derived by this method. Total energies of all transition states are collected in Table IV.

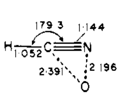
The Formonitrile Oxide–Isocyanic Acid Rearrangement. The interconversion of formonitrile oxide (**3**) and isocyanic acid (**1**) may, in principle, take the five different routes shown in Figure 3. In pathway A, the oxygen atom moves first, followed by the migration of the hydrogen atom. Conceivable intermediates on this path are oxazirine (**7**) and formylnitrene (**5**). In path B, it is the hydrogen atom which moves first, followed by an oxygen migration. Potential intermediates along this path are the nitronylidene (**8**) and oxaziridinylidene (**10**) molecules. Thirdly, one has to consider a synchronous reaction (path C) in which both migrating atoms move simultaneously. Path D involves an initial ring closure to oxazirine (**7**) which is followed by a hydrogen shift from the carbon to the nitrogen atom. Breaking the N–O bond in **10** leads to isocyanic acid (**1**). Path E sets out as does path B, but ends with the same hydrogen shift as path A. A key step in this sequence is the transformation **8** → **5**, the simultaneous migration of the oxygen and hydrogen atoms from nitrogen to carbon.

Our STO-3G surface (Figure 1) does in fact show path A quite clearly. Starting at the formonitrile oxide minimum ($\theta \simeq 180°$, $\phi \simeq 180°$), it leads via a saddle point at $\theta \simeq 180°$, $\phi \simeq 260°$ into the oxazirine minimum ($\theta \simeq 150°$, $\phi \simeq 300°$) from where it has to surmount a second saddle at $\theta \simeq 130°$, $\phi \simeq 320°$ and pass through the formylnitrene valley to finally reach the isocyanic acid basin ($\theta \simeq 30°$, $\phi \simeq 360°$). The fact that we did find a stable formylnitrene at the STO-3G level implies that, in Figure 1, there must be an energy barrier between formylnitrene (**5**) and isocyanic acid (**1**). Detailed investigation of the STO-3G energies listed in Table V shows that this barrier is approximately 4 kcal mol^{-1} and thus too low to be visible on the contour plot. The reaction path on the 4-31G surface (Figure 2) is very similar to the STO-3G path, even though there are now apparently no secondary minima between formonitrile oxide and isocyanic acid. However, the minimum energy route **3** → **1** does involve geometries close to those of **7** and **5**.

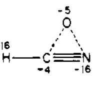
Using the direct transition state procedure, we find the saddle point **15** between formonitrile oxide (**3**) and oxazirine



15a
($\theta = 180$, $\phi = 265$)
(STO-3G, C_s)

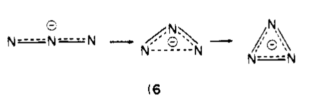


15b
($\theta = 179$, $\phi = 274$)
(4-31G; C_s)



15c
($\mu = 2.85$D)

(7) at $\theta = 180°$, $\phi = 256°$ (STO-3G) or $\theta = 179°$, $\phi = 273°$ (4-31G). With very long C-O and N-O bonds, an essentially linear HCN group, and a C-N bond typical of triple bonds, this transition state resembles a weak complex between hydrogen cyanide and an oxygen atom. At the single determinant level, it is bound with respect to HCN + O by 4 kcal mol^{-1} (4-31G/4-31G) and lies 33 kcal mol^{-1} (4-31G/4-31G) above formonitrile oxide. According to the Woodward-Hoffmann rules,[46] the interconversion of the azide and triazirinyl anions via the C_{2v} transition state **16** is a thermally forbidden process.

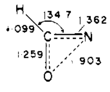


16

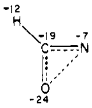
(1)

Although it is uncertain whether such arguments can be applied to the interconversion of the less symmetrical isoelectronic formonitrile oxide and oxazirine molecules, there may be a residual "symmetry" barrier of this kind which causes the C-O and N-O bonds in **15** to be so weak. Furthermore, the lowest singlet state of the free oxygen atom is not well described by a single determinant of doubly occupied real orbitals. Part of this error is presumably also present in the single determinant wave function for weak complexes between an oxygen atom and closed-shell molecules such as HCN. These considerations weaken our conclusions regarding the structure and relative energy of **15** and emphasize the desirability of multiconfiguration calculations for this part of the surface.

The second transition state on path A, **17,** links the oxazirine



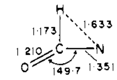
17a
(θ=135, ϕ=319)
(STO-3G, C_s)



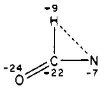
17b
(μ=2.60D)

(7) and formylnitrene (5) minima and lies 23 kcal mol^{-1} (STO-3G/STO-3G) above the three-membered ring. However, the 4-31G calculations, carried out at the optimum STO-3G geometries, place **17** 9 kcal mol^{-1} *below* oxazirine (**7**) and hence suggest that there is no barrier between oxazirine (**7**) and formylnitrene (**5**).

The last transition state on the STO-3G path A is the hydrogen-bridged structure **18.** On our contour surface, this point



18a
(θ=80, ϕ=346)
(STO-3G, C_s)



18b
(μ=1.21D)

corresponds to $\theta = \simeq 80°$, $\phi \simeq 346°$. As would be expected from Hammond's postulate,[48] the transition state **18** for the strongly exothermic reaction **5** → **1** resembles the reactant rather than the product; the migrating hydrogen atom is still firmly bound to the carbon atom and the N-H bond is long. The STO-3G/STO-3G barrier for this step is 4 kcal mol^{-1}. As in the case of **17**, the 4-31G/STO-3G calculations suggest that the transition state (**18**) is more stable than the reactant (**5**) and hence does not correspond to a true barrier. This result is in line with the 4-31G optimization studies for oxazirine and formylnitrene and indicates that there are no intermediates on path A.

