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Molecular Structure, Rotational Constants, and Vibrational Frequencies for Ethynamine ($NH_2–C\equiv CH$): A Possible Interstellar Molecule

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Abstract: Ab initio molecular orbital calculations with the STO-3G, 3-21G, and 6-31G* basis sets have been carried out for ethynamine and the related cyanamide molecule. Optimized structures and harmonic vibrational frequencies have been obtained. Ethynamine is found to be nonplanar with a pyramidal amino group. The calculated inversion barrier is 6.9 kJ mol^{-1} (6-31G*). Correction for systematic deficiencies in the basis sets yields a prediction of the r_0 structure and of microwave spectral frequencies for ethynamine. In particular, predictions of 74.1 ± 0.4 and 92.6 ± 0.5 GHz for the 4_{13}–3_{12} and 5_{14}–4_{13} transitions, respectively, may facilitate the possible identification of ethynamine in interstellar space. In a similar manner, vibrational frequencies have been calculated and corrected for systematic deficiencies; these may prove useful in the laboratory identification of ethynamine.

Examination of a list of molecules which have been identified in interstellar space[2] reveals that more than 20% of the total contain either an amino group (NH_3, $NH_2–CN$, $NH_2–CHO$) or a $C\equiv C$ triple bond ($HC\equiv C$, $HC\equiv CH$, $C\equiv C—C\equiv N$, $HC\equiv C—C\equiv C$, $HC\equiv C—C\equiv N$, $CH_3C\equiv CH$, $HC\equiv C—C\equiv C—C\equiv N$, $HC\equiv C—C\equiv C—C\equiv C—C\equiv N$, and $HC\equiv C—C\equiv C—C\equiv C—C\equiv C—C\equiv N$). On this basis, an attractive candidate for a new interstellar molecule is ethynamine ($NH_2—C\equiv CH$), which is the simplest molecule containing *both* these components. Identification of interstellar molecules is generally accomplished by matching observed interstellar emission frequencies with those from authenticated molecules in the laboratory. Unfortunately, in the case of ethynamine no such information on which to base an interstellar search is currently available.

Theory provides, in principle, an alternative source of such information. Several ab initio studies of ethynamine have in fact been reported.[3-12] These include calculations with minimal,[4,6,7,10-12] lobe-function,[5] and split-valence[3,8,9,11,12] basis sets. None of the previous studies, however, were carried out with the possibility of interstellar observation of ethynamine in mind and, consequently, none of the previous calculations have yielded a structure for ethynamine of sufficient accuracy to be useful in predicting reliable microwave transition frequencies.

We have recently carried out a detailed investigation of the vinylamine (ethenamine) molecule,[13] and a study of ethynamine provides a natural extension of this work. In our previous studies of vinylamine,[13] vinyl alcohol,[14] propenenitrile,[15] and aminopropenenitrile,[15] we demonstrated that accurate r_0 structures, thence rotational constants, can be estimated from relatively simple ab initio molecular orbital calculations by correcting the directly calculated results for systematic deficiencies in the basis sets. We use a similar approach here for ethynamine, not only to obtain an empirically corrected r_0 structure but also to obtain empirically corrected vibrational frequencies. Ab initio calculations with complete geometry optimization have been carried out with three different basis sets for ethynamine and the related cyanamide ($NH_2—C\equiv N$) molecule. The predicted r_0 structure, rotational constants for eight isotopic species, microwave transition frequencies, and vibrational frequencies for ethynamine are reported.

