Structure Determination of Methyl Nicotinate and Methyl Picolinate by Gas Electron Diffraction Combined with ab Initio Calculations

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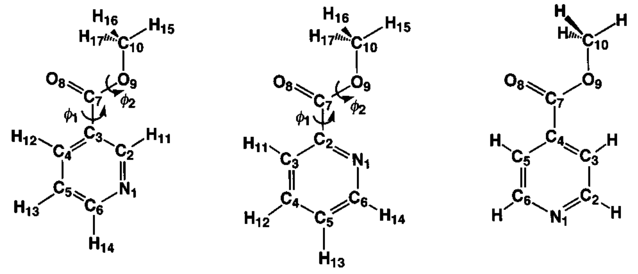
The molecular structures of isomers, methyl nicotinate and methyl picolinate, have been studied by gas electron diffraction. The samples were heated to 341−343 K by using a high-temperature nozzle to get enough vapor pressure. HF/6-31G* ab initio calculations were carried out, and structural constraints were taken from their results. Vibrational amplitudes and shrinkage corrections were calculated from the harmonic force constants given by normal coordinate analyses. The principal structural parameters of the s-trans conformer of methyl nicotinate are as follows (angle brackets mean averaged values): $\langle r_g(\mathrm{N-C})\rangle = 1.337(7)$ Å; $\langle r_g(\mathrm{C-C})_{\mathrm{ring}}\rangle = 1.402(3)$ Å; $r_g(\mathrm{C_{ring}-C({=}O)}) = 1.480(12)$ Å; $r_g(\mathrm{C{=}O}) = 1.199(7)$ Å; $\langle r_g(\mathrm{C-O})\rangle = 1.380(11)$ Å; $\angle_\alpha\mathrm{CNC} = 119.0(14)°$; $\langle\angle_\alpha\mathrm{NCC}\rangle = 122.8(11)°$; $\angle_\alpha\mathrm{(N{=})C-C_{ring}-C({=}O)} = 118.3(12)°$; $\angle_\alpha\mathrm{C_{ring}-C{=}O} = 121.5(12)°$; $\angle_\alpha\mathrm{C_{ring}-C-O} = 115.6(10)°$. Those of the s-trans conformer of methyl picolinate are as follows: $\langle r_g(\mathrm{N-C})\rangle = 1.344(7)$ Å; $\langle r_g(\mathrm{C-C})_{\mathrm{ring}}\rangle = 1.398(4)$ Å; $r_g(\mathrm{C_{ring}-C({=}O)}) = 1.497(11)$ Å; $r_g(\mathrm{C{=}O}) = 1.209(7)$ Å; $\langle r_g(\mathrm{C-O})\rangle = 1.380(11)$ Å; $\angle_\alpha\mathrm{CNC} = 117.2(12)°$; $\langle\angle_\alpha\mathrm{NCC}\rangle = 123.9(12)°$; $\angle_\alpha\mathrm{N-C-C({=}O)} = 115.1(10)°$; $\angle_\alpha\mathrm{C_{ring}-C{=}O} = 121.0(12)°$; $\angle_\alpha\mathrm{C_{ring}-C-O} = 115.1(12)°$. The structural parameters of the two isomers and methyl isonicotinate have been compared and their similarity and differences have been discussed.

Introduction

In a series of recent papers,[1−3] we reported the geometrical structures and conformations of alkyl acetates $\mathrm{CH_3-COO-R}$ (R = Et,[1] *i*-Pr,[2] *t*-Bu[3]), determined by gas electron diffraction (GED). One of the important findings was that the (O=)C−O bond tends to decrease with the increasing size of substituent R, and we attributed this phenomenon to the electron-releasing inductive effect of alkyl groups.[3] In a new series of investigations,[4,5] we are determining the molecular structures of methyl esters, $\mathrm{R'-COO-CH_3}$, and it has so far been found that the (O=)C−O bond length of methyl isonicotinate (MI, 4-pyridinecarboxylic acid methyl ester) (1.331 Å)[5] is considerably shorter than those of methyl acetate (1.360 Å)[6] and methyl acrylate (1.349 Å).[4]

As an extension of these studies, the present study has been undertaken to determine the molecular structures of methyl nicotinate (MN, 3-pyridinecarboxylic acid methyl ester) and methyl picolinate (MP, 2-pyridinecarboxylic acid methyl ester). These molecules and MI are structural isomers that differ from each other only in the position of the methoxycarbonyl group (see Figure 1). In the gas phase, few structural data are available for such a series of ring compounds consisting of three or more structural isomers that only differ in the position of substituents.[7,8] The structural similarity and differences of these isomers are our interest.

In the case of MN and MP, coexistence of two conformers, s-trans and s-cis, seems possible due to the C−C single bond connecting the pyridine ring and the methoxycarbonyl group. The conformational composition of each isomer is also our concern. Only a few conformational studies have been reported for MN,[9] and no data are available for the conformation of MP. In addition, these isomers are biochemically important substances because MN is a derivative of nicotinic acid, which is an antipellagra factor and a component of the vitamin B complex as well.



