Proton Affinities of Dicyanogen Isomers: Is There a Preferred Site of Protonation for CNCN?

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A variety of high-level ab initio techniques [including G2(QCI) and CBS-APNO] have been employed to characterize the various isomers of neutral and protonated C_2N_2. Notable findings of this study are the following: first, that the calculated proton affinity of NCCN (655 kJ mol^{-1}) is approximately 20 kJ mol^{-1} below the accepted experimental value, and second that the respective proton affinities of the two terminal atoms of cyanogen cyanide, CNCN, are virtually identical (~692 kJ mol^{-1}). The barrier to unimolecular isomerization between $HCNCN^+$ and $CNCNH^+$ is large; thus, protonation of CNCN at room temperature should generate these two species, as distinct isomers, in comparable amounts. In consequence, we anticipate that the investigation of CNCN protonation presents a considerable experimental challenge.

Introduction

Proton transfer

$$XH^+ + Y \rightarrow YH^+ + X \qquad (1)$$

is one of the fundamental reaction mechanisms observed in the gas-phase ion/molecule chemistry of hydrogenated ions. The phenomenon that such reactions are generally very efficient when exothermic implies that a study of the reactivity of an ion with regard to proton transfer can yield useful thermochemical data which may not otherwise be easily obtainable, and a very extensive database now exists[1,2] of the proton affinities of gas-phase neutrals:

$$XH^+ \rightarrow X + H^+ \qquad (2)$$

where the proton affinity is the enthalpy change associated with reaction **2**.

In the field of gas-phase ion/molecule chemistry, several examples[3−6] have been observed where proton transfer affords a mechanism for isomerization of a protonated ion:

$$ABH^+ + Y \rightarrow [AB\cdots HY]^+ \rightarrow [BA\cdots HY]^+ \rightarrow [BAH\cdots Y]^+ \rightarrow BAH^+ + Y \qquad (3)$$

Such isomerization, which has been variously described as “forth-and-back proton transfer”,[5] “proton shuttling”,[7] and “proton transport catalysis”,[8] is facilitated by the general tendency for different atoms within a molecule to possess different proton affinities. For example, the proton affinities of CO are 427 kJ mol^{-1} for protonation at O,[3] and 594 kJ mol^{-1} for C-atom protonation.[1] Other well-characterized species, such as CN,[4] SiO,[6] and NNO,[5,9] possess smaller, but still considerable, differences in the proton affinities of their terminal atoms.

The small number of reactions of type 3 which have been reported to date reflects several factors: namely, difficulties in distinguishing between isomeric ions; a lack of neutrals having an appropriate intermediate proton affinity; and often the existence of competing product channels such as adduct formation or functional group abstraction. Nevertheless, the potential exists for any two isomeric ions to be distinguished on the basis of their proton-transfer reactivity by virtue of the difference between proton affinities of the different sites on the corresponding neutral.

In the present work, we report the results of high-level ab initio calculations upon neutral and protonated C_2N_2 isomers. The various “CN dimers” NCCN, CNCN, and CNNC have been proposed as likely constituents of dense interstellar clouds,[10,11] and the lowest-energy isomer, NCCN, has been detected within the atmosphere of Titan.[12] Protonation of these species is especially important with respect to their interstellar detection, since the NCCN and CNNC isomers are of $D_{\infty h}$ symmetry and hence do not possess active microwave spectra. Notably, while many experimental[13] and theoretical[11,14] studies of the various C_2N_2 isomers have been reported, $NCCNH^+$ is the only protonated isomer to have been investigated experimentally,[15] and the present work appears to be the first detailed ab initio study of the $C_2N_2H^+$ potential energy surface. Our study suggests, among other things, that the accepted experimental value for the proton affinity of NCCN[1,2,15b−d] may require reevaluation in the light of our ab initio results. We also suggest that identification of the two lowest-energy isomers of protonated cyanogen cyanide, on the basis of their proton-transfer reactivity, may prove especially difficult: unexpectedly, the two terminal atoms of CNCN possess virtually identical proton affinities.

