J. Org. Chem. **1997,** *62,* 8063−8070

Trends in Inversion Barriers of Group 15 Compounds. 3. Are Fluorinated Pyridone Derivatives Planar or Nonplanar?

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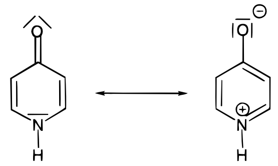
Received June 9, 1997⊗

Fluorinated compounds of 4-pyridone are studied using the semiempirical PM3 method, and the ab initio HF and MP2 methods. The perfluorinated derivative of 4-pyridone is predicted to have a nonplanar ring structure with the fluorine ligand at the nitrogen atom lying above the pyridine ring. The inversion barrier for the pentafluoro-4-pyridone is predicted to be 26 kJ/mol similar to that found for NH_3. This distortion corresponds to a static second-order Jahn−Teller effect and is expected to be experimentally detectable at low temperatures. *N*-Fluoro-4-pyridone is predicted to be nonplanar and has a small inversion barrier of 0.2 kJ/mol at the MP2 level. However, the maximum point of this barrier lies below the lowest zero-point out-of-plane inversion vibrational mode ($^1/_2$ 84 $cm^{-1} \equiv 0.5$ kJ/mol). This corresponds to a dynamic Jahn−Teller effect and thus is experimentally difficult to verify. The MP2 calculations indicate that at least one fluorine atom is required at the ring nitrogen in order to achieve nonplanarity. Schleyer's negative-independent chemical shift method (NICS) is applied, and the results are used to discuss aromaticity in fluorinated pyridones. The NICS values show that succesive fluorination increases aromaticity. The vibrational spectra of all fluorinated pyridone derivatives are predicted. The vibrational spectrum of 4-pyridone is discussed in detail using a normal-mode analysis defined within a set of nonredundant internal coordinates.

Introduction

It is well-known that the inversion barrier of NH_3 is quite small (24.2 kJ/mol),[1] the smallest in the series of Group 15 trihydrides.[2] It therefore comes as no surprise that some nitrogen-containing compounds, like pyrrole or pyridone, appear as planar species.[3] In pyridone the driving force for planarity at the nitrogen center is probably the conservation of aromaticity.[4] For example, for 4-pyridone one can draw the following resonance structures.



1 **2**

A more detailed discussion of possible resonance forms is given in ref 6. The tautomeric form of **1**, 4-hydroxypyridine, is aromatic in character and therefore has a planar ring system. From NMR ring-current measurements it was estimated that 2-pyridone has about 35% the aromaticity of benzene.[6] Even so, if valence bond theory predicts a lesser percentage of the zwitterionic structure **2** compared to **1**, the small inversion barrier predicted for N-containing compounds[7] like **1** and the

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[†] This work is dedicated to Prof. Con Cambie (Auckland) on the occasion of his emeritus.

⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.

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S0022-3263(97)01034-7 CCC: $14.00

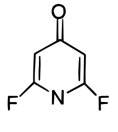
Table 1. Optimized PM3, HF/6-31G*, and MP2/6-31G* Geometries for the Structures 2−5[a]

	2			**3**			**4**			**5**			**6**		
parameter	PM3	HF	MP2	PM3	HF	MP2	PM3	HF	MP2	PM3	HF	MP2	PM3	HF	MP2
Distances															
NC_2	1.400	1.365	1.370	1.413	1.361	1.368	1.409	1.361	1.365	1.411	1.355	1.362	1.419	1.364	1.368
	1.408	–	–	*1.420*	–	–	*1.416*	–	*1.365*	*1.430*	*1.371*	*1.357*	*1.441*	*1.394*	*1.394*
C_2C_3	1.352	1.337	1.360	1.356	1.327	1.348	1.370	1.329	1.358	1.350	1.338	1.361	1.369	1.330	1.362
	1.350	–	–	*1.354*	–	–	*1.369*	–	*1.358*	*1.345*	*1.332*	*1.363*	*1.364*	*1.318*	*1.349*
C_3C_4	1.470	1.467	1.460	1.473	1.470	1.465	1.484	1.466	1.460	1.473	1.469	1.462	1.488	1.468	1.460
	1.472	–	–	*1.474*	–	–	*1.369*	–	*1.460*	*1.477*	*1.473*	*1.462*	*1.491*	*1.477*	*1.468*
C_4O	1.225	1.206	1.243	1.222	1.201	1.238	1.214	1.195	1.235	1.223	1.204	1.242	1.212	1.193	1.235
	1.224	–	–	*1.221*	–	–	*1.213*	–	*1.235*	*1.220*	*1.201*	*1.242*	*1.210*	*1.186*	*1.229*
NX_1	0.991	0.993	1.011	0.995	0.996	1.013	0.995	0.997	1.015	1.384	1.340	1.387	1.373	1.327	1.366
	0.992	–	–	*0.996*	–	–	*0.996*	–	*1.015*	*1.392*	*1.353*	*1.381*	*1.381*	*1.367*	*1.431*
C_2X_2	1.095	1.074	1.086	1.335	1.311	1.341	1.332	1.305	1.335	1.098	1.071	1.084	1.328	1.295	1.325
	1.095	–	–	*1.335*	–	–	*1.332*	–	*1.335*	*1.099*	*1.072*	*1.084*	*1.328*	*1.298*	*1.326*
C_3X_3	1.098	1.073	1.085	1.096	1.071	1.014	1.336	1.319	1.341	1.096	1.072	1.084	1.336	1.317	1.339
	1.098	–	–	*1.096*	–	–	*1.336*	–	*1.341*	*1.096*	*1.072*	*1.084*	*1.335*	*1.312*	*1.335*
Angles															
NC_2C_3	120.8	121.9	121.0	123.4	123.7	123.2	122.8	122.3	121.6	119.0	119.4	118.2	121.0	120.0	118.9
	121.2	–	–	*123.7*	–	–	*123.0*	–	*121.6*	*120.0*	*120.1*	*118.5*	*122.2*	*122.6*	*121.7*
$C_2C_3C_4$	121.3	121.1	121.9	120.3	119.7	120.2	122.0	121.6	122.4	121.7	121.4	122.3	122.4	122.2	123.2
	121.2	–	–	*120.2*	–	–	*121.9*	–	*122.4*	*121.4*	*121.1*	*122.1*	*122.1*	*121.5*	*121.8*
C_3C_4O	122.4	123.1	123.2	122.1	122.6	122.6	123.5	123.6	123.8	122.1	122.9	123.1	123.2	123.5	123.7
	122.4	–	–	*122.1*	–	–	*123.5*	–	*123.8*	*122.3*	*122.9*	*123.0*	*123.4*	*123.3*	*123.3*
C_2NX_1	119.7	119.9	119.7	121.6	120.8	120.7	121.3	120.3	120.2	118.6	117.9	117.4	120.2	118.7	118.4
	117.0	–	–	*118.8*	–	–	*118.9*	–	*120.2*	*114.9*	*114.5*	*116.3*	*115.6*	*108.8*	*107.8*
NC_2X_2	116.6	115.5	115.8	112.3	112.1	112.4	113.6	113.7	114.4	117.2	115.4	115.7	114.6	114.7	115.5
	116.2	–	–	*112.2*	–	–	*113.6*	–	*114.4*	*116.4*	*114.7*	*115.5*	*113.9*	*113.0*	*113.7*
$C_2C_3X_3$	120.5	120.6	119.9	121.1	120.7	120.3	119.5	120.3	119.2	120.2	120.3	119.3	119.4	119.7	118.4
	120.7	–	–	*121.2*	–	–	*119.7*	–	*119.2*	*120.6*	*120.7*	*119.5*	*119.8*	*121.3*	*120.4*
$C_2C_3C_4O$	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180
	177.9	–	–	*177.9*	–	–	*178.3*	–	*−179.1*	*173.9*	*178.6*	*179.7*	*175.7*	*−179.6*	*−175.8*
$X_3C_3C_4O$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−2.4	–	–	*−2.7*	–	–	*−2.5*	–	*−0.1*	*−7.0*	*−2.6*	*−0.6*	*−5.5*	*2.1*	*1.9*
$X_2C_2C_3C_4$	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180
	179.7	–	–	*179.4*	–	–	*179.3*	–	*179.4*	*179.1*	*178.8*	*179.1*	*178.8*	*178.6*	*177.7*
$N_1C_2C_3C_4$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	−3.8	–	–	*−4.0*	–	–	*−4.3*	–	*−1.4*	*−5.8*	*−5.4*	*−4.4*	*−7.0*	*−4.9*	*−11.1*
$X_1N_1C_2C_3$	180	180	180	180	180	180	180	180	180	180	180	180	180	180	180
	160.5	–	–	*161.2*	–	–	*163.0*	–	*177.8*	*160.4*	*159.0*	*168.5*	*157.3*	*132.2*	*135.6*

