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## Ab Initio and $^{17}\text{O}$ NMR Studies of the Substituent Effects on the Tautomeric Equilibrium in 6-X-1H-2-Pyridones

Julio C. Facelli,\*

Utah Supercomputing Institute and Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Anita M. Orendt,

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Rubén H. Contreras, Maria F. Tufro, and Dora G. de Kowalewski

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellon I, Ciudad Universitaria, Buenos Aires 1428, Argentina (Received: March 30, 1992)

$^{17}\text{O}$  chemical shifts are found to be highly sensitive probes in the study of keto-enol tautomeric equilibria due to the strong sensitivity of these shifts to the coordination of the oxygen atom. The large shielding effect observed, both experimentally and theoretically, for the carbonyl oxygen atom in 2-pyridone suggests that the carbonyl  $\pi$ -electronic system is undergoing a strong conjugation with the formal  $\text{C}_3=\text{C}_4$  double bond and/or the nitrogen lone pair. A Cl or  $\text{NH}_2$  substitution at position 6 of the pyridine ring shifts the tautomeric equilibrium toward the 2-hydroxypyridine form, while a  $\text{CH}_3$  substitution results in the keto form being predominant, as is the case in the parent compound.

### Introduction

The tautomeric equilibrium between the keto and enol forms of 2-hydroxypyridines has been studied from different points of view.<sup>1-16</sup> Among them, two approaches merit mention, namely, the theoretical analysis<sup>11-13</sup> and the measurement of NMR spectroscopic data.<sup>9,10,14,15</sup> Several NMR parameters have been used to probe which of the two forms is preferred for a given compound under the conditions used. Takeuchi and Dennis<sup>14</sup> suggest that the  $^2J(\text{C}_5\text{H}_6)$  coupling corresponding to the  $\alpha$  proton is different between the two forms and, therefore, can be used to differentiate 2-pyridones from 2-hydroxypyridines. Lumbroso-Bader et al.<sup>15</sup> suggest that the best probe to differentiate between the two structures is the measurement of the three-bond  $^3J(\text{C}_2\text{H}_6)$  coupling. For the pyridine structure, this coupling is ca. 12 Hz, while for the 2-pyridone structure it drops to at least 7 Hz.  $^3J(\text{H}_5\text{H}_6)$  is another NMR spectral parameter that has been found to be very sensitive to this tautomeric equilibrium. The pyridine structure exhibits a small  $^3J(\text{H}_5\text{H}_6)$  coupling,<sup>17</sup> due to the relative orientation between the coupling pathway and the nitrogen lone pair.<sup>18</sup> Its value is 4.862 Hz in pyridine<sup>17</sup> and 5.05 Hz in 2-methoxypyridine, while it increases to 6.55 Hz for 1H-2-pyridone.<sup>19</sup> A comparison of  $J(\text{HH})$  and  $J(\text{CH})$  couplings for pyrazinone and pyrazine structures has been reported by Tobias and Günther.<sup>20</sup> This work also reported that the  $^{15}\text{N}$  chemical shift is very sensitive to the tautomeric equilibrium in these compounds.

It is important to note that the most sensitive  $J(\text{HH})$  and  $J(\text{CH})$  couplings to the -ine and -one structures involve the proton placed at ring position 6. Therefore, those couplings are not available as indicators of the tautomeric equilibrium in 6-X-1H-2-pyridone

derivatives. When X is a polar substituent, the equilibrium is shifted toward the -ine form.<sup>21</sup> In a previous paper,<sup>22</sup> the substituent additivity rule for  $^1J(\text{CH})$  coupling and for  $^{13}\text{C}$  chemical shifts was employed as a means for detecting changes in the tautomeric equilibrium due to the presence of a substituent. Those results indicate that for X = Cl and  $\text{NH}_2$ , the equilibrium is shifted toward the 2-hydroxypyridine form.

