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Ab Initio Vibrational Analysis of Three Rotamers of 2-Propen-1-Imine, $\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{N}-\text{H}$, and Methanimine, $\text{H}_2\text{C}=\text{N}-\text{H}$

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The results of complete Hartree-Fock (HF)/6-31G geometry optimization and HF/6-31G//HF/6-31G force fields evaluations of three rotamers of the $\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{N}-\text{H}$ molecule (*s-trans-d-trans*-, *s-trans-d-cis*- and *s-cis-d-trans*-2-propen-1-imine) and the $\text{H}_2\text{C}=\text{N}-\text{H}$ molecule are reported. All three conformers were found to be planar with the *s-trans-d-trans* conformer lowest in energy. This was corroborated by further complete optimizations of the geometries of the *s-trans-d-trans* and *s-trans-d-cis* conformers at the HF/6-31G*(5D) level as well as single-point MP4/6-31G**/HF/6-31G*(5D) calculations. The assignment of the vibrational frequencies of the propenimine rotamers and some isotopomers of methanimine are also reported. The majority of the experimental frequencies of propenimine in the gaseous phase are found to belong to the *s-trans-d-trans* form, but a few frequencies are attributed to the high-energy *s-trans-d-cis* conformer.

INTRODUCTION

2-Propen-1-imine is of considerable interest since conformers involving rotation around the single C—C bond as well as *trans* and *cis* positions of the hydrogen atom in the imine moiety are both possible. This leads to four stable rotamers, of which three are shown in Figure 1. The experimental realization of the fourth is highly unlikely.

An analysis of the microwave spectrum of a gaseous sample of propenimine showed that

this substance exists as a mixture of two planar conformers, viz. the *s-trans-d-trans* and *s-trans-d-cis* forms.^{1,2} The *s-trans-d-trans* conformer was expected to be more stable.^{1,2} (Here *s* means the single bond, *d* is for double bond, *s-trans* denotes the *trans* position with respect to the single C—C bond, *d-cis* is the *cis* position concerning the double C=N bond). An *ab initio* analysis of the rotational isomerism in this compound at the HF/4-31G and HF/4-31G(N*) levels corroborated this conclusion.³⁻⁶ Contrary to experimental

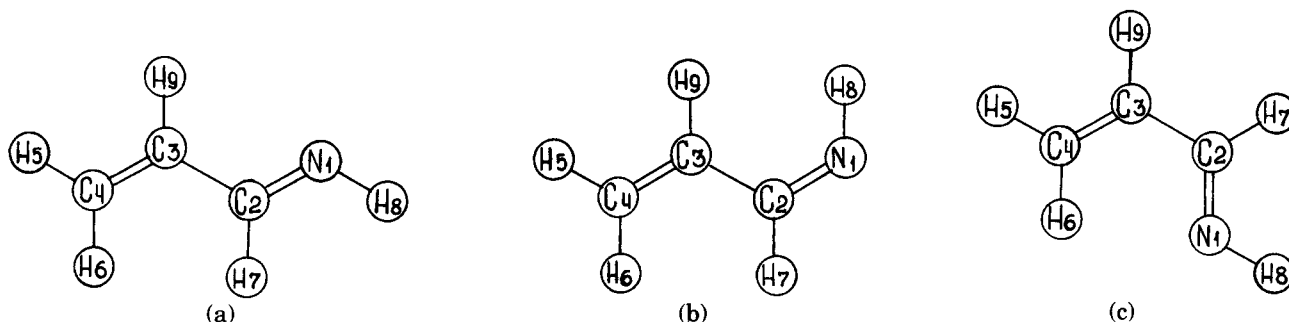


Figure 1. Three rotamers of 2-propen-1-imine: (a) is *s-trans-d-trans*, (b) is *s-trans-d-cis* and (c) is *s-cis-d-trans*.

data^{1,2} the STO-3G basis set favors the conformer (*s-trans-d-cis*) as the lower energy structure.³ Later the influence of internal rotation on electronic structure of this molecule was studied.^{7,8}

The infrared vibrational spectrum of a mixture of these conformers was recently investigated.^{5,6,9} In refs. 5 and 6, the effective force constants were obtained by revising the diagonal constants starting from the *ab initio* values [HF/4-31G(N*)//HF/4-31G(N*)], with off-diagonal constants fixed to the *ab initio* values. The observed frequencies as assigned to certain vibrations were involved in the corresponding least-squares fitting.^{5,6}

In this connection it is of interest to repeat an *ab initio* analysis of the structures, energy differences, and vibrational spectra of the propenimine rotamers using more complete basis sets and assessing the effect of electron correlation. Besides, it is desirable not to involve the experimental vibrational frequencies of these rotamers, unlike the analysis of refs. 5 and 6.

