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## Theoretical study of the possible isomers and high-energy intermediates of HCN–H<sub>2</sub>O complexes

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### Abstract

All chemically significant structures and some possible intermediates involving unimolecular and bimolecular complexes of CH<sub>3</sub>NO were studied by using the 6-311G\*\* basis set at the Hartree–Fock, MP2 and density functional levels employing the three-parameter Becke functional (B3-LYP). Calculated structures and thermodynamic properties are presented. Formamide was found to be the most stable structure in all methods. Minor structural and energetic differences among the methods are discussed. Density functional computations were carried out on selected structures incorporating diffuse functions into the basis set (6-311++G\*\*), and the results are compared with experimental values where available. © 1998 Elsevier Science B.V.

**Keywords:** Formamide; Hydrogen cyanide; HCN; Density functional; Energetic intermediates

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### 1. Introduction

The isomers of CH<sub>3</sub>NO range from species such as formamide and nitrosomethane to bimolecular complexes such as H<sub>2</sub>O⋯HCN and CO⋯NH<sub>3</sub>, and complexes involving HCNO and HNCO. The present study was prompted by our interest in the decomposition products of HCN in the presence of trace amounts of water. A polymerization pathway exists, involving the release of a substantial amount of energy [1]. The mechanism for this reaction, which involves trace amounts of water as a catalyst, is not known. Since HCN is an important industrial chemical, the results of this study have implications in devising strategies for long-term storage and safe handling procedures for bulk quantities of the compound. We have presented a preliminary study which examined chemically

feasible structures which included possible intermediates in the reaction involving HCN and H<sub>2</sub>O. That study presented thermodynamic quantities and vibrational structures for 22 isomers computed at the Hartree–Fock (HF) level of theory. Several high-energy intermediates were described, and care was taken to ensure that only singlet states existed by using the quadratic convergence method in the self-consistent field (SCF) procedure [2].

The present study was extended to include seven additional structures which were not considered in our earlier study. We also expanded the present study to explore the effect of electron correlation in the energetics of the various isomers. Since the HCN polymerization mechanism may involve several H<sub>2</sub>O and HCN molecules, we further expanded the present study to evaluate the applicability of density

functional theory (DFT) to the description of these structures. We were particularly interested in the applicability of DFT to the high-energy intermediate structures presented in this study. We report herein the results obtained by use of HF, second-order Møller–Plesset (MP2) and DFT methods to describe the structures presented.

## 2. Theoretical method

There are numerous isomers and complexes of empirical formula  $\text{CH}_3\text{NO}$ . We address in this study not only the monomeric form of  $\text{CH}_3\text{NO}$ , but also a number of bimolecular complexes. A geometry

optimization procedure was applied to over 50 chemically significant combinations. In this paper we limit the structures to those in which oxygen is divalent, nitrogen is trivalent, and carbon is tetravalent; i.e., the most chemically significant structures. The unimolecular structures were arrived at by placing H atoms onto all possible linear and triangular arrangements of C, N and O, and the bimolecular complexes were arrived at by considering: HCN or HNC to be complexed to  $\text{H}_2\text{O}$ ;  $\text{HCNO}$ ,  $\text{HNCO}$  or  $\text{HOCN}$  to be complexed to  $\text{H}_2$ ; and the  $\text{NH}_3\cdots\text{CO}$  complex.

All structures were first optimized using the HF method of the GAUSSIAN 94 series of programs employing the 6-311G\*\* basis set [3]. The HF

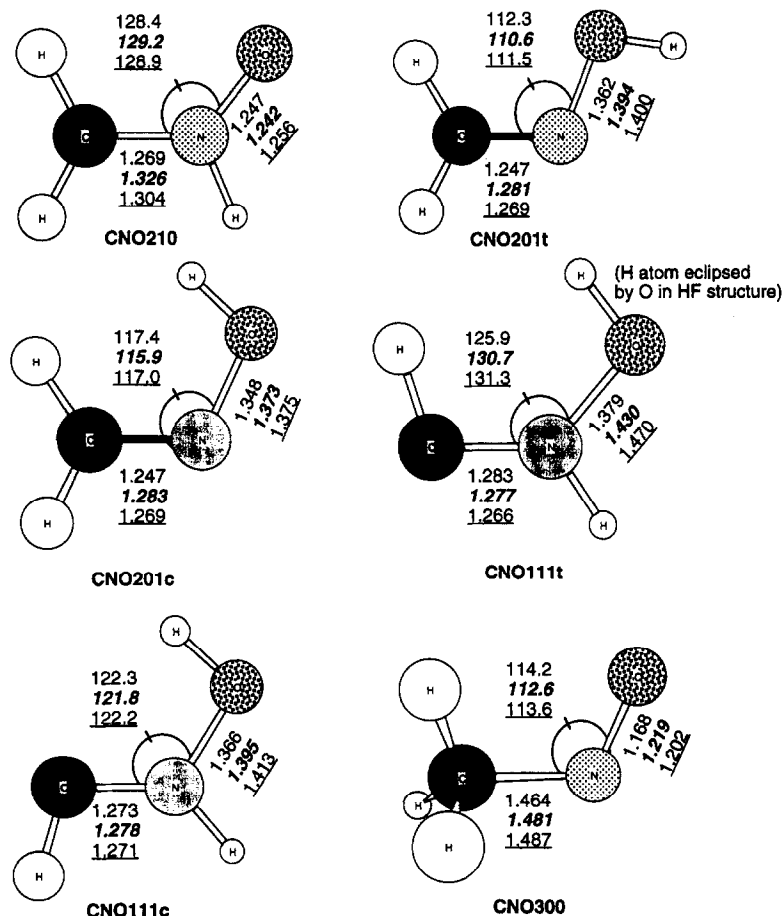


Fig. 1. Optimized structures of the formula  $\text{CH}_3\text{NO}$ , with structural parameters computed at HF (normal) MP2 (bold) and DFT (underlined) levels of theory using the 6-311G\*\* basis. Multiple bonds are shaded.