$^{17}\text{O}$  chemical shifts are known to be very sensitive to changes in the coordination of the oxygen atom.<sup>23-25</sup> Therefore, it is expected that  $^{17}\text{O}$  NMR would be an important tool to determine the changes in the tautomeric equilibrium due to the presence of a substituent in the 6 position. In this paper,  $^{17}\text{O}$  NMR spectra of 6-X-2-hydroxypyridines (X = H, Cl,  $\text{NH}_2$ ,  $\text{CH}_3$ ), compounds I, II, III, and IV, respectively, are reported. Ab initio optimized geometries are calculated for all these compounds in both the -one and -ine structures. To estimate the relative importance of the substituent effect on  $^{17}\text{O}$  chemical shifts with respect to the change due to the tautomeric structure, the LOG (localized orbitals/local origin)<sup>26</sup> method is used to calculate the  $^{17}\text{O}$  chemical shifts for both tautomeric forms in compounds I-IV. (See Figure 1).

### Experimental Section

**NMR Measurements.** Natural abundance  $^{17}\text{O}$  NMR spectra were recorded on a Varian XL-400 spectrometer using 5-mm sample tubes. All compounds were of commercial origin and were used without further purification. Samples were prepared using pyridine- $d_5$  (Aldrich, 99 atom % D) as a solvent, with the concentration being dependent upon solubility. All measurements were carried out at 28 °C.  $^{17}\text{O}$  chemical shifts were externally