In order to obtain a set of scale factors for the vibrational analysis of the =N—H moiety it was necessary to repeat an *ab initio* analysis of the vibrational frequencies of methanimine at the HF/6-31G level. The experimental spectra of methanimine under high resolution were recently measured.^{10–12} Earlier vibrational frequencies of its isotopomers can be found in refs. 13 and 14. Recently *ab initio* calculations of the vibrational frequencies,^{13,15–17} and geometry^{13,17–20} were reported and will be compared to results of this work.

COMPUTATIONAL DETAILS

Optimization of the geometry of the 2-propen-1-imine rotamers (*s-trans-d-trans*, *s-trans-d-cis* and *s-cis-d-trans* conformers) and methanimine was carried out using the standard gradient technique at the HF//6-31G level with the Gaussian-82 program²¹ (Tables I and II). For the *s-trans-d-trans* and *s-trans-d-cis* conformers the geometry was also optimized at the HF/61-31G*(5D) level²⁴ (see Table III). Single-point calculations of the total energy were also performed at the

MP2/6-31G//HF/6-31G and MP2,3,4SDQ/6-31G*//HF/6-31G*(5D) levels²⁵ (Table III).

Sets of force constants for methanimine and three conformers of 2-propen-1-imine were obtained at the HF/6-31G//HF/6-31G level using the FREQ=ANAL option in Gaussian-82.

The starting force constant matrix in cartesian coordinates for methanimine was transformed into the local symmetry (valence) coordinates.²⁶ The list of these coordinates is given in Table IV. The procedure of scaling is reduced to congruent transformation of the force constant matrix.²⁷ As starting scale factors the value 0.8 was taken since it is well known that *ab initio* calculations usually overestimate the values of vibrational frequencies by ~20%. Results of computing the vibrational frequencies of methanimine and its isotopomers with this set of scale factors for its force field are given in Table V (column A). Then the 0.8 factors were refined by the least-squares method, controlling the Jacobian ill condition by the singular expansion method.²⁸ In the refinement procedure of the scale factors, the experimental frequencies of the H₂CNH, D₂CNH, and H₂CND molecules were involved. The calculated vibrational frequencies with the refined scale factors for the force constants are collected in columns B of Table V.

The set of scale factors obtained for the =N—H moiety and the corresponding scale factors from H₂C=CH—HC=CH₂²⁹ (Table VI) were employed to calculate the scaled force fields of the three conformers of propenimine in the local symmetry coordinates (Fig. 1 and Table VII). The scaled quantum mechanical (SQM) force fields of the methanimine molecule and the 2-propen-1-imine rotamers are given in Tables VIII and IX.

The resulting SQM force fields of the propenimine rotamers are *a priori* in the sense that they do not make any direct use of the experimental information of the propenimine molecule. However, they do involve the transfer of experimental information from the related molecules mentioned above in the form of the scale factors.³⁰

Table X contains the computed vibrational frequencies of the three propenimine rotamers.

Table I. Experimental and calculated geometry of methanimine (angstroms, degrees, and atomic units).

Parameter	Experimental ^{1a,b} (22,23)	Ab initio calculation							
		STO-3G (19)	4-31G (13)	7.3/3 (20)	4-31G* (13)	4-31G(N*) (13)	6-31G* (17)	MP2/ 6-31G* (17)	6-31G this work
$r(\text{N}-\text{H})$	1.021	1.049	1.008	1.018	1.007	1.008	1.006	1.027	1.007
$r(\text{C}-\text{H})_{\text{cis}}$	1.092	1.091	1.079	1.081	1.082	1.080	1.084	1.097	1.080
$r(\text{C}-\text{H})_{\text{trans}}$	1.092	1.089	1.073	1.075	1.078	1.076	1.080	1.091	1.074
$r(\text{C}=\text{N})$	1.273	1.274	1.257	1.257	1.247	1.252	1.250	1.283	1.261
$\angle \text{C}=\text{N}-\text{H}$	110.4	109.0	115.8	114.1	111.5	111.3	111.5	109.8	115.8
$\angle \text{N}=\text{C}-\text{H}_{\text{cis}}$	125.1	125.0	124.7	125.2	124.5	124.5	124.7	125.3	124.6
$\angle \text{N}=\text{C}-\text{H}_{\text{trans}}$	117.9	119.0	119.2	119.1	119.7	119.5	119.2	118.4	119.0
Energy (a.u.)									-93.98145

^aPseudo-Kraitchman structural parameters (22).^bCostain Uncertainties for the $\text{N}-\text{H}$, $\text{C}-\text{H}_{\text{cis}}$, $\text{C}-\text{H}_{\text{trans}}$, and $\text{C}=\text{N}$ bonds are 0.017, 0.081, and 0.077, and 0.008 Å respectively, for $\angle \text{C}=\text{N}-\text{H}$, $\angle \text{N}=\text{C}-\text{H}_{\text{cis}}$ and $\angle \text{N}=\text{C}-\text{H}_{\text{trans}}$ angles are 4.3°, 6.5°, and 7.0° respectively.

Table II. Experimental and calculated geometry of three rotamers of 2-propen-1-imine (angstroms and degrees)^a.