optimized geometries were then used as the initial geometries in the MP2 and DFT computations. The same basis set was employed for the higher computational procedures. The structures were optimized at each level of theory by using analytical gradient methods. The VERY TIGHT thresholds of forces and displacements were applied in all cases. The quadratic convergence (QC) method was applied to the SCF procedure for all computations [4]. The QC method runs significantly slower than the GAUSSIAN

94 default methods, but we have found that this method gave more consistent results, particularly in many of the high-energy structures which may have low-lying excited states.

Since most of these structures are unimolecular, our chosen basis set (involving polarization functions on all atoms) is sufficiently large to address the variety of structures and bond orders and types presented. Studies involving molecular complexes typically further incorporate diffuse functions into the basis set

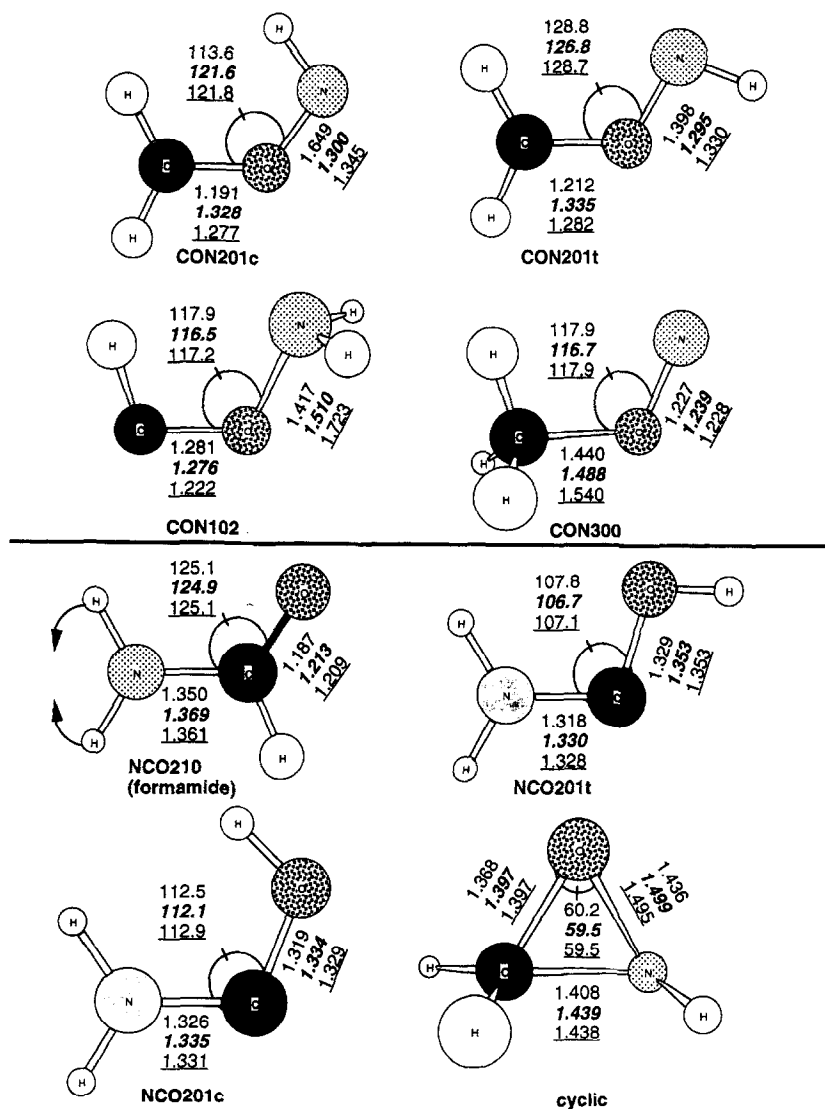


Fig. 1. (continued)

(i.e., 6-311(++)G\*\* [5–8]). We expect the 6-311G\*\* basis set to be applicable to all complexes and unimolecular species presented herein. As a check on the DFT results, we apply the 6-311(++)G\*\* basis set to the bimolecular species presented herein. Since most of the structures involve high-energy intermediates, single-point MP4 computations were applied to each MP2 optimized geometry. The three-parameter Becke functional with Lee, Yang and Parr exchange correlation (B3-LYP) was chosen for the DFT calculations. This functional, which

contains gradient corrections for both exchange and correlation, has produced favorable results for a number of similar species in the literature [9–11]. All calculations were run on the SGI Power Challenge Array at Aberdeen Proving Grounds.