Method

Standard ab initio molecular orbital calculations were carried out by using a modified version[16] of the GAUSSIAN 80 system of programs.[17] The geometries were fully optimized by using analytical gradient procedures, and the force constants, thence the vibrational frequencies, were obtained

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Table I. Optimized Structures and Energies for Ethynamine

	STO-3G		3-21G	6-31G*	
parameter	C_s	C_{2v}	$C_s \rightarrow C_{2v}$	C_s	C_{2v}
C≡C	1.170	1.172	1.191	1.187	1.189
C–N	1.407	1.367	1.330	1.357	1.337
C–H	1.062	1.061	1.049	1.055	1.055
N–H	1.031	1.013	0.996	0.999	0.992
∠CCH[a]	180.2	180.0	180.0	179.6	180.0
∠CCN[a]	177.3	180.0	180.0	178.3	180.0
∠CNH	109.8	120.9	120.9	113.8	120.8
∠HNH	107.3	118.2	118.1	111.3	118.5
E[b]	−130.17681	−130.16988	−131.12430	−131.84557	−131.84295
ΔE[c]	0.0	18.2	0.0	0.0	6.9

[a] For definition of the CCH and CCN angles, see Figure 1. [b] E is the total energy (in hartrees). [c] ΔE is the energy (in kJ mol^{-1}) relative to the most stable (C_s or C_{2v}) structure.

Table II. Optimized Structures and Energies for Cyanamide

	STO-3G		3-21G	6-31G*		predicted r_0
parameter	C_s	C_{2v}	$C_s \rightarrow C_{2v}$	C_s	C_{2v}	structure, C_s
C–N	1.399	1.360	1.324	1.344	1.326	1.349
C≡N	1.158	1.160	1.145	1.138	1.140	1.162
N–H	1.031	1.014	0.996	0.998	0.993	1.003
∠CNH	110.4	120.5	120.5	114.5	120.4	114.3
∠HNH	108.8	119.0	119.1	113.2	119.3	112.3
∠NCN	176.7	180.0	180.0	178.2	180.0	178.2
E[a]	−145.99801	−145.99270	−147.08464	−147.90866	−147.90695	
ΔE[b]	0.0	13.9	0.0	0.0	4.5	

[a] E is the total energy (in hartrees). [b] ΔE is the energy (in kJ mol^{-1}) relative to the most stable (C_s or C_{2v}) structure.

by numerical differentiation of the energy gradient. Three different basis sets were used: the minimal STO-3G basis set,[18] the split-valence 3-21G basis set,[19] and the split-valence plus *d*-polarization 6-31G* basis set.[20]

Throughout this paper, total energies are given in hartrees, relative energies in kJ mol^{-1}, bond lengths in angstroms, and bond angles in degrees.

Results and Discussion

Optimized Structures and Calculated Inversion Barriers for Ethynamine. Optimized structures and energies for ethynamine are given in Table I. As was the case for vinylamine,[13] STO-3G and 6-31G* predict that ethynamine is nonplanar with a pyramidal amino group whereas 3-21G predicts a planar C_{2v} structure. This basis-set dependence of the description of the amino group is consistent with previous studies.[21] Vibrational analyses were carried out on the STO-3G, 3-21G, and 6-31G* optimized structures (with the same basis sets as used for optimization) to confirm that they correspond to minima on the appropriate potential energy surfaces. The calculated vibrational frequencies are all found to be real, as required. The 6-31G* results are the most reliable with respect to the pyramidality of the amino group and indicate that ethynamine is nonplanar, with an amino-group geometry very similar to that of vinylamine.

If the amino group is pyramidal, there are no symmetry reasons that the N—C≡C—H chain should be linear; accordingly, both STO-3G and 6-31G* give N—C≡C and C≡C—H angles that differ slightly from 180.0° (Table I). The distortions are, however, very small and, if both these angles are constrained to be 180.0°, the increase in energy is only 0.2 kJ mol^{-1} (6-31G*).

Additional calculations were performed with the STO-3G and 6-31G* basis sets on structures constrained to planarity. A vibrational analysis on the STO-3G planar structure yielded one imaginary frequency, which demonstrates that the planar C_{2v} form is a saddle point on the potential surface; it corresponds to the transition structure for inversion of the amino group.