A crucial step in path B is the hydrogen shift which converts formonitrile oxide (**3**) into nitronylidene (**8**). Our contour surfaces show a suitable saddle point **19** near $\theta \simeq 50°$, $\phi \simeq 190°$ and detailed calculations confirm that **19** does indeed link **3** and **8**. The refined structures indicate that this transition state is best written with an N-O single bond and a C-N double bond. The calculated barrier for the direct process **3** → **8** via **19** is 74 kcal mol^{-1} (4-31G/4-31G). The high energy of **19** makes it unlikely that the formonitrile oxide-isocyanic acid rearrangement can proceed via routes B or E.

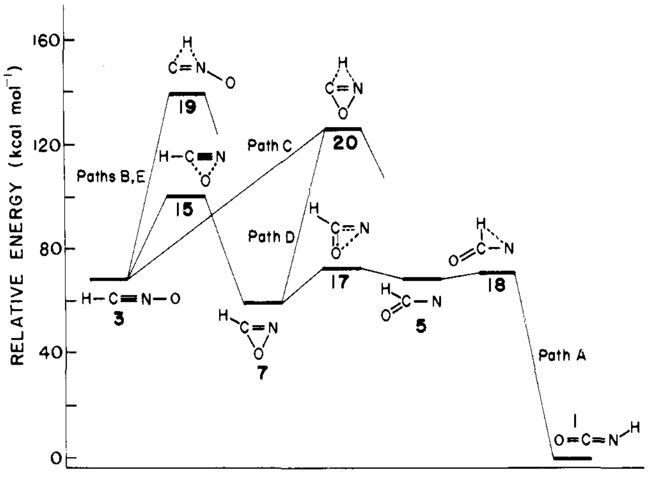
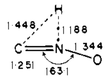
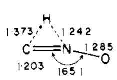


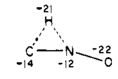
Figure 4. STO-3G energies along the formonitrile oxide (**3**)-isocyanic acid (**1**) reaction path.



19a
(θ=52, ϕ=197)
(STO-3G; C_s)

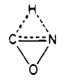


19b
(θ=57, ϕ=195)
(4-31G; C_s)

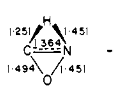


19c
(μ=2.25D)

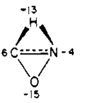
The reaction scheme in Figure 3 suggests that an edge-protonated oxazirinyl anion **20a** could serve as a transition state



20a



20b
(θ=64, ϕ=293)
(STO-3G)



20c
(μ=1.09D)

for paths C, D, or E. The STO-3G surface (Figure 1) does in fact show such a saddle point. We find that this transition state **20b** has a geometry reminiscent of bicyclobutane, with an angle between the CNO and CNH planes of 103°. Presumably a planar species **20** would be of higher energy owing to the antiaromaticity of the oxazirine ring. On the STO-3G surface (Figure 1) this saddle point is an energy maximum along direct routes from oxazirine (**7**) to oxaziridinylidene (**10**) (path D), from formonitrile oxide (**3**) to isocyanic acid (**1**) (path C), and from nitronylidene (**8**) to formylnitrene (**5**) (path E); it corresponds to a barrier of 117 kcal mol^{-1} (4-31G/STO-3G) along these reaction paths.

In Figures 4 and 5, we schematically summarize energies and structures along the STO-3G and 4-31G reaction paths A. Included also are the first steps in the high-energy routes B-E. Note that in both diagrams the reaction coordinate has no quantitative meaning. From these diagrams, the results of our 4-31G optimization studies for oxazirine (**7**) and formylnitrene (**5**), and the contour surfaces (Figures 1 and 2) it appears that the formonitrile oxide-isocyanic acid rearrangement involves successive 1,2 migrations of the oxygen and hydrogen atoms, the former moving first. The best reaction path passes through nuclear geometries corresponding to oxazirine (**7**) and formylnitrene (**5**). However, our most reliable calculations

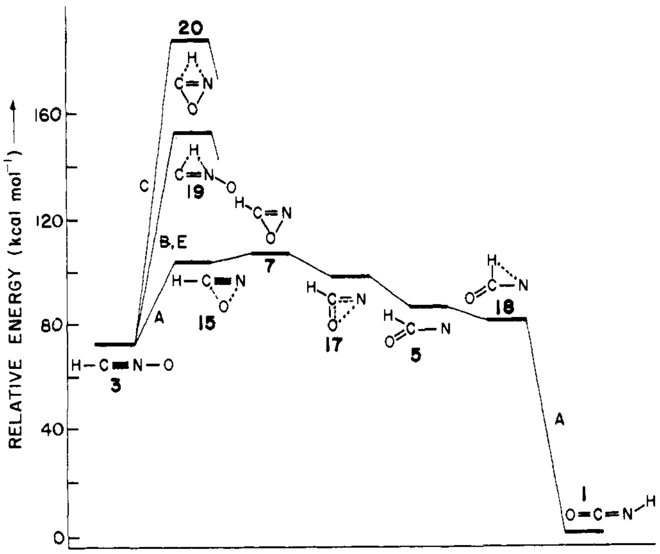
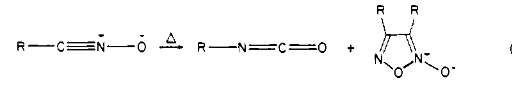


Figure 5. 4-31G energies along the formonitrile oxide (3)–isocyanic acid (1) reaction path.

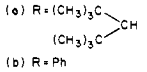
suggest that there are no secondary minima on the reaction path which could be associated with metastable intermediates.

