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Band Assignments of the Infrared Spectrum of 1-Methyl-2(1*H*)-pyridinimine

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The band assignments of the IR spectrum of 1-methyl-2(1*H*)-pyridinimine in solution were carried out with the normal coordinate treatment by the *ab initio* 6-31G method. The IR spectrum of the compound is characterized by three prominent strong absorption bands in the 1700 to 1500 cm^{-1} region. These three bands are mainly attributed to the stretching modes of the C=C bonds of the ring and the C=N group. All another bands are relatively weak compared with the intensities of these bands. The normal coordinate treatment suggests that 1-methyl-2(1*H*)-pyridinimine has three out-of-plane fundamental bands in the frequency region lower than the lowest fundamental band of pyridine. The calculated lowest fundamental band is near 129 cm^{-1}. It was assigned to the twisting mode of the CH_3 group. The second and third lowest bands correspond to the twisting vibration of the CH_3 group and the out-of-plane bending vibration of the ring framework. This suggests that the ring framework of 1-methyl-2(1*H*)-pyridinimine may be more flexible than that of pyridine. The vibrational features of the IR spectrum of 1-methyl-2(1*H*)-pyridinimine are similar to that of 1-methyl-2-pyridone. In the liquid state, 1-methyl-2(1*H*)-pyridinimine forms an inter-molecular hydrogen bond between the imino groups.

In a previous paper,[1)] 1-methyl-2(1*H*)-pyridinimine was synthesized as a model compound of the imino-form of 2-aminopyridine to investigate its spectroscopic properties, and its UV absorption and fluorescence spectra were measured in solution. The UV absorption and fluorescence spectra have vibrational structures in solution and the fluorescence quantum yield is very small at room temperature.

In this paper, the band assignments of the IR spectra were carried out to analyze the vibrational structure of the UV absorption and fluorescence spectra and to ascertain whether the ring framework is rigid like that of pyridine or not, because the rigidity influences the fluorescence quantum yield at room temperature. The IR spectrum of the compound was recorded in the range 4000—400 cm^{-1}. A normal coordinate analysis was performed to confirm the proposed assignments. The calculations were carried out by assuming C_s symmetry for the molecule.

As the band assignments of the IR spectra of 2-pyridone and 1-methyl-2-pyridone were already made by Katritzky et al.,[2)] their band assignments were referred to for 1-methyl-2(1*H*)-pyridinimine, because these compounds are similar to each other with respect to the molecular structure of the ring framework and the π-conjugated system.

Experimental

The IR spectrum (4000—400 cm^{-1}) was measured on a JEOL JIR-RFX3001 spectrophotometer. 1-Methyl-2(1*H*)-pyridinimine was prepared according to the procedure of Taylor et al.,[3)] and purified by alumina column chromatography using isooctane (2,2,4-trimethylpentane) as an eluent. CCl_4 was used as solvent. It was commercially available and was further purified by distillation. The sample concentration was about 0.1 mol dm^{-3}.

Method of Calculation and Molecular Model

The molecular model of 1-methyl-2(1*H*)-pyridinimine was optimized by the *ab initio* 6-31G method with an assumption that the ring framework of the model is planar. The normal coordinate calculation within the *ab initio* 6-31G level was carried out using the Gaussian 90 source program[4)] on a VAX-6420 VMS-5.4-2 computer at the Process Technology Center, Daicel Chemical Industries, Ltd. and on a FACOM VP-100E computer at the TDU Computing Center. The Calculated vibrational frequencies were scaled by 0.9, because the present method overestimates the vibrational frequencies.[5)]

Results and Discussion

In Fig. 1 the geometry-optimized model of 1-methyl-2(1*H*)-pyridinimine prepared by the *ab initio* 6-31G method is shown. As shown in Fig. 1, the molecular framework of the compound has a clear bond alterna-

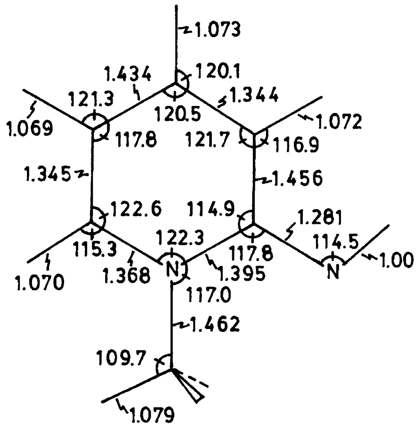


Fig. 1. The geometry-optimized model of 1-methyl-2(1*H*)-pyridinimine prepared by the *ab initio* 6-31G approximation.