Parameter	<i>s-trans-d-trans</i>						<i>s-trans-d-cis</i>						<i>cis-trans</i>	
	Calculated						Calculated						Calculated	
	Exp. ^c (1)	4-31G (4)	4-31G (N*) (5,6)	6-31G this work	6-31G *(5D) this work	6-31G *(5D) this work	4-31G (4)	4-31G (N*) (5,6)	6-31G this work	6-31G *(5D) this work	4-31G (4)	6-31G this work	4-31G (4)	6-31G this work
$r(N1=C2)$	1.274	1.262	1.256	1.266	1.256	1.256	1.261	1.255	1.266	1.255	1.255	1.262	1.262	1.266
$r(C2-C3)$	1.454	1.460	1.465	1.464	1.471	1.471	1.467	1.470	1.469	1.475	1.475	1.469	1.469	1.472
$r(C3=C4)$	1.336	1.322	1.320	1.326	1.322	1.322	1.321	1.321	1.326	1.321	1.321	1.321	1.321	1.326
$r(N1-H8)$	1.014	1.014	1.006	1.005	1.005	1.005	1.018	1.008	1.009	1.007	1.007	1.014	1.014	1.005
$r(C2-H7)$	1.086 ^b	1.087	1.084	1.083	1.086	1.086	1.082	1.078	1.077	1.082	1.082	1.085	1.085	1.082
$r(C3-H9)$	1.086 ^b	1.077	1.074	1.074	1.076	1.076	1.081	1.075	1.077	1.078	1.078	1.078	1.078	1.075
$r(C4-H5)$	1.086 ^b	1.078	1.075	1.072	1.075	1.075	1.078	1.073	1.072	1.075	1.075	1.078	1.078	1.073
$r(C4-H6)$	1.086 ^b	1.081	1.071	1.075	1.077	1.077	1.080	1.071	1.075	1.076	1.076	1.078	1.078	1.072
$\angle C2-N1-H8$	111.7	115.0	111.1	115.6	111.6	111.6	114.9	111.8	115.7	111.7	111.7	115.0	115.0	115.6
$\angle N1=C2-C3$	121.5	121.4	121.9	121.1	121.1	121.1	126.5	127.7	126.7	126.8	126.8	122.9	122.9	122.7
$\angle C2-C3=C4$	122.9	123.2	122.2	123.2	122.8	122.8	123.4	122.4	123.0	122.7	122.7	124.0	123.9	123.9
$\angle C3=C4-H5$	120.0 ^b	122.0	121.3	121.9	121.8	121.8	121.8	121.6	121.9	121.8	121.8	121.0	121.5	121.5
$\angle C3=C4-H6$	120.0 ^b	121.9	122.5	121.9	121.8	121.8	121.8	122.4	121.7	121.6	121.6	121.5	121.5	121.0
$\angle C2-C3-H9$	120.0 ^b	115.4	116.0	115.2	115.7	115.7	116.5	117.2	116.8	116.9	116.9	115.8	115.9	115.9
$\angle C3-C2-H7$	120.0 ^b	115.9	115.0	116.1	115.7	115.7	115.8	115.0	116.3	115.8	115.8	115.0	115.0	115.2

^aFor numbering of atoms see Fig. 1.^bAssumed values from ref. 1.^cr, parameters. Standard deviations are listed in ref. 1 only for the parameters N1=C2, C3=C4 and ∠C2-C3=C4 and are 0.002Å, 0.002Å, and 0.2°, respectively.

Table III. The total energy of the 2-propen-1-imine rotamers at different computational levels (a.u.) and energy difference $\Delta E = E_{Tc} - E_{Tr}$ (kcal/mol).

Computational level	<i>s-trans-d-trans</i>	<i>s-trans-d-cis</i>	ΔE	<i>s-cis-d-trans</i>	<i>s-cis-d-cis</i>
1. HF/STO-3G (3)	-168.76958	-168.76996	-0.24	-168.76824	-168.76751
2. HF/4-31G (3)	-170.66209	-170.66066	0.90	-170.65906	-170.65626
3. HF/4-31G (4)	-170.66516	-170.66341	1.10	-170.66229	-170.65910
4. HF/4-31G(N*) (5,6)	-170.69672	-170.69554	0.74		
5. HF/6-31G ^a	-170.84672	-170.84468	1.2 ₈	-170.84302	
6. HF/6-31G*(5D) ^b	-170.91972	-170.91838	0.8 ₄		
7. HF/6-311G**(5D) ^b	-170.96622	-170.96465	0.9 ₈		
8. HF/6-31G*(6D) ^b	-170.92052	-170.91913	0.8 ₇		
9. MP2/6-31G//HF6-31G	-171.22273	-171.22071	0.7 ₄	-171.21927	
10. MP2/6-31G*(6D) ^b	-171.45374	-171.45243	0.8 ₂		
11. MP3/6-31G*(6D) ^b	-171.48126	-171.47996	0.8 ₂		
12. MP4SDQ/6-31G*(6D) ^b	-171.48987	-171.48871	0.7 ₃		

^aStarting from HF/6-31G all the calculations were performed in the present work.^bAt HF/6-31G*(5D) geometry.**Table IV.** Definition of local symmetry coordinates of methanimine.