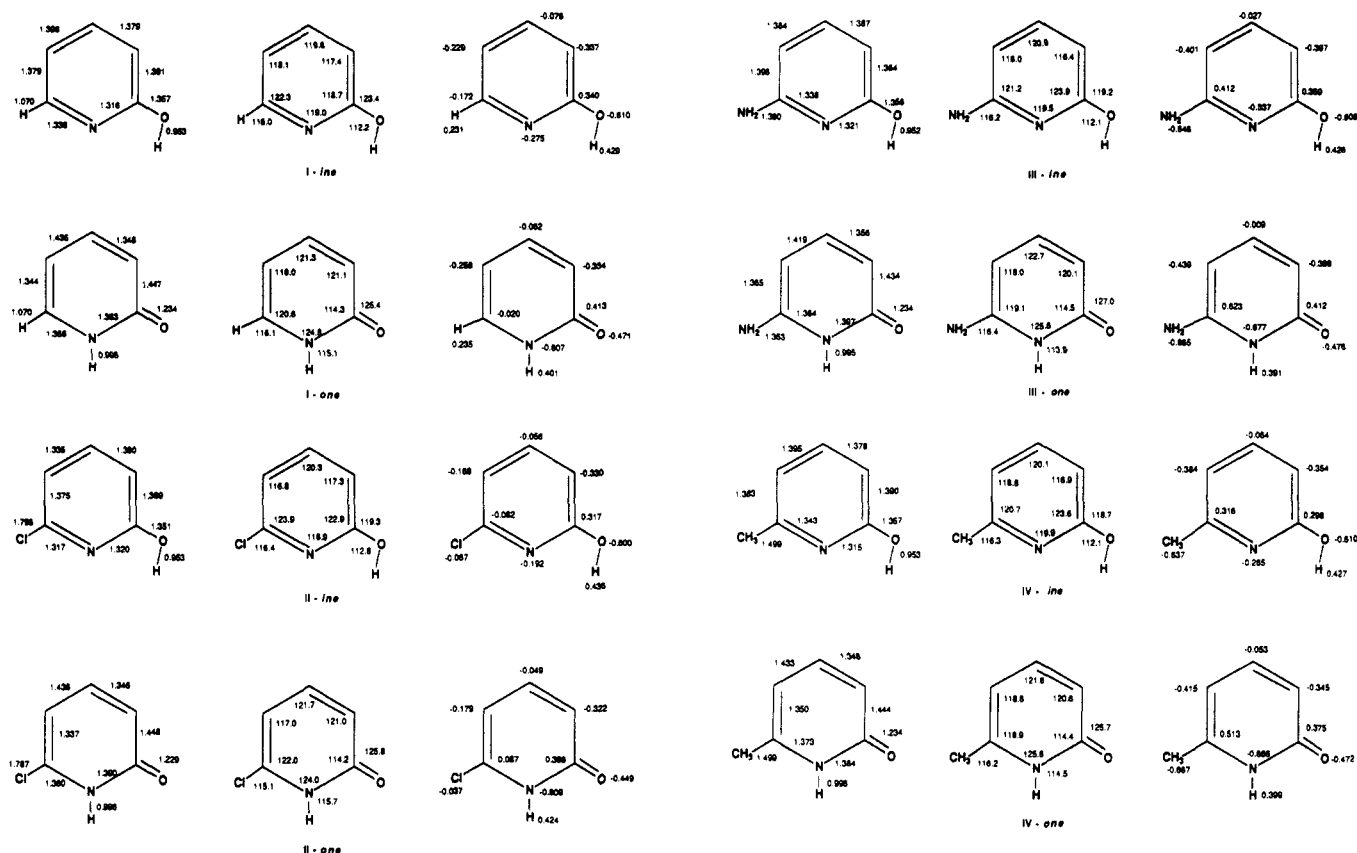


Figure 1. Ab initio optimized structures and Mulliken atomic charges in 6-X-1H-2-pyridones, X = H, Cl, NH<sub>2</sub>, CH<sub>3</sub>. Atomic distances in Å and atomic charges in au.

TABLE I: <sup>17</sup>O Chemical Shifts (in ppm) for 6-X-1H-2-Pyridones<sup>a</sup>

compd	X	$\delta(^{17}\text{O})$	compd	X	$\delta(^{17}\text{O})$
I	H	262	III	NH <sub>2</sub>	170
II	Cl	126	IV	CH <sub>3</sub>	269

<sup>a</sup> All measurements at 28 °C. Chemical shifts referenced externally to water at room temperature.

referenced to water at the same temperature.

**Calculations.** Geometry optimizations were carried out for the -one and -ine structures of compounds I-IV using the GAUSSIAN 86 molecular package<sup>27</sup> and D95 basis sets.<sup>28</sup> C<sub>s</sub> symmetry was assumed for compounds I, II, and IV. This assumption was relaxed in compound III. <sup>17</sup>O magnetic shielding values were calculated with the LORG program<sup>26</sup> using the same D95 basis set.<sup>28</sup>

## Results and Discussion

The <sup>17</sup>O chemical shifts measured for compounds I-IV are displayed in Table I. It is, in general, accepted that in solution there is a fast tautomeric exchange between the -ine and -one forms; for compound I, the equilibrium is notably shifted toward the -one form.<sup>7</sup> Therefore, it can be assumed that independently of the solvent used, the oxygen atom in I is a carbonyl oxygen and its chemical shift of 262 ppm corresponds to a strongly shielded carbonyl oxygen. For comparison, the <sup>17</sup>O chemical shift in benzaldehyde is 564 ppm.<sup>23</sup> The <sup>17</sup>O chemical shift of an aldehyde oxygen depends strongly on the resonance interactions of the aldehyde group; in particular, the larger the resonance interaction is the smaller the chemical shift value. Other strongly shielded carbonyl <sup>17</sup>O nuclei have been reported in the literature for chromone (V), at 446 ppm,<sup>29</sup> and coumarin (VI), at 352 ppm.<sup>23</sup> In these compounds, the corresponding dicoordinated <sup>17</sup>O chemical shifts are 162 and 219 ppm, respectively, which are also strongly deshielded for dicoordinated <sup>17</sup>O atoms (see Figure 2). Comparison of these values with those of chromanone (VII), at 515 and 70 ppm,<sup>29</sup> for the carbonyl and dicoordinate oxygen, respectively, indicates that the resonance interaction between the carbonyl and the  $\pi$ -electronic system shifts the <sup>17</sup>O resonance