Theoretical Methods

Computational techniques utilized in the present work include the Gaussian-2 (G2),[16] G2(QCI),[17] CBS-Q,[18] and CBS-APNO[19] procedures. All of these, except G2(QCI), are composite techniques which use a sequence of comparatively inexpensive single-point calculations to emulate a more computationally intensive single-point calculation. In the case of G2 and its related techniques, the aim is to produce a result comparable in quality to that of a QCISD(T)/6-311+G(3df,2p) calculation;[16,17] in contrast, the complete basis set methods (CBS) attempt an extrapolation to the complete basis set limit through the use of a sequence of basis sets of various levels of correlation.[18−20] Detailed assessments of the performance of these techniques

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TABLE 1: G2 Total Energies and Enthalpies of Formation for Neutral and Protonated C_2N_2 Isomers

	species	ZPE[a]	$n(i)$[b]	E_0(G2)[c]	$\Delta H°_{f,0}$[d]
I	NCCN	16.252	0	−185.38647	311.2
II	CNCN	15.566	0	−185.34798	412.2
III	CNNC	14.562	0	−185.27234	610.8
IV	CNCN → NCCN TS	12.037[e]	1	−185.29189[f]	559.5[f]
V	CNNC → CNCN TS	11.019[e]	1	−185.22048[f]	747.0[f]
VI	$NCCNH^+$	26.985	0	−185.63347	1191.5
VII	$NC(H)CN^+$	22.600[e]	0	−185.48313[f]	1586.2[f]
VIII	$NC(H)CN^+ \rightarrow NCCNH^+$ TS	18.625[e]	1	−185.49099[f]	1565.5[f]
IX	$CNCNH^+$	26.017	0	−185.60882	1256.2
X	$HCNCN^+$	26.947	0	−185.60971	1253.9
XI	$CN(H)CN^+$	24.950	0	−185.51572	1500.6
XII	$CN(H)CN^+ \rightarrow HCNCN^+$ TS	18.846[e]	1	−185.44813[f]	1678.0[f]
XIII	$CN(H)CN^+ \rightarrow CNCNH^+$ TS	18.095[e]	1	−185.49531[f]	1554.2[f]
XIV	$CNNCH^+$	25.688	0	−185.54385	1426.8
XV	$CN(H)NC^+$	22.676[e]	0	−185.45065[f]	1671.5[f]
XVI	$CN(H)NC^+ \rightarrow CNNCH^+$ TS	18.131[e]	1	−185.43304[f]	1717.7[f]
XVII	$CN(H)NC^+ \rightarrow CNN(H)C^+$ TS	16.589[e]	1	−185.37504[f]	1870.0[f]
XVIII	$CNCNH^+ \rightarrow NCCNH^+$ TS	22.382[e]	1	−185.55166[f]	1406.3[f]
XIX	$CNNCH^+ \rightarrow NCNCH^+$ TS	21.710[e]	1	−185.49007[f]	1568.0[f]
XX	$CN \cdots H \cdots NC^+$	30.168[e]	0	−185.46278[f]	1639.6[f]
XXI	$CN \cdots H \cdots CN^+$	23.774[e]	0	−185.41198[f]	1773.1[f]
XXII	$NC \cdots H \cdots CN^+$	19.126[e]	0	−185.36944[f]	1884.7[f]

[a] Zero-point vibrational energy in mHartrees (1 mHartree = 2.6255 kJ mol^{-1}), obtained at the HF/6-31G* level of theory (corrected by a factor of 0.8929) unless otherwise indicated. [b] Number of imaginary frequencies obtained in the frequency calculation used to determine ZPE. [c] Calculated G2 total energy (in Hartrees), including ZPE. [d] Calculated G2 (zero Kelvin) enthalpy of formation, in kJ mol^{-1}. [e] ZPE obtained for the MP2(full)/6-31G* optimized geometry (and scaled by a factor of 0.9427).[27] [f] G2(ZPE=MP2) value, obtained according to the method given in ref 28.

TABLE 2: G2(QCI), CBS-Q, and CBS-APNO Total Energies and Enthalpies of Formation for Selected Neutral and Protonated C_2N_2 Isomers

	G2(QCI)		CBS-Q		CBS-APNO	
species	E_0[a]	$\Delta H°_{f,0}$[b]	E_0[a]	$\Delta H°_{f,0}$[b]	E_0[a]	$\Delta H°_{f,0}$[b]
NCCN	−185.38702	316.1	−185.39272	311.2	−185.63648	312.0
CNCN	−185.34830	417.7	−185.35446	411.6	−185.59721	415.1
CNNC	−185.27352	614.1	−185.27884	610.2	−185.52144	614.1
$NCCNH^+$	−185.63401	1196.4	−185.64023	1189.6	−185.88402	1190.7
$CNCNH^+$	−185.60986	1259.8	−185.61502	1255.8	−185.85852	1257.7
$HCNCN^+$	−185.61024	1258.8	−185.61436	1257.6	−185.86002	1253.8
$CN(H)CN^+$	−185.51665	1504.1	−185.51925	1507.3	−185.76255	1509.7
$CNNCH^+$	−185.54479	1430.6	−185.55093	1424.1	−185.79483	1424.9