Direct comparison of our theoretical results with experimental data is difficult. Free formonitrile oxide polymerizes rapidly above −15 °C,[49] and there is no evidence for the formation of isocyanic acid under these conditions. Isocyanic acid has been obtained as a minor by-product from the reaction of acetyl chloride with mercuric fulminate in ether or ligroin.[50] However, it remains unclear whether free formonitrile oxide is involved in this reaction. On the other hand, the rearrangement of larger nitrile oxides to isocyanates is a well-known process,[51] which can be initiated by rapidly heating the starting material. For example, the nitrile oxide **21a** is converted in quantitative yield into the isocyanate **22a**.[52] With sterically less hindered nitrile oxides (e.g., **21b**[53]) dimerization to furoxans **23** is often the major route. The rearrangement to isocyanates has been studied in detail by Grundmann and coworkers,[54] who find that the reaction is intramolecular and proceeds with complete retention of optical asymmetry and stereochemical configuration. They consider several of the reaction paths sketched in Figure 3, but prefer a doubly bridged transition state **24** in which the migration of the oxygen atom has proceeded further than the migration of R. This corresponds roughly to the high-energy route C in Figures 3–5. Our best reaction path (A) is similar to Grundmann's earlier suggestion:[55]



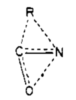
(2)

21 22 23

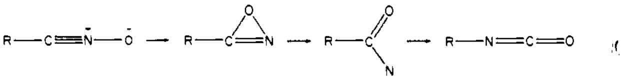


(a) R = $[(CH_3)_3C]_2CH$

(b) R = Ph



24

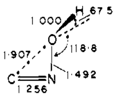


(3)

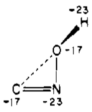
According to our calculations, however, neither oxazirine nor formylnitrene are true intermediates.

The Carboxime–Cyanic Acid Rearrangement. Carboxime HONC (**4**) and fulminates RONC have never been positively identified in the laboratory. Since our calculations suggest that carboxime (**4**) and formonitrile oxide (**3**) are of comparable thermodynamic stability, it is of interest to examine the kinetic stability as well and to study theoretically the reaction channels which connect carboxime with its more stable CHNO isomers. We begin with the rearrangement to cyanic acid (**2**).

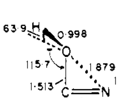
It is tempting to speculate that this reaction involves, either as an intermediate or as a transition state, the oxygen-protonated oxazirinyl anion **9**. Our STO-3G contour surface (Figure 1) does show a valley which can be associated with such a reaction path. This path sets out at $\theta \simeq 20°$, $\phi \simeq 180°$ and leads via an intermediate **9** at $\theta \simeq 70°$, $\phi \simeq 70°$ (which is not visible in the plot because of the wide spacing of contour lines) into the cyanic acid minimum at $\theta \simeq 150°$, $\phi \simeq 0°$. The first transition state **25** on this route lies only 3 kcal mol⁻¹ (STO-3G/STO-3G) above the intermediate **9**. At the 4-31G level, **25** is *more* stable than **9** by 10 kcal mol⁻¹, and hence does not seem to correspond to a true barrier. We find the second transition state **26** on the STO-3G reaction path at $\theta = 97°$, $\phi = 53°$, 45 kcal mol⁻¹ above carboxime (**4**). The geometry of this species, but not its relative energy, is rather sensitive to a change of basis sets, since the potential energy surface is rather flat in the transition state region. Our best (4-31G/4-31G) estimate for the barrier between carboxime (**4**) and cyanic acid (**2**) is 39 kcal mol⁻¹. Our most reliable theoretical results furthermore suggest that the carboxime-cyanic acid rearrangement is a one-step process and does not involve metastable intermediates (cf. Figure 6).



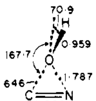
25a
(θ = 52, ϕ = 87)
(STO-3G)



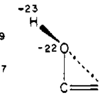
25b
(μ = 1.78D)



26a
(θ = 97, ϕ = 53)
(STO-3G)

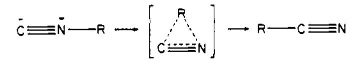


26b
(θ = 78, ϕ = 63)
(4-31G)



26c
(μ = 1.70D)

The carboxime-cyanic acid rearrangement may be considered as a special case of the more general class of isonitrile-nitrile rearrangements:



(4)

This reaction has been studied experimentally for various alkyl and aryl isonitriles, and has been successfully interpreted using RRKM rate theory and a cyclic model for the transition state.[57] Theoretical studies have been carried out using semiempirical[58,59] and ab initio[60–62] molecular orbital methods. In Table VI, we compare our 4-31G results with ab initio data reported by Liskow et al.[60] and Pearson et al.[61]

Even though theoretical results obtained with different basis sets are not strictly comparable, it may be noted that the computed exothermicity of the carboxime-cyanic acid rearrangement is much higher than for the reactions of hydrogen isocyanide and methyl isocyanide. The barrier for R = CH_3 as calculated by Liskow et al.[60] with a basis set similar to ours is considerably higher than our value for R = OH, and also higher than the experimental value by approximately 50%. In the light of this deviation, and in view of the known tendency

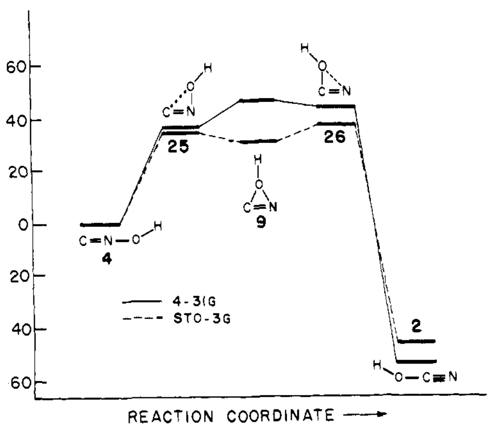
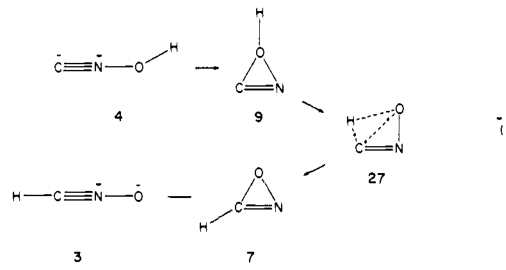


Figure 6. STO-3G and 4-31G energies along the carboxime (4)–cyanic acid (2) reaction path.