### 3. Results and discussion

In order to classify the unimolecular structures presented, we employ a system based on all chain or ring

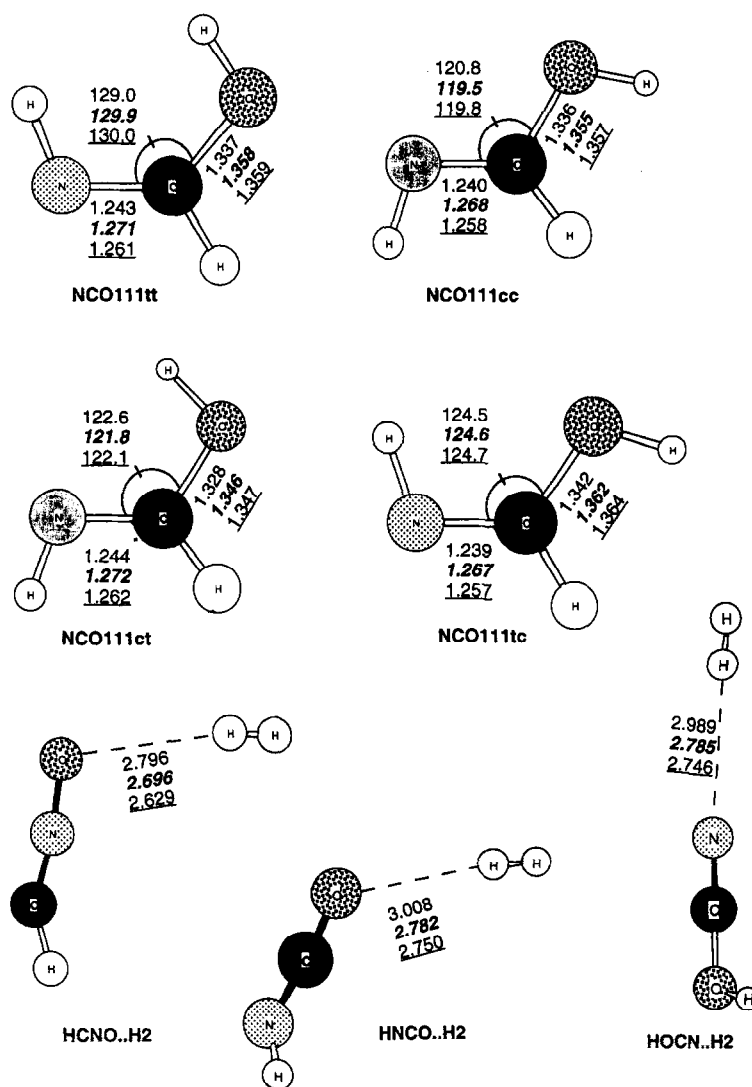


Fig. 1. (continued)

arrangements of the backbone, made up of the atoms C, N and O. The number of hydrogens on each of the heavy atoms is accounted for in this description. Each structure is characterized by a name consisting of three letters followed by three numbers. The letters correspond to the backbone of the system, while the numbers correspond to the placement of the three hydrogens. There are only three possible linear arrangements of the three heavy atoms: NCO, CNO and CON. Thus a molecule such as formamide would be given the description NCO210; i.e., two hydrogens on the nitrogen, one on the carbon and none on the oxygen. Nitrosomethane is described as CNO300. With our constraint of a trivalent nitrogen, there is only one chemically significant ring structure. Within any linear arrangement there are possible diastereomers,

usually involving *cis* and *trans* positions of the H atoms. We use the designation cc, ct, tc or tt for describing these structures. Fig. 1 groups the structures using our classification scheme and indicates the heavy atom bond lengths and angles computed using the three computational methods.

The bimolecular structures are named on the basis of their unimolecular constituents. Two structures of the H<sub>2</sub>O and HCN complex involved two different hydrogen bond structures (Fig. 1). There is only one complex found involving CO and NH<sub>3</sub>. We have investigated bimolecular complexes of H<sub>2</sub> and HCNO, HNCO and HOCN respectively.

In Table 1 we list the HF calculated electronic energies, enthalpies, entropies and free energies of all species. Tables 2 and 3 give the MP2 and

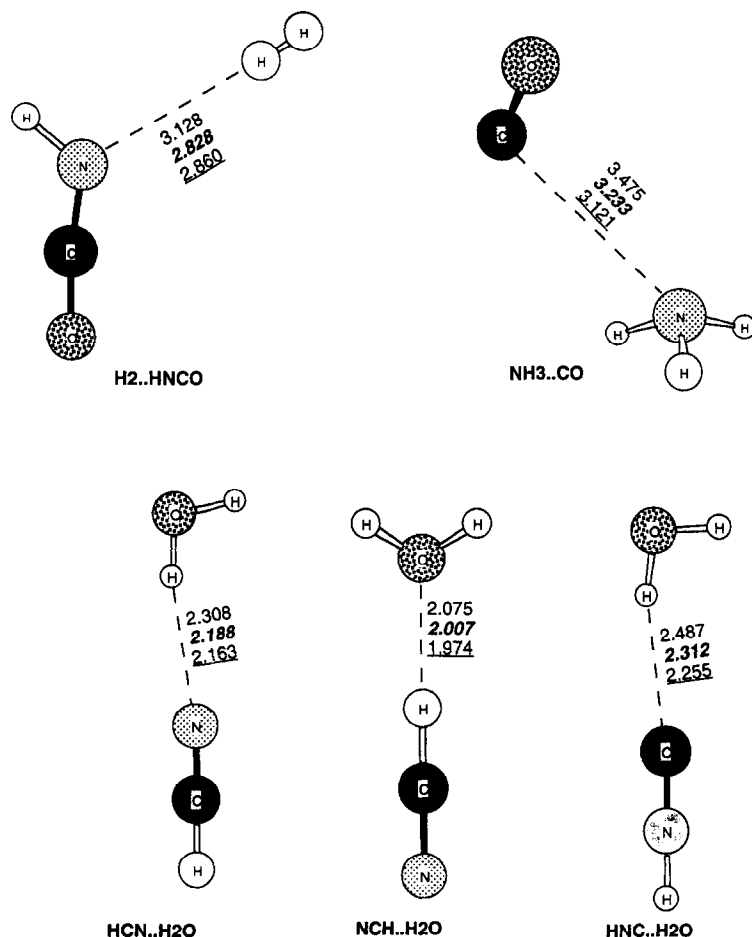


Fig. 1. (continued)