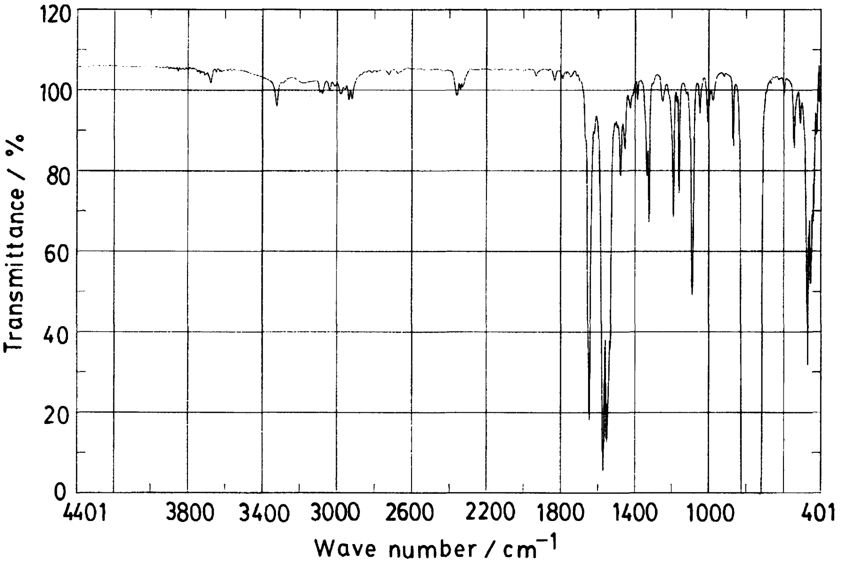


Fig. 2. The IR spectrum of 1-methyl-2-(1*H*)-pyridinimine measured in CCl_4 solution at room temperature.

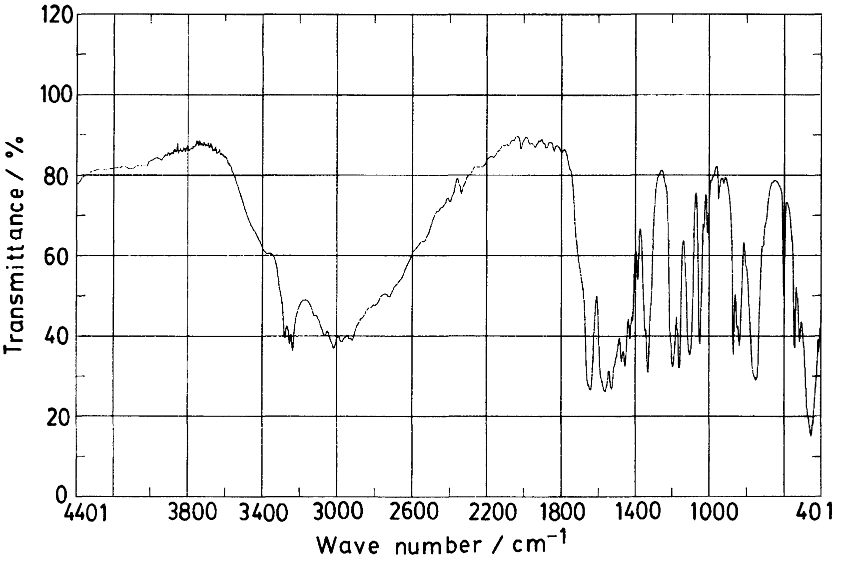


Fig. 3. The IR spectrum of 1-methyl-2(1*H*)-pyridinimine measured in the liquid state at room temperature.

tion and it looks more like a polyene-type structure than an aromatic ring structure. As the experimental data of its molecular geometry are unavailable, the geometry of the ring framework of 1-methyl-2(1*H*)-pyridinimine was compared with the experimental data of 2-pyridone.[6] The differences in the results are approximately below 0.05 Å and 2 degrees for the bond lengths and bond angles of the ring framework. Therefore, the geometry of 1-methyl-2(1*H*)-pyridinimine is close to that of 2-pyridone with respect to the ring framework.