Methyl nicotinate (s-*trans*) **Methyl picolinate (s-*trans*)** **Methyl isonicotinate**

Figure 1. Methyl nicotinate (MN), methyl picolinate (MP), and methyl isonicotinate (MI). For MN and MP, the s-trans conformers are shown. Dihedral angle ϕ_1 ($\mathrm{C_2C_3C_7O_8}$ for MN and $\mathrm{N_1C_2C_7O_8}$ for MP) is defined to be 180° and ϕ_2 ($\mathrm{O_8C_7O_9C_{10}}$) is defined to be 0° for the conformers given here.

TABLE 1: Experimental Conditions

	methyl nicotinate	methyl picolinate
nozzle temperature, K	341	343
camera distance, mm	244.5	244.6
electron wavelength, Å	0.06348	0.06363
background pressure, 10^{-6} Torr	2.4−3.6	2.5−4.5
exposure time, s	51−58	30−45
beam current, μA	2.1	3.6
uncertainty in the scale factor, %	0.04	0.1
no. of plates used	4	3

As in the case of the esters that we investigated previously,[1−5] the molecular structures of MN and MP are difficult to be determined by GED alone because each molecule has many

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TABLE 2: Observed and Calculated Vibrational Wavenumbers (cm^{-1}) and Assignments

		ν_{calc}			
$\nu_{\text{obs}}{}^{a}$		s-trans	s-cis	S^{b}	assignment^{c}
					Methyl Nicotinate
3056	sh	3060	3056	A'	C−H$_{\text{ring}}$ str.(99)
3043	m	3043	3042	A'	C−H$_{\text{ring}}$ str.(98)
3025	w	3029	3034	A'	C−H$_{\text{ring}}$ str.(101)
3006	w	3013	3013	A'	C−H$_{\text{ring}}$ str.(101)
2982	w	2987	2986	A'	CH$_3$ asym. str.(101)
2957	m	2959	2959	A''	CH$_3$ asym. str.(100)
2907	w	2885	2885	A'	CH$_3$ sym. str.(101)
1728	vs	1734	1736	A'	C═O str.(87)
1592	s	1597	1595	A'	C−C$_{\text{ring}}$ str.(51) + C−H$_{\text{ring}}$ in-plane bend.(33)
1574	m	1576	1577	A'	C−C$_{\text{ring}}$ str.(65) + C−H$_{\text{ring}}$ in-plane bend.(29)
1480	m	1487	1488	A'	C−H$_{\text{ring}}$ in-plane bend.(67)
1476	m	1472	1472	A'	CH$_3$ asym. def.(99)
1461	sh	1461	1461	A''	CH$_3$ asym. def.(95)
1438	s	1431	1436	A'	CH$_3$ sym. def.(31) + C−H$_{\text{ring}}$ in-plane bend.(27)
1420	s	1422	1422	A'	CH$_3$ sym. def.(58)
1328	m	1336	1331	A'	C−H$_{\text{ring}}$ in-plane bend.(81)
1288	vs	1277	1273	A'	C−O str.(30) + C$_{\text{ring}}$−C str.(29)
1238	sh	1219	1220	A'	C−H$_{\text{ring}}$ in-plane bend.(74)
1193	m	1184	1183	A'	CH$_3$ asym. def.(72)
1131	sh	1144	1144	A''	CH$_3$ rock.(93)
		1131	1140	A'	C−C$_{\text{ring}}$ str.(42) + C−N str.(31) + C−H$_{\text{ring}}$ in-plane bend.(22)
1113	s	1124	1118	A'	O−C$_{\text{Me}}$ str.(29)
1089	sh	1084	1084	A'	C−C$_{\text{ring}}$ str.(103) + C−N str.(72)
1038	w	1031	1032	A'	C−C$_{\text{ring}}$ str.(35) + C−N str.(30)
1025	s	1027	1025	A''	C−H out-of-plane bend.(80)+ C$_{\text{ring}}$−C out-of-plane bend.(50)
1013	sh	1001	1001	A''	C−H out-of-plane bend.(85) + C$_{\text{ring}}$−C out-of-plane bend.(36)
994	vw	988	991	A'	ring def.(46) + C−C$_{\text{ring}}$ str.(30)
961	m	966	968	A''	C−H$_{\text{ring}}$ out-of-plane bend.(114) + ring tor.(20)
938	sh	957	949	A'	O−C$_{\text{Me}}$ str.(45) + ring def.(31)
826	m	837	834	A''	C−H out-of-plane bend.(78) + ring tor.(25)
		802	803	A'	C−O str.(24) + O−C═O def.(21)
741	s	735	735	A''	C═O out-of-plane bend.(55) + C−H$_{\text{ring}}$ out-of-plane bend.(43)
702	m	698	697	A''	ring tor.(134) + C−H$_{\text{ring}}$ out-of-plane bend.(29)
		697	697	A'	ring def.(60)
620	w	611	613	A'	ring def.(90)
501	vw	511	512	A'	O−C═O rock.(40)
465	vw	440	440	A''	ring tor.(113) + C−H$_{\text{ring}}$ out-of-plane bend.(58)
406	vw	407	406	A''	ring tor.(131) + C−H$_{\text{ring}}$ out-of-plane bend.(22)
		355	356	A'	C$_{\text{ring}}$−C str.(29) + ring def.(27)
331	m	329	327	A'	C−O−C$_{\text{Me}}$ bend.(40) + O═C−O def.(30) + C$_{\text{ring}}$−C in-plane bend.(27)
212	w	211	211	A''	C−O tor.(49) + ring tor.(30)
		172	174	A'	C$_{\text{ring}}$−C in-plane bend.(33) + O═C−O rock.(32)
		129	130	A''	O−C$_{\text{Me}}$ tor.(64)
		107	108	A''	C−O tor.(33) + O−C$_{\text{Me}}$ tor.(31) + C$_{\text{ring}}$−C out-of-plane bend.(25)
		80	78	A''	C$_{\text{ring}}$−C tor.(77)
					Methyl Picolinate
			3085		
3075	m	3068		A'	C−H$_{\text{ring}}$ str.(99)
3060	m	3047	3047	A'	C−H$_{\text{ring}}$ str.(99)
3028	w	3030	3030	A'	C−H$_{\text{ring}}$ str.(101)
		3020	3019	A'	C−H$_{\text{ring}}$ str.(101)
3001	w	2989	2983	A'	CH$_3$ asym. str.(98)
2962	m	2956	2956	A''	CH$_3$ asym. str.(100)
2914	vw				
2887	sh	2884	2883	A'	CH$_3$ sym. str.(98)
2856	w				
1777	m		1788		
1744	vs	1739		A'	C═O str.(92)
1701	w				
1603	sh	1607	1603	A'	C−C$_{\text{ring}}$ str.(61) + C−H$_{\text{ring}}$ in-plane bend.(38)
1581	m	1591	1593	A'	C−C$_{\text{ring}}$ str.(47) + C−H$_{\text{ring}}$ in-plane bend.(34)+ C−N str.(21)
1575	sh				
1503	m	1508	1506	A'	C−H$_{\text{ring}}$ in-plane bend.(61) + C−C$_{\text{ring}}$ str.(21)
		1495	1494	A'	C−H$_{\text{ring}}$ in-plane bend.(73)
1476	m	1480	1482	A'	CH$_3$ asym. def.(98)
1470	m	1471	1471	A''	CH$_3$ asym. def.(96)
1446	s	1437	1434	A'	CH$_3$ sym. def.(81)
1430	sh				
1335	sh	1338	1331	A'	C−H$_{\text{ring}}$ in-plane bend.(40)
1315	vs	1310		A'	C−O str.(21)