Table 1

Calculated electronic energies, entropies, enthalpies and free energies (HF)

Structure	$E(\text{scf})$ u	$S(298 \text{ K})$ ( $\text{J mol}^{-1} \text{ K}^{-1}$ )	$H(298 \text{ K})$ u	$G(298 \text{ K})$ u
HCN + H <sub>2</sub> O	– 168.946968377	388.16	– 168.90	– 168.94
HCNO + H <sub>2</sub>	– 168.807325954	318.59	– 168.77	– 168.80
HNC + H <sub>2</sub> O	– 168.929617779	391.32	– 168.88	– 168.93
HNCO + H <sub>2</sub>	– 168.942898195	367.43	– 168.90	– 168.94
HOCN + H <sub>2</sub>	– 168.905123196	369.56	– 168.86	– 168.91
NCO210	– 168.982285178	260.71	– 168.93	– 168.96
NH <sub>3</sub> + CO	– 168.979872241	389.02	– 168.93	– 168.97
CON201t	– 168.772339071	255.79	– 168.72	– 168.75
NCO111tc	– 168.955467823	251.99	– 168.90	– 168.93
HOCN...H <sub>2</sub>	– 168.905924466	334.62	– 168.86	– 168.90
CNO201t	– 168.892875263	251.53	– 168.84	– 168.87
HCNO...H <sub>2</sub>	– 168.808456246	305.67	– 168.77	– 168.80
HCN...H <sub>2</sub> O	– 168.952465396	313.58	– 168.90	– 168.94
NCH...H <sub>2</sub> O	– 168.957164837	306.45	– 168.91	– 168.94
CNO201c	– 168.883223485	251.28	– 168.83	– 168.86
NCO111cc	– 168.951425275	251.74	– 168.90	– 168.93
NCO111ct	– 168.962329907	248.98	– 168.91	– 168.94
NCO111tt	– 168.956377173	250.27	– 168.90	– 168.93
HNCO...H <sub>2</sub>	– 168.943436146	336.27	– 168.90	– 168.94
CNO300	– 168.875523047	257.84	– 168.82	– 168.85
cyclic	– 168.857571668	245.40	– 168.80	– 168.83
H <sub>2</sub> ...HNCO	– 168.943495121	341.18	– 168.90	– 168.94
NH <sub>3</sub> ...CO	– 168.981595357	354.02	– 168.93	– 168.97
CON102	– 168.802642406	257.96	– 168.75	– 168.78
NCO201c	– 168.916989015	252.23	– 168.86	– 168.89
HNC...H <sub>2</sub> O	– 168.934540761	316.16	– 168.89	– 168.92
CON201c	– 168.784417459	274.14	– 168.74	– 168.77
CNO111t	– 168.830731132	254.91	– 168.78	– 168.81
CON300	– 168.807713632	260.47	– 168.76	– 168.79
CNO210	– 168.858120023	247.75	– 168.81	– 168.83
CNO111c	– 168.833860558	252.95	– 168.78	– 168.81
NCO201t	– 168.928694511	251.37	– 168.87	– 168.90

Table 2

Calculated electronic energies, entropies, enthalpies and free energies (MP2)

Structure	MP2 $E(\text{scf})$ u	MP4	$S(298 \text{ K})$ ( $\text{J mol}^{-1} \text{ K}^{-1}$ )	$H(298 \text{ K})$ u	$G(298 \text{ K})$ u
HCN + H <sub>2</sub> O	– 169.46417845600	– 169.499931378	390.11	– 169.42	– 169.46
HCNO + H <sub>2</sub>	– 169.35569973200	– 169.397027514	366.49	– 169.32	– 169.36
HNC + H <sub>2</sub> O	– 169.43410258100	– 169.474392418	393.04	– 169.39	– 169.43
HNCO + H <sub>2</sub>	– 169.46457105000	– 169.503444724	369.20	– 169.43	– 169.47
HOCN + H <sub>2</sub>	– 169.42611790400	– 169.463295084	372.55	– 169.39	– 169.43
NCO210	– 169.49455273348	– 169.532078830	254.61	– 169.44	– 169.47
NH <sub>3</sub> + CO	– 169.48354524600	– 169.524486146	389.89	– 169.44	– 169.48
CNO201t	– 169.32257016533	– 169.364867040	260.80	– 169.27	– 169.30
NCO111tc	– 169.46969634104	– 169.507808260	253.21	– 169.42	– 169.45
HOCN...H <sub>2</sub>	– 169.42753696953	– 169.464658930	333.52	– 169.39	– 169.42
CNO201t	– 169.41010785075	– 169.448291650	253.22	– 169.36	– 169.39
HCNO...H <sub>2</sub>	– 169.35723427022	– 169.398470640	326.05	– 169.32	– 169.35
HCN...H <sub>2</sub> O	– 169.47097781954	– 169.495432310	313.47	– 169.42	– 169.46
NCH...H <sub>2</sub> O	– 169.47543969477	– 169.511203670	301.56	– 169.43	– 169.46
CNO201c	– 169.40192137135	– 169.443808630	252.63	– 169.35	– 169.38
NCO111cc	– 169.46600313095	– 169.503998280	252.78	– 169.42	– 169.44