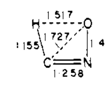
of the 4-31G basis set to overestimate the energy of small cyclic molecules relative to their acyclic isomers (cf. Table 7 in ref 12), it appears likely that the barrier we compute for the carboxime–cyanic acid rearrangement is too high by about 15 kcal mol^{-1}.

The Carboxime–Formonitrile Oxide Rearrangement. Our STO-3G and 4-31G contour surface both suggest that the lowest energy path linking carboxime (**4**) and formonitrile oxide (**3**) follows the route shown as eq 5.

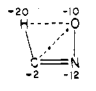


(5)

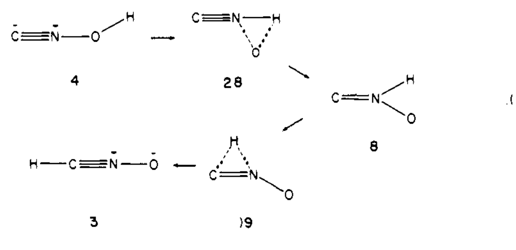
Structure **27** could be associated with the seemingly flat regions of the STO-3G and 4-31G surfaces around $\theta \simeq 160°$, $\phi \simeq 100°$ (cf. Figures 1 and 2). However, the surfaces are somewhat unreliable in this region because of the wide spacing of the grid points and do in fact suggest the presence of low-lying saddle points. Attempts to obtain additional grid points were unsuccessful owing to severe convergence difficulties. The directly calculated transition state structure **27** has very high energy at STO-3G/STO-3G and 4-31G/STO-3G (87 and 91 kcal mol^{-1}, respectively, above carboxime) levels and repeated attempts to resolve the transition state on the 4-31G surface were unsuccessful. The most favorable pathway that we are able to find for the carboxime–formonitrile oxide rearrangement proceeds via nitronylidene (**8**) as shown in eq 6.



27a
(θ = 117, ϕ = 77)
(STO-3G; C_s)



27b
(μ = 1.84D)



(6)

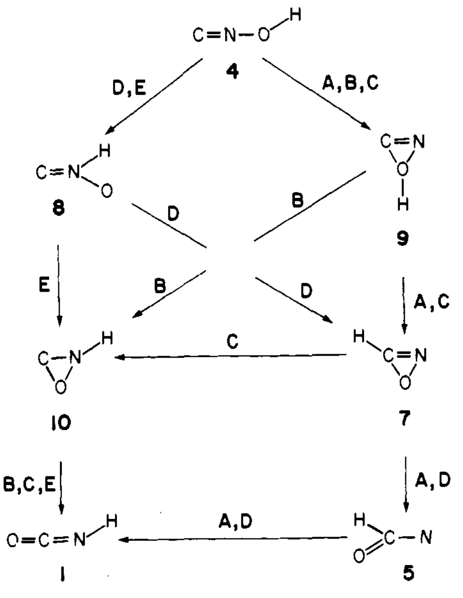
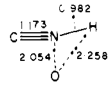


Figure 7. Five hypothetical routes from carboxime HONC (4) to isocyanic acid HNCO (1).

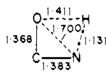
A search for the transition state for the first step in this process yielded a saddle point **28** with a geometry and energy quite close to that of nitronylidene itself. We were not able to explicitly demonstrate that **28** links **4** and **8** on the CHNO surface but its structure and energy as a transition state for the transformation **4** → **8** are consistent with data in our 4-31G contour surface (Figure 2). This point is not particularly important for our purposes here since examination of Figure 2 also indicates that the highest point on the reaction path is almost certainly the second transition state **19** linking **8** and **3**. This leads to a barrier of 73 kcal mol^{-1} (4-31G/4-31G) for the pathway shown in eq 6.



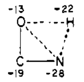
28a
(θ = 1, ϕ = 268)
(4-31G; C_s)

The Carboxime–Isocyanic Acid Rearrangement. The third—and most stable—CHNO isomer into which carboxime might rearrange is isocyanic acid (**1**). As in the case of the formonitrile oxide–isocyanic acid isomerization, one may postulate several reaction paths (Figure 7) which differ in the phase of the oxygen and hydrogen movements. Many of the individual steps in these reaction sequences have been discussed above in connection with other rearrangements. This is the case for the whole of path A. The highest barrier for this path is the transition state **27** linking **9** and **7** and which lies 91 kcal mol^{-1} (4-31G/STO-3G) above carboxime.