The calculated barriers to inversion in ethynamine with STO-3G and 6-31G* are 18.2 and 6.9 kJ mol^{-1}, respectively. On the basis of previous experience,[13,22] the true barrier is likely to be close to the latter value. Comparative values for vinylamine are 19.5 (STO-3G),[13] 7.2 (6.31G*),[13] and 4.6 (experimental)[23,24] kJ mol^{-1}, while for cyanamide the values are 13.9 (STO-3G), 4.5 (6-31G*, see below), and 5.4–5.6 (experimental)[25,26] kJ mol^{-1}.

Table III. Corrections for Bonds at Nitrogen, Taken from the Vinylamine and Cyanamide Structure Analyses

	STO-3G			6-31G*		
parameter	vinylamine[a]	cyanamide	average	vinylamine[a]	cyanamide	average
C–N	−0.047	−0.050	−0.049	0.002	0.005	0.004
N–H	−0.025	−0.028	−0.027	0.006	0.005	0.005
∠CNH	3.2	3.9	3.6	−0.9	−0.2	−0.5
∠HNH	2.8	3.5	3.2	−0.6	−0.9	−0.8

[a] From ref 13.

Predicted r_0 Structure for Ethynamine. One of the main aims of the present study was to estimate the r_0 structure and rotational constants for ethynamine in order to facilitate its identification in interstellar space. To this end, the directly calculated geometries were corrected for systematic deficiencies in the basis sets by utilizing data on related molecules for which experimental structures are known. Where possible, we selected experimental r_0 structures; thus, adjustments from theoretical r_e values to vibrationally averaged r_0 values are incorporated in our correction scheme which is straightforward and described in detail elsewhere.[14]

For the C–N bond length and the geometrical parameters associated with the amino group, we have used the average of corrections based on our previous theoretical analysis of vinylamine[13] and a current analysis of cyanamide. Structural parameters for the latter are listed in Table II and include a predicted r_0 structure where the corrections are based on vinylamine (C–N)[13] and propenenitrile (C≡N)[15] together with an adjustment of the

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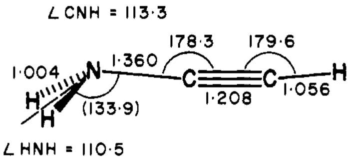

Figure 1. Predicted r_0 structure for ethynamine.

Table IV. Calculated and Experimental Rotational Constants (*A*, *B*, *C*, GHz) for Cyanamide and Vinylamine[a]

species		*A*	*B*	*C*
$NH_2—C≡N$	calcd	309.0	10.107	9.879
	exptl	310.9	10.130	9.866
$^{15}NH_2—C≡N$	calcd		9.831	9.615
	exptl		9.854	9.604
$NHD—C≡N$	calcd		9.592	9.278
	exptl		9.605	9.257
$ND_2—C≡N$	calcd		9.147	8.769
	exptl		9.156	8.743
$NH_2—C≡^{15}N$	calcd		9.781	9.567
	exptl		9.803	9.555
$^{15}ND_2—C≡N$	calcd		8.946	9.585
	exptl		8.956	8.562
$ND_2—C≡^{15}N$	calcd		8.848	8.494
	exptl		8.858	8.470
$NH_2—CH=CH_2$	calcd	56.4	10.011	8.584
	exptl	56.3	10.035	8.565

[a] Evaluated for structures derived by using average corrections from Table III.

Table V. Structural Data for Reference Molecules and Derived Corrections for C≡C and C–H Bonds

molecule	parameter	STO-3G[a]	3-21G[a]	6-31G*[a]	exptl
H—C≡C—H	C≡C	1.168	1.188	1.185	1.207[b]
	C—H	1.065	1.051	1.057	1.058
$CH_3C≡C—H$	C≡C	1.170	1.188	1.187	1.207[c]
	C—H	1.064	1.051	1.057	1.060
F—C≡C—H	C≡C	1.168	1.178	1.178	1.198[d]
	C—H	1.062	1.048	1.055	1.053
corrn	C≡C	0.035	0.019	0.021	
	C—H	−0.007	0.007	0.001	

[a] From ref 12. [b] From ref 29. [c] From ref 30. [d] From ref 31.