Table 2 (continued)

Structure	MP2 $E(\text{scf})$ u	MP4	$S(298 \text{ K})$ ( $\text{J mol}^{-1} \text{ K}^{-1}$ )	$H(298 \text{ K})$ u	$G(298 \text{ K})$ u
NCO111ct	– 169.47634492044	– 169.514033590	250.27	– 169.43	– 169.45
HNCO $\cdots$ H <sub>2</sub>	– 169.46564072545	– 169.504533800	327.52	– 169.42	– 169.46
NCO111tt	– 169.47078055536	– 169.508886050	251.53	– 169.42	– 169.45
NO300	– 169.39274777360	– 169.437387500	260.55	– 169.34	– 169.37
H <sub>2</sub> $\cdots$ HNCO	– 169.46570782070	– 169.504572190	307.08	– 169.43	– 169.46
cyclic	– 169.37896524796	– 169.419601380	247.09	– 169.33	– 169.36
NH <sub>3</sub> $\cdots$ CO	– 169.48605678735	– 169.529025790	334.39	– 169.44	– 169.48
CON102	– 169.30686755836	– 169.354883500	264.39	– 169.26	– 169.29
NCO201c	– 169.42097726142	– 169.461564990	253.55	– 169.37	– 169.40
HNC $\cdots$ H <sub>2</sub> O	– 169.44113906652	– 169.481159330	315.59	– 169.39	– 169.43
CON201c	– 169.32677050072	– 169.370218640	259.49	– 169.28	– 169.31
CN0111t	– 169.33990169887	– 169.383796610	257.04	– 169.29	– 169.32
CON300	– 169.30355284379	– 169.354423130	260.82	– 169.25	– 169.28
CNO210	– 169.39014977144	– 169.432040630	250.75	– 169.34	– 169.37
CNO111c	– 169.34319071267	– 169.386432080	252.56	– 169.29	– 169.32
NCO201t	– 169.43170253558	– 169.471839490	253.33	– 169.38	– 169.41

Table 3

Calculated electronic energies, entropies, enthalpies and free energies (DFT)

Structure	$E(\text{scf})$ u	$S(298 \text{ K})$ ( $\text{J mol}^{-1} \text{ K}^{-1}$ )	$H(298 \text{ K})$ u	$G(298 \text{ K})$ u
HCN + H <sub>2</sub> O	– 169.899466706	389.70	– 169.85	– 169.90
HCNO + H <sub>2</sub>	– 169.802174014	328.14	– 169.76	– 169.80
HNC + H <sub>2</sub> O	– 169.875837486	393.65	– 169.83	– 169.88
HNCO + H <sub>2</sub>	– 169.912535806	368.74	– 169.87	– 169.92
HOCN + H <sub>2</sub>	– 169.867050988	371.78	– 169.83	– 169.87
NCO210	– 169.946262472	257.76	– 169.90	– 169.93
NH <sub>3</sub> + CO	– 169.922271552	389.82	– 169.88	– 169.92
CON201t	– 169.775698245	251.98	– 169.73	– 169.76
NCO111tc	– 169.919553006	252.89	– 169.87	– 169.90
HOCN $\cdots$ H <sub>2</sub>	– 169.868216919	326.54	– 169.83	– 169.86
CNO201t	– 169.864140920	252.88	– 169.82	– 169.84
HCNO $\cdots$ H <sub>2</sub>	– 169.803513739	312.53	– 169.76	– 169.80
HCN $\cdots$ H <sub>2</sub> O	– 169.906104225	312.29	– 169.86	– 169.89
NCH $\cdots$ H <sub>2</sub> O	– 169.911725630	299.83	– 169.86	– 169.90
CNO201c	– 169.855868728	252.35	– 169.81	– 169.84
NCO111cc	– 169.915598869	252.42	– 169.87	– 169.89
NCO111ct	– 169.925698276	250.26	– 169.88	– 169.90
NCO111tt	– 169.920371529	251.48	– 169.87	– 169.90
HNCO $\equiv$ H <sub>2</sub>	– 169.913370287	325.15	– 169.87	– 169.91
CNO300	– 169.843959352	259.67	– 169.80	– 169.83
cyclic	– 169.828317206	247.18	– 169.78	– 169.81
H <sub>2</sub> $\cdots$ HNCO	– 169.913375323	329.50	– 169.87	– 169.91
NH <sub>3</sub> $\cdots$ CO	– 169.924578863	337.16	– 169.88	– 169.91
CON102	– 169.772795500	270.22	– 169.73	– 169.76
NCO201c	– 169.876418757	253.07	– 169.83	– 169.86
HNC $\cdots$ H <sub>2</sub> O	– 169.882773586	313.95	– 169.84	– 169.87
CON201c	– 169.782913958	251.96	– 169.74	– 169.76
CN0111t	– 169.801232097	258.57	– 169.75	– 169.78
CON300	– 169.768765344	263.91	– 169.72	– 169.75
CNO210	– 169.847797410	249.71	– 169.80	– 169.83
CNO111c	– 169.803236697	253.11	– 169.75	– 169.78
NCO201t	– 169.885294920	252.94	– 169.84	– 169.86



DFT results. Since the MP4 results were only from single-point calculations using MP2 optimized structures, we include the calculated electronic energy in Table 2. It was found in all cases that formamide (NCO210) has the lowest electronic energy. We present energy differences using formamide as the reference for all species in Table 4 for HF, Table 5 for MP2 (MP4) and in Table 6 for DFT computations.