[a] Total energy (including ZPE, at zero Kelvin) in Hartrees. [b] Enthalpy of formation (at zero Kelvin) in kJ mol^{-1}.

have found that all are able to deliver enthalpies of formation[21,22] and proton affinities[23−25] of small molecules to a typical accuracy of ± 6 kJ mol^{-1} or better. All calculations were performed using the GAUSSIAN94 software package.[26]

TABLE 3: Calculated Proton Affinities of C_2N_2 Isomers

	method				
PA[a]	G2[b]	G2(QCI)[b]	CBS-Q[b]	CBS-APNO[b]	expt
NCC***N***	654.0	654.7	655.2	655.3	674.3 ± 4[c,d]
CNC***N***	693.3	692.9	689.1	691.1	
CNCN	690.2	693.9	688.4	696.0	
C***N***CN	446.1	447.7	438.3	439.7	
CNN***C***	719.6	718.4	720.0	723.6	

[a] Proton affinity (at 298 K), in kJ mol^{-1}. [b] Obtained from the calculated 298 K enthalpies for C_2N_2 and $C_2N_2H^+$, and using also the value $H_{0,298}(H^+) = +0.00236$ Hartrees.[23] [c] Ref 15d. [d] A theoretical (CEPA-1) value of 657 ± 5 kJ mol^{-1} has been reported by Botschwina and Sebald.[11]

Results and Discussion

Optimized geometries, for stationary points located upon the MP2(full)/6-31G* potential energy surfaces for C_2N_2 and $C_2N_2H^+$, are detailed in Figures 1−3. Total energies and enthalpies of formation for these species, using the G2, G2(QCI), CBS-Q, and CBS-APNO techniques, are reported in Tables 1 and 2. Proton affinities of C_2N_2 isomers, obtained at various levels of theory, are given in Table 3. Total energies and enthalpies for other species of relevance to the present discussion, calculated using G2 and CBS theory, are listed in Table 4; the calculated proton affinities derived from these values are shown in Table 5.

C_2N_2 Isomerism. While the principal focus of this study is on protonated forms of C_2N_2, it is of some relevance also to assess the performance of G2 and other methods for the C_2N_2 surface itself. Several previous studies of C_2N_2 isomerism have been reported,[11,14a−d,14h] but few such studies have included investigations of the transition states involved.[14c,d] A detailed analysis of this surface has very recently been reported: Ding et al.[14h] have located five minima (the additional species being CCNN, and a cyclic species featuring a CNN three-membered ring) and many transition states to isomerization. The present study therefore samples only a small portion of the surface; however, the linear minima NCCN, CNCN, and CNNC are the three lowest-energy isomers, and the transition states **IV** and **V** identified in our study describe the lowest-energy pathway for interconversion of these species. The calculations of Ding et al.[14h] are at a level of theory (CCSD(T)/6-311G**//B3-LYP/6-311G**) which is expected to be somewhat inferior to G2, CBS-Q, and related methods in its ability to estimate enthalpies of formation; nevertheless, agreement with G2 to within ± 6 kJ mol^{-1} is noted for the relative energies of all species except **V**

TABLE 4: G2, CBS-Q, and CBS-APNO Total Energies and Enthalpies of Formation for Various Species

	G2		CBS-Q		CBS-APNO	
species	E_0[a]	$\Delta H^\circ_{f,0}$[b]	E_0[a]	$\Delta H^\circ_{f,0}$[b]	E_0[a]	$\Delta H^\circ_{f,0}$[b]
HCN	−93.28490[c]	131.0	−93.28618	135.3	−93.40873	134.3
HNC	−93.26209[c]	190.8	−93.26427	192.8	−93.38589	194.3
$HCNH^+$	−93.55388[c]	953.3	−93.55533	957.0	−93.67894	953.5
C_2H_4	−78.41592[c]	62.0	−78.41567	65.1	−78.53220	59.4
$C_2H_5^+$	−78.67358[c]	914.3	−78.67128	922.3	−78.78970	912.0
CH_3Cl	−499.55383	−77.7	−499.56065	−78.4	d	
CH_3ClH^+	−499.79939	806.3	−499.80420	810.4	d	
HCCCN	−169.29975	381.8	−169.30846	371.1	−169.54223	377.0
$HCCCNH^+$	−169.58307	1166.7	−169.59376	1150.3	−169.82732	1157.1