TABLE 2 (Continued)

		ν_{calc}			
ν_{obs}[a]		s-trans	s-cis	S[b]	assignment[c]
1298	sh				
1282	s		1276		
1247	s	1242	1244	A′	C−H$_{\mathrm{ring}}$ in-plane bend.(83) + C−N str.(22)
1219	m				
1199	m	1187	1187	A′	CH$_3$ asym. def.(73)
1134	vs	1144	1146	A′	O−C$_{\mathrm{Me}}$ str.(22) + C−C$_{\mathrm{ring}}$ str.(21)
		1144	1145	A″	CH$_3$ rock.(93)
		1117	1112	A′	C−C$_{\mathrm{ring}}$ str.(45) + C−H$_{\mathrm{ring}}$ in-plane bend.(27)
1094	m				
1084	sh	1083	1084	A′	C−C$_{\mathrm{ring}}$ str.(107) + C−N str.(79)
1050	m				
1046	m	1046	1044	A″	C−H$_{\mathrm{ring}}$ out-of-plane bend.(133)
		1037	1039	A′	C−C$_{\mathrm{ring}}$ str.(62)
1000	vw	1010	1007	A″	C−H$_{\mathrm{ring}}$ out-of-plane bend.(123)
980	w	971	977	A′	O−C$_{\mathrm{Me}}$ str.(66) + C−C$_{\mathrm{ring}}$ str.(23)
		949	945	A′	ring def.(74) + C−N str.(20)
927	vw	939	936	A″	C−H$_{\mathrm{ring}}$ out-of-plane bend.(111)
828	w	836	835	A″	C−H$_{\mathrm{ring}}$ out-of-plane bend.(41) + ring tor.(35) + C$_{\mathrm{ring}}$−C out-of-plane bend.(34) + C═O out-of-plane bend.(26)
816	w	818	811	A′	O═C−O def.(23) + C−O str.(21) + C−O−C$_{\mathrm{Me}}$ bend.(20)
775	s	755	755	A″	C−H$_{\mathrm{ring}}$ out-of-plane bend.(89) + ring tor.(62)
752	m				
706	m	704	702	A″	ring tor.(65)
		702	701	A′	ring def.(62)
		620	620	A′	ring def.(90)
		513	499	A′	O═C−O rock.(45)
		460	457	A″	ring tor.(102) + C$_{\mathrm{ring}}$−C out-of-plane bend.(48)
		421	421	A″	ring tor.(134)
		358	364	A′	C$_{\mathrm{ring}}$−C str.(30) + ring def.(22)
		327	323	A′	C−O−C$_{\mathrm{Me}}$ bend.(40) + O═C−O def.(28) + C$_{\mathrm{ring}}$−C in-plane bend.(27)
		211	211	A″	C−O tor.(51) + ring tor.(37)
		168	175	A′	C$_{\mathrm{ring}}$−C in-plane bend.(39) + O═C−O rock.(28)
		136	133	A″	O−C$_{\mathrm{Me}}$ tor.(85)
		111	109	A″	C−O tor.(40) + C$_{\mathrm{ring}}$−C out-of-plane bend.(26)
56	vw	69	68	A″	C$_{\mathrm{ring}}$−C tor.(92)