[a] The geometries for the nonplanar structures are set in italics and are given below the ones kept in the planar arrangement (C_{2v} symmetry). The notation for the different atoms is given in Figure 1. All distances are in angstroms, bond and torsion angles are in degrees.

strong tendency for aromatic compounds to be planar[5] rationalizes a planar C_5N ring arrangement for 4-pyridone. Similar arguments hold for 2-pyridone. All pyridone derivatives studied so far by spectroscopic methods have been predicted to be planar.[8]

A nonplanar pyridone ring system may be achieved by either decreasing the aromatic character in **2** or by increasing the inversion barrier at the nitrogen center in **1**. For example, we expect that the phosphorus analogue of **1** would be nonplanar due to the fact that the inversion barrier of PH_3 is 132 kJ/mol.[9] On the other hand, Liebman et al. pointed out that a subsequent substitution of hydrogen by more electronegative fluorine ligands in NH_3 raises the inversion barrier substantially,[10] i.e., NF_3 has an inversion barrier of approximately 300 kJ/mol.[11] Thus, introducing electronegative substituents into the ring system **1** may eventually overcome the aromatic stabilization resulting in a nonplanar structure. The question is, at what stage of fluorination will the ring system become nonplanar? The fluorinated compounds of pyridone have not been studied in detail (in contrast to the fluorine-substituted compounds of pyridine), and we predict structures and vibrational frequencies for the compounds shown below. Moreover, theoretical studies in the past have concentrated on the 2-hydroxypyridine derivatives and its lactam tautomers[12−15] because of their role in biologically relevant systems.[16] There are only a few Hartree−Fock or semiempirical studies on 4-hydroxypyridine or 4-pyridone.[17−20] For example, Fraga et al. studied the tautomeric equilibrium between 4-hydroxypyridine and 4-pyridone by theoretical methods including solvent effects.[18]



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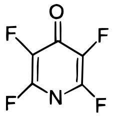

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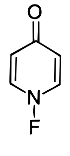

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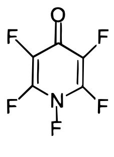

6

There has been considerable discussion of the infrared and Raman spectrum of 4-pyridone.[21,22] The assignment

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Table 2. HF/6-31G* and MP2/6-31G* Harmonic Frequencies for the Minimum Planar Structures (C_{2v} Symmetry) of Compound 2−4[a]