[a] Total energy (including ZPE, at zero Kelvin) in Hartrees. [b] Enthalpy of formation (at zero Kelvin) in kJ mol^{-1}. [c] G2 value previously reported by Smith and Radom.[23] [d] The CBS-APNO technique is not defined for atoms heavier than Ne.[19]

TABLE 5: Calculated Proton Affinities of Various Species

	method			
PA[a]	G2[b]	CBS-Q[b]	CBS-APNO[b]	expt[c]
HC***N***	712.1[d]	712.4	715.2	712.9
HN***C***	772.8	770.7	775.9	772.3
C_2H_4	681.9[d]	676.6	681.5	680.5
CH_3***Cl***	649.8[e]	643.4	f	648.2
HCC***CN***	736.3	754.5	753.8	751.5

[a] Proton affinity (at 298 K), in kJ mol^{-1}. [b] Obtained from the calculated 298 K enthalpies for C_2N_2 and $C_2N_2H^+$, and using also the value $H_{0,298}(H^+) = +0.00236$ Hartrees.[23] [c] From the review of Hunter and Lias.[2] [d] Value previously reported by Smith and Radom.[23] [e] Value previously reported by Glukhovtsev et al.[24] [f] The CBS-APNO technique is not defined for atoms heavier than Ne.[19]

[for which the CCSD(T) value, assessed relative to NCCN, is 12.8 kJ mol^{-1} above the G2 value). The agreement between the two studies thus appears to be good. Our results for the three linear isomers are also in very good agreement with those reported by Botschwina and Sebald;[11] their coupled-electron-pair-approximation calculations, which probably represent the most precise values obtained in any calculations on C_2N_2 isomers, are in agreement with our G2, G2(QCI), CBS-Q, and CBS-APNO relative energies to within ± 5 kJ mol^{-1} in all cases.

Protonation of NCCN. Of the various C_2N_2 isomers, NCCN (dicyanogen) is the only species whose PA has been characterized by experiment. The agreement between the various calculated values reported here is very good—only 1.5 kJ mol^{-1} separates the PA values determined by the G2, G2(QCI), CBS-Q, and CBS-APNO techniques, for protonation at a terminal nitrogen—but there is a significant discrepancy between the theoretical values and those resulting from experimental studies. It is pertinent, therefore, to review the various experimental investigations of this issue.

The proton affinity of C_2N_2 listed in the compilation of Lias et al.[1] is 679 ± 8 kJ mol^{-1}, obtained from a Selected-Ion Flow Tube (SIFT) study by Raksit and Bohme:[15b] this is a bracketed value, based on the occurrence of rapid proton transfer from protonated SO_2 (PA = 676 kJ mol^{-1})[1] to C_2N_2, and from protonated C_2N_2 to C_2H_4 (PA = 680 kJ mol^{-1}),[1] in hydrogen buffer gas at 296 K. Deakyne et al.[15c] have performed a combined experimental and theoretical study, involving ion cyclotron resonance (ICR) bracketing experiments and calculations at levels of theory up to MP3(fc)/6-31+G**/HF/6-31G**. The ICR results yielded PA(C_2N_2) = 674 ± 8 kJ mol^{-1} [based on rapid proton transfer from protonated CF_3CFO (PA = 670 kJ mol^{-1})[1] to C_2N_2 and from protonated C_2N_2 to C_2H_4, and no reaction between protonated C_2H_4 and C_2N_2],[15c] while the calculated value obtained in this study was 668 kJ mol^{-1}. Petrie et al.[15d] also performed a SIFT study, involving measurement of both the forward and reverse reactions for proton transfer between C_2N_2 and C_2H_4, and between C_2N_2 and CH_3Cl (PA = 682 kJ mol^{-1}):[1] this study reported a value PA(C_2N_2) = 674.3 ± 4 kJ mol^{-1}. The experimental measurements are thus in good mutual agreement, with a marginally lower PA value being suggested by the calculations of Deakyne et al.[15c] using a modest level of theory. More serious disagreement between theory and experiment, among the various literature values, involves the CEPA-1 study of Botschwina and Sebald[11] which yielded PA(C_2N_2) = 657 kJ mol^{-1}; the uncertainty ascribed to the latter value is ± 5 kJ mol^{-1}. In the present work, values of 654.0 (G2), 654.7 (G2Q), 655.2 (CBS-Q), and 655.3 (CBS-APNO) kJ mol^{-1} have been determined, in excellent agreement with the value of Botschwina and Sebald[11] but in serious disagreement with all of the experimental values.[15b−d] Why should there be such a discrepancy between the experimental and theoretical results for this proton affinity value?