As expected, the arrangement of these energy differences is the same for MP2 and MP4. Additionally, HF and MP2 ordering are consistent. This is most likely a result of the QC procedure, which guarantees the convergence on the lowest singlet state within the SCF procedure.

We have found more significant variance when comparing MP2 and DFT energy differences. However, when comparing unimolecular MP2 and DFT differences, the ordering is consistent. Within the bimolecular species the ordering is largely consistent between MP2 and DFT with one exception. DFT favored the HCNO $\cdots$ H<sub>2</sub> and H<sub>2</sub> $\cdots$ HCNO structures over HCN $\cdots$ H<sub>2</sub>O and NCH $\cdots$ H<sub>2</sub>O. MP2 favors HCN $\cdots$ H<sub>2</sub>O and NCH $\cdots$ H<sub>2</sub>O over HCNO $\cdots$ H<sub>2</sub> and H<sub>2</sub> $\cdots$ HCNO.

These energy difference orderings are consistent over a range of *ca.* 100 kcal mol<sup>-1</sup>. A possible explanation for the variance within the bimolecular species is the choice of the 6-311G\*\* basis set rather than one which includes very diffuse basis functions

Table 4

Changes in calculated electronic energies, entropies, enthalpies and free energies ( $\Delta G = \Delta H - 298\Delta S$ ) (HF)

Structure	$\Delta E$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H(298\text{ K})$ (kJ mol <sup>-1</sup> )	$\Delta G(298\text{ K})$ (kJ mol <sup>-1</sup> )
NCO210	0	0	0	0
NH <sub>3</sub> $\cdots$ CO	1.81	93.31	- 5.27	- 33.10
NH <sub>3</sub> + CO	6.33	128.32	- 4.60	- 42.84
NCO111ct	52.39	- 11.72	54.48	57.99
NCH $\cdots$ H <sub>2</sub> O	65.95	45.74	56.78	43.14
NCO111tt	68.02	- 10.44	69.45	72.55
NCO111tc	70.41	- 8.71	71.55	74.14
HCN $\cdots$ H <sub>2</sub> O	78.29	52.87	69.12	53.39
NCO111cc	81.02	- 8.97	82.17	84.85
HCN + H <sub>2</sub> O	92.72	127.46	78.78	40.75
H <sub>2</sub> $\cdots$ HNCO	101.84	80.48	72.59	48.62
HNCO $\cdots$ H <sub>2</sub>	102.00	75.56	72.63	50.12
HNCO + H <sub>2</sub>	103.41	106.73	69.96	38.12
HNC $\cdots$ H <sub>2</sub> O	125.35	55.46	114.68	98.11
HNC + H <sub>2</sub> O	138.28	130.61	122.80	83.85
NCO201t	140.70	- 9.34	141.80	144.60
NCO201c	171.44	- 8.48	170.46	172.97
HOCN + H <sub>2</sub>	200.49	73.92	174.05	152.05
HOCN + H <sub>2</sub>	202.59	108.86	171.80	139.33
CNO201t	234.75	- 9.18	232.97	235.68
CNO201c	260.09	- 9.43	257.19	259.99
CNO300	280.30	- 2.86	275.10	275.93
CNO210	326.00	- 12.95	325.18	329.07
cyclic	327.44	- 15.31	328.28	332.84
CNO111c	389.69	- 7.76	387.48	389.78
CNO111t	397.91	- 5.79	395.35	397.10
HCNO $\cdots$ H <sub>2</sub>	456.39	44.97	425.64	412.25
CON300	458.34	- 0.23	452.67	452.75
HCNO + H <sub>2</sub>	459.36	57.89	422.46	405.22
CON102	471.65	- 2.74	467.48	468.27
CON201c	519.50	13.43	508.19	504.17
CON201t	551.21	- 4.91	541.66	543.13

such as the 6-311(++)G\*\* set, which has been reported for similar complexes in the literature. A test of this assumption was performed on the reference molecules H<sub>2</sub>O, H<sub>2</sub>, HNC, HCN, HOCN, HNCO, HCNO, NH<sub>3</sub> and CO using the 6-311(++)G\*\* basis under DFT. The results of this test are shown in Table 7, along with some experimental values extracted from the literature. The thermodynamic values in Table 7 are presented as differences between the combined molecular pair energies and formamide to maintain consistency with Tables 4–6.

Energies of complexation can easily be obtained by subtracting the appropriate table entries. We have included the combined energies of the isolated molecule pairs within all tables. Of the bimolecular

species, the most stable is the NH<sub>3</sub>...CO complex, which is slightly more than 5 kcal mol<sup>-1</sup> less stable than formamide as calculated by the MP2 method, and more than 10 kcal mol<sup>-1</sup> by the DFT method. The second most stable complex is HCN...H<sub>2</sub>O according to the MP2 method, but it is the HNCO...H<sub>2</sub> complex via DFT. Both DFT and MP2 give the isocyanuric acid HNCO...H<sub>2</sub> complex as being *ca.* 70 kcal mol<sup>-1</sup> more stable than the fulminic acid HCNO...H<sub>2</sub> complex.