An alternative path (B) involves, in **9**, a migration of the hydrogen atom from oxygen to nitrogen. The resulting oxaziridinylidene (**10**) could then presumably open the ring and collapse to isocyanic acid (**1**). On the STO-3G surface, we find a saddle point **29** which connects the minima associated with the three-membered ring isomers **9** and **10**. This saddle point is not visible on the contour plot since it occurs in a region where the energy is so sensitive to a small change in θ and ϕ that



29a
(θ = 32, ϕ = 51)
(STO-3G; C_s)



29b
(μ = 1.53D)

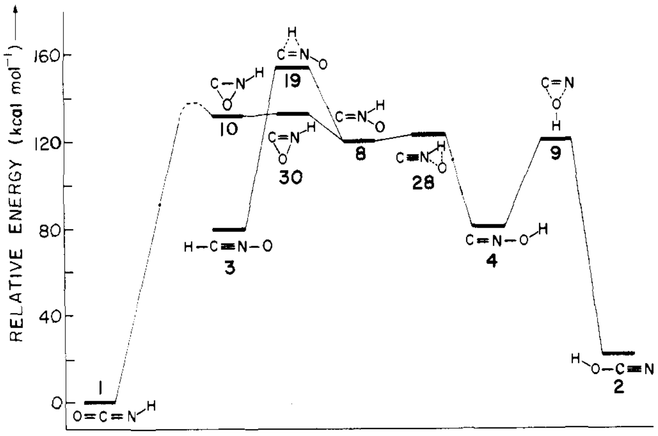
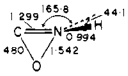


Figure 8. 4-31G energies along reaction paths from carboxime (4) to its more stable isomers.

the surface appears to be discontinuous. We have verified that **29** does relax to **9** and **10**. At the 4-31G/STO-3G level, this species lies 44 kcal mol⁻¹ above **9**. Since **29** is less stable than carboxime by 87 kcal mol⁻¹ (4-31G/STO-3G), path B is clearly a high-energy route. Similarly, paths C and D can probably be excluded on the basis of the high barriers between oxazirine (**7**) and oxaziridinylidene (**10**), and the nitronylidene (**8**) and oxazirine (**7**) regions, respectively.

The remaining path to be discussed is the direct route E. This path would involve nitronylidene (**8**) and oxaziridinylidene (**10**) intermediates. We have already discussed the transformation of carboxime (**4**) to nitronylidene (**8**) and its probable transition state **28** lying 41 kcal mol⁻¹ (4-31G/4-31G) above carboxime. On the 4-31G surface, we find that the transition state **30** for the next step on path E, the ring closure reaction **8** → **10**, has a geometry which resembles oxaziridinylidene **10**. The C-N bond, however, is significantly shorter than in **10** (4-31G: 1.464 Å) and seems to have some double bond character, whereas the C-O bond is weakened relative to **10** (4-31G: 1.293 Å). The computed (4-31G/4-31G) barrier between nitronylidene (**8**) and oxaziridinylidene (**10**) is 13 kcal mol⁻¹. Since we have—owing to SCF convergence difficulties[64]—not been able to locate the transition state between oxaziridinylidene and isocyanic acid, we use the relative energy of **30** as a lower limit for the barrier along path E. This estimate is quite high, 52 kcal mol⁻¹ (4-31G/4-31G), and indicates that carboxime (**4**) can rearrange more easily to cyanic acid (**2**) rather than to the more stable isomer isocyanic acid (**1**).



30a
(θ=20, ϕ=298)
(4-31G)

The Existence of Carboxime. In Figure 8, we summarize our findings concerning the reaction paths which lead from carboxime (**4**) to the more stable CHNO isomers.

At the 4-31G level the lowest barrier between carboxime and any of its isomers is 39 kcal mol⁻¹ and corresponds to a 1,2 shift of the hydroxyl group. Even if one allows for an error of 15 kcal mol⁻¹ in the theoretical barrier height, our results suggest that carboxime should be a reasonably stable species.

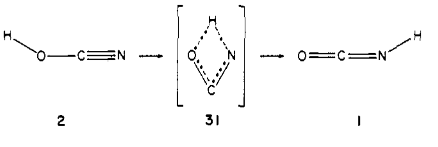
It is then rather puzzling that carboxime has never been observed experimentally.[65] One might suspect that this is due to a tendency of free HONC to polymerize[66] or to rearrange in hydroxylic solvents to the more stable formonitrile oxide via their common anion CNO^-.[67] Heterolytic rearrangement via the fulminate anion and presumably polymerization reactions as well could be blocked by attaching suitable substituents to the oxygen end of carboxime. Relevant theoretical data for fulminates RONC and their isomers will be presented elsewhere.[68]

Table VI. Theoretical and Experimental Data for Isonitrile (RNC)-Nitrile (RCN) Rearrangements (Equation 4)

R	Method	Exothermicity, kcal mol⁻¹	Barrier, kcal mol⁻¹	Ref
H	SCF	9.5	40.2	61
	CI	14.6	34.9	61
CH_3	SCF	17.3	60.4	62
	Exptl	15[a]	38.4	63
OH	SCF	60.1	38.8	This work

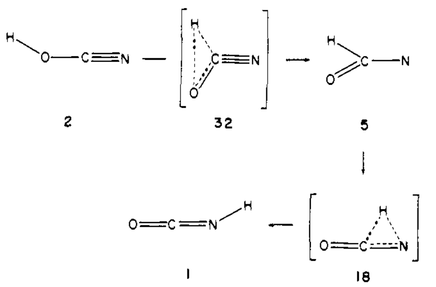
[a] Empirical estimate: S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

The Cyanic Acid-Isocyanic Acid Rearrangement. Intuitively, and without detailed calculations, it is difficult to predict whether the intramolecular cyanic acid-isocyanic acid rearrangement involves a single 1,3 migration (path A)



(7)

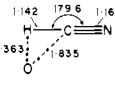
or two successive 1,2 shifts (path B)

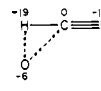


(8)

or would follow an entirely different course. As we have mentioned above, a transition state resembling **31** does exist on the STO-3G surface (stationary point **29**). It connects, however, the cyclic CHNO isomers **9** and **10**. Our more reliable (4-31G) results demonstrate that the intermediate **9** is an artifact of the minimal basis set; hence **29** should rather be viewed as a saddle point between cyanic acid (**2**) and oxaziridinylidene (**10**) (which could then open the N-C bond and collapse to isocyanic acid). The high energies of **29** (4-31G/STO-3G: 145 kcal mol⁻¹ above cyanic acid) and oxaziridinylidene (**10**) (4-31G/4-31G: 110 kcal mol⁻¹ above cyanic acid) clearly imply that path A is not a chemically important route from cyanic acid (**2**) to isocyanic acid (**1**). This is also true for an alternative path via carboxime (**4**) (cf. the carboxime-isocyanic acid rearrangement).