Some additional points should be noted. The measured equilibrium constant for the reaction

$$C_2N_2H^+ + CH_3Cl \leftrightarrow CH_3ClH^+ + C_2N_2 \qquad (4)$$

indicates that PA(C_2N_2) − PA(CH_3Cl) = 2.1 ± 2 kJ mol^{-1}.[15d] A recent study,[24] combining G2 calculations with high-pressure mass spectrometry measurements of proton-transfer equilibria, has recommended a value of PA(CH_3Cl) = 649.8 kJ mol^{-1}, substantially lower than the longstanding literature value[1] of 682 kJ mol^{-1}. With the incorporation of the low PA(CH_3Cl) value in a revision of the proton affinity scale,[2] the body of measurements for PA(C_2N_2) is no longer internally consistent: the observation[15d] of detectable proton transfer from $C_2N_2H^+$ to CH_3Cl and from $C_2H_5^+$ to C_2N_2 implies that the proton affinities of C_2N_2, C_2H_4, and CH_3Cl, are all fairly close ($\Delta PA < 10$ kJ mol^{-1}), in contradiction with the comparatively large gulf (30 kJ mol^{-1}) separating the current "benchmark" values for PA(C_2H_4) and PA(CH_3Cl).[2,24] We note, also, that other neutrals (CS_2 and CF_3CN) which were previously listed as possessing proton affinities greater than ethylene (PA(CS_2) = 688 kJ mol^{-1}; PA(CF_3CN) = 687 kJ mol^{-1})[1] have now had significantly lower values (675 and 667 kJ mol^{-1}, respectively) recommended as the result of a high-pressure mass spectrometric study of proton-transfer equilibria.[29] In light of these three instances, of compounds (CH_3Cl, CS_2, and CF_3CN) whose experimental proton affinities have recently been "devalued" by between 13 and 32 kJ mol^{-1},[24,29] and given the close consistency between PA values for C_2N_2 obtained from very high-level calculations using several different approaches (CEPA-1,[11] G2 and variants, and CBS), we feel that there is sufficient circumstantial evidence to call into question the literature value for PA(C_2N_2).[30] Indeed, a more detailed experimental reevaluation − of all compounds having listed proton affinities in the vicinity of C_2H_4—may be in order.

A high-energy local minimum, **VII**, involving protonation perpendicular to the NC−CN bond midpoint, is also found on the MP2(full)/6-31G* surface for $C_2N_2H^+$. However, this species corresponds to a transition state on the HF/6-31G* surface, and the G2 total energy for the supposed minimum **VII** is 22.7 kJ mol^{-1} higher than the G2 value for the associated transition state **VIII**; therefore, it appears that only one isomer of protonated NCCN, **VI**, is viable.

Protonation of CNCN. There do not appear to have been any previous studies of CNCN protonation. Analysis of the MP2/6-31G* potential energy surface finds two low-lying linear isomers, $HCNCN^+$ and $CNCNH^+$. G2 calculations of the enthalpies of formation of these species are in good agreement with the G2(QCI) values, as well as those of the various CBS techniques. The assignment of the preferred site of protonation is, at present, too close to call, with all of the high-level calculations indicating that the isomerization process

$$HCNCN^+ \leftrightarrow CNCNH^+ \tag{5}$$

is virtually thermoneutral; the enthalpy change for this process, at 298 K, is calculated to be −3.1, +1.0, −0.7, and +4.9 kJ mol^{-1} using, respectively, the G2, G2(QCI), CBS-Q, and CBS-APNO approaches.