The model has C_s symmetry: two of the hydrogen atoms of the CH_3 groups are placed above and below the symmetry plane, respectively, while the third hydrogen atom lies in the plane itself. 1-Methyl-2-(1*H*)-pyridinimine has the 42 fundamentals, all IR and Raman active. They are distributed as $28A'+14A''$. The A' mode is in-plane vibration and the A'' mode is out-of-plane vibration.

The IR spectra of 1-methyl-2(1*H*)-pyridimine are shown in Figs. 2 and 3 in CCl_4 and the liquid state. The calculated results of the normal coordinate treatment are summarized in Table 1 with the observed fundamentals ranging from 4000 to 400 cm^{-1} and with the corresponding assignments. The fundamental frequencies of the model of deuterium-substituted 1-methyl-2(1*H*)-pyridinimine were calculated by the *ab initio* 6-31G approximation and are listed in Table 2.

(a) In-Plane Vibrations. The weak and sharp absorption band at 3323 cm^{-1} (CCl_4) was assigned to the N–H stretching vibration which corresponds to the calculated value 3373 cm^{-1} in Table 1. In the liquid state, the N–H stretching band shifted to the lower frequency side from 3323 in CCl_4 to 3236 cm^{-1} due to the inter-molecular hydrogen bond formation between the

Table 1. Normal Coordinate Treatment of Vibrational Frequencies and Their Intensities of the Optimized Model of 1-Methyl-2(1*H*)-pyridinimine by the *Ab Initio* 6-31G Approximation