			2		**3**		**4**
n	IRREP	mode	HF	MP2	HF	MP2	HF
1	B_1	out-of-plane	178 *3*	150 *0.3*	176 *3*	140 *0.2*	111 *2*
2	B_1	out-of-plane	423 *133*	392 *82*	194 *5*	172 *8*	151 *40*
3	A_2	out-of-plane	460 *0*	412 *0*	257 *0*	232 *0*	151 *0*
4	B_2	in-plane	496 *10*	452 *5*	400 *13*	364 *8*	303 *0.02*
5	A_1	in-plane	555 *10*	520 *7*	355 *4*	324 *5*	290 *0.2*
6	B_1	H_1 out-of-plane	541 *21*	526 *31*	355 *135*	328 *116*	236 *104*
7	B_2	in-plane	672 *0.9*	629 *0.9*	533 *16*	493 *14*	363 *10*
8	B_1	out-of-plane	799 *3*	665 *16*	738 *12*	591 *3*	398 *19*
9	A_2	out-of-plane	888 *0*	799 *0*	680 *0*	581 *0*	406 *0*
10	B_1	out-of-plane	944 *110*	823 *84*	776 *3*	681 *4*	661 *12*
11	A_1	in-plane	866 *8*	835 *3*	543 *19*	508 *12*	350 *4*
12	B_1	out-of-plane	1096 *0.6*	906 *1*	929 *156*	796 *100*	753 *6*
13	A_2	out-of-plane	1099 *0*	913 *0*	928 *0*	823 *0*	676 *0*
14	A_1	in-plane	1069 *77*	1007 *50*	654 *15*	608 *10*	488 *8*
15	A_1	in-plane	1103 *2*	1045 *50*	997 *6*	949 *7*	651 *6*
16	B_2	in-plane	1161 *0.05*	1103 *3*	633 *0.3*	578 *0.4*	469 *0.3*
17	A_1	in-plane	1304 *30*	1232 *16*	1123 *33*	1048 *33*	803 *10*
18	B_2	in-plane	1344 *0.6*	1289 *0.1*	1119 *13*	1051 *26*	775 *0.5*
19	B_2	in-plane	1374 *29*	1299 *8*	1293 *84*	1193 *55*	1045 *172*
20	B_2	in-plane	1552 *0.09*	1456 *0.1*	1333 *6*	1258 *1*	1270 *17*
21	A_1	in-plane	1568 *0.5*	1461 *0.5*	1369 *82*	1264 *44*	1270 *66*
22	B_2	in-plane	1679 *176*	1594 *116*	1460 *29*	1363 *10*	1375 *177*
23	B_2	in-plane	1788 *10*	1657 *0.5*	1693 *371*	1603 *367*	1468 *22*
24	A_1	in-plane	1844 *77*	1688 *1*	1551 *6*	1452 *9*	1444 *276*
25	A_1	in-plane	1932 *736*	1764 *367*	1901 *529*	1729 *6*	1543 *112*
26	B_2	in-plane	3397 *4*	3254 *5*	1836 *135*	1712 *54*	1747 *205*
27	A_1	in-plane	3397 *8*	3254 *4*	1947 *709*	1780 *647*	1935 *748*
28	B_2	in-plane	3417 *16*	3274 *5*	3434 *0.6*	3296 *3*	1900 *161*
29	A_1	in-plane	3418 *0.8*	3275 *0.5*	3435 *4*	3296 *5*	1974 *161*
30	A_1	N_1H_1 stretch	3909 *122*	3669 *123*	3880 *217*	3653 *211*	3873 *262*

[a] Frequencies are given in cm^{-1}, infrared intensities in km mol^{-1} are set in italics. The atomic labeling is given in Figure 1. For 4-pyridone **2** the modes are shown in Figure 2. Only 4-pyridone is shown in increasing frequency order; the other frequencies are assigned to their original C_{2v} structure as best as possible. In-plane modes: A_2 or B_1, out-of-plane modes: A_1 or B_2.

of the C=O stretching mode especially seems to cause difficulties. This problem will be addressed using a harmonic frequency analysis within the ab initio framework allowing for a detailed analysis of different vibrational contributions.

Computational Details

To predict if nonplanar pyridone derivatives exist, we present theoretical studies[23] at the PM3[24] and Hartree−Fock (HF) level for compound **1**, the difluoro derivative **3**, the tetrafluoro compound **4**, the *N*-fluoro compound **5**, and the pentafluoro compound **6**. We include electron correlation by applying second-order Møller−Plesset theory (MP2).[25] A 6-31G* split-valence basis set was used throughout. The geometries were fully optimized by gradient techniques[23] and followed by a harmonic frequency analysis. The orbital space has been kept fully active in the MP2 calculation. In particular for compound **6** the MP2 geometry optimization and frequency analysis using analytical first- and second-order derivatives with respect to nuclear coordinates were very computer time expensive and required about 7.9 GB of disk space, 512 MB of memory, and 26 h of CPU on 8-processors of a multiprocessor SIC R10000 computer system. Some of the optimized planar structures are first-order transition states for the nitrogen ligand out-of-plane motion, and only the frequencies for the optimized nonplanar structures are shown. The PM3, HF, and MP2 geometries are collected in Table 1. Frequency analyses at the PM3 and MP2 level are shown in Tables 2 and 3. Inversion barriers and dipole moments are listed in Table 4. As a reference to future work total electronic energies for the HF and MP2 6-31G* calculations are listed in Table 5. A code was developed to transform the Cartesian harmonic MP2 force-field into Pulay's force field defined in nonredundant internal coordinates (Table 6).[26] For 4-pyridone a normal-mode analysis using Pulay's M-matrix method was carried out allowing us to discuss the vibrational distribution of the fundamental modes (Table 7). For the tetrafluoro compound **4** and the N-fluorinated species **5** the location of a nonplanar structure was not trivial, and we had to apply very tight convergence criteria, i.e., $<10^{-10}$ au for the total electronic energy and $<10^{-4}$ au for the root-mean-square of the force field.

To discuss the widely used term aromaticity in more detail, we applied Schleyer's recently published negative-

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Table 3. PM3, HF/6-31G*, and MP2/6-31G* Harmonic Frequencies for the Minimum Nonplanar Structures (C_s Symmetry) of Compounds 2−6[a]