It is interesting to note that, although the calculated $\Delta H°_{f,0}$ values for $HCNCN^+$ and $CNCNH^+$ are higher than that of $NCCNH^+$, the difference is not so great as that between the $\Delta H°_{f,0}$ values of CNCN and NCCN. This phenomenon is, of course, reflected in the respective proton affinities; apparently, protonation serves to reduce (by ~35 kJ mol^{-1}) the instability of the CNCN skeleton. In the case of $HCNCN^+$ production, this is understandable since it results in formation of a carbenium ion from a carbene, but the difference between nitrogen-protonation of CNCN and of NCCN is less easily fathomed. In any event, we anticipate that it will be a significant experimental challenge to distinguish between the two protonated CNCN isomers, or to characterize the true preferred site of protonation. We hazard that, while the proton-transfer reactivity of the two isomers must be virtually identical—implying that an observation of proton shuttling between the two terminal atoms, as in the mechanism described by reaction 3, is extremely unlikely for these isomers—their ion/molecule reactivity may differ in other respects. For example, the species $CNCNH^+$ (which is an isocyanide) may be more prone to association with various neutrals than might be the case for the carbenium ion $HCNCN^+$.[32]

As with protonated NCCN, a high-energy minimum (**XI**) is obtained on the MP2/6-31G* potential energy surface. Unlike **VI**, however, the stability of **XI** is supported by both the HF/6-31G* frequency calculations, and the G2 results which indicate that the smallest barrier to isomerization is 53.6 kJ mol^{-1}. Nevertheless, experimental production of this structure is likely to be extremely inefficient, both because of the relatively low proton affinity of the inner N atom of CNCN and because of the significant bending of the CNC fragment required to produce **XI**.

Protonation of CNNC. Two isomers are seen for protonation of this species. As with the other examples, the linear structure $CNNCH^+$ is by far the lower-energy isomer, and the high-energy structure (**XV**) involves protonation of an inner N atom with a 46.2 kJ mol^{-1} barrier to isomerization. It is interesting to note, also, that although the $\Delta H°_{f,0}$ value for $CNNCH^+$ is the highest of any of the linear isomers of protonated C_2N_2, the proton affinity of the terminal C atoms in CNNC is also the highest PA for any C_2N_2 structure—a further example of protonation stabilizing the carbene skeleton.

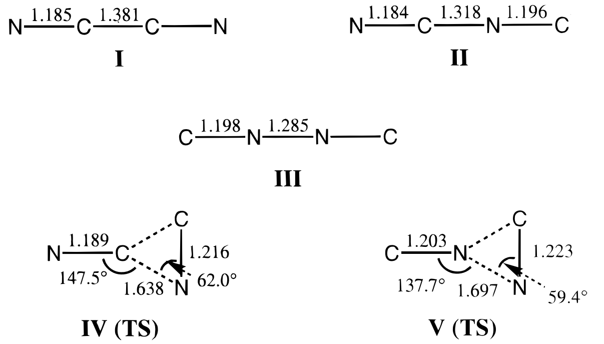

Figure 1. Optimized geometries (bond lengths in Å), obtained at the MP2(full)/6-31G* level of theory, for C_2N_2 isomers and transition states.

No experimental studies of CNNC protonation have been performed, and so the present theoretical measurements cannot readily be assessed against previous results. Nevertheless, the very good agreement seen between G2, G2(QCI), CBS-Q, and CBS-APNO values for these is encouraging.

Isomerism of the (Protonated) Heavy-Atom Skeleton. We have located two transition states (**XVIII** and **XIX**) upon the $C_2N_2H^+$ potential energy surface which relate to the lowest-energy pathways for the interconversions

$$HCNNC^+ \leftrightarrow HCNCN^+ \tag{6}$$

and

$$CNCNH^+ \leftrightarrow NCCNH^+ \tag{7}$$

The G2 total energies for these respective transition states indicate, somewhat unexpectedly, that the most accessible isomerization pathways available to $CNNCH^+$ and $CNCNH^+$ involve rearrangement of the heavy-atom skeleton rather than migration of the proton. Nevertheless, the higher-energy isomer in the interconversions (reactions 6 and 7) is, in each case, protected by a barrier of at least 140 kJ mol^{-1}. Therefore, all four linear isomers of protonated C_2N_2 should exist as isolable species at room temperature.