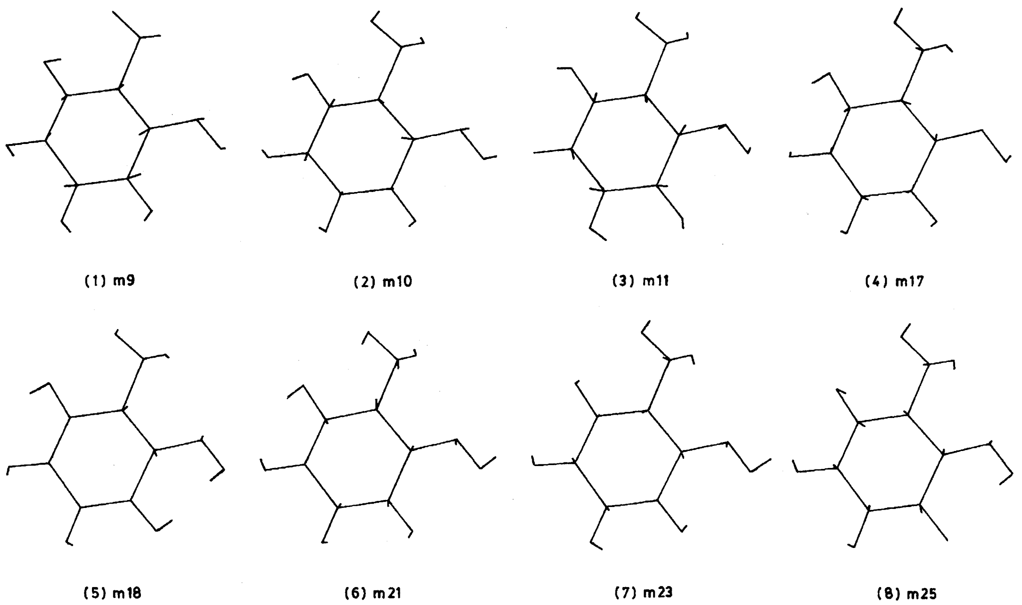
Mode	Sym.	$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}c/\mathrm{cm}^{-1}$	Int.	Raman	Depol.	CCl_4	liq.	Assign.
1	A'	3748	3373	5.2	155.3	0.330	3323	3236	NH str
2	A'	3425	3083	14.0	174.1	0.147	3076	3066	CH str
3	A'	3401	3061	3.5	49.8	0.690	3039		CH str
4	A'	3389	3050	17.3	105.4	0.244			CH str
5	A'	3364	3028	7.7	70.6	0.693	3013	3014	CH str
6	A''	3320	2988	15.1	55.4	0.750	2980	2972	CH_3 antisym str
7	A'	3314	2983	16.2	51.1	0.710	2959		CH_3 antisym str
8	A'	3231	2908	39.9	110.8	0.010	2918	2918	CH_3 sym str
9	A'	1870	1683	337.9	19.1	0.429	1647	1644	C=C, C=N str
10	A'	1787	1608	306.2	61.6	0.181	1572	1563	C=N, C=C str
11	A'	1736	1562	86.0	51.6	0.355	1533	1529	C=C, C=N str
12	A'	1664	1498	14.3	25.3	0.699	1479	1475	δCH_3
13	A'	1642	1478	27.9	9.2	0.736	1456	1456	δCH_3, δCH
14	A''	1641	1477	6.3	22.5	0.750	1425	1430	δCH_3
15	A'	1611	1450	3.4	9.5	0.558	1410	1415	δCH_3
16	A'	1562	1406	7.1	14.6	0.137	1387	1390	δCH, δNH
17	A'	1491	1342	51.5	53.6	0.127	1336		δCH, CH_3 rock, NC_2, NC_6 str
18	A'	1483	1335	88.8	12.3	0.177	1325	1331	δNH, δCH
19	A'	1333	1200	12.8	9.7	0.728	1246		δCH
20	A'	1316	1184	4.3	13.2	0.617	1192	1196	δCH, δNH
21	A'	1294	1165	74.7	6.2	0.318	1161	1159	N-CH_3 str, δNH
22	A''	1283	1155	1.7	3.3	0.750			CH_3 out-of-plane
23	A'	1202	1082	151.2	6.9	0.339	1088	1103	δNH
24	A''	1167	1050	2.1	4.7	0.750			CH out-of-plane
25	A'	1160	1044	13.2	0.8	0.277	1047	1049	CH_3 rock, δNH, Ring def
26	A''	1127	1014	0.2	2.8	0.750			CH out-of plane
27	A'	1090	981	5.9	7.0	0.638	1005	1009	Ring def
28	A'	968	871	19.1	3.2	0.269	870	872	Ring def
29	A''	964	868	79.4	7.5	0.750			CH, NH out-of-plane
30	A''	890	801	128.9	1.1	0.750	823	841	NH, CH out-of-plane
31	A''	850	765	19.3	9.6	0.750	750	750	NH, CH out-of-plane
32	A''	823	741	0.1	1.4	0.750			CH, NH out-of-plane
33	A'	815	734	11.0	20.0	0.133			Ring def
34	A'	664	598	1.7	8.5	0.391	598	604	Ring def
35	A'	602	542	18.0	5.0	0.604	546	544	Ring def, NH rock
36	A''	581	523	4.7	1.6	0.750	513	517	Ring frame out-of-plane
37	A'	498	448	0.9	2.7	0.625			NH rock, ring def
38	A''	464	418	32.9	2.4	0.750		457	Ring frame out-of-plane
39	A'	395	356	7.6	1.0	0.731			CH_3, NH rock
40	A''	257	231	2.7	2.2	0.750			CH_3 twist, ring frame out-of-plane
41	A''	153	138	3.3	0.3	0.750			CH_3 twist
42	A''	143	129	2.3	1.0	0.750			CH_3 twist

N–H groups. The very weak absorption bands located around 3100—3000 cm^{-1} were attributed to the four-ring C–H stretches, and the very weak bands ranging 3000—2900 cm^{-1} to the C–H stretching vibrations of the CH_3 group. The calculated frequencies for the C–H stretching vibrations are in good agreement with the observed frequencies. 1-Methyl-2(1*H*)-pyridinimine shows three prominent strong bands at 1647, 1572, and 1533 cm^{-1} in CCl_4, which correspond to modes 9,10, and 11, respectively, in Table 1. The first two bands are much stronger in intensity than all the another bands and seem to be characteristic of the IR spectrum of 1-methyl-2(1*H*)-pyridinimine. However, they are similar to the three bands of 1-methyl-2-pyridone which appear at 1665, 1590, and 1545 cm^{-1} in its spectroscopic feature.[2)] These bands were attributed to the stretching vibrations of the C=O group and the C=C bonds of the ring framework of 1-methyl-2-pyridone.[2)] In Fig. 4 (1), (2), and (3), the atomic displacements of the vibrational modes of the prominent three strong bands (modes 9,10,