[a] Abbreviations used: vs,very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] Symmetry of vibrational modes. [c] Assignments for the s-trans conformer. Numbers in parentheses denote potential energy distribution (%). Contributions of less than 20% are not shown.

closely spaced interatomic distances. Also, the precise determination of conformational compositions is not easy because the atomic scattering factors of carbon and nitrogen atoms are similar. For these reasons, vibrational spectroscopic data and ab initio calculations are combined with the data of GED in the present study. To use accurate mean amplitudes and shrinkage corrections in the analysis is one of the essential factors for resolving similar distances. Therefore normal coordinate analyses have been performed on the gas-phase vibrational frequencies to derive harmonic force constants, which are used to calculate mean amplitudes and shrinkage corrections. In addition, RHF ab initio calculations have been performed by using the 6-31G* basis set to obtain structural constraints in the data analyses of GED.[10]

Experimental Section

Commercial samples with a purity of better than 99% (Tokyo Chemical Industry Co., Ltd.) were used with no further purification. Electron diffraction patterns were recorded on 8 × 8 in. Kodak projector slide plates by using an apparatus equipped with an r^3-sector[11] and a high-temperature nozzle.[12] The acceleration voltage of electrons was about 37 kV. Diffraction patterns of carbon disulfide were recorded at room temperature (298 K) in the same sequence of exposures and the electron wavelength was calibrated to the r_{a}(C−S) distance (1.5570 Å).[13] Other experimental conditions are listed in Table 1.

Optical densities were measured by using a microphotometer of a double-beam autobalanced type at intervals of 100 μm along the diameter. Five optical densities were averaged, and thus the densities taken at intervals of 500 μm were converted to intensities. The intensities obtained for four or three plates were averaged and divided by a theoretical background. Elastic and inelastic atomic scattering factors were taken from refs 14 and 15, respectively.

Vapor-phase IR spectra were measured on a BOMEM DA3.16 Fourier transform spectrometer with a resolution of 0.5 cm^{-1}. Sample pressures were the saturated vapor pressure at 320 K and about 0.2 Torr for MN and MP, respectively. Absorption cells with KBr windows were used. The path lengths of the cells were 7 cm and 10 m for MN and MP, respectively. Table 2 lists the observed vibrational wavenumbers of MN and MP.

Ab Initio Calculations

As shown later, each molecule has a planar skeleton in the gas phase. Figure 1 shows the s-trans conformer of each molecule and the numbering of atoms. Ab initio calculations were performed with the program GAUSSIAN 92.[16] Preliminary calculations at the RHF/4-21G level[17] for MN and MP revealed that the internal rotation around the C$_{\mathrm{ring}}$−C(═O) bond has the energy minima at ϕ_1 ($C_2C_3C_7O_8$ for MN and $N_1C_2C_7O_8$ for MP) = 0° (s-cis) and 180° (s-trans). On the other hand, the internal rotation of the (O═)C−O bond has only one energy minimum at ϕ_2 ($O_8C_7O_9C_{10}$) = 0° as expected from a strong dipole−dipole interaction. Therefore, harmonic force constants were calculated in the Cartesian coordinates for s-trans and s-cis forms.

To obtain more reliable information, the structures of the s-trans and s-cis conformers were optimized at the RHF/6-31G* level,[18] and the results are listed in Table 3. The RHF/6-31G* calculations show that the s-trans conformer is more stable than the s-cis conformer. The energy difference is about 0.29 and 1.65 kcal mol^{-1} for MN and MP, respectively.

Normal Coordinate Analysis

The Cartesian force constants given by the 4-21G ab initio calculations were transformed to the force constants in internal coordinates, f_{ij}. They were modified by using scale factors, c_i,[19] as f_{ij}(scaled) = $(c_i c_j)^{1/2}$ f_{ij}(unscaled). The scale factors for the s-trans and s-cis conformers were assumed to be the same. The scale factors were divided into several groups and were determined so as to reproduce the observed vibrational wavenumbers. Definitions of the internal coordinates, the scale factors, and the modified force constants in internal coordinates are listed in Tables S2, S3, and S4, respectively, in the Supporting Information. Table 2 lists the wavenumbers calculated from the modified force constants. The free energy differences, ΔG, were calculated from these vibrational wavenumbers, and the rotational constants obtained from the RHF/6-31G* calculations. Then the mole fractions of the s-trans conformers of MN and MP at the nozzle temperatures of the diffraction experiment were estimated to be 60 and 91%, respectively.

Mean amplitudes and shrinkage corrections were calculated from the modified force constants. Table S5 in the Supporting Information lists calculated mean amplitudes.

Analysis of Electron Diffraction Data

According to the 4-21G calculations mentioned above, the potential barriers for the C_{ring}−C and (O═)C−O torsions exceed 9 kcal mol^{-1}. Therefore each torsion was treated as a small-amplitude motion.

To reduce the number of adjustable structure parameters, data analysis was performed under the following assumptions: (1) the pyridine ring and the skeleton of the $COOCH_3$ group are planar as shown in Figure 1; (2) the methyl group has local C_{3v} symmetry; (3) the C−H bond lengths in the pyridine ring are the same; (4) the C_3C_2H, C_3C_4H, C_4C_5H, and C_5C_6H bond angles of MN and the N_1C_6H, C_2C_3H, C_3C_4H, and C_4C_5H bond angles of MP are equal to the corresponding 6-31G* values; (5) the OCH bond angles are equal to the average of 6-31G* values; (6) the differences between the values of similar parameters in each conformer are equal to the values given by the 6-31G* calculations; (7) the differences between the corresponding structural parameters of s-trans and s-cis conformers are equal to the 6-31G* values; (8) the $C_7O_9C_{10}$ angle of the major conformer of each molecule is 115.4°.