On path B, the relative energy of formylnitrene (**5**) (4-31G/STO-3G: 70 kcal mol⁻¹) places a lower limit on the theoretical activation barrier. The 4-31G contour plot (Figure 2) suggests that the highest barrier on path B is considerably above this value, possibly as high as 100 kcal mol⁻¹ (cf. the region around θ = 100°, ϕ = 0°). Our search for transition state **32** produced a saddle point **33** which lies 103 kcal mol⁻¹ above cyanic acid and 11 kcal mol⁻¹ above HCN + O(4-31G/STO-3G). Because of the high energy of this species, it





33a
(θ=180, ϕ=330)
(STO-3G; C_s)

33b
(μ=2.19D)

is of little consequence whether it is in fact a saddle point which connects the cyanic acid and formylnitrene regions and hence a transition state on path B, or rather the transition state for the expulsion of an oxygen atom from HOCN, and we have not investigated this problem in greater detail. In either case the theoretical results suggest that cyanic acid is more stable towards intramolecular rearrangement than is the experimentally characterized molecule formonitrile oxide and thus should be observable under nonionizing conditions.[69,70]

The Existence of Cyclic CHNO Isomers. At various points in the preceding discussion we have mentioned reaction paths leading from cyclic to open-chain CHNO isomers. Since one of these species, oxazirine (**7**), has been invoked as an intermediate in chemical reactions,[71] we find it appropriate to review our results for the cyclic isomers in a more concise form.

Isomer **9**, which may alternatively be viewed as an oxygen-protonated oxazirinyl anion or a complex of OH and CN, is unstable at the 4-31G level, and not a true intermediate. In fact, our calculations suggest that it is rather close to the transition state for the carboxime–cyanic acid rearrangement.

On the other hand, our extended basis set calculations do predict the existence of an oxaziridinylidene molecule (**10**). We estimate that this species is 131 kcal mol^{-1} less stable than isocyanic acid. Our theoretical data suggest that oxaziridinylidene could collapse virtually without activation (the overall barrier is only 2 kcal mol^{-1}) to carboxime or to HNC + O.

The third potentially stable cyclic CHNO isomer is oxazirine (**7**). Our most reliable results indicate that oxazirine is not a stable molecule. Attempts to synthesize this species will most likely result in the formation of isocyanic acid.

Galactochemical Speculations. On the basis of our calculations, we have predicted that both cyanic acid (HOCN) and carboxime (HONC) should be quite stable with respect to intramolecular rearrangement. Failure to observe these molecules to date may well be due to complicating *inter*molecular reactions. It is of interest that the related molecule, hydrogen isocyanide (HNC), which has likewise been predicted[61] to be stable toward intramolecular rearrangement but which for a long time had eluded experimental observation, has recently been detected in the laboratory.[72]

A major impetus for the experimental studies on HNC has been the conjecture that this molecule might exist in the galactic sources W51 and DR21.[73] In these circumstances, individual molecules are widely separated and intermolecular side reactions are not a problem. Such conditions are similarly likely to enhance the probability of detection of our cyanic acid and carboxime molecules. We note that isocyanic acid has already been detected in the galactic center source Sgr B2.[74] It is tempting to speculate that the other stable CHNO isomers may also be observable in interstellar space.

Summary and Conclusions

In this paper we have used ab initio molecular orbital theory to examine the potential energy surface for the lowest singlet state of the smallest organic molecule consisting of four different atoms (C, H, N, and O). Since relatively little is known experimentally about this system, most of our results are of a predictive nature. Our main results are as follows:

(a) Isocyanic acid (HNCO) is the most stable CHNO isomer, followed by cyanic acid (HOCN), formonitrile oxide (HCNO), and carboxime (HONC).
(b) HCNO is predicted to have a linear equilibrium geometry; HNCO, HOCN, and HONC are found to have planar, trans bent structures.
(c) Cyanic acid is a low-energy CHNO isomer with a high activation energy toward intramolecular rearrangement. It should therefore be observable under appropriate conditions. Such conditions exist in the interstellar medium.
(d) Carboxime is a somewhat higher energy isomer of CHNO. However, the barrier to intramolecular rearrangement is sufficiently high that this species should also be observable under appropriate conditions.
(e) The rearrangement of formonitrile oxide to isocyanic acid does not proceed via metastable intermediates. However, a minimum energy path may be drawn which involves geometries resembling oxazirine and formylnitrene.
(f) Singlet formylnitrene is predicted to collapse without activation to isocyanic acid.
(g) The cyclic CHNO isomers correspond to very shallow minima or no minima at all. Our results suggest that none of the cyclic species is stable enough to be observable.

We are aware of the possible pitfalls in using single determinant molecular orbital theory to calculate entire potential energy surfaces. We believe nevertheless that our study has provided the overview of the CHNO potential surface that will facilitate the application of more sophisticated theoretical procedures. Although we do not expect that our more important qualitative conclusions will have to be revised, we regard the more refined calculations as necessary,[75] and we have stated where additional theoretical work would be of greatest interest. We note that to carry out a study of the full CHNO surface at the double ζ + polarization + correlation level in a detail comparable to that of the present work would be an immense computational task and well beyond our current computational resources. Many of our predictions can be checked experimentally and await verification. We hope that further experimental work will be forthcoming and we expect that such work will demonstrate that theoretical chemistry has reached the state of a useful predictive tool.