Table 2. Normal Coordinate Treatment of Vibrational Frequencies and Their Intensities of the Optimized Model of Deuterium-Substituted 1-Methyl-2(1*H*)-pyridinimine by the *Ab Initio* 6-31G Approximation

Mode	Sym.	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$c/cm^{-1}	Int.	Raman	Depol.	Assign.
1	A$'$	3425	3083	14.0	173.9	0.147	CH str
2	A$'$	3401	3061	3.5	49.8	0.689	CH str
3	A$'$	3389	3050	17.3	106.0	0.243	CH str
4	A$'$	3364	3028	7.7	70.9	0.695	CH str
5	A$''$	3320	2988	15.1	55.4	0.750	CH$_3$ antisym str
6	A$'$	3314	2983	16.4	51.6	0.714	CH$_3$ antisym str
7	A$'$	3231	2908	39.9	110.4	0.010	CH$_3$ sym str
8	A$'$	2746	2471	12.9	67.7	0.332	ND str
9	A$'$	1868	1681	321.8	17.1	0.441	C=C, C=N str
10	A$'$	1775	1598	376.6	71.2	0.167	C=N, C=C str
11	A$'$	1734	1561	85.0	50.0	0.369	C=C, C=N str
12	A$'$	1664	1498	9.8	26.3	0.679	δCH$_3$
13	A$'$	1642	1478	27.8	9.2	0.735	δCH$_3$ δCH
14	A$''$	1641	1477	6.1	22.6	0.750	δCH$_3$
15	A$'$	1611	1450	3.0	9.7	0.537	δCH$_3$
16	A$'$	1555	1399	4.9	7.2	0.153	δCH, δNH
17	A$'$	1490	1341	72.9	41.2	0.133	δCH, CH$_3$ rock NC2, NC6 str
18	A$'$	1445	1301	14.5	29.8	0.166	δCH,δND
19	A$'$	1333	1200	9.2	11.9	0.744	δCH
20	A$'$	1307	1176	38.5	6.0	0.402	δCH
21	A$''$	1283	1155	1.8	3.3	0.750	CH$_3$ out-of plane
22	A$'$	1272	1145	12.8	8.9	0.251	N–CH$_3$ str
23	A$'$	1172	1055	50.2	1.8	0.729	CH$_3$ rock, ring def
24	A$''$	1167	1050	1.5	4.8	0.750	CH out-of plane
25	A$''$	1127	1014	0.2	2.8	0.750	CH out-of-plane
26	A$'$	1095	986	14.3	8.3	0.633	Ring def
27	A$'$	981	883	46.5	3.4	0.610	δ ND
28	A$'$	964	868	30.7	4.1	0.183	Ring def
29	A$''$	952	857	26.2	5.8	0.750	CH out-of-plane
30	A$''$	864	778	124.7	9.2	0.750	CH out-of-plane
31	A$''$	825	743	0.8	2.8	0.750	CH out-of-plane
32	A$'$	799	719	20.4	17.0	0.143	Rind def
33	A$''$	661	595	27.2	0.5	0.750	ND out-of-plane
34	A$'$	661	595	1.3	8.5	0.374	Ring def
35	A$'$	592	533	20.4	4.8	0.597	Ring def, ND rock
36	A$''$	581	523	4.7	1.6	0.750	Ring frame out-of-plane
37	A$'$	478	430	0.8	2.7	0.545	ND rock, ring def
38	A$''$	461	415	37.4	2.2	0.750	Ring frame out-of-plane
39	A$'$	386	347	8.8	1.0	0.748	CH$_3$, ND rock
40	A$''$	254	229	3.5	2.3	0.750	CH$_3$ twist, ring frame out-of-plane
41	A$''$	152	137	2.5	0.3	0.750	CH$_3$ twist
42	A$''$	142	128	2.5	1.1	0.750	CH$_3$ twist