		2	**3**	**4**		**5**			**6**		
n	IRREP	PM3	PM3	PM3	MP2	PM3	HF	MP2	PM3	HF	MP2
1	$A'(B_1)$	121	114	70	31	79	111	84	53	86	85
		3	*0.7*	*0.3*	*13*	*8*	*17*	*16*	*0.2*	*3*	*4*
2	$A''(A_2)$	369	205	113	134	407	468	418	112	137	122
		0.7	*0.003*	*0.03*	*0.002*	*16*	*7*	*2*	*0.04*	*0.002*	*0.01*
3	$A'(B_1)$	391	178	168	139	224	182	143	116	139	130
		139	*4*	*5*	*10*	*24*	*49*	*22*	*2*	*5*	*5*
4	$A'(B_1)$	423	426	321	230	416	458	406	332	223	199
		164	*235*	*7*	*92*	*42*	*24*	*18*	*5*	*17*	*9*
5	$A''(B_2)$	475	369	337	274	346	389	362	316	290	251
		11	*17*	*0.7*	*0.008*	*3*	*13*	*11*	*0.06*	*1*	*0.02*
6	$A'(A_1)$	509	308	309	262	442	489	455	317	291	263
		28	*3*	*0.8*	*0.7*	*1*	*0.1*	*12*	*3*	*0.1*	*0.1*
7	$A''(B_2)$	612	484	350	325	498	511	467	342	312	280
		0.1	*2*	*11*	*6*	*3*	*3*	*0.8*	*1*	*0.1*	*0.009*
8	$A'(B_1)$	651	588	422	352	665	774	632	586	440	405
		3	*17*	*232*	*19*	*15*	*54*	*18*	*0.9*	*6*	*5*
9	$A''(A_2)$	801	556	382	376	798	874	769	388	441	401
		0.1	*2*	*0.3*	*0.01*	*0.002*	*0.05*	*0.05*	*6*	*3*	*2*
10	$A'(B_1)$	851	647	575	458	863	943	812	623	622	564
		104	*2*	*16*	*7*	*114*	*119*	*83*	*9*	*14*	*8*
11	$A'(A_1)$	878	495	338	325	764	817	761	332	343	319
		7	*61*	*1*	*3*	*35*	*79*	*58*	*5*	*1*	*1*
12	$A''(A_2)$	965	903	644	555	973	1095	913	653	684	592
		0.03	*0.1*	*0.6*	*0*	*0.3*	*0*	*0.4*	*2*	*0.6*	*0.01*
13	$A'(B_1)$	972	948	773	638	983	1085	901	787	766	647
		27	*155*	*34*	*0.3*	*4*	*5*	*6*	*28*	*10*	*68*
14	$A'(A_1)$	977	643	444	601	914	856	835	384	478	448
		16	*13*	*53*	*4*	*67*	*25*	*24*	*17*	*0.3*	*1.6*
15	$A'(A_1)$	1032	981	636	461	992	1099	1036	416	684	618
		41	*25*	*19*	*5*	*37*	*2*	*0.04*	*5*	*2*	*6*
16	$A''(B_2)$	1088	575	424	434	624	690	647	363	374	335
		0.08	*0.5*	*0.5*	*0.5*	*0.08*	*0.9*	*2*	*10*	*13*	*8*
17	$A'(A_1)$	1140	1060	770	737	1120	1280	1198	662	738	681
		0.1	*6*	*0.4*	*3*	*0.9*	*12*	*4.3*	*59*	*48*	*3*
18	$A''(B_2)$	1158	1073	701	704	1109	1185	1117	431	467	439
		12	*0.02*	*1*	*1*	*1*	*5*	*9.7*	*0.07*	*0.2*	*0.3*
19	$A''(B_2)$	1234	1227	1046	973	1191	1354	1284	764	868	778
		0.6	*3*	*30*	*143*	*7*	*11*	*4*	*0.6*	*0.9*	*0.2*
20	$A''(B_2)$	1361	3331	1320	1180	1308	1457	1389	1062	1083	1004
		2	*25*	*51*	*1*	*4*	*20*	*3*	*53*	*223*	*167*
21	$A'(A_1)$	1364	1308	1240	1179	1188	1342	1225	1085	1107	937
		10	*2*	*13*	*62*	*9*	*32*	*18*	*50*	*195*	*113*
22	$A''(B_2)$	1534	1434	1359	1287	1466	1604	1552	1323	1273	1186
		91	*20*	*22*	*73*	*76*	*108*	*55*	*65*	*17*	*10*
23	$A''(B_2)$	1769	1573	1487	1411	1796	1767	1614	1488	1476	1391
		18	*252*	*125*	*84*	*4*	*2*	*5*	*67*	*125*	*131*
24	$A'(A_1)$	1793	1543	1503	1363	1354	1570	1456	1274	1284	1151
		277	*18*	*157*	*163*	*8*	*10*	*6*	*4*	*8*	*25*
25	$A'(A_1)$	1934	1875	1641	1444	1815	1849	1667	1489	1443	1326
		503	*567*	*101*	*45*	*191*	*45*	*1*	*88*	*74*	*20*
26	$A''(B_2)$	3019	1854	1672	1630	3020	3415	3272	1634	1611	1499
		20	*22*	*63*	*190*	*32*	*0.4*	*0.07*	*29*	*143*	*80*
27	$A'(A_1)$	3021	1947	1886	1738	1951	1956	1751	1631	1516	1405
		34	*283*	*315*	*145*	*449*	*671*	*319*	*149*	*296*	*223*
28	$A''(B_2)$	3073	3071	1878	1739	3066	3440	3288	1893	1946	1742
		79	*99*	*24*	*129*	*91*	*1*	*0.3*	*36*	*113*	*150*
29	$A'(A_1)$	3075	3074	1959	1775	3022	3415	3271	1907	1991	1739
		12	*35*	*298*	*291*	*49*	*0.05*	*0.3*	*228*	*236*	*157*
30	$A'(A_1)$	3412	3380	3379	3642	3069	3441	3290	1971	2021	1779
		17	*52*	*65*	*254*	*6*	*0.04*	*0.4*	*276*	*368*	*87*

[a] Frequencies are given in cm^{-1}, infrared intensities in $km\ mol^{-1}$ are set in italics. The irreducible representation for the fundamental mode resulting from the undistorted C_{2v} structures is set in brackets. Only 4-pyridone is shown in increasing frequency order; the other frequencies are assigned to their original C_{2v} structure as best as possible.

independent chemical shift method (NICS).[27] The gauge invariant atomic orbital approach (GIAO) is used[23,28] to calculate the negative isotropic component of the diamagnetic shielding tensor at the center of the ring system (NICS), which is determined by mean value of the ring atom coordinates.[27] Schleyer has demonstrated that NICS values correlate well with other definitions of aromaticity; in addition NICS values are more readily obtained than most other indicators for aromaticity.[27,29]

Results and Discussion

A comparison of the bond distances and bond angles shows that the PM3 method performs reasonably well.

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Table 4. Energy Differences and Dipole Moments of Compounds 2–6[a]

compound	method	ΔE	$\mu_z(C_{2v})$	$\mu_z(C_s)$	$\mu_x(C_s)$
2	PM3	1.1	6.01	5.11	0.61
	HF	0	7.03	–	–
	MP2	0	6.69	–	–
3	PM3	1.1	3.99	3.59	0.62
	HF	0	5.21	–	–
	MP2	0	4.94	–	–
4	PM3	0.9	5.08	4.70	0.38
	HF	0	6.45	–	–
	MP2	$<10^{-3}$	6.20	6.20	0.05
5	PM3	0.6	4.85	3.59	0.84
	HF	0.1	4.72	3.97	0.24
	MP2	0.02	4.60	4.33	0.05
6	PM3	9.3	3.14	2.10	0.25
	HF	25.1	4.43	2.26	0.29
	MP2	26.4	4.40	1.98	0.27

[a] Energy differences ΔE between the planar and nonplanar structures in kJ/mol and dipole moments μ in Debye. The dipole moments are listed for the planar structures (C_{2v}) and for the nonplanar structures (C_s). Dipole moments are defined in direction N (+) to O (−) and ligand X_1 (+) to the ring (−) (see Figure 1).