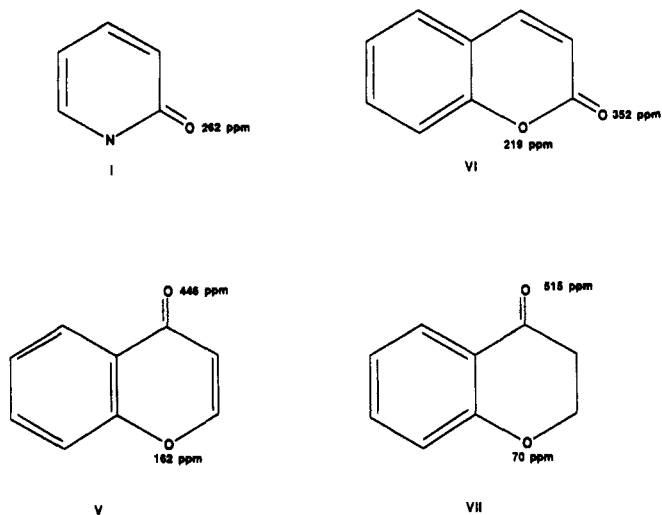


Figure 2. <sup>17</sup>O chemical shifts in 2-pyridone (I), chromone (V), coumarin (VI), and chromonone (VII). Values for compounds V and VII were taken from ref 29 and for compound VI from ref 23.

upfield for the carbonyl and downfield for the dicoordinated oxygen. Therefore, the small chemical shift observed in I suggests that the  $\pi$ -electronic system of the C=O double bond is undergoing rather strong conjugation either with the N lone pair or with the C<sub>3</sub>=C<sub>4</sub> formal double bond of the pyridone ring, or both.

For the substituted compounds, a strong shielding effect is observed for X = Cl and NH<sub>2</sub>. This strong shielding effect suggests that there is a shift in the tautomeric equilibrium toward the enol form for both II and III, in agreement with the results of studies using the additivity rule for the <sup>13</sup>C chemical shifts of C<sub>6</sub> and for the <sup>1</sup>J(C<sub>5</sub>H<sub>5</sub>) coupling.<sup>22</sup> The slight deshielding effect observed in IV suggests that in this compound, the predominant form is the -one. This conclusion is in agreement with previous measurements of the J coupling constants in VI,<sup>31-33</sup> which in-

TABLE II: Total Optimized SCF Energies for the -One and -Ine Forms for the 6-X-1H-2-Pyridones

compd	E, au	kJ/mol
I-one	-321.474 086 981	-3.22 <sup>a</sup>
I-ine	-321.472 852 285	
II-one	-780.331 120 846	+9.54
II-ine	-780.334 753 881	
III-one	-376.500 966 998	+12.09
III-ine	-376.505 579 609	
IV-one	-360.505 337 299	-5.73
IV-ine	-360.503 153 508	

<sup>a</sup>The best theoretical value, without zero-point vibration correction, previously reported in the literature is  $-5.0 \pm 1.6$  kJ/mol.<sup>13</sup>

TABLE III: LORG-Calculated <sup>17</sup>O Isotropic Chemical Shieldings for 6-X-1H-2-Pyridones<sup>a</sup>

	$\sigma_d^{\text{LORG}}$	$\sigma_p^{\text{LORG}}$	$\sigma^{\text{LORG}}$	SCS <sup>b</sup>
I-one	421.7	-514.2	-92.5	
I-ine	420.4	-237.1	183.3	
II-one	421.4	-526.8	-105.4	12.9
II-ine	420.8	-239.9	180.9	2.4
III-one	421.8	-504.0	-82.2	-10.3
III-ine	419.8	-241.8	178.0	5.3
IV-one	421.6	-510.5	-88.9	-3.6
IV-ine	420.2	-238.1	182.1	1.2

<sup>a</sup>All values are in ppm.  $\sigma$  values correspond to absolute shieldings, i.e., referenced to the bare nucleus. <sup>b</sup>SCS: substituent effects on chemical shifts.

icates that the methyl substitution at position 6 does not significantly change the tautomeric equilibrium found in the parent compound (IV).