Acknowledgments. We thank Dr. U. Klement, University Regensburg, for help with the contour plots. This research was supported in part by the National Science Foundation Grant GP-25617 (Carnegie-Mellon University).

Supplementary Material Available: Table V (optimized geometric parameters and total energies for points in the CHNO potential surface) (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Australian National University; (b) Institute of Organic Chemistry, University of Erlangen-Nürnberg, 8520 Erlangen, West Germany; (c) Carnegie-Mellon University.
(2) R. Kewley, K. V. L. N. Sastry, and M. Winnewisser, *J. Mol. Spectrosc.*, **10**, 418 (1963).
(3) W. Beck and K. Feldl, *Angew. Chem., Int. Ed. Engl.*, **5**, 722 (1966).
(4) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 1 and 2, W. A. Benjamin, New York, N.Y., 1966.
(5) C. Grundmann and P. Grünanger, "The Nitrile Oxides," Springer-Verlag, West Berlin, 1971.
(6) W. Lwowski, Ed., "Nitrenes", Wiley, New York, N.Y., 1970.
(7) L. Pauling and S. B. Hendricks, *J. Am. Chem. Soc.*, **48**, 641 (1926).
(8) R. Bonaccorsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, **48**, 1500 (1968).
(9) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 289 (1971).
(10) J. M. Howell, I. Absar, and J. R. Van Wazer, *J. Chem. Phys.*, **59**, 5895 (1973).
(11) J. Baside and J. P. Maier, *Chem. Phys.*, **12**, 177 (1976).
(12) W. A. Lathan, L. Radom, P. C. Hariharan, W. J. Hehre, and J. A. Pople, *Fortschr. Chem. Forsch.*, **40**, 1 (1973).
(13) J. F. Harrison and G. Shalhoub, *J. Am. Chem. Soc.*, **97**, 4172 (1975).
(14) P. F. Alewood, P. M. Kazmaier, and A. Rauk, *J. Am. Chem. Soc.*, **95**, 5466 (1973).
(15) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(16) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).
(17) P. C. Hariharan and J. A. Pople, *Mol. Phys.*, **27**, 209 (1974).