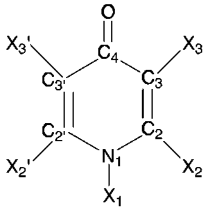

Figure 1. Atomic labeling for the 4-pyridone derivatives.

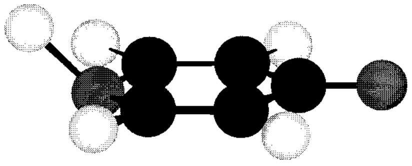

Figure 2. Molecular structure of pentafluoro-4-pyridone.

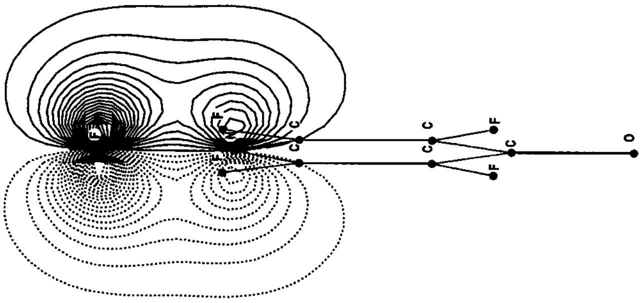

Figure 3. Contour diagram of the lowest lying totally bonding π-orbital ($\epsilon_\pi = -0.830$ au) of pentafluoro-4-pyridone.

Our calculated bond distances and angles for 4-pyridone agree nicely with the ones previously published by Schlegel et al. or Scanlan et al. who used Hartree–Fock theory within a 6-31G* or 6-31G** basis set, respectively.[19,20] Interestingly, the PM3 approximation predicts a nonplanar structure for all compounds in contrast to the more accurate ab initio method. This may be explained by comparing the inversion barriers for NH_3 at different levels of theory. For NH_3 we obtain 41.8 kJ/mol at the PM3 level, 27.2 kJ/mol at the HF/6-31G* level, and 27.4 kJ/mol at the MP2/6-31G* level. It was shown recently that the PM3 method overestimates the inversion barrier in NF_3 significantly.[11] Thus there is a greater tendency for PM3 to predict a nonplanar structure. However, for NH_2F we obtain a smaller barrier at the PM3 level compared to the other methods: 58.3 kJ/mol at the PM3 level, 72.2 kJ/mol at the HF/6-31G* level, and 77.2 kJ/mol at the MP2/6-31G* level. The ab initio results show that 4-pyridone **1** and its difluoro derivative **3** are both planar, hence the increase in electronegativity and subsequent increase in the inversion barrier is not sufficient to overcome aromaticity. This is in contrast to the pentafluoro-4-pyridone **6**, and possibly to the tetrafluoro-4-pyridone **4** and N-fluoro-4-pyridone **5** compounds, these are nonplanar at the 6-31G* MP2 level. The molecular structure of compound **6** is depicted in Figure 2. The predicted inversion barrier for this compound is 26 kJ/mol and is only slightly larger than that for NH_3. In contrast to NH_3, however, the large mass of the fluorine ligand implies that it will not readily undergo quantum tunneling, and therefore the nonplanar structure should be observable by standard spectroscopic methods (vibrational spectroscopy or gas-phase electron diffraction).

The accurate detection of nonplanar arrangements for floppy molecules is problematic because they exhibit shallow minima on the potential energy surface and can result in a dynamic Jahn–Teller effect. For example, planar structures of compounds **4** and **5** have very small imaginary frequencies of 22 cm^{-1} and 73 cm^{-1} respectively, where this mode corresponds to the *N*-hydrogen (or *N*-fluorine) out-of-plane motion. Moreover, improvement of the basis set and correlation method may eventually result in a planar structure for these compounds. If we assume that compound **4** is nonplanar, then the inversion motion involving the *N*-hydrogen in **4** can be approximated by a one-dimensional double-minimum potential and tunneling splitting will occur. However, the barrier is extremely small (<0.1 cm^{-1}) and below the accuracy of the method applied, with the lowest frequency of 31 cm^{-1} lying well above the maximum. There are only very small differences in bond lengths (<0.001 Å) and bond angles ($<0.1°$) between the planar and the nonplanar structures of compound **4**; the only sizable difference is calculated for some of the torsion angles (Table 1). The trend toward a nonplanar arrangement with increasing fluorine substitution can be seen, for example, in the lowest frequency corresponding to the *N*-hydrogen out-of-plane mode. If we compare the HF results for the planar structures, we have 178 cm^{-1} for compound **1**, 176 cm^{-1} for compound **3**, and 111 cm^{-1} for compound **4**.

In a previous paper (paper 2 in this series)[11] we discussed second-order (or pseudo) Jahn–Teller (JT) distortions in Group 15 containing compounds in some detail. For symmetric (C_{2v}) pyridone derivatives, the ligand-nitrogen (H–N or F–N) out-of-plane motion is of b_1-symmetry, hence this must be the symmetry of the distortion second-order Hamiltonian, $\partial^2 H_0/\partial q^2$, H_0 being the Hamiltonian fixed at the planar arrangement and q being the distortion coordinate (which is of b_1-symmetry). We therefore expect a low lying ${}^1B_1$ state to be responsible for symmetry breaking and thus the a_1(HOMO)/b_1(LUMO) energy gap to give some insight into the magnitude of the second-order JT-term. However, analyzing these orbital energies we cannot find a clear trend in the HOMO/LUMO gap with respect to increasing fluorination. We note however, that the b_1-LUMO in the pentafluorinated pyridone is the lowest lying of all pyridione compounds studied here.

Table 5. Total Electronic Energies within the 6-31G* Basis Set[a]

method	geometry	**2**	**3**	**4**	**5**	**6**
HF	linear	−321.550314	−519.253082	−716.914423	−420.309532	−815.653042
	bent	–	–	–	−420.310038	−815.662593
MP2	linear	−322.543025	−520.583750	−718.590345	−421.477139	−817.504465
	bent	–	–	−718.590345	−421.477211	−817.514523

[a] All values are in atomic units.