Number	Description	Definition
1	$\nu(\text{C}=\text{N})\text{str.}$	$r(\text{C1}=\text{N2})$
2	$\nu(\text{C}-\text{H})\text{str.}$	$r(\text{C1}-\text{H3})$
3	$\nu(\text{C}-\text{H})\text{str.}$	$r(\text{C1}-\text{H5})$
4	$\nu(\text{N}-\text{H})\text{str.}$	$r(\text{N2}-\text{H4})$
5	$\delta(=\text{CH}_2)\text{sci.}$	$(2 \angle \text{H5}-\text{C1}-\text{H3} - \angle \text{N2}=\text{C1}-\text{H3} - \angle \text{N2}=\text{C1}-\text{H5})/\sqrt{6}$
6	$\rho(=\text{CH}_2)\text{rock.}$	$(\angle \text{N2}=\text{C1}-\text{H3} - \angle \text{N2}=\text{C1}-\text{H5})/\sqrt{2}$
7	$\delta(\text{C}=\text{N}-\text{H})\text{bend.}$	$\angle \text{C1}=\text{N2}-\text{H4}$
8	$\chi(=\text{CH}_2)\text{wag.}$	$\text{N2 out of H3}-\text{C1}-\text{H5 plane}$
9	$\tau(=\text{CH}_2)\text{twist.}$	$(\tau_{3124} + \tau_{5124})/2$

DISCUSSION

Methanimine

Comparison of the results for the methanimine geometry calculations using different basis sets^{13,17,19,20} with the microwave data^{22,23} shows that the completeness of the basis set and account of electron correlation affect primarily the estimates of the internuclear distances, see the C=N bond length in Table I for example. The use of the polarization functions has a favorable effect on the valence angles. Indeed, for the C=N—H angle the best results were obtained for the basis sets including polarization functions (Table I).

The vibrational frequencies assignment as obtained in the present work for the H₂CNH and H₂C¹⁵NH molecules coincide with that of refs. 13, 15–17. It should be noted that the assignment of the experimental frequencies may be carried out from the calculated variant A (Table V). Indeed, the calculations suggest the following changes in assignment.

In the case of D₂CNH the assignment of the experimental bands at 1280 cm⁻¹ and at 1074 cm⁻¹ was mutually interchanged in comparison with the assignment in ref. 13. In the experimental spectrum of H₂CND molecule¹³ the assignments of the 1256 cm⁻¹ and 857 cm⁻¹ bands and the out-of-plane vibrational bands at 1062 cm⁻¹ and 946 cm⁻¹ were changed. In the heavy methanimine, D₂CND, the bands at 1067 cm⁻¹, 821 cm⁻¹, and 770 cm⁻¹ were also reassigned in comparison with that of Ref. 14.

The behavior of rocking vibration ν_7 of the methylene moiety $\rho(=\text{CH}_2)_{\text{rock}}$, in the series of the methanimine isotopomers is of definite interest. In the case of the D₂CNH molecule the position of this band decreases by almost 200 cm⁻¹ with respect to the light methanimine (Table V). In the H₂CND spectrum it increases by approximately 200 cm⁻¹. The latter effect is connected with inverse isotopic shift (see, for example, ref. 31). In the heavy methanimine, D₂CND, these two effects, the direct and inverse isotopic shifts, compensate

Table V. Experimental and calculated vibrational frequencies of methanimine (cm^{-1}).

Assignment	Sym.	$\text{H}_2\text{C}=\text{NH}$			$\text{H}_2\text{C}=\text{N}^{15}\text{H}$			$\text{D}_2\text{C}=\text{NH}$			$\text{H}_2\text{C}=\text{ND}$			$\text{D}_2\text{C}=\text{ND}$		
		Exptl.		Calc.		Exptl.	Calc.		Exptl.	Calc.	Exptl.	Calc.		Exptl.	Calc.	
		(10-12) ^a	A	B	A		(13) ^a	A	B	(13) ^a	A	B	(14) ^b	A	B	
$\nu(\text{N}-\text{H})_{\text{str.}}$	a'	3262.6	3298	3266	3290	3237	3290	3259	3265	3297	2417	2393	—	2420	2396	
$\nu(=\text{CH}_2)_{\text{a.str.}}$		3024.5	3019	3033	3019	3037	3019	3033	2269	3017	3020	3034	2269	2247	2258	
$\nu(=\text{CH}_2)_{\text{s.str.}}$		2914.2	2910	2924	2910	2905	2910	2924	2175	2918	2911	2925	2184	2135	2141	
$\nu(\text{C}=\text{N})_{\text{str.}}$		1638.3	1670	1646	1625	1625	1655	1633	1580	1630	1658	1636	1577	1587	1558	
$\delta(=\text{CH}_2)_{\text{sci.}}$		1452.0	1464	1457	1445	1445	1455	1446	1074	1079	1460	1452	—	1089	1097	
$\delta(\text{C}=\text{N}-\text{H})_{\text{bend.}}$		1344.3	1320	1345	1336	1336	1313	1338	1280	1249	1283	857	770	751	764	
$\rho(=\text{CH}_2)_{\text{rock.}}$		1058.2	1039	1054	—	—	1038	1054	867 ^b	855	861	1256 ^b	1067	1048	1059	
$\tau(=\text{CH}_2)_{\text{tw.}}$	a''	1127.0	1143	1127	1130	1130	1140	1124	1032	1054	946	951	821	831	813	
$\chi(=\text{CH}_2)_{\text{wag.}}$		1060.8	1108	1063	1059	1059	1107	1062	849	883	847	1108	—	893	863	