It is of some interest to compare the barriers to skeletal rearrangement on the neutral and protonated surfaces. The barriers to rearrangement of neutral C_2N_2 isomers

$$CNNC \leftrightarrow CNCN \tag{8}$$

and

$$CNCN \leftrightarrow NCCN \tag{9}$$

are, respectively, found to be 136.2 and 147.3 kJ mol^{-1} above the energy of the higher-energy isomer according to our G2 results. On the protonated surface, the analogous reactions 6 and 7 are impeded by barriers of 141.2 and 150.1 kJ mol^{-1}, respectively. There is thus very little change in barrier height induced by protonation, and we conclude that protonation should have little effect on the prospects for interconversion [except that, since the pathway from $HCNCN^+$ to $HNCCN^+$ is more convoluted (involving the sequence **X** → **XII** → **XI** → **XIII** → **IX** → **XVIII** → **VI**)[34] than the pathway from CNCN to NCCN (involving only **II** → **IV** → **I**), C-protonation of CNCN might be considered as an effective means of stabilizing the CNCN skeleton].

Proton-Bound Dimers. We have located a further three, very high-energy, linear minima upon the $C_2N_2H^+$ singlet

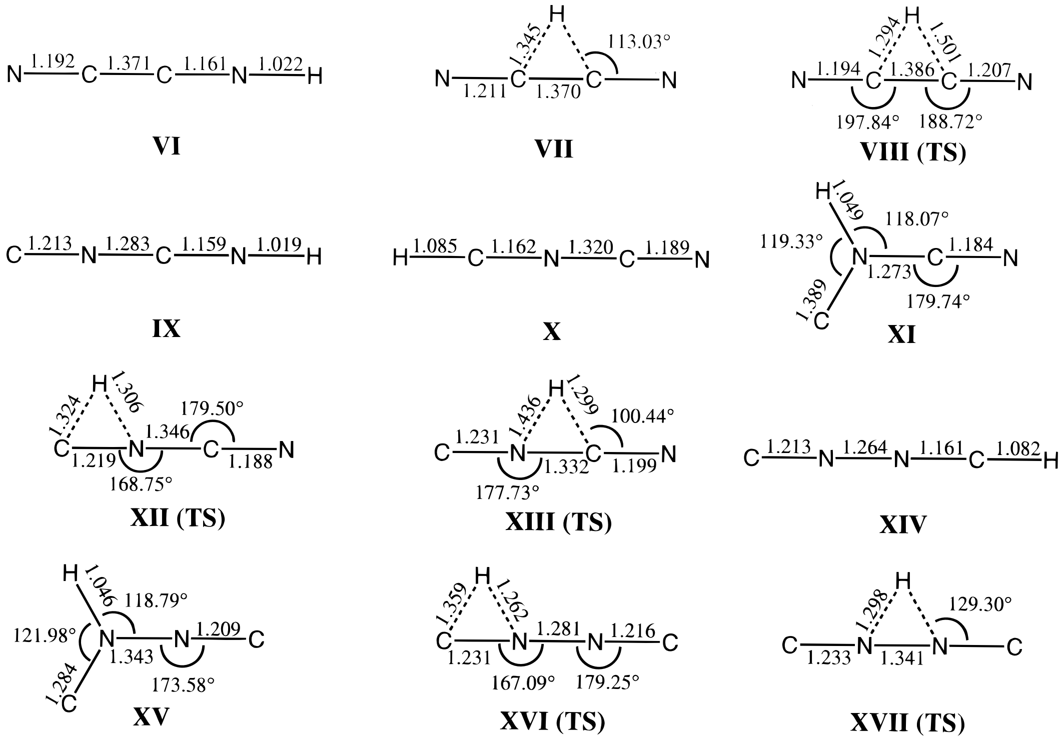

Figure 2. Optimized geometries (bond lengths in Å), obtained at the MP2(full)/6-31G* level of theory, for protonated C_2N_2 isomers and transition states.