In a preliminary data analysis, least-squares calculations were carried out by fixing the C_{ring}−C_7 torsion angles at various values and the skeletons of both molecules were found to be planar, and hence, assumption 1 was adopted. Assumption 8 was required because of the strong correlation between the $C_7O_9C_{10}$ bond angle and the abundance of s-trans conformer. The assumed value of the $C_7O_9C_{10}$ angle was taken from the corresponding bond angle of MI.[5] This is because MI has only one conformer, and consequently, this angle has been determined rather precisely, i.e., with an uncertainty of ±1.5° in the data analysis of GED. The constraints on the structural parameters are summarized in Table S6 (Supporting Information).

TABLE 3: Optimized RHF/6-31G* Geometries[a]

parameter	s-trans	s-cis
Methyl Nicotinate		
Bond Length (Å)		
$r(N_1-C_2)$	1.320	1.318
$r(N_1-C_6)$	1.321	1.322
$r(C_2-C_3)$	1.389	1.390
$r(C_5-C_6)$	1.386	1.385
$r(C_3-C_4)$	1.389	1.388
$r(C_4-C_5)$	1.380	1.382
$r(C_3-C_7)$	1.487	1.487
$r(C_7=O_8)$	1.191	1.190
$r(C_7-O_9)$	1.322	1.324
$r(O_9-C_{10})$	1.418	1.418
$\langle r(C-H_{ring})\rangle^b$	1.074	1.074
$\langle r(C-H_{Me})\rangle^b$	1.080	1.080
Bond Angle (deg)		
$\angle C_2N_1C_6$	117.8	117.7
$\angle N_1C_2C_3$	123.3	123.5
$\angle N_1C_6C_5$	123.8	123.8
$\angle C_2C_3C_4$	118.2	118.2
$\angle C_6C_5C_4$	118.1	118.2
$\angle C_3C_4C_5$	118.7	118.6
$\angle C_2C_3C_7$	122.8	118.7
$\angle C_3C_7O_8$	123.6	124.0
$\angle C_3C_7O_9$	113.0	112.7
$\angle C_7O_9C_{10}$	117.0	116.9
$\angle C_3C_2H_{11}$	120.3	119.5
$\angle C_3C_4H_{12}$	119.6	120.4
$\angle C_4C_5H_{13}$	121.5	121.3
$\angle C_5C_6H_{14}$	120.2	120.2
$\angle O_9C_{10}H_{15}$	105.7	105.8
$\angle O_9C_{10}H_{16}$	110.4	110.4
$\angle O_9C_{10}H_{17}$	110.4	110.4
ΔE(s-cis − s-trans)^c	0.0^d	0.29
Methyl Picolinate		
Bond Length (Å)		
$r(N_1-C_2)$	1.321	1.322
$r(N_1-C_6)$	1.317	1.314
$r(C_2-C_3)$	1.386	1.386
$r(C_5-C_6)$	1.388	1.389
$r(C_3-C_4)$	1.384	1.386
$r(C_4-C_5)$	1.382	1.380
$r(C_2-C_7)$	1.503	1.506
$r(C_7=O_8)$	1.192	1.184
$r(C_7-O_9)$	1.313	1.327
$r(O_9-C_{10})$	1.416	1.417
$\langle r(C-H_{ring})\rangle^b$	1.074	1.074
$\langle r(C-H_{Me})\rangle^b$	1.080	1.080
Bond Angle (deg)		
$\angle C_2N_1C_6$	118.0	118.3
$\angle N_1C_2C_3$	123.5	123.2
$\angle N_1C_6C_5$	123.3	123.3
$\angle C_2C_3C_4$	118.1	118.2
$\angle C_6C_5C_4$	118.4	118.2
$\angle C_3C_4C_5$	118.7	118.8
$\angle N_1C_2C_7$	118.6	115.3
$\angle C_2C_7O_8$	122.3	124.7
$\angle C_2C_7O_9$	113.8	111.8
$\angle C_7O_9C_{10}$	116.8	116.6
$\angle N_1C_6H$	116.2	116.3
$\angle C_2C_3H$	119.8	120.5
$\angle C_3C_4H$	120.5	120.4
$\angle C_4C_5H$	121.4	121.5
$\angle O_9C_{10}H_{15}$	105.7	105.9
$\angle O_9C_{10}H_{16,17}$	110.5	110.5
ΔE(s-cis − s-trans)^c	0.0^e	1.65

[a] See Figure 1 for the atom numbering. [b] Brackets denote averaged values. [c] Relative energy in kcal mol^{-1}. [d] $E = -473.343\ 80E_h$ (hartree) [e] $E = -473.339\ 35E_h$ (hartree).