^aThe IR spectrum in the gas phase.^bThe IR spectrum in the Ar matrix.

Table VI. Scale factors of methanimine and 2-propen-1-imine.

Number	Type of scale factor	Methanimine	Propenimine
1	C—C stretch	—	0.8514 ^a
2	C=C stretch	—	0.7573 ^a
3	C—H stretch	0.8077	0.8301 ^a
4	C=C—C, C=C—H in-plane	0.8042	0.7944 ^a
5	C—C torsion	—	0.9979 ^a
6	C=C twist	—	0.7980 ^a
7	C=N stretch	0.7658	0.7658
8	N—H stretch	0.7848	0.7848
9	C=N—H bend	0.8521	0.8521
10	C=N twist	0.7777	0.7777
11	=C—H rock /	—	0.7290 ^b
12	C—H, =CH ₂ wag	0.7358	0.6706 ^a

^aScale factors transferred from butadiene-1,3 (29).^bThe value of this scale factor was fitted for the 1251 cm⁻¹ band of vinyl group (ν_{32}) in hexatriene-1,3,5 (30).

Table VII. Definition of local symmetry coordinates of 2-propen-1-imine.

Number	Description	Definition
1	$\nu(\text{C}—\text{C})$ str.	$r(\text{C2}—\text{C3})$
2	$\nu(\text{C}=\text{C})$ str.	$r(\text{C1}=\text{C2})$
3	$\nu(\text{C}=\text{N})$ str.	$r(\text{C3}=\text{N4})$
4	$\nu(\text{C}—\text{H})$ str.	$r(\text{C1}—\text{H5})$
5	$\nu(\text{C}—\text{H})$ str.	$r(\text{C1}—\text{H6})$
6	$\nu(\text{C}—\text{H})$ str.	$r(\text{C2}—\text{H7})$
7	$\nu(\text{C}—\text{H})$ str.	$r(\text{C3}—\text{H9})$
8	$\nu(\text{N}—\text{H})$ str.	$r(\text{N4}—\text{H8})$
9	$\delta(\text{C}=\text{C}—\text{C})$ bend.	$\angle \text{C1}=\text{C2}—\text{C3}$
10	$\delta(\text{N}=\text{C}—\text{C})$ bend.	$\angle \text{N4}=\text{C3}—\text{C2}$
11	$\delta(\text{C}—\text{H})$ bend.	$(\angle \text{C1}=\text{C2}—\text{H7} - \angle \text{C2}=\text{C2}—\text{H7})/\sqrt{2}$
12	$\delta(\text{C}—\text{H})$ bend.	$(\angle \text{C2}—\text{C3}—\text{H9} - \angle \text{N4}=\text{C3}—\text{H9})/\sqrt{2}$
13	$\delta(=\text{CH}_2)$ sci.	$(2\angle \text{H5}—\text{C1}—\text{H6} - \angle \text{C2}=\text{C1}—\text{H5} - \angle \text{C2}=\text{C1}—\text{H6})/\sqrt{6}$
14	$\rho(=\text{CH}_2)$ rock.	$(\angle \text{C2}=\text{C1}—\text{H5} - \angle \text{C2}=\text{C1}—\text{H6})/\sqrt{2}$
15	$\delta(\text{C}=\text{N}—\text{H})$ bend.	$\angle \text{C3}=\text{N4}—\text{H8}$
16	$\chi(\text{C}—\text{H})$ wag.	H7 out of C1=C2—C3 plane
17	$\chi(\text{C}—\text{H})$ wag.	H9 out of C2—C3=N4 plane
18	$\chi(=\text{CH}_2)$ wag.	C2 out of H5—C1—H6 plane
19	$\tau(\text{C}—\text{C})$ tors.	$(\tau_{1234} + \tau_{1239} + \tau_{7234} + \tau_{7239})/2$
20	$\tau(=\text{CH}_2)$ twist.	$(\tau_{5123} + \tau_{5127} + \tau_{6123} + \tau_{6127})/2$
21	$\tau(\text{C}=\text{N})$ twist.	$(\tau_{2348} + \tau_{9348})/2$

Table VIII. Scaled quantum mechanical (SQM) force field of methanimine (mdyn/A, mdyn, mdyn × Å)^a.