Table 6. Definition of the Internal Coordinates for the Normal Mode Analysis of 4-Pyridone[a]

Ring Stretches s

$s_1 = C_4C_3$, $s_2 = C_3C_2$, $s_3 = C_2N_1$, $s_4 = C_{2'}N_1$, $s_5 = C_{3'}C_{2'}$, $s_6 = C_{3'}C_{4'}$

Ring Deformations d

$\alpha_1 = C_{3'}C_4C_3$, $\alpha_2 = C_4C_3C_2$, $\alpha_3 = C_3C_2N_1$, $\alpha_4 = C_2N_1C_{2'}$, $\alpha_5 = N_1C_{2'}C_{3'}$, $\alpha_6 = C_{2'}C_{3'}C_4$

$$d_7 = \frac{1}{2\sqrt{3}}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6),\ d_8 = \frac{1}{2}(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6),$$

trigonal deformation $d_9 = \frac{1}{\sqrt{6}}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$

Ring Torsions t

$\tau_1 = C_4C_3C_2N_1$, $\tau_2 = C_{3'}C_4C_3C_2$, $\tau_3 = C_3C_5N_1C_{2'}$, $\tau_4 = N_1C_{2'}C_{3'}C_4$, $\tau_5 = C_2N_1C_{2'}C_2$, $\tau_6 = C_{2'}C_{3'}C_4C_3$

asymmetric torsions $t_{10} = \frac{1}{2\sqrt{3}}(-\tau_1 + 2\tau_2 - \tau_3 - \tau_4 + 2\tau_5 - \tau_6)$, $t_{11} = \frac{1}{2}(\tau_1 - \tau_3 + \tau_4 - \tau_6)$,

puckering $t_{12} = \frac{1}{\sqrt{6}}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6)$

Carbonyl Group Motions c

$\beta_1 = OC_4C_3$, $\beta_2 = OC_4C_{3'}$

stretching $c_{13} = C_4O$, CO rocking $c_{14} = \frac{1}{\sqrt{2}}(\beta_1 - \beta_2)$, oxygen out-of-plane $c_{15} = OC_4C_3C_{3'}$

Ring Hydrogen r

$\gamma_1 = H_3C_3C_4$, $\gamma_2 = H_3C_3C_2$, $\gamma_3 = H_2C_2C_3$, $\gamma_4 = H_2C_2N_1$, $\gamma_5 = H_1N_1C_2$, $\gamma_6 = H_1N_1C_{2'}$, $\gamma_7 = H_{2'}C_{2'}N_1$,
$\gamma_8 = H_{2'}C_{2'}C_3$, $\gamma_9 = H_{3'}C_{3'}C_{2'}$, $\gamma_{10} = H_{3'}C_{3'}C_4$

stretching $r_{16} = C_3H_3$, CH rocking $r_{17} = \frac{1}{\sqrt{2}}(\gamma_1 - \gamma_2)$, H out of plane $r_{18} = H_3C_3C_4C_2$

stretching $r_{19} = C_2H_2$, CH rocking $r_{20} = \frac{1}{\sqrt{2}}(\gamma_3 - \gamma_4)$, H out of plane $r_{21} = H_2C_2C_3N_1$

stretching $r_{22} = N_1H_1$, NH rocking $r_{23} = \frac{1}{\sqrt{2}}(\gamma_5 - \gamma_6)$, H out of plane $r_{24} = H_1N_1C_2C_{2'}$

stretching $r_{25} = C_{2'}H_{2'}$, CH rocking $r_{26} = \frac{1}{\sqrt{2}}(\gamma_7 - \gamma_8)$, H out of plane $r_{27} = H_{2'}C_{2'}N_1C_4$

stretching $r_{28} = C_{3'}H_{3'}$, CH rocking $r_{29} = \frac{1}{\sqrt{2}}(\gamma_9 - \gamma_{10})$,, H out of plane $r_{30} = H_{3'}C_{3'}C_{2'}C_4$

[a] See Figure 1 for the atomic numbering.

In the planar arrangement we expect a larger contribution from the benzenoid resonance structure **2** within the valence bond picture. NMR measurements of the ring current for the different compounds may give some insight.[5] A larger contribution by resonance structure **2** should result in an increased dipole moment of the compound. Indeed, the PM3 and ab initio results of **6** show a significantly reduced dipole moment for the nonplanar compared to the planar form, Table 4. We also calculate slightly enhanced infrared A′ out-of-plane intensities for the bent compared to the planar structure. Note also that the A_2-modes become infrared active when moving from the planar C_{2v} structure to the nonplanar C_s structure. However, Table 3 shows that the corresponding A″-modes are very weak (as expected) and are not very useful for the prediction of a nonplanar arrangement.

To discuss aromaticity in these compounds in more detail, we calculated NICS values as outlined in the computational section (in ppm): −3.07 for compound **2**, −5.66 for **3**, −9.48 for **4**, −7.33 for **5**, and −10.07 for **6**. The NICS values show that fluorination *increases* aromaticity. Such effects have been discussed previously with respect to fluorinated pyridines and have been explained by an increase in π-electron density in the ring system due to a positive mesomeric effect from the fluorine ligands.[6] Analyzing the MO-coefficients we find considerable p_π-interactions between the fluorine ligands

Table 7. MP2/6-31G* Vibrational Contributions[a]