Table VI. Calculated Rotational Constants (*A*, *B*, *C*, GHz) for Ethynamine[a]

species	*A*	*B*	*C*
$NH_2—C≡C—H$	306.2	9.305	9.121
$^{15}NH_2—C≡C—H$	305.7	9.064	8.890
$NH_2—^{13}C≡C—H$	306.2	9.301	9.118
$NH_2—C≡^{13}C—H$	306.2	9.009	8.837
$NH_2—C≡C—D$	306.2	8.423	8.272
NHD—C≡C—H	211.0	8.862	8.605
NHD—C≡C—D	210.8	8.035	7.823
$ND_2—C≡C—H$	156.8	8.475	8.166
$ND_2—C≡C—D$	156.7	7.694	7.438

[a] Evaluated for the structure shown in Figure 1.

Table VII. Predicted Rotational Transition Frequencies (GHz) for Ethynamine

transition	frequency	transition	frequency
$1_{01}–0_{00}$	18.4 ± 0.1	$5_{24}–4_{23}$	92.1 ± 0.5
$2_{12}–1_{11}$	36.7 ± 0.2	$5_{23}–4_{22}$	92.1 ± 0.5
$2_{02}–1_{01}$	36.9 ± 0.2	$5_{42}–4_{41}$	92.1 ± 0.5
$2_{11}–1_{10}$	37.0 ± 0.2	$5_{41}–4_{40}$	92.1 ± 0.5
$3_{13}–2_{12}$	55.0 ± 0.3	$5_{33}–4_{32}$	92.1 ± 0.5
$3_{03}–2_{02}$	55.3 ± 0.3	$5_{32}–4_{31}$	92.1 ± 0.5
$3_{22}–2_{21}$	55.3 ± 0.3	$5_{14}–4_{13}$	92.6 ± 0.5
$3_{21}–2_{20}$	55.3 ± 0.3	$6_{16}–6_{15}$	110.0 ± 0.6
$3_{12}–2_{11}$	55.6 ± 0.3	$6_{06}–6_{05}$	110.6 ± 0.6
$4_{14}–3_{13}$	73.3 ± 0.4	$6_{25}–6_{24}$	110.6 ± 0.6
$4_{23}–3_{22}$	73.7 ± 0.4	$6_{24}–6_{23}$	110.6 ± 0.6
$4_{22}–3_{21}$	73.7 ± 0.4	$6_{43}–6_{42}$	110.6 ± 0.6
$4_{32}–3_{31}$	73.7 ± 0.4	$6_{42}–6_{41}$	110.6 ± 0.6
$4_{31}–3_{30}$	73.7 ± 0.4	$6_{52}–6_{51}$	110.6 ± 0.6
$4_{04}–3_{03}$	73.7 ± 0.4	$6_{51}–6_{50}$	110.6 ± 0.6
$4_{13}–3_{12}$	74.1 ± 0.4	$6_{34}–6_{33}$	110.6 ± 0.6
$5_{15}–4_{14}$	91.7 ± 0.5	$6_{33}–6_{32}$	110.6 ± 0.6
$5_{05}–4_{04}$	92.1 ± 0.5	$6_{15}–6_{14}$	111.1 ± 0.6

N–H length and the CNH and HNH bond angles to best fit the observed[25,27,28] microwave rotational constants. The empirical corrections derived for the C–N and N–H lengths and CNH and HNH angles from the predicted r_0 structures for vinylamine and cyanamide are summarized in Table III. As 3-21G predicts a planar structure at the nitrogen atom, the 3-21G results at this center are considered less reliable than STO-3G or 6-31G* results and have therefore not been included in the correction scheme.