	1	2	3	4	5	6	7	8	9
1	10.420								
2	0.201	4.761							
3	0.201	0.034	5.007						
4	-0.012	0.025	-0.017	5.908					
5	-0.289	0.072	0.062	-0.005	0.493				
6	-0.072	0.100	-0.095	-0.078	0.0	0.684			
7	0.477	-0.056	0.006	0.222	-0.010	-0.051	0.784		
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.318	
9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.21	0.095

^aFor definition of internal coordinates see Table IV.

Table IX. Scaled quantum mechanical (SQM) force field of *s-trans-d-trans*-, *s-trans-d-cis*-, and *s-cis-d-trans*-2-propen-1-imine (mdyn/Å, mdyn, mdyn × Å).^a

<i>s-trans-d-trans</i>									
	1	2	3	4	5	6	7	8	9
1	5.103								
2	0.277	8.584							
3	0.473	-0.060	10.131						
4	-0.007	0.045	0.013	5.230					
5	0.0	0.068	0.003	0.026	5.131				
6	0.032	0.050	0.013	0.012	-0.004	5.186			
7	0.052	0.025	0.199	-0.001	0.012	0.005	4.792		
8	-0.016	0.010	-0.033	0.002	0.002	-0.005	0.024	5.997	
9	0.197	0.185	0.085	0.043	-0.058	-0.138	-0.037	0.017	1.038
10	0.229	0.090	0.320	0.015	0.001	-0.069	-0.168	0.099	0.179
11	-0.158	0.165	0.017	-0.009	0.024	-0.014	-0.021	0.008	-0.009
12	0.172	-0.010	-0.223	-0.003	0.011	0.020	0.016	0.031	-0.045
13	-0.007	-0.195	-0.005	0.057	0.057	-0.005	-0.007	-0.002	-0.016
14	0.034	0.010	0.022	0.095	-0.107	-0.027	-0.003	0.003	0.087
15	0.009	0.003	0.478	0.001	0.0	0.005	-0.054	0.222	0.020
	10	11	12	13	14	15			
10	1.253								
11	0.079	0.451							
12	0.056	-0.033	0.533						
13	-0.014	-0.013	-0.002	0.449					
14	0.010	-0.036	0.0	0.005	0.525				
15	0.070	-0.005	0.019	-0.001	0.003	0.782			
	16	17	18	19	20	21			
16	0.237								
17	-0.017	0.307							
18	0.024	-0.006	0.245						
19	0.007	0.0	0.003	0.032					
20	0.002	-0.018	0.0	0.006	0.127				
21	-0.012	0.021	-0.004	0.003	-0.007	0.091			
<i>s-trans-d-cis</i>									
	1	2	3	4	5	6	7	8	9
1	4.882								
2	0.264	8.592							
3	0.424	-0.084	10.095						
4	-0.009	0.042	0.009	5.229					
5	-0.006	0.063	-0.004	0.023	5.156				
6	0.043	0.063	0.051	0.013	-0.001	5.048			
7	0.059	0.026	0.211	-0.001	0.011	0.002	5.023		
8	0.015	-0.008	0.007	0.001	0.0	0.010	-0.011	5.840	
9	0.214	0.179	0.072	0.042	-0.057	-0.155	-0.037	-0.021	1.032
10	0.205	0.069	0.108	0.014	-0.004	-0.044	-0.144	-0.101	0.202
11	-0.158	0.177	0.012	-0.008	0.025	-0.004	-0.018	-0.018	-0.011
12	0.179	-0.012	-0.288	-0.004	0.010	0.022	0.008	-0.039	-0.041
13	-0.004	-0.196	0.0	0.057	0.054	-0.007	-0.007	0.002	-0.014
14	0.033	0.008	0.019	0.093	-0.103	-0.033	-0.004	0.004	0.080
15	-0.046	-0.012	0.458	-0.002	-0.005	0.015	0.005	0.234	0.001
	10	11	12	13	14	15			
10	1.213								
11	0.059	0.471							
12	0.053	-0.032	0.527						
13	0.013	-0.014	-0.003	0.447					
14	0.013	-0.037	-0.001	0.004	0.524				
15	0.039	-0.005	-0.029	0.002	-0.002	0.779			
	16	17	18	19	20	21			
16	0.235								
17	-0.011	0.265							
18	0.023	-0.004	0.247						

Table IX. (continued)