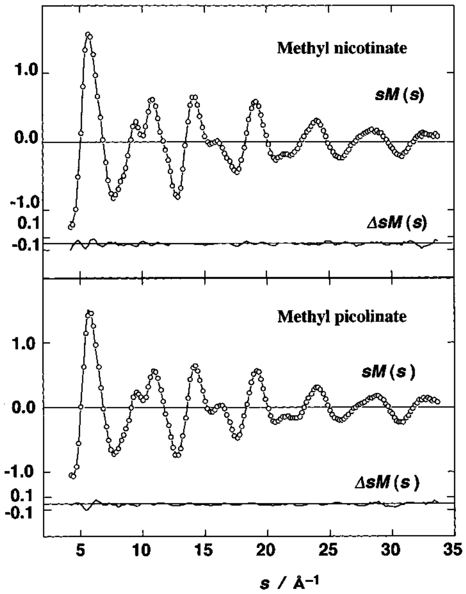

Figure 2. Experimental (open circles) and theoretical (solid curves) molecular scattering intensities of MN and MP; $\Delta sM(s) = sM(s)^{\text{obs}} - sM(s)^{\text{calc}}$. The theoretical curves were calculated from the best fitting parameters.

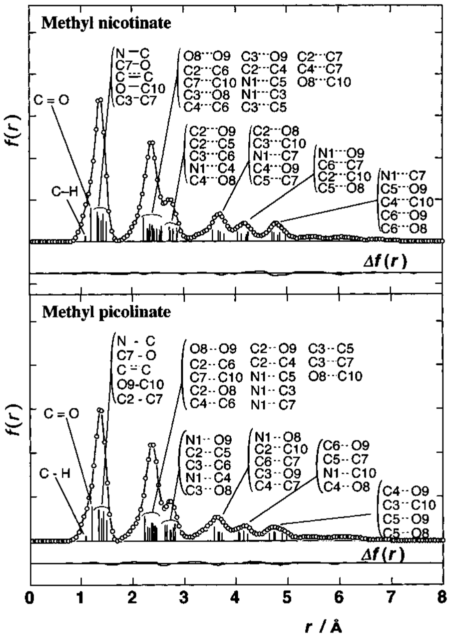

Figure 3. Experimental (open circles) and theoretical (solid curves) radial distribution curves of MN and MP; $\Delta f(r) = f(r)^{\text{obs}} - f(r)^{\text{calc}}$. Vertical bars indicate relatively important atom pairs of the s-trans conformers.

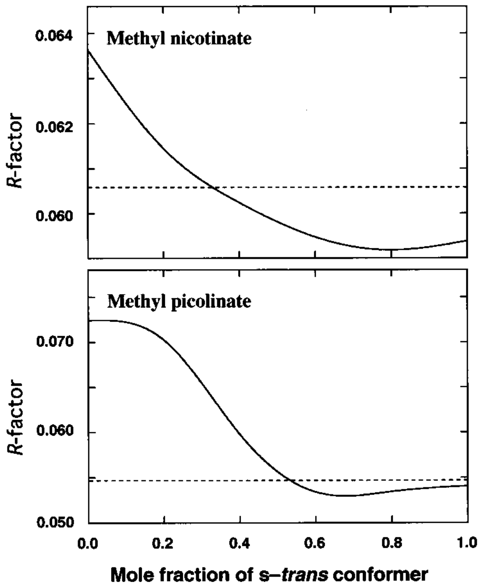

Figure 4. R-factor values versus the mole fractions of the s-trans conformers of MN and MP. $R = \{\Sigma_i W_i(\Delta sM(s)_i)^2/\Sigma_i W_i(sM(s)^{\text{obs}}{}_i)^2\}^{1/2}$, where W_i is a diagonal element of the weight matrix. Dashed lines show the 99% significant levels.

Vibrational mean amplitudes and shrinkage corrections were fixed at calculated values. Asymmetry parameters κ_{ij} were estimated in the same way as described in refs 20 and 21. Adjustable structure parameters and the index of resolution were determined by least-squares calculations on molecular scattering intensities.

Results and Discussion

Molecular scattering intensities and radial distribution curves are displayed in Figures 2 and 3, respectively. Figure 4 shows the R-factors against the relative abundance of the s-trans conformer for MN and MP. The mole fraction of the s-trans conformer of MN is 66(34)%. This is consistent with the predicted value 60%, which has been obtained from the results of the 6-31G* calculations and the vibrational analyses as described above. Similarly, the mole fraction of the s-trans conformer of MP, 77(23)%, is found to be consistent with the prediction (91%). Considering the uncertainty of the $C_7O_9C_{10}$ angle, ±1.5°, analyses were also carried out by fixing this angle at 114° and 117°. No significant change in the abundance was obtained.

Table 4 lists the determined molecular structures. The limits of error were estimated from three times standard deviations and the systematic errors accompanied with the estimated uncertainty (±1.5°) of $\angle C_7O_9C_{10}$. A correlation matrix is listed in Table S7. None of the absolute values of correlation coefficients exceeded 0.89. The planar skeletons of MN, MP, and MI show that their C=O double bonds are conjugated with the pyridine rings. This explains that the distances of the $C_{\text{ring}}-C(=O)$ bonds are shorter than the C−C distance of ethane (1.5351(1) Å)[22] and the $C_{\text{ring}}-C$ distance of toluene (1.515(2) Å).[23]

Table 5 compares the structures of MN, MP, and MI.[5] There is no significant difference between the structures of pyridine rings. That is, the structure of the pyridine ring is not significantly dependent on the position of the substituent. On the other hand, there is some difference between the ring structure of each isomer and that of pyridine.[24]

The comparison of the structural parameters of MN, MP, and MI with those of methyl acetate[6] and methyl acrylate[4] revealed the following differences in the structure of the COO moiety. First, the $C_{\text{ring}}-C_7=O_8$ angles of MN, MP, and MI are about 4° smaller than the corresponding angles of methyl acetate (125.5°)[6] and methyl acrylate (126.1°).[4] On the other hand, the $C_{\text{ring}}-C_7-O_9$ angles of the three isomers are about 3° larger than the corresponding angles of methyl acetate (111.4°)[6] and methyl acrylate (110.3°).[4] That is, the difference between $\angle C_{\text{ring}}-C=O$ and $\angle C_{\text{ring}}-C-O$ is much smaller for MN, MP, and MI than for methyl acetate and methyl acrylate.