(18) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
(19) For a general review, see L. Radom and J. A. Pople, *MTP Int. Rev. Sci.: Theor. Chem., Ser. One* (1972).
(20) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 289 (1971).
(21) L. Radom, W. J. Hehre, W. A. Lathan, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 5339 (1971).
(22) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).
(23) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).
(24) L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc. A*, 2299 (1971).
(25) M. J. S. Dewar and J. Kelemen, *J. Chem. Educ.*, **48**, 494 (1971).
(26) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).
(27) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(28) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(29) D. Poppinger, *Chem. Phys. Lett.*, **34**, 332 (1975).
(30) D. Poppinger, *Chem. Phys. Lett.*, **35**, 550 (1975).
(31) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, QCPE, University of Indiana, Bloomington, Ind.
(32) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(33) L. H. Jones, J. N. Shoolery, R. G. Shulman, and D. M. Yost, *J. Chem. Phys.*, **18**, 990 (1955).
(34) W. H. Hocking, M. C. L. Gerry, and G. Winnewisser, *Astrophys. J.*, **187**, L89 (1974); W. H. Hocking, M. C. L. Gerry, and G. Winnewisser, *Can. J. Phys.*, **53**, 1869 (1975). These authors point out that despite an abundance of isotopic data, they are unable to distinguish rigorously between a linear and slightly nonlinear (<10°) NCO chain.
(35) (a) B. M. Rode, W. Kosmus,and E. Nachbaur, *Chem. Phys. Lett.*, **17**, 186 (1972); *Z. Naturforsch. A*, **29**, 650 (1974). (b) A very recent paper from the same group: P. Botschwina, E. Nachbaur, and B. M. Rode, *Chem. Phys. Lett.*, **41**, 486 (1976), gives the results of ab initio calculations on HNCO which also yield a trans bent geometry.
(36) A trans bent equilibrium structure has been found experimentally in chlorine isocyanate[37a] and in silyl isocyanate.[37b]
(37) (a) H. Oberhammer, *Z. Naturforsch. A*, **26**, 280 (1971); W. H. Hocking and M. C. L. Gerry, *J. Mol. Spectrosc.*, **42**, 547 (1972). (b) W. Airey, C. Glidewell, A. G. Robiette, and G. M. Sheldrick, *J. Mol. Struct.*, **8**, 435 (1971). See, however, M. C. L. Gerry, J. C. Thompson, and T. M. Sugden, *Nature (London)*, **211**, 846 (1966).
(38) H. K. Bodenseh and M. Winnewisser, *Z. Naturforsch. A*, **24**, 1973 (1969).
(39) (a) B. T. Hart, *Aust. J. Chem.*, **28**, 1 (1976); (b) L. Radom, J. S. Binkley, and J. A. Pople, *ibid.*, **30**, 699 (1977).
(40) P. A. Giguere and I. D. Lew, *Can. J. Chem.*, **30**, 948 (1952).
(41) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).
(42) B. P. Winnewisser, M. Winnewisser, and F. Winther, *J. Mol. Spectrosc.*, **51**, 65 (1974); K. Yamada, B. P. Winnewisser, and M. Winnewisser, *ibid.*, **56**, 449 (1975); B. P. Winnewisser and M. Winnewisser, *ibid.*, **56**, 471 (1975).
(43) The only CHNO isomer which is not contained in our contour surfaces is the complex **6**. We have been interested mainly in the interconversion of bound isomers and have therefore not investigated reaction paths connecting **6** with other minima.
(44) The contour plots were generated on the Siemens 4004 at Regensburg University using routines written by Dr. U. Klement.
(45) There are regions on the $E(\theta, \phi)$ surfade in which the cisoid ($\phi < 180°$) structures collapse without activation and via rotation around the C–N bond to their transoid ($\phi \geqslant 180°$) counterparts or vice versa. This occurs, for example, at $\theta = 10°$, $\phi = 10°$. In these cases, we use the energy of the resulting most stable structure to generate both the cisoid and the transoid parts of the surface.
(46) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **10**, 781 (1969).
(47) For some of the molecules which we designate as planar (C_s symmetry), the geometry optimization program terminates at slightly nonplanar structures. The distances of the H atom from the plane of the heavy atom in these cases are as follows: **15b,** 0.005 Å; **17a,** 0.005 Å; **18a,** 0.002 Å; **19b,** 0.062A Å; **28a,** 0.002 Å. These small deviations from planarity do not significantly affect the total energies.
(48) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
(49) Reference 5, p 16.
(50) R. Scholl, *Ber. Dtsch. Chem. Ges.*, **23**, 3505 (1894).
(51) Reference 5, Chapter IV.
(52) C. Grundmann and S. K. Datta, *J. Org. Chem.*, **34**, 2016 (1969).
(53) H. Wieland, *Ber. Dtsch. Chem. Ges.*, **42**, 4207 (1909).
(54) C. Grundmann, P. Kochs, and J. R. Boal, *Justus Liebigs Ann. Chem.*, **761**, 162 (1972).
(55) Reference 5, p 65.
(56) Acyl nitrenes have been trapped in the photochemical rearrangement of nitrile oxides to isocyanates: G. Just and W. Zehetner, *Tetrahedron Lett.*, 3389 (1967).
(57) For a review, see K. M. Maloney and B. S. Rabinovitch, in "Isonitrile Chemistry," I. Ugi, Ed., Academic Press, New York, N.Y., 1971.
(58) G. W. Van Dine and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 3227 (1968).
(59) M. J. S. Dewar and M. C. Kohn, *J. Am. Chem. Soc.*, **94**, 2705 (1972).
(60) D. H. Liskow, C. F. Bender, and H. F. Schaefer, *J. Am. Chem. Soc.*, **94**, 5178 (1972).
(61) P. K. Pearson, H. F. Schaefer, and U. Wahlgren, *J. Chem. Phys.*, **62**, 350 (1975).
(62) D. H. Liskow, C. F. Bender, and H. F. Schaefer, *J. Chem. Phys.*, **57**, 4509 (1972).
(63) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 4215 (1962).
(64) Severe convergence difficulties arose for many points on the CHNO potential energy surface. We found that in all but the most fatal cases convergence can be enforced by damping the change in the density matrix D according to $D^{i+1} = \alpha D^{i+1} + (1 - \alpha)D^{i}$, where i denotes the iteration cycle and α is a dimensionless damping factor (usually 0.3).
(65) There are indications that carboxime can be stabilized in a transition metal complex: W. Beck and E. Schuirer, *Chem. Ber.*, **95**, 3048 (1962).
(66) Polymerization is a well-known reaction of free formonitrile oxide and isocyanic acid; cf. ref 4 and 5.
(67) The nitrogen analogue of carboxime, *N*-isocyanamine $H_2NN{=}C$, is known to rearrange base catalyzed to diazomethane: E. Müller, R. Beutler, and B. Zeeh *Justus Liebigs Ann. Chem.*, **719**, 72 (1968).
(68) D. Poppinger and L. Radom, manuscript in preparation.
(69) The rearrangement of cyanates and thiocyanates to isocyanates and isothiocyanates, respectively, is acid catalyzed and appears to involve solvated ion pairs: D. Martin, *Angew. Chem.*, **76**, 303 (1964); P. A. S. Smith and D. W. Emerson, *J. Am. Chem. Soc.*, **82**, 3076 (1960); A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *ibid.*, **83**, 2729 (1961).
(70) Indirect evidence for the existence of cyanic acid has been obtained by N. Groving and A. Holm, *Acta Chem. Scand.*, **19**, 1768 (1965).
(71) S. Ranganathan, B. B. Singh, and C. S. Panda, *Tetrahedron Lett.*, 1225 (1970); M. Georgarakis, H. J. Rosenkranz, and H. Schmid, *Helv. Chim. Acta*, **54**, 819 (1971); R. S. Berry in ref 6, p 42.
(72) (a) G. L. Blackman, R. D. Brown, P. D. Godfrey, and H. I. Gunn, *Nature (London)*, in press; (b) R. J. Saykally, T. G. Szanto, T. G. Anderson, and R. C. Woods, *Astrophys. J. Lett.*, **204**, L143 (1976); (c) R. A. Creswell, E. F. Pearson, M. Winnewisser, and G. Winnewisser, *Z. Naturforsch. A*, **31**, 221 (1976).
(73) L. E. Snyder and D. Buhl, *Ann. N.Y. Acad. Sci.*, **194**, 17 (1972).
(74) L. E. Snyder and D. Buhl, *Astrophys. J.*, **177**, 619 (1972).
(75) After this manuscript was completed, we became aware of an independent theoretical study of the four CHNO isomers **1–4** by A. D. McLean and coworkers at IBM (San Jose). Their calculations have been carried out at a higher level of sophistication than have ours but the conclusions are in substantial agreement with those reported herein. We are indebted to Dr. McLean for bringing this work to our attention.