19	0.004	0.002	0.001	0.025					
20	-0.001	-0.015	-0.001	0.007	0.127				
21	-0.009	-0.016	-0.003	0.003	-0.002	0.091			
<i>s-cis-d-trans</i>									
	1	2	3	4	5	6	7	8	9
1	5.039								
2	0.318	8.568							
3	0.499	-0.115	10.035						
4	0.0	0.046	0.0	5.199					
5	-0.033	0.060	0.012	0.017	5.257				
6	0.031	0.072	0.029	0.014	-0.002	5.094			
7	0.056	0.006	0.208	0.005	0.001	0.020	4.813		
8	-0.026	-0.009	-0.034	0.002	-0.001	0.005	0.025	6.006	
9	0.318	0.162	-0.033	0.051	-0.071	-0.151	0.041	-0.027	1.104
10	0.340	-0.070	0.250	-0.003	-0.034	0.058	-0.162	0.091	0.008
11	-0.179	0.182	-0.038	-0.009	0.021	0.001	-0.002	-0.011	0.002
12	0.182	0.032	-0.228	0.007	0.001	-0.001	0.012	0.031	0.060
13	-0.001	-0.190	-0.006	0.057	0.033	-0.008	-0.002	0.003	0.010
14	0.019	0.011	0.003	0.097	-0.108	-0.036	0.013	0.003	0.081
15	0.003	0.007	0.487	-0.002	0.005	0.004	-0.056	0.218	-0.009
	10	11	12	13	14	15			
10	1.364								
11	-0.069	0.484							
12	0.054	0.007	0.548						
13	0.022	-0.015	-0.005	0.436					
14	-0.022	-0.041	0.010	-0.004	0.522				
15	0.068	-0.011	0.018	-0.006	-0.004	0.777			
	16	17	18	19	20	21			
16	0.237								
17	0.011	0.312							
18	0.021	0.007	0.246						
19	0.004	-0.003	-0.001	0.009					
20	0.004	0.013	-0.005	-0.003	0.128				
21	0.008	0.020	0.002	-0.006	0.003	0.087			

*For definition of internal coordinates see Table VII.

each other and the ν_7 band lies at 1067 cm^{-1} , that is it manifests approximately the same value as in the light methanimine, *viz.* 1058.2 cm^{-1} . It should be emphasized that the vibrational frequencies of the D_2CND molecule were not involved in the refinement of the scale factors. In all other instances the expected isotopic shifts are observed for the isotopomers under consideration.

2-Propen-1-imine

The calculations of the total energy and optimized geometry of the propenimine rotamers (Tables II and III) demonstrated that all three conformers are planar and the *s-trans-d-trans* form is the most stable. The next most stable conformer according to the energy scale is the *s-trans-d-cis* form. This coincides with data from the microwave spectra^{1,2} and earlier *ab initio* calculations at the HF/4-31G^{3,4} and HF/4-31G(N*) levels.^{5,6} The probability of realization of the *s-cis-d-trans* conformer is quite low since its en-

ergy is higher by far than the energy of the *s-cis-d-trans* form.^{3,4}

All the *ab initio* calculations support the suggestion of ref. 1 that the C—C=N angle of the *s-trans-d-cis* form is greater than that of the *s-trans-d-trans* conformer by as much as 5° . This explains the values of the observed rotational constants.^{1,2}

The 6-31G energy difference, $\Delta E = E_{\text{Tc}} - E_{\text{Tt}}$, between the two most stable conformers is lowered by the inclusion of polarization functions on the heavy atoms by $\sim 0.4\text{ kcal/mol}$ and raised by $\sim 0.1\text{ kcal/mol}$ when *p* functions are included on the hydrogen atoms (admittedly with no further optimization). Maintenance of the energy difference ΔE when going from second to third-order perturbation theory and its subsequent decrease on going from third to fourth order demonstrates that the singly and doubly excited configurations provide only a small contribution to the energy difference. This suggests that the main contribution to ΔE is due to the coupling of localized electron pairs, and

Table X. Experimental and calculated vibrational frequencies of 2-propen-1-imine (cm^{-1}).