The average corrections listed in Table III have been used to derive new structures and rotational constants for cyanamide and vinylamine, as shown in Table IV. The comparison with experiment provides some guide as to the reliability of these corrections when applied to ethynamine.

In order to obtain the empirical corrections for the C–C and C–H bond lengths, we used STO-3G, 3-21G, 6-31G* and experimental structural data for acetylene,[12,29] propyne,[12,30] and fluoroacetylene.[12,13,31] The results are summarized in Table V.

Corrected geometrical parameters for ethynamine are obtained, for each basis set, by adding the corrections listed in Tables III and V to the directly calculated values of Table I. This procedure gives either two or three values for each parameter, and our final prediction is the average of these values. For the angles describing the deviation from linearity of the N—C≡C—H chain, as no relevant experimental data are available, 6-31G* optimized values were used directly.

The resultant structure, i.e., our predicted r_0 structure for ethynamine, is shown in Figure 1. We believe that the geometrical parameters of Figure 1 are predicted to accuracies of within 0.01 Å for the bond lengths and 1° for the bond angles.

The NH_2 group in ethynamine is predicted to be bent by 46.1° from coplanarity with the C–N bond. This is comparable with the degree of nonplanarity predicted for vinylamine (46.3°)[13] and slightly greater than that predicted for cyanamide (42.4°, derived from the data in Table II).

Calculated Rotational Constants and Microwave Spectral Frequencies. The rotational constants based on the structure displayed in Figure 1 are given in Table VI for eight different isotopic species. A sensitivity analysis for the rotational constants shows that the *A* constant is very sensitive to the location of the amino hydrogens but not to the remainder of the structure. The resulting uncertainty in *A* may be as large as 5 GHz. The uncertainties in the *B* and *C* constants are much smaller and in this case dominated by the uncertainties in the N—C and C≡C lengths; they are estimated as ±0.05 GHz. Again, the comparisons in Table IV give some measure of the likely errors.

The large uncertainty in *A* is unlikely to pose a problem in identifying interstellar ethynamine. Ethynamine is a near-prolate asymmetric rotor (calculated $\kappa = -0.9988$), with the dipole moment closely aligned with the *a*-axis. By analogy with cyanamide,[28] we expect that only low *J*, μ_a-type transitions will be observable, and these are insensitive to the value of *A*.

We have used the computed rotational constants (Table VI) to predict, using standard equations for an asymmetric rotor,[32] transition frequencies for ethynamine; these are presented in Table VII. We list only R-branch transitions since the Q-branch frequencies depend on *B*–*C* and have very large uncertainties. The

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Table VIII. Comparison of Calculated and Experimental[a] Rotational Transition Frequencies (GHz) for Cyanamide

	frequency			frequency	
transition	calcd	exptl	transition	calcd	exptl
1_{01}–0_{00}	19.98	19.99	5_{24}–4_{23}	99.93	99.95
2_{12}–1_{11}	39.77	39.73	5_{23}–4_{22}	99.93	99.96
2_{02}–1_{01}	39.97	39.99	5_{42}–4_{41}	99.93	99.93
2_{11}–1_{10}	40.20	40.25	5_{41}–4_{40}	99.93	99.93
3_{13}–2_{12}	59.61	59.59	5_{33}–4_{32}	99.93	100.07
3_{03}–2_{02}	59.96	59.99	5_{32}–4_{31}	99.93	100.07
3_{22}–2_{21}	59.96	59.97	5_{14}–4_{13}	100.50	100.63
3_{21}–2_{20}	59.96	59.97	6_{16}–5_{15}	119.23	119.17
3_{12}–2_{11}	60.30	60.38	6_{06}–5_{05}	119.91	119.97
4_{14}–3_{13}	79.49	79.45	6_{25}–5_{24}	119.92	119.94
4_{23}–3_{22}	79.94	79.96	6_{24}–5_{23}	119.92	119.95
4_{22}–3_{21}	79.95	79.96	6_{43}–5_{42}	119.92	119.91
4_{32}–3_{31}	79.94	80.06	6_{42}–5_{41}	119.92	119.91
4_{31}–3_{30}	79.94	80.06	6_{52}–5_{51}	119.92	119.86
4_{04}–3_{03}	79.94	79.98	6_{51}–5_{50}	119.92	119.86
4_{13}–3_{12}	80.40	80.50	6_{34}–5_{33}	119.92	120.08
5_{15}–4_{14}	99.36	99.31	6_{33}–5_{32}	119.92	120.08
5_{05}–4_{04}	99.93	99.97	6_{15}–5_{14}	120.60	120.75