and 11) are shown. These vibrational modes come from the stretching vibrations of the C=C and C=N bonds. However, in mode 11 the above stretching vibrations couple with the bending mode of the N–H group. The band at 1479 cm^{-1} in CCl$_4$ was assigned to the asymmetric bending vibration of the CH$_3$ group by referring to the assignment of the CH$_3$ group of 1-methyl-2-pyridone (1466 cm^{-1}).[2] The medium band at 1456 cm^{-1} in CCl$_4$ corresponded to the calculated band at 1478 cm^{-1} in Table 1. This vibrational mode was assigned to the bending vibrations of CH$_3$ group and C–H bonds. The weak band at 1410 cm^{-1} was assigned to the symmetric vibration of the CH$_3$ group. The weak band at 1387 cm^{-1} in CCl$_4$ was attributed to mode 16 in Table 1. From the atomic displacement of mode 16, the corresponding band was mainly assigned to the in-plane bending vibrations of the C–H and N–H bonds. The split bands appear at 1336 and 1325 cm^{-1} in CCl$_4$, and their intensities are relatively strong compared with other bands in the 1500 to 1400 cm^{-1} region. As 2-pyridone has no bands near 1330 cm^{-1}, the bands near 1330 cm^{-1} may come from the CH$_3$ or N–H groups. The for-



(1) m9 (2) m10 (3) m11 (4) m17

(5) m18 (6) m21 (7) m23 (8) m25

Fig. 4. The atomic displacements of the vibrational modes are as shown; (1) m9, (2) m10, (3) m11, (4) m17, (5) m18, (6) m21, (7) m23, and (8) m25.

mer band at 1336 cm^{-1} is weaker in intensity than the latter one at 1325 cm^{-1}. These split bands were attributed to modes 17 (1342 cm^{-1}) and 18 (1335 cm^{-1}), respectively, in Table 1. According to the atomic displacements of modes 17 and 18 as shown in Fig. 4, (4) and (5), the former mode was assigned to the stretching mode of the N–C2 and N–C6 bonds coupled with the rocking vibration of the CH$_3$ group and the bending vibration of the C–H bond. The latter mode was assigned mainly to the in-plane bending vibrations of the N–H and C–H bonds. From Table 2 the deuteration changed the frequency of mode 18 from 1335 to 1301 cm^{-1} and gave rise to a marked reduction of its band intensity. Such large variations in the frequency and intensity suggest that mode 18 is involved with the vibrational mode of the N–H group. The weak band at 1246 cm^{-1} was assigned to the bending vibration of the C–H bonds.

The medium band at 1192 cm^{-1} in CCl$_4$ was attributed to the in-plane bending vibrations of the ring C–H and N–H groups. The medium band at 1161 cm^{-1} (CCl$_4$) which corresponds to mode 21 (1165 cm^{-1}) was assigned to the stretching vibration of the N–CH$_3$ bond coupled with the in-plane bending vibration of the N–H group as shown in Fig. 4 (6).

In CCl$_4$, the band at 1088 cm^{-1} is the strongest in intensity except for two prominent bands in the region 1700 to 1500 cm^{-1}. This band at 1088 cm^{-1} corresponds to mode 23 (1082 cm^{-1}) in Table 1. In 1-methyl-2-pyridone and 2-pyridone there is no band corresponding to the band at 1088 cm^{-1}.[2)] In Fig. 4 (7), the atomic displacement of mode 23 is shown. From Fig. 4 (7), the absorption band at 1088 cm^{-1} may be mainly assigned to the in-plane bending vibration of the N–H group. Table 2 suggests that the corresponding band of the deuterated compound occurs at 883 cm^{-1}, and the frequency ratio of the two compounds is 0.816. It is noted that in the liquid state the corresponding band appears at 1103 cm^{-1}, and its shift to the higher frequency side may be due to the inter-molecular hydrogen bond formation of the N–H group.

The weak band at 1047 cm^{-1} in CCl$_4$ was attributed to the calculated value 1044 cm^{-1} which corresponds to mode 25. This mode was mainly assigned to the rocking vibration of the CH$_3$ group coupled with the ring deformation vibration and the in-plane bending vibration of the N–H group according to the atomic displacement as shown in Fig. 4 (8). The corresponding band is observed at 1050 cm^{-1} for 1-methyl-2-pyridone but not for 2-pyridone.[2)] There is a very weak band at 1005 cm^{-1} in CCl$_4$. This weak band was attributed to mode 27 (981 cm^{-1}) in Table 1 and it was assigned to the ring deformation mode. The very weak band at 598 cm^{-1} in CCl$_4$ was attributed to mode 34 in Table 1 and it was assigned to the in-plane ring deformation which is similar to the vibrational mode (E_{2g}: 606 cm^{-1}) of benzene. The medium band appears at 546 cm^{-1}. This band corresponds to mode 35 and the calculated frequency is in good agreement with the observed value. Its vibrational mode is attributed to the ring deformation coupled with the rocking vibrations of the CH$_3$ and N–H groups.