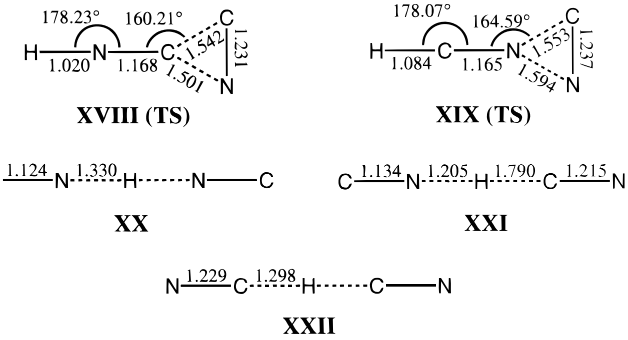

Figure 3. Optimized geometries (bond lengths in Å), obtained at the MP2(full)/6-31G* level of theory, for transition states to (protonated) skeletal C_2N_2 rearrangement, and proton-bound dimers of CN.

potential energy surface. These species are best considered as proton-bound dimers of the CN radical. The lowest-energy of these three species, $[CN{\cdots}H{\cdots}NC]^+$, features the most favorable combination of proton/dipole orientations, while the most unfavorable proton/dipole orientations (viz. $[NC{\cdots}H{\cdots}CN]^+$) give rise to the highest-energy structure. Indeed, $[NC{\cdots}H{\cdots}CN]^+$ is the highest-energy minimum which we have located upon the singlet $C_2N_2H^+$ surface, and of the other proton-bound dimers only $[CN{\cdots}H{\cdots}NC]^+$ has an enthalpy of formation ($\Delta H^\circ_{f,0}$ = 1639.6 kJ mol^{-1} at G2) which is below that of the highest-energy form of any protonated C_2N_2 isomer (namely **XV**, $\Delta H^\circ_{f,0}$ = 1671.5 kJ mol^{-1} at G2). Bonds between the hydrogen and the respective heavy atoms are, in all cases, somewhat long (see Figure 3); this is especially true of the H···C bond in $[CN{\cdots}H{\cdots}CN]^+$. For completeness, it might appear desirable to characterize transition states between these proton-bound dimers and the more conventional protonated C_2N_2 isomers; however, a cursory examination of the MP2/6-31G* surface has failed to reveal any such transition states. Since these species are expected to be comparatively unimportant features on the potential energy surface (by virtue of their very high energies), a more detailed search for the transition states in question does not currently seem warranted. For this reason, also, we have not attempted further high-level calculations [G2(QCI), CBS-Q, or CBS-APNO] to supplement the G2 values for the proton-bound dimers themselves.

Calculations on Related Species. As detailed above, the proton affinities of CNCN and CNNC have not been subjected to previous study, while the theoretical proton affinity for NCCN is in serious disagreement with experimental values[15b−d] for this quantity. It is thus important to test the validity of the various theoretical techniques used here. To this end, we have used various Gaussian-type and CBS model chemistry procedures to characterize the theoretical proton affinities of the structurally related species HCN, HNC, and HCCCN, and of the two species (C_2H_4 and CH_3Cl) to which the proton affinity of NCCN is most closely linked.[15d] Total energies and enthalpies of formation for these neutrals and their corresponding protonated forms are reported in Table 4, while the proton affinities for these species are summarized in Table 5.

It is apparent from Table 5 that the agreement between experiment and the various model chemistries is good, with the exception of the G2 result for PA(HCCCN) which is almost 20 kJ mol^{-1} below the CBS and experimental values. The excellent agreement seen in all cases, between CBS methods and experimental results, adds support to the CBS values (and the very similar results obtained from G2 and G2(QCI)) for the various isomers of protonated C_2N_2.

Conclusions

Calculations using Gaussian-2 and Complete Basis Set model chemistries provide values for the proton affinity of dicyanogen, PA(NCCN) ~ 655 kJ mol^{-1}, which are in excellent agreement with a previous CEPA-1 calculation[11] but in disagreement with previous experimental studies[15b−d] which have indicated a value of ~680 kJ mol^{-1}. We propose that the discrepancy between theory and experiment (as well as the discrepancy inherent in the observation of significant proton transfer from CH_3ClH^+ to C_2N_2, and from $C_2N_2H^+$ to C_2H_4)[15d] constitutes sufficient grounds to call into question the existing experimental value for PA(NCCN).

The two proton affinities PA(***C***NCN) and PA(CNC***N***) are predicted to lie within 3 kJ mol^{-1} of each other, based on the results of high-level calculations at several different levels of theory. Calculations at existing levels of theory appear incapable of unambiguously assigning the lowest-energy isomer of protonated CNCN, and we recommend an experimental investigation of this issue.[30]

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(34) Our G2 calculations indicate that the largest barrier along this sequence is 424.1 kJ mol^{-1} above the total energy of $HCNCN^+$.