ν	Assignment Sym.	<i>s-trans-d-trans</i>				<i>trans-cis</i>		<i>cis-trans</i>	
		$\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{NH}$		$\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{ND}$		$\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{NH}$		$\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{NH}$	
		Exp. (9) ^a	(5,6) ^b	Calc.	Exp. (5,6) ^b	Calc.	Exp. (5,6) ^b	Calc.	Calc.
1	$\nu(\text{N}-\text{H})$ str. a'	—	—	3291	—	2411	—	3246	3293
2	$\nu(=\text{CH}_2)$ a. str.	—	—	3115	—	3115	—	3117	3129
3	$\nu(\text{C}-\text{H})$ str. v. ^c	—	—	3073	—	3073	—	3039	3053
4	$\nu(=\text{CH}_2)$ s. str.	—	—	3030	—	3030	—	3030	3036
5	$\nu(\text{C}-\text{H})$ str. i. ^c	—	2955	2950	—	2951	—	3022	2955
6	$\nu(\text{C}=\text{N})$ str.	1640	1651	1674	1640	1665	1649	1667	1644
7	$\nu(\text{C}=\text{C})$ str.	1600	1600	1598	1595	1590	1598	1592	1625
8	$\delta(=\text{CH}_2)$ sci.	—	1416	1424	—	1421	—	1419	1422
9	$\delta(\text{C}=\text{N}-\text{H})$ bend.	1370	1368	1369	833	828	1374	1342	1374
10	$\delta(\text{C}-\text{H})$ bend. v.	—	1260	1260	1252	1256	—	1265	1271
11	$\delta(\text{C}-\text{H})$ bend. i.	1252	1251	1224	1288	1321	—	1241	1194
12	$\nu(\text{C}-\text{C})$ str.	—	1089	1086	1185	1187	—	1097	900
13	$\rho(=\text{CH}_2)$ rock.	—	—	906	970	966	—	908	1059
14	$\delta(\text{C}-\text{C}=\text{N})$ bend.	—	557	547	545	538	—	537	643
15	$\delta(\text{C}=\text{C}-\text{C})$ bend.	—	—	312	—	302	—	308	286
16	$\chi(\text{C}-\text{H})$ wag. i. a''	1100	1096	1082	—	983	1092	1087	1079
17	$\chi(\text{C}-\text{H})$ wag. v.	1000	991	999	1018	1015	994	986	997
18	$\chi(=\text{CH}_2)$ wag.	935	—	934	—	931	—	940	956
19	$\tau(\text{C}=\text{N})$ tw.	840	839	812	—	719	852	832	799
20	$\tau(\text{C}=\text{C})$ tw.	—	568	562	519	517	557	552	526
21	$\tau(\text{C}-\text{C})$ tors.	—	—	176	—	174	—	158	126

^aThe IR spectrum in the Ar matrix.^bThe IR spectrum in the gas phase.^cv. is vinyl group, i. is imine group.

explains why an adequate description of the localized molecular orbitals (MOs) requires polarization functions in the basis set. This is corroborated by the data of Table III from which it may be seen that correlation effects play a smaller role than including polarization functions.

The experimental infrared spectra of propenimine^{5,6,9} were interpreted in terms of the *s-trans-d-trans* \leftrightarrow *s-trans-d-cis* equilibrium (Table X). The successful transfer of scale factors from the force fields of methanimine and butadiene-1,3²⁹ to that of propenimine means that the accuracy of the calculation for a given type of force constant and the anharmonicity corrections for the corresponding vibrations are similar in these three related molecules. Taking this into account the agreement between calculated and experimental values of the vibrational frequencies of the *s-trans-d-trans* form of the $\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{N}-\text{H}$ and $\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{N}-\text{D}$ molecules and the *s-trans-d-cis* conformer (Table X) may be accepted as quite good. Among the experimental vibrational frequencies as detected in the Ar matrix⁹ only the weak band at 3230 cm^{-1} and the middle intensity band at 854 cm^{-1} are not identified. In the infrared spectrum of the gaseous mixture of the *s-trans-d-trans* and *s-trans-d-cis* forms the weak band at 855 cm^{-1} and bands at 979 cm^{-1} and 770 cm^{-1} are unassigned.^{5,6} All the other bands are attributed to the fundamental vibrations of the two conformers mentioned above (Table X).

It should be noted that the present calculation reproduces correctly the experimentally observed inverse isotopic shifts for the ν_{11} , ν_{12} , and ν_{13} vibrations of *s-trans-d-trans*- $\text{H}_2\text{C}=\text{CH}-\text{HC}=\text{N}-\text{D}$. Due to the diagonal elements of the force constant matrix in refs. 5 and 6, which were revised to fit the observed frequencies, the present assignment for some infrared bands is different from description given in the previous analysis.^{5,6}

Judging from the calculated and experimental vibrational frequencies, the difference between the vibrational spectra of the *s-trans-d-trans* and *s-trans-d-cis* conformers is not great. That is why the identification of these conformers by their vibrational spectra is obviously unreasonable. The set of calculated vibrational frequencies of the

s-cis-d-trans conformer differs more from the vibrational frequencies of the two more stable forms. This is especially noticeable in the region of deformational skeleton vibrations of these molecules (ν_{14} and ν_{15}).

CONCLUSIONS

The *ab initio* calculation of the vibrational frequencies of the methanimine molecule allow one to explain the practical absence of isotopic shift of the ν_7 vibration on going from $\text{H}_2\text{C}=\text{N}-\text{H}$ to the $\text{D}_2\text{C}=\text{N}-\text{D}$ molecule.

The calculations performed in this work corroborate the planar structures of the 2-propen-1-imine conformers and give a consistent assignment of the experimental vibrational frequencies for the two lower energy forms (*s-trans-d-trans* and *s-trans-d-cis*).

Therefore, the substitution of the terminal carbon atom in the conjugated system of butadiene-1,3 by the nitrogen atom results in the planar structure of all the possible conformers of 2-propen-1-imine. Meanwhile, the butadiene-1,3 molecule and its 2-methyl- and 2,3-dimethyl-derivatives manifest the non-planar structure of their high energy conformers.^{29,32-35}

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