Second, the (O=)C−O distances of MP and MN are considerably shorter than those of methyl acetate (1.360 Å)[6] and methyl acrylate (1.349 Å),[4] as found in the case of MI.[5]

TABLE 4: Observed Structural Parameters[a]

parameter	s-trans		s-cis	
	Methyl Nicotinate[b]			
	Bond Length (Å)			
$r_g(N_1-C_2)$	1.336	(7)	1.334	(7)
$r_g(N_1-C_6)$	1.337		1.338	
$r_g(C_2-C_3)$	1.405	(3)	1.406	(3)
$r_g(C_5-C_6)$	1.401		1.400	
$r_g(C_3-C_4)$	1.405		1.404	
$r_g(C_4-C_5)$	1.396		1.398	
$r_g(C_3-C_7)$	1.480(12)		1.480(12)	
$r_g(C_7{=}O_8)$	1.199(7)		1.198(7)	
$r_g(C_7-O_9)$	1.332	(11)	1.334	(11)
$r_g(O_9-C_{10})$	1.428		1.428	
$r_g(C_2-H)$	1.092	(12)	1.092	(12)
$r_g(C_{10}-H)$	1.098		1.098	
	Bond Angle (deg)			
$\angle_\alpha C_2N_1C_6$	119.0(14)		119.0(14)	
$\angle_\alpha N_1C_2C_3$	122.5	(11)	122.7	(11)
$\angle_\alpha N_1C_6C_5$	123.0		123.0	
$\angle_\alpha C_2C_3C_4{}^c$	118.5		118.4	
$\angle_\alpha C_6C_5C_4{}^c$	118.6		118.6	
$\angle_\alpha C_3C_4C_5{}^c$	118.5		118.5	
$\angle_\alpha C_2C_3C_7$	118.3(12)		123.8(12)	
$\angle_\alpha C_3C_7O_8$	121.5(12)		121.9(12)	
$\angle_\alpha C_3C_7O_9$	115.6(10)		115.3(10)	
$\angle_\alpha C_7O_9C_{10}$	115.4[d]		115.3[d]	
$\phi_1(C_2C_3C_7O_8)$	180.0		0.0	
	Methyl Picolinate[e]			
	Bond Length (Å)			
$r_g(N_1-C_2)$	1.346	(7)	1.347	(7)
$r_g(N_1-C_6)$	1.342		1.339	
$r_g(C_2-C_3)$	1.399	(4)	1.399	(4)
$r_g(C_5-C_6)$	1.401		1.402	
$r_g(C_3-C_4)$	1.397		1.399	
$r_g(C_4-C_5)$	1.396		1.394	
$r_g(C_2-C_7)$	1.497(11)		1.500(11)	
$r_g(C_7{=}O_8)$	1.209(7)		1.205(7)	
$r_g(C_7-O_9)$	1.328	(11)	1.342	(11)
$r_g(O_9-C_{10})$	1.431		1.432	
$r_g(C_3-H)$	1.093	(13)	1.093	(13)
$r_g(C_{10}-H)$	1.099		1.099	
	Bond Angle (deg)			
$\angle_\alpha C_2N_1C_6$	117.2(12)		117.5(12)	
$\angle_\alpha N_1C_2C_3$	124.0	(12)	123.7	(12)
$\angle_\alpha N_1C_6C_5$	123.8		123.8	
$\angle_\alpha C_2C_3C_4{}^c$	117.3		117.3	
$\angle_\alpha C_6C_5C_4{}^c$	117.7		117.5	
$\angle_\alpha C_3C_4C_5{}^c$	120.0		120.2	
$\angle_\alpha N_1C_2C_7$	115.1(10)		118.8(10)	
$\angle_\alpha C_2C_7O_8$	121.0(12)		123.8(12)	
$\angle_\alpha C_2C_7O_9$	115.1(12)		113.5(12)	
$\angle_\alpha C_7O_9C_{10}$	115.4[d]		115.2[d]	
$\phi_1(N_1C_2C_7O_8)$	180.0		0.0	

[a] See Figure 1 for the atom numbering. Parenthesized numbers are the estimated limits of error (3σ) referring to the last significant digit. The structures of s-trans and s-cis forms are not independent (see Table S6). [b] The index of resolution is 0.96(5). [c] Dependent parameter. [d] Assumed. [e] The index of resolution is 0.90(5).

There is a conjugation between the (O═)C−O single bond and the C═O double bond of esters,[25,26] which increases the double-bond character of the (O═)C−O bond and thus decreases its bond length. This effect is enhanced when the COO moiety is attached to the aromatic ring because of the additional conjugation with the ring. Therefore the (O═)C−O bonds of MI, MN, and MP are shorter than those of nonaromatic esters, methyl acetate and methyl acrylate. In addition, it seems to make the C_{ring}−C═O and C_{ring}−C−O angles of MI, MN, and MP closer to each other.