(b) Out-of-Plane Vibrations. The band at 1425 cm^{-1} (CCl$_4$) was assigned to the asymmetric out-of-plane bending vibration of the H atoms of the CH$_3$ group. 1-Methyl-2(1*H*)-pyridinimine has two medium bands at 870 and 823 cm^{-1} in CCl$_4$, and at 872 and 841 cm^{-1} in the liquid state. In 1-methyl-2-pyridone, two such medium bands appear at 876 and 845 cm^{-1}, and they were assigned to the out-of-plane bending vibration of the C–H group.[2)] However, with respect to the band at 870 cm^{-1} in CCl_4, Table 1 shows that there are two very close vibrational bands at 871 and 868 cm^{-1} which correspond to modes 28 and 29. Mode 28 corresponds to the in-plane ring deformation vibration, but mode 29 corresponds to the out-of-plane bending vibration of the C–H group. The intensity of the former is weaker than that of the latter. Therefore, the observed band at 870 cm^{-1} may be assigned to the overlapped band of the two different vibrational modes. The vibrational character of the band at 870 cm^{-1} may be more predominant in the out-of-plane bending mode of the C–H group than in the in-plane vibrational modes. The observed band at 823 cm^{-1} in CCl_4 shifts to a higher frequency (841 cm^{-1}) in the liquid state. This band corresponds to mode 30 in Table 1, and it was assigned to the out-of-plane bending vibration of the N–H group. This assignment may be in line with the higher frequency shift of the band in th liquid state due to the hydrogen bond formation of the N–H group.

In the region from 800 to 600 cm^{-1}, a strong broad band appears at 750 cm^{-1}. However, the normal coordinate calculation suggests the existence of three fundamental vibrations, modes 31, 32, and 33, in this region. Therefore, the observed band at 750 cm^{-1} may be attributed to these three vibrational bands. The vibrational modes of these bands were assigned as shown in Table 1. In CCl_4, a clear weak band appears at 513 cm^{-1} which corresponds to the calculated band at 523 cm^{-1} in Table 1, and it was assigned to the out-of-plane bending vibration of the ring framework. In the liquid state, the strong broad band appears at 457 cm^{-1}. This band was assigned to the out-of-plane bending vibration of the ring framework which corresponds to mode 38 in Table 1.

From Table 1, 1-methyl-2(1*H*)-pyridinimine has three out-of-plane fundamental bands (modes 40, 41, and 42) in the frequency region lower than the lowest fundamental band of pyridine at 374 cm^{-1} which was observed in the Raman spectrum.$^{7)}$ These three bands correspond to the out-of-plane bending vibration of the ring framework and the twisting vibration of the CH_3 group. The lower frequency of the out-of-plane bending vibration of the ring framework suggests that the ring framework in 1-methyl-2(1*H*)-pyridinimine may be more flexible than in pyridine.

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References

1) A. Fujimoto and K. Inuzuka, *Bull. Chem. Soc. Jpn.*, **64**, 3758 (1991).

2) A. R. Katritzky and R. A. Jones, *J. Chem. Soc.*, **1960**, 2947.

3) E. C. Taylor and R. O Kan, *J. Am. Chem. Soc.*, **85**, 776 (1963).

4) Gaussian 90, Revision J. M. J. Frish, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian. Inc., Pittsburgh PA. 1990.

5) J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, *Int. J. Quantum Chem., Quantum Chem. Symp.*, **15S**, 269 (1981).

6) J. Almolt, A. Kvick, and I. Olovsson, *Acta Crystallogr., Sect B*, **B27**, 1201 (1971).

7) L. Corrsin, B. J. Fax, and R. C. Lord, *J. Chem. Phys.*, **21**, 1170 (1953).