The optimized geometries of the various structures are generally quite similar over the three computational methods. However, some notable exceptions exist, the most remarkable of which is that of the structure CNO111t is planar in the MP2 and DFT

Table 5

Changes in calculated electronic energies, entropies, enthalpies and free energies ( $\Delta G = \Delta H - 298\Delta S$ ) (MP2)

Structure	$\Delta E$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H(298\text{ K})$ (kJ mol <sup>-1</sup> )	$\Delta G(298\text{ K})$ (kJ mol <sup>-1</sup> )
NCO210	0	0	0	0
NH <sub>3</sub> ...CO	22.31	79.78	16.28	- 7.53
NH <sub>3</sub> + CO	28.90	135.28	18.91	- 21.42
NCO111Ct	47.80	- 4.34	48.58	49.87
NCH...H <sub>2</sub> O	50.18	46.95	40.46	26.44
HCN...H <sub>2</sub> O	61.90	58.86	51.97	34.39
NCO111tt	62.41	- 3.08	62.51	63.43
NCO111tc	65.26	- 1.40	65.10	65.52
NCO111cc	74.96	- 1.83	74.85	75.40
H <sub>2</sub> ...HNCO	75.73	52.47	47.32	31.67
HNCO...H <sub>2</sub>	75.91	72.91	49.87	28.16
HNCO + H <sub>2</sub>	78.72	114.59	48.37	14.18
HCN + H <sub>2</sub> O	79.75	135.50	65.02	24.60
HNC...H <sub>2</sub> O	140.24	60.98	130.12	111.92
HNC + H <sub>2</sub> O	158.71	138.43	143.85	102.59
NCO201t	165.01	- 1.28	165.44	165.81
HOCN...H <sub>2</sub>	175.95	78.91	150.71	127.19
HOCN + H <sub>2</sub>	179.68	117.94	149.79	114.60
NCO201c	193.17	- 1.06	190.96	191.29
CNO201t	221.71	- 1.39	218.28	218.70
CNO201c	243.20	- 1.98	238.24	238.86
CNO300	267.29	5.94	261.12	259.37
CNO210	274.11	- 3.86	271.25	272.42
cyclic	303.47	- 7.51	302.46	304.68
HCNO...H <sub>2</sub>	360.53	71.44	331.25	309.95
HCNO + H <sub>2</sub>	364.56	111.88	330.75	297.40
CNO111c	397.40	- 2.05	394.17	394.80
CNO111t	406.04	2.43	401.87	401.12
CON201c	440.51	4.88	434.51	433.09
CON201t	451.54	6.19	443.96	442.12
CON102	492.77	9.78	486.01	483.08
CON300	501.47	6.21	495.80	493.92

Table 6

Changes in calculated electronic energies, entropies, enthalpies and free energies ( $\Delta G = \Delta H - 298\Delta S$ ) (DFT)

Structure	$\Delta E$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H(298\text{ K})$ (kJ mol <sup>-1</sup> )	$\Delta G(298\text{ K})$ (kJ mol <sup>-1</sup> )
NCO210	0	0	0	0
NCO111ct	53.99	- 7.50	54.98	57.20
NH <sub>3</sub> ...CO	56.93	79.40	51.55	27.91
NH <sub>3</sub> + CO	62.99	132.06	53.68	14.31
NCO111tt	67.98	- 6.28	68.24	70.12
NCO111tc	70.13	- 4.87	70.21	71.63
NCO111cc	80.51	- 5.33	80.63	82.22
H <sub>2</sub> ...HNCO	86.35	71.74	61.59	40.17
HNCO...H <sub>2</sub>	86.36	67.39	61.50	41.42
HNCO + H <sub>2</sub>	88.55	110.98	59.37	26.28
NCH...H <sub>2</sub> O	90.68	42.07	82.59	70.04
HCN...H <sub>2</sub> O	105.44	54.53	97.11	80.88
HCN + H <sub>2</sub> O	122.86	131.94	109.79	70.46
NCO201t	160.07	- 4.82	160.46	161.92
HNC...H <sub>2</sub> O	166.69	56.19	157.11	140.33
NCO201c	183.37	- 4.69	180.58	181.96
HNC + H <sub>2</sub> O	184.90	135.89	170.54	130.00
HOCN...H <sub>2</sub>	204.91	68.78	181.29	160.79
HOCN + H <sub>2</sub>	207.97	114.02	179.66	145.69
CNO201t	215.61	- 4.88	212.76	214.22
CNO201c	237.33	- 5.41	232.84	234.43
CNO210	258.52	- 8.05	256.69	259.12
CNO300	268.60	1.91	262.59	262.04
cyclic	309.67	- 10.58	308.44	311.58
HCNO...H <sub>2</sub>	374.79	54.77	346.73	330.41
CNO111c	375.51	- 4.65	371.37	372.79
HCNO + H <sub>2</sub>	378.30	70.38	345.31	324.30
CNO111t	380.78	0.81	375.60	375.39
CON201c	428.87	- 5.80	423.25	424.97
CON201t	447.82	- 5.78	440.70	442.42
CON102	455.44	12.46	445.05	441.33
CON300	466.02	6.15	457.94	456.10