n	IRREP	$\tilde{\nu}$ [cm^{-1}]	distribution (in %)
1	B_1	150	60 t_{10}, 26 t_{12}, 20 t_{11}
2	B_1	392	34 t_{12}, 44 r_{24}, 13 t_{11}, 6 c_{15}
3	A_2	412	88 t_{11}, 29 t_{10}, −5 r_{18}, −5 r_{30}
4	B_2	452	75 c_{14}, 12 d_8
5	A_1	520	83 d_7
6	B_1	526	51 r_{24}, 25 c_{15}, 8 t_{10}, 5 r_{18}, 5 r_{30}
7	B_2	629	76 d_8, 9 s_1, 9 s_6
8	B_1	665	57 t_{12}, 35 c_{15}, 7 r_{21}, 7 r_{27}
9	A_2	799	31 r_{21}, 31 r_{27}, 18 r_{18}, 18 r_{30}
10	B_1	823	33 c_{15}, 32 r_{18}, 32 r_{30}, 8 r_{21}, 8 r_{27}, −7 t_{12}
11	A_1	835	36 s_1, 36 s_6, 6 d_7, 6 d_9, 5 c_{13}
12	B_1	906	36 r_{21}, 36 r_{27}, 17 r_{18}, 17 r_{30}, −9 t_{12}
13	A_2	913	36 r_{18}, 36 r_{30}, 24 r_{21}, 24 r_{27}, −15 t_{11}, −5 t_{10}
14	A_1	1007	68 d_9, 9 s_3, 9 s_4
15	A_1	1045	25 s_3, 25 s_4, 14 d_9, 10 r_{17}, 10 r_{29}
16	B_2	1103	15 r_{17}, 15 r_{29}, 11 s_3, 11 s_4, 11 s_2, 11 s_5, 6 r_{20}, 6 r_{26}
17	A_1	1232	19 r_{17}, 19 r_{29}, 18 r_{20}, 18 r_{26}, 6 s_2, 6 s_5, 5 s_3, 5 s_4
18	B_2	1289	23 r_{17}, 23 r_{29}, 15 r_{23}, 9 c_{14}, 8 s_3, 8 s_4, 6 s_1, 6 s_6
19	B_2	1299	22 r_{23}, 20 r_{20}, 20 r_{26}, 9 s_1, 9 s_6, 5 c_{14}
20	B_2	1456	18 r_{20}, 18 r_{26}, 16 r_{23}, 15 s_1, 15 s_6
21	A_1	1461	19 r_{20}, 19 r_{26}, 15 r_{17}, 15 r_{29}, 8 c_{13}
22	B_2	1594	29 r_{23}, 25 s_3, 25 s_4, 7 d_8
23	B_2	1657	33 s_2, 33 s_5, 14 r_{23}
24	A_1	1688	34 c_{13}, 18 s_2, 18 s_5, 8 r_{20}, 8 r_{26}
25	A_1	1764	47 c_{13}, 10 s_2, 10 s_5, 8 d_7, 5 s_1, 5 s_6
26	B_2	3254	40 r_{19}, 40 r_{25}, 9 r_{16}, 9 r_{28}
27	A_1	3254	39 r_{19}, 39 r_{25}, 11 r_{16}, 11 r_{28}
28	B_2	3274	40 r_{16}, 40 r_{28}, 9 r_{19}, 9 r_{25}
29	A_1	3275	39 r_{16}, 39 r_{28}, 11 r_{19}, 11 r_{25}
30	A_1	3669	100 r_{22}

[a] Vibrational contributions are according to the M-matrix method of Pulay. The definitions of the internal coordinates are given in Table 6. Only contributions greater than 5% are listed.

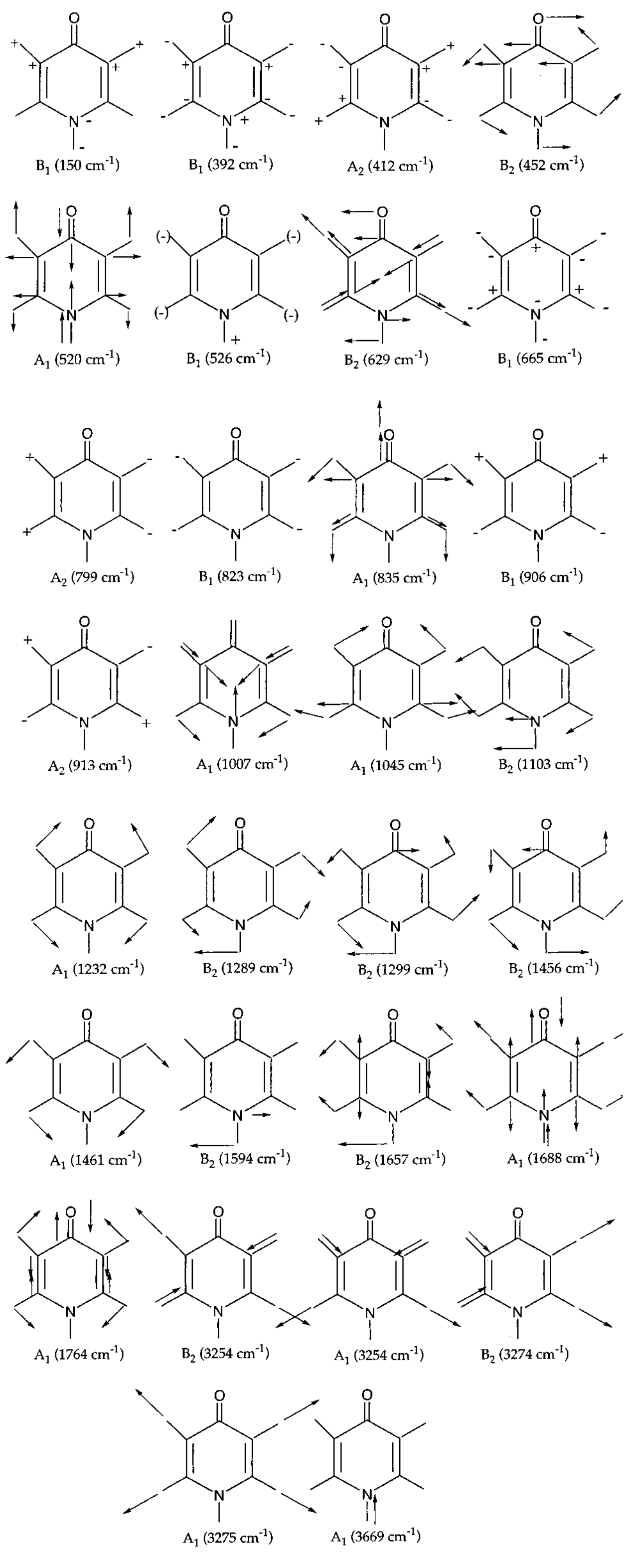

Figure 4. Approximate diagrams for the fundamental vibrational modes of 4-pyridone derived from a MP2 harmonic frequency analysis.

and the aromatic ring π-system; especially strong π-overlap is calculated between the nitrogen atom and the fluorine ligand attached to it. This is shown for the totally bonding π-orbital in Figure 3. This increased aromaticity due to subsequent fluorination may rationalize why five fluorine ligands are necessary to obtain a substantial inversion barrier at the ring N-center.