Optimized geometries and the Mulliken atomic charges for the -one and -ine forms of compounds I-IV are shown in Figure 1. The total SCF energies for the optimized structures are displayed in Table II. It can be observed that the ab initio calculations predict as the more stable form the -one structure for both I and IV, i.e., for X = H and X = CH<sub>3</sub>, by 3.22 and 5.73 kJ/mol, respectively, in agreement with the experimental observations. In addition, the calculations predict that the equilibrium is shifted toward the -ine form for both X = Cl and NH<sub>2</sub>, with the 2-hydroxypyridine structures being preferred by 9.54 and 12.09 kJ/mol, respectively. These last two values are not in the same order expected from the experimental values, which predict that the tautomeric equilibrium is more shifted toward the 2-hydroxypyridine form in III than in II. However, as the calculations refer to an isolated molecule and as it is known that tautomeric equilibria in general depend on the solvent, this discrepancy could easily originate in medium effects.

The changes in the <sup>17</sup>O chemical shifts observed in Table I for the substituted compounds could also be attributed to electronic substituent effects on each type of structure due to the presence of the group at position 6 of the pyridine ring. To estimate the relative importance of this effect, LORG calculations<sup>26</sup> were carried out for both -one and -ine structures of compounds I-IV. The results obtained are given in Table III, where the LORG diamagnetic and paramagnetic contributions to the magnetic shielding constants and the calculated substituent effects are shown. The substituent effects for either structure are by far much smaller than the experimental changes observed in Table I, confirming the assumption that the chemical shift changes observed in II and III are mainly due to changes in their tautomeric equilibrium. Nonetheless, it is interesting to observe that the calculations predict that the <sup>17</sup>O chemical shift of the carbonyl in a pyridone structure is more sensitive to substituent effects than the <sup>17</sup>O chemical shift of the hydroxy oxygen in an -ine structure.

It is important to verify from a theoretical point of view whether the strongly shielded <sup>17</sup>O nucleus reported in Table I for compound I actually corresponds to a carbonyl oxygen atom or whether the tautomeric equilibrium is shifted more toward the -ine form than is commonly accepted. The calculated value of the magnetic

TABLE IV: Comparison of the Larger Paramagnetic LORG Bond-Bond Contributions to the Chemical Shieldings in Acetone with Those in 2-Pyridone<sup>a</sup>

	acetone	I-one	$\Delta$
C=O <sup>b</sup>	-261	-190	-71
LPs <sup>c</sup>	-562	-294	-268
total	-823	-484	-339

<sup>a</sup>All values are in ppm. <sup>b</sup>Contribution from the carbonyl double bond. <sup>c</sup>Contribution from oxygen lone pairs.

shielding constant in I-one, -92.6 ppm, can be compared with the value for the carbonyl oxygen in acetone calculated using the same basis set, -460.8 ppm. The value in I-one is more shielded by 368.2 ppm. Experimentally, the difference between the <sup>17</sup>O chemical shift for I and acetone (569 ppm<sup>23</sup>) is 307 ppm, which is in favorable agreement with the theoretical difference.

A comparison of the paramagnetic LORG bond-bond contributions to the magnetic shielding constant between acetone and I-one shows that the large difference between the shieldings originates mainly in the paramagnetic contributions from the lone pairs and the C=O double bond. These two contributions account for a difference of 399 ppm between the shielding calculated for acetone and I-one. The diamagnetic contributions, not shown in Table IV, depend only slightly on the compound, and are not affected by the conjugative effects. The calculations support the assumptions made above by attributing the large upfield shift in the <sup>17</sup>O chemical shift of I to the conjugative effect of the pyridone carbonyl group.