[a] From ref 28.

errors listed for each band of frequencies are based on a variation of ±0.05 GHz in *B* and *C*, as estimated above. We do not have the information necessary to predict within each band fine structure associated with the effects of centrifugal distortion, nor can we allow for perturbations due to excitation of the NH_2 inversion mode. Corrections due to these factors are, however, likely to be smaller than the quoted uncertainties.

We have carried out a similar determination of the microwave spectral frequencies for cyanamide using the calculated rotational constants of Table IV. The results are compared with experimental frequencies[28] in Table VIII and suggest that the quoted uncertainties for ethynamine (Table VII) are probably overestimated. Of particular interest are the observed[33] interstellar transitions for cyanamide at 80.50 (4_{13}–3_{12}) and 100.63 (5_{14}–4_{13}) GHz for which the calculated frequencies of 80.40 and 100.50 GHz are in good agreement. Corresponding calculated frequencies for ethynamine are 74.1 ± 0.4 (4_{13}–3_{12}) and 92.6 ± 0.5 (5_{14}–4_{13}) GHz. DeFrees and McLean (DM) have noted in a theoretical study of the ethynol molecule[34] that the error in the calculated triplet splittings within specific *J* transitions is less than the error in the individual transitions. We find for cyanamide triplet splittings of 0.46 GHz for the $J = 4$–3 band and 0.57 GHz for the $J = 5$–4 band compared with experimental values of 0.53 and 0.66 GHz, respectively. The errors (0.07 and 0.09 GHz) are considerably larger than the uncertainty (±0.01 GHz) suggested by DM for such splittings for ethynol, and we consider that ±0.01 GHz may be somewhat optimistic. Our ethynamine triplet splittings are calculated to be 0.37 ($J = 4$–3) and 0.46 ($J = 5$–4) GHz. On the basis of the cyanamide results, we suggest as better estimates of the ethynamine splittings 0.43 ($J = 4$–3) and 0.53 ($J = 5$–4) GHz. We hope that these values and perhaps other calculated frequencies from Table VII might be helpful in identifying ethynamine in the laboratory and in interstellar space.

Predicted Vibrational Frequencies for Ethynamine. It is well-known[35] that harmonic vibrational frequencies calculated at the HF/6-31G* level are generally 10–15% greater than observed values, owing partly to the neglect of anharmonicity and partly to the neglect of electron correlation effects. Correction for these errors may be accomplished in an approximate manner by scaling by 0.9, and indeed, for many purposes (e.g., evaluation of zero-point vibrational energies), this is a quite satisfactory procedure.

In order that the calculated frequencies might have useful predictive value, however, it would be desirable to apply such corrections in a more refined manner. The procedure we have used here stems from the observation, based on the data in ref 35 and elsewhere,[36] that errors for certain specific frequencies tend to be roughly constant. For example, the average ratio, $\nu_{\text{exptl}}/\nu_{\text{3-21G}}$, for 26 isolated C–H frequencies[35] is 0.904, with a mean absolute deviation from this value of ±0.010 and a maximum deviation of 0.030. It might be expected that a scheme in which individual frequencies are corrected by appropriate, differing scale factors would yield more precise results than one based on average corrections.