Table 7

Comparison of calculated enthalpies computed at various levels of theory with experimental values

Structure	$\Delta H$ (HF) (kJ mol <sup>-1</sup> )	$\Delta H$ (MP2) (kJ mol <sup>-1</sup> )	$\Delta H$ (DFT) (kJ mol <sup>-1</sup> )	$\Delta H$ (DFT++) (kJ mol <sup>-1</sup> )	EXP	Ref.
Formamide	0	0	0	0	0	[12,13]
HCN + H <sub>2</sub> O	78.78	65.02	109.79	94.14	74	[14,15]
HCNO + H <sub>2</sub>	422.46	330.75	345.31	350.62		
HNC + H <sub>2</sub> O	122.80	143.85	170.54	153.39	139	[15,16]
HNCO + H <sub>2</sub>	69.96	48.37	59.37	64.22	80	[17]
HOCN + H <sub>2</sub>	171.80	149.79	179.66	183.89		
NH <sub>3</sub> + CO	- 4.60	18.91	53.68	48.91	23	[14,15]
HOCN...H <sub>2</sub>	174.05	150.71	181.29	189.37		
HCNO...H <sub>2</sub>	425.64	331.25	346.73	356.48		
NCH...H <sub>2</sub> O	56.78	40.46	82.59	77.11		
HNCO...H <sub>2</sub>	72.63	49.87	61.50	70.12		
H <sub>2</sub> ...HNCO	72.59	47.32	61.59	70.17		
NH <sub>3</sub> ...CO	- 5.27	16.28	51.55	50.04		
HNC...H <sub>2</sub> O	114.68	130.12	157.11	144.77		

All computations were performed utilizing the 6-311G\*\* basis except (DFT++), which utilized 6-311++G\*\*.

Values are relative to that of formamide (computed by the same method, or - 186 kJ mol<sup>-1</sup> from [12]).

optimized geometry, but not in the HF optimized geometry. The latter geometry places the OH hydrogen atom behind the plane of the molecule as depicted in Fig. 1. The formamide structure is found to be planar in the HF and DFT optimized structure, whereas the MP2 structure exhibits a pyramidal structure, with the  $\text{NH}_2$  moiety  $23.8^\circ$  behind the plane of the molecule as depicted in Fig. 1. This is in agreement with previously published ab initio results of formamide computations [18]. The bimolecular species exhibit variances in the intermolecular distances as a function of computational method, with the HF distances often significantly greater than the MP2 and DFT distances, while the latter methods give distances which are more generally in agreement. The intramolecular bond distances are generally greater via the MP2 and DFT methods than the corresponding HF bond lengths, and again the MP2 and DFT geometries are more often in agreement.

In conclusion, HF, MP2 and B3-LYP methods were applied to a large variety of possible intermediate structures in the reaction of HCN and  $\text{H}_2\text{O}$ . The density functional methods produced structures in general agreement with those computed at the MP2 level, but typically overestimated the thermodynamic properties relative to MP2 and experimental data where available. Both HF and DFT methods, however, failed to predict the pyramidal formamide structure, which has been reported in a microwave study [19].

## References

- [1] H.S. Gutowsky, T.C. Germann, J.D. Auspurger, C.E. Dykstra, *J. Chem. Phys.* 96 (1992) 5808.
- [2] J.O. Jensen, P.N. Krishnan, L.A. Burke, *J. Mol. Struct. (Theochem)* 370 (1996) 245.
- [3] G.B. Bacskay, *Chem. Phys.* 61 (1981) 385.
- [4] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez and J.A. Pople, *GAUSSIAN 94*, Revision D.2, Gaussian, Inc., Pittsburgh, PA, 1995.
- [5] A.T. Pudzianowski, *J. Phys. Chem.* 100 (1996) 4781.
- [6] J. Florián, B.G. Johnson, *J. Phys. Chem.* 99 (1995) 5899.
- [7] J.J. Novoa, C. Sosa, *J. Phys. Chem.* 99 (1995) 15837.
- [8] R.C.M.U. Araújo, M.N. Ramos, *J. Mol. Struct. (Theochem)* 366 (1996) 233.
- [9] W.-G. Han, S. Suhai, *J. Phys. Chem.* 100 (1996) 3943.
- [10] P. Politzer, P. Lane, *J. Mol. Struct. (Theochem)* 388 (1996) 51.
- [11] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [12] A. Bauder, Hs.H. Günthard, *Helv. Chim. Acta* 83 (1958) 670.
- [13] D.R. Stull, E.F. Westrum, Jr. and G.C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley, New York, 1969.
- [14] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, S.M. Bailey, K.L. Churney, R.L. Nutall, *The NBS Tables of Chemical Thermodynamic Properties (NBS Tech Note 270)* *J. Phys. Chem. Ref. Data, Suppl.* 1 (1982) 11.
- [15] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, *JANAF Thermochemical Tables (Third Edition)* *J. Phys. Chem. Ref. Data, Suppl.* 1 (1985) 14.
- [16] C.F. Pau, W.J. Hehre, *J. Phys. Chem.* 86 (1982) 321.
- [17] T.A. Spiglanin, R.A. Perry, D.W. Chandler, *J. Phys. Chem.* 90 (1986) 6184.
- [18] J.S. Kwiatkowski, J. Leszynski, *J. Mol. Struct.* 297 (1993) 277.
- [19] C.C. Costain, J.M. Dowling, *J. Chem. Phys.* 32 (1960) 158.