TABLE 5: Molecular Structures of Methyl Picolinate, Methyl Nicotinate, and Methyl Isonicotinate[a]

	methyl picolinate[b]		methyl nicotinate[b]		methyl isonicotinate[c]	
			Bond Length (Å)			
$r_g(N_1-C_2)$	1.346	(7)	1.336	(7)	1.343	(10)
$r_g(N_1-C_6)$	1.342		1.337		1.343	
$r_g(C_2-C_3)$	1.399	(4)	1.405	(3)	1.401	(4)
$r_g(C_5-C_6)$	1.401		1.401		1.401	
$r_g(C_3-C_4)$	1.397		1.405		1.401	
$r_g(C_4-C_5)$	1.396		1.396		1.401	
$r_g(C_{ring}-C_7)^d$	1.497 (11)		1.480 (12)		1.499 (9)	
$r_g(C_7{=}O_8)$	1.209 (7)		1.199 (7)		1.205 (5)	
$r_g(C_7-O_9)$	1.328	(11)	1.332	(11)	1.331	(8)
$r_g(O_9-C_{10})$	1.431		1.428		1.430	
			Bond Angle (deg)			
$\angle_\alpha C_6N_1C_2$	117.2 (12)		119.0 (14)		117.6 (9)	
$\angle_\alpha N_1C_2C_3$	124.0	(12)	122.5	(11)	123.6[e]	
$\angle_\alpha N_1C_6C_5$	123.8		123.0		123.6[e]	
$\angle_\alpha C_2C_3C_4$	117.3[e]		118.5[e]		118.2[e]	
$\angle_\alpha C_6C_5C_4$	117.7[e]		118.6[e]		118.2[e]	
$\angle_\alpha C_3C_4C_5$	120.0[e]		118.5[e]		118.7(9)	
$\angle_\alpha C_{ring}-C_7{=}O_8{}^d$	121.0(12)		121.5(12)		121.4(12)	
$\angle_\alpha C_{ring}-C_7-O_9{}^d$	115.1(12)		115.6(10)		114.2(10)	
$\angle_\alpha C_7O_9C_{10}$	115.4[f]		115.4[f]		115.4(15)	

[a] Atom numbering is shown in Figure 1. Parenthesized numbers are the estimated limits of error (3σ) referring to the last significant digits. [b] Present work. The structure of s-trans conformer. [c] Determined by GED combined with ab initio calculations. The symmetry of the pyridine ring was assumed to be C_{2v}. [d] C_{ring} is C_2, C_3, and C_4 for MP, MN, and MI, respectively. [e] Dependent parameter. [f] Assumed parameter.

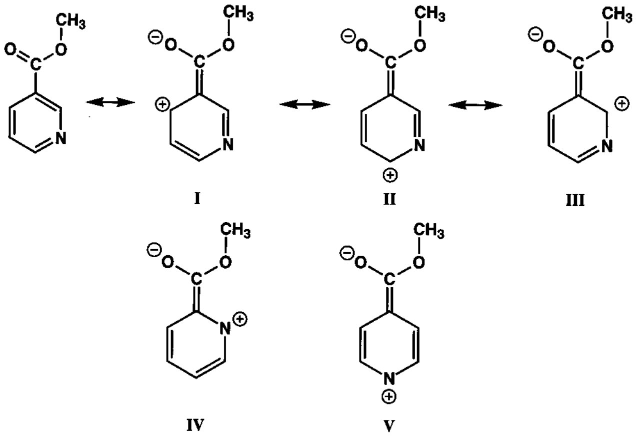

Figure 5. Resonance structures of MN, MP, and MI.

The C_{ring}−C(═O) bond length of MN (1.480(12) Å) is shorter than the corresponding ones of MP (1.497(11) Å) and MI (1.499(9) Å). The difference between the C_{ring}−C(═O) bond lengths of MN and MP is 0.017(16) Å, and the corresponding difference between MI and MP is 0.019(15) Å. The RHF/6-31G* calculations show a similar tendency: the C_{ring}−C(═O) distances of MN, MP, and MI are 1.487, 1.503, and 1.497 Å, respectively (see Table 3 and ref 5). The similarity of the C−C bond lengths of MP and MI indicates that the steric repulsion between the pyridine ring and the $COOCH_3$ group is not the main factor of the variation of the C−C bond length. Their difference can be explained in terms of resonance as shown in Figure 5. The resonance structures of **I**, **II**, and **III** give positive charges on the α and γ positions in the pyridine ring. The nitrogen atom in the pyridine ring is considered to be electronegative.[27] This electronegativity destabilizes the resonance structures in MP (**IV**) and MI (**V**). Therefore the number of stable resonance structures in MN is larger compared with MP and MI. Thus the C−C bond length of MN is shorter than those of MI and MP because of the increase in the double-bond character of the C−C bond.

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Supporting Information Available: The leveled total intensities and the backgrounds (Table S1), the internal coordinates (Table S2), the scale factors (Table S3), the modified force constants (Table S4), the mean amplitudes (Table S5), the structural constraints (Table S6) and the correlation matrixes (Table S7) (21 pages). Ordering information is given on any current masthead page.

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