Table IX. Calculated (6-31G*)[a] and Experimental[b] Vibrational Frequencies (cm^{-1}) for Some Molecules Related to Ethynamine

	6-31G*	exptl	$\nu_{\text{exptl}}/\nu_{\text{calcd}}$
NH_2 asym. stretch			
NH_2CN	3890	3365	0.865
NH_2CH_3	3813	3427	0.899
NH_2CHO	3972	3330	0.838
NH_2 sym. stretch			
NH_2CN	3787	3272	0.864
NH_2CH_3	3730	3361	0.901
NH_2CHO	3837	3190	0.831
NH_2 sciss.			
NH_2CN	1804	1585	0.879
NH_2CH_3	1838	1623	0.883
NH_2CHO	1789	1608	0.899
NH_2 twist or rock			
NH_2CN	1323	*c*	*c*
NH_2CH_3	1481	1419	0.958
NH_2CHO	1160	1090	0.940
NH_2 wag			
NH_2CN	691	539	0.780
NH_2CH_3	946	780	0.825
≡C—H stretch			
CH_3CCH	3665	3334	0.910
HCCH (sym)	3719	3374	0.907
HCCH (asym)	3607	3289	0.912
C≡CH bend			
CH_3CCH	797	633	0.795
HCCH (sym)	794	612	0.771
HCCH (asym)	883	730	0.827
C≡C stretch			
CH_3CCH	2419	2142	0.885
HCCH	2247	1974	0.879
C—N stretch			
NH_2CN	1159	1128	0.973
NH_2CH_3	1151	1044	0.907
NH_2CHO	1378	1309	0.950
NC≡C bend[d]			
CH_3CCH	393	328	0.835
NH_2CN	531	532	1.002
CH_3CN	426	362	0.851
CH_2CCH_2	410	354	0.863
NC≡C bend[e]			
CH_3CCH	393	328	0.835
NH_2CN	463	430	0.929
CH_3CN	426	362	0.851
CH_2CCH_2	410	354	0.863

[a] See ref 37. [b] See ref 38. [c] Not assigned; see ref 39. [d] In symmetry plane. [e] Orthogonal to symmetry plane.

To obtain such individual scale factors, we have selected a set of reference molecules whose vibrational motions include modes comparable with the stretching and/or bending motions of ethynamine. The number of molecules available for comparison, however, including those for which calculations were made specifically for the present purposes, is small. Our selection of reference molecules for ethynamine is shown in Table IX along with calculated (6-31G*)[37] and experimental[38] vibrational fre-

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(38) Experimental frequencies for NH_2CN are taken from ref 39, those for NH_2CHO from ref 40 while the remaining values are included in ref 35.

Table X. Calculated (6-31G*) and Predicted Experimental Vibrational Frequencies (cm^{-1}) for Ethynamine

description	symmetry	calcd (6-31G*)	corrn factor[a]	pred exptl
NH_2 asym. stretch	a″	3868	0.865	3346
NH_2 sym. stretch	a′	3771	0.864	3258
C—H stretch	a′	3675	0.910	3344
C≡C stretch	a′	2432	0.885	2152
NH_2 sciss	a′	1815	0.88	1597
NH_2 rock	a″	1330	0.95	1264
C—N stretch	a′	1138	0.97	1104
CCH bend	a″	831	0.795	661
NH_2 wag	a′	754	0.80	603
CCH bend	a′	645	0.795	513
NCC bend	a′	506	0.89	450
NCC bend	a″	426	0.87	371

[a] From data in Table IX; see text.

quencies. For some modes, values of the ratio ν_{exptl}/ν_{calcd}, lie close together (e.g., those for C≡C or ≡C—H stretch), but for others the ratio may vary widely from molecule to molecule. As we have at most four values for comparison and in some cases only two, we are unable to assess magnitudes of probable error. Instead, we show in Table X the calculated (6-31G*) vibrational frequencies for ethynamine along with a correction factor obtained for each mode by judicious selection and/or weighting of those shown in Table IX. We suggest that the resulting "predicted" experimental vibrational frequencies for ethynamine be regarded as midpoints of ranges of up to 100 cm^{-1} within which the corresponding experimental frequency is likely to lie; for the favorable cases noted above (e.g., C≡C and ≡C—H stretch), we believe the experimental frequency may lie within 10 cm^{-1} of that predicted, but in other cases predicted frequencies are subject to much greater uncertainties.