Nowak et al. has studied the harmonic vibrational spectrum of 2-pyridone in detail[14] using a potential energy distribution. We have carried out a similar analysis for 4-pyridone at the MP2 level. The internal coordinates and the major vibrational contributions are listed in Tables 6 and 7. Approximate diagrams for the major atomic displacements in 4-pyridone are presented in Figure 4. The irreducible representations (IRREPs) in the correct C_s and approximate C_{2v} symmetry are given for the nonplanar structures, Table 3. Note that in the low-frequency range the IRREP notation in C_{2v} symmetry for the nonplanar structures is only very approximate because the frequencies of the same symmetry (A′ or A″) resulting from different IRREPs in C_{2v} symmetry can mix substantially, especially if they are nearly degenerate. Moreover, in the reduced C_s symmetry in-plane and out-of-plane modes can mix.

Our results for 4-pyridone may be compared with those of Batts and Spinner published in 1969,[21] i.e., we compare our Figure 4 with Figure 1 given in their paper. Some of the modes are similar to those predicted by Batts and Spinner, but others show evidence of significant mixing between bending and stretching modes, Figure 4 and Table 7. The highest frequency of 3669 cm^{-1} can be assigned to a pure and intense N−H stretching mode. This compares to 3445 cm^{-1} given by Bellamy and Rogasch[30] or Costa et al.[31] The PM3 value (Table 4) is 3412 cm^{-1} and in better agreement with experiment than the MP2 result. We assume that a larger basis set would

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(30) (a) Bellamy, L. J.; Rogasch, P. E. *Proc. Roy. Soc. (A)* **1960**, *257*, 98. (b) Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*; Chapman and Hall: London, 1975.

(31) Costa, G.; Blasina, P.; Sartori, G. *Z. Physik Chem. (Frankfurt)* **1956**, *7*, 123.

improve the MP2 frequencies. The carbonyl stretching band in 2-pyridone is found at 1730 cm^{-1}, above the ring breathing modes which are in the 1400−1650 cm^{-1} range for all pyridine derivatives.[30] Due to difficulties in making an accurate assignment, this band has been discussed intensively in the literature. Figure 4 shows that the CO stretching mode at the MP2 level (A_1 mode at 1688 and 1764 cm^{-1}) is heavily admixed with C═C stretching modes. This is shown in more detail in Table 7. However, only the mode at 1764 cm^{-1} is intense, probably corresponding to the 1635 cm^{-1} mode assigned by Batts and Spinner. Other intense modes are calculated at 392 cm^{-1} (B_1 out-of-plane mode), 823 cm^{-1} (B_1 out-of-plane mode), 1007 and 1045 cm^{-1} (A_1 ring breathing and bending modes), and 1594 cm^{-1} (B_2 N−H rocking).

Intense Raman bands are observed experimentally in the 750−1050 cm^{-1} region,[21] and this agrees with our calculated Raman intensities. From the HF Raman intensities, and a comparison of the HF with the MP2 frequencies, we can assign the following bands as intense Raman modes (in cm^{-1}): 835 (A_1), 799 (A_2), 1007 (A_1), 1044 (A_1), 1232 (A_1), 1461 (A_1), 1688 (A_1), 1764 (A_1), and all the modes in the 3000 cm^{-1} region. The C═O out-of-plane mode (B_1) is calculated to contribute to the 665 cm^{-1} and 823 cm^{-1} frequencies and is higher than that predicted by Dellepiane and Overend.[32]

The measured dipole moment of 4-pyridone is approximately 6.0−6.3 D,[33] in reasonable agreement with our MP2 value of 6.7 D, Table 6. Notable is the change in the dipole moment for tetrafluoro-4-pyridone **4** when moving from the planar arrangement (4.40 D) to the nonplanar minimum structure (2.00 D). An indication that this might be due to partial loss of the zwitterionic aromatic resonance structure comes from the Mulliken population analysis. For the planar structure we obtain the following gross atomic charges: N −0.19, O −0.46. In the bent arrangement the difference between these charges is reduced (N −0.23, O −0.40). Finally we note that Adamowicz studied 2-pyridone at the HF/6-31G* level.[13] A comparison with our HF/6-31G* result shows that 2-pyridone is more stable in the gas phase compared to 4-pyridone by 45 kJ/mol (not including zero-point vibrational contributions).

Conclusion

Our calculations have shown that one fluorine ligand at the ring nitrogen is required to obtain a significant deviation from planarity. Structure **6** has a relatively high barrier for the fluorine out-of-plane motion, and therefore it should not be difficult to confirm the predicted nonplanar arrangement using experimental methods, for example by matrix isolation spectroscopy. PM3 seems to favor nonplanar structures for all ligands. Higher level calculations are needed to decide if the tetrafluoro or N-fluoro derivatives of 4-pyridone are planar or not. For the vibrational assignment of 4-pyridone larger basis sets are required to eliminate small discrepancies.

This work can be extended to different ligands which have a nonbenzenoid tautomer. It has been estimated, for example, that 2-hydroxypyridine has an aromatic stabilization energy of 30 kJ/mol estimated from the tautomeric enthalpy difference.[6,22] In contrast, 2-methylpyridine has an aromatic stabilization energy of approximately 75 kJ/mol. Hence, changing the substituents in pyridine ring systems which undergo tautomerism (X = O, CH_2, S, ...)[34] may significantly change the inversion barrier. Such effects have not been studied to date. We note that Facalli et al. studied derivatives of 2-pyridone.[15] It was concluded that different substituents significantly influence the aromatic stabilization and the tautomeric equilibrium of 2-pyridone. It will also be interesting to examine the effects of less electronegative substituents such as chlorine; these should reduce the inversion barrier significantly. For example, the chloro derivatives of **4** and **5** may be planar.

Acknowledgment. This work was supported by the Auckland University Research Committee, the New Zealand/Federal Republic of Germany Science and Technology Agreement, the Humboldt Foundation (Bonn), and the Marsden Fund. The supply of large amounts of computer time by the High Performance Computer Committee, the SIC New Zealand, and the Marsden Fund is gratefully acknowledged. We thank Prof. Paul D. Woodgate for critically reading this paper.

Supporting Information Available: PM3, HF, and MP2 Cartesian coordinates and electronic energies for compounds **2**−**6** (Tables A1−A25, 25 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9710341

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