Concluding Remarks

Ethynamine has yet to be synthesized in the laboratory or observed in interstellar space. Theory has the opportunity of contributing to its discovery. We hope that the present predictions of the structure, rotational constants, microwave frequencies, and vibrational frequencies for ethynamine will facilitate its identification, both in the laboratory and in interstellar space.

Acknowledgment. We thank Professor W. M. Irvine for helpful correspondence.

Registry No. NH_2—C≡CH, 52324-04-6; NH_2—C≡N, 420-04-2.

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Nuclear Spin-Spin Coupling via Nonbonded Interactions. 6. The Importance of Bridgehead Interactions on $^1H-^1H$, $^1H-^{13}C$, and $^{13}C-^{13}C$ Coupling Constants in Bicycloalkanes

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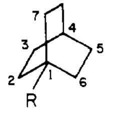
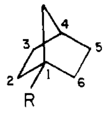
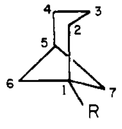
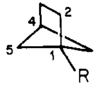
Abstract: Experimental and theoretical methods are used to investigate the importance of the nonbonded interactions associated with the bridgehead carbon atoms (C_{1b} and C_{nb}) of a series of bicycloalkanes and their 1-substituted methyl and carboxylic acid derivatives. Within the $H_1-C_{1b}\cdots C_{nb}-H_n$ and $C_1-C_{1b}\cdots C_{nb}-H_n$ moieties of these compounds, the long-range $^1H_1-^1H_n$, $^{13}C_1-^1H_n$, vicinal $^1H_1-^{13}C_{nb}$, $^{13}C_1-^{13}C_{nb}$, and interbridgehead $^{13}C_{1b}-^{13}C_{nb}$ coupling constants were measured. The trends within these series of compounds are reproduced quite well by the INDO-FPT molecular orbital results; for example, the experimental (calculated) results for coupling between the bridgehead carbon atoms in bicyclo[2.2.2]octane-1-carboxylic acid and bicyclo[1.1.1]pentane-1-carboxylic acid are (+)13.2 (14.2) and (−)25.2 (−24.8) Hz, respectively; the pattern of experimental coupling constants in the series is consistent with the calculated sign change. In contrast to all of the other coupling constants in these series, contributions of nonbonded interactions to the bridgehead coupling constants are small and relatively constant for this type of coupling.

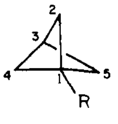
Previous papers from these laboratories[2-5] have demonstrated the importance of nonbonded interactions (NBI), which involve the bridgehead carbon atoms in the series of bicycloalkanes **1–5**, to the $^{13}C-^1H$,[2] $^{13}C-^{13}C$,[2,5] and $^{13}C-^{19}F$[3,4] coupling constants involving the bridgehead carbons (C4 in **1**, **2**, and **4**, C5 in **3**, and C3 in **5**) and the substituent X bonded to the C1 carbon atom. All couplings measured so far increase in magnitude in the series **1** to **5**. However, depending on the number of intervening bonds and which nuclei are coupled, the magnitude of the increase is substantially greater or substantially less than would be expected on the basis of simple additivity of coupling contributions over "equivalent" two- or three-bond paths. Moreover, the long-range $^1H-^{19}F$ coupling constants in the series of compounds **1d–5d** range


1a–d


2a–d


3a–d


4a–d


5a–d

a, R = ^1H, ^2H; b, R = $^{13}CH_3$⁻ c, R = $^{13}CO_2H$; d, R = ^{19}F

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