### Concluding Remarks

<sup>17</sup>O chemical shifts have been found to be adequate probes to study the position of the keto-enol tautomeric equilibrium due to their strong dependence on the coordination of the oxygen atom. The results presented in this paper show that a pyridone structure is more efficient than a pyridine structure in transmitting substituent effects in the <sup>17</sup>O chemical shifts for substituents at ring position 6. However, these substituent effects are much smaller than the experimental changes observed in the <sup>17</sup>O chemical shifts. Theoretical calculations also confirm that the large changes in the <sup>17</sup>O chemical shifts originate in shifts of their tautomeric equilibria.

The large upfield shift observed, both theoretically and experimentally, for the carbonyl oxygen in 2-pyridone suggests that the carbonyl  $\pi$ -electronic system is largely delocalized due to rather strong conjugative effects with the C<sub>3</sub>=C<sub>4</sub> double bond and/or with the nitrogen lone pair, which is of  $\pi$ -type character. By comparing this result with those chemical shifts for chromone and coumarine, where the B ring exhibits delocalization of the  $\pi$  electrons,<sup>23</sup> it can be concluded that a pyridone ring may also exhibit some  $\pi$ -electron delocalization.

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**Registry No.** I-one, 142-08-5; I-ine, 72762-00-6; II-one, 16879-02-0; II-ine, 73018-09-4; III-one, 5154-00-7; III-ine, 59315-47-8; IV-one, 3279-76-3; IV-ine, 91914-07-7.

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## Anharmonic Force Field of CO<sub>2</sub>

Attila G. Császár

Failure Analysis Associates, Inc., 149 Commonwealth Drive, P.O. Box 3015, Menlo Park, California 94025  
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A group theoretical algorithm to calculate the number of independent force constants of a molecule at any given order has been extended to treat linear molecules in a fashion analogous to nonlinear molecules. Using this algorithm to determine the independent force constants and a finite-difference formalism to obtain higher-order force constants from low-order analytic geometric derivatives of the electronic energy, the anharmonic force field of CO<sub>2</sub> has been determined at the ab initio TZ2P SCF and QZ2P CCSD(T) levels. It is shown that accurate sextic force fields can be calculated from only analytic first derivatives if the wave function is tightly converged and the calculated forces are highly accurate. The calculated anharmonic force fields are compared to experimentally determined sextic force fields of CO<sub>2</sub>, and uncertainties and discrepancies in the experimental fields are discussed.

### Introduction

The present paper describes, to our best knowledge, the first quantum chemical calculation of the complete sextic force field of any molecule larger than diatomic. This study complements and extends several recent investigations<sup>1-8</sup> which showed the unique value of ab initio calculations in the determination of molecular constants which characterize the vibration-rotation spectra of semirigid<sup>9</sup> molecules and the considerable accuracy of the underlying anharmonic molecular force fields. Some important results of these earlier studies are the following: (a) For most constants the self-consistent-field (SCF) cubic and quartic force fields show little variation with basis set extension; the values can be considered as converged using a basis set of triple-zeta plus double-polarization function (TZ2P) quality. (In many cases, especially for molecules not having multiple bonds, the convergence at the SCF level is nearly achieved even at the rather low double-zeta plus polarization function (DZP) level.) (b) Particularly accurate values can be obtained using methods incorporating substantial part of the electron correlation energy; the improvement is especially pronounced for the quadratic part of the force field and becomes less and less important for higher-order constants. (c) A substantial part of the discrepancy between force constants calculated at theoretical stationary points and force constants obtained from experiments comes from differences in the underlying reference geometries; shifting the theoretical reference geometry close to the true equilibrium geometry results in force constants which are in dramatically better agreement with their experimental counterparts. These and some other important results are especially well reviewed in a paper by Allen and Császár.<sup>5</sup> The accumulated knowledge about theoretical anharmonic force fields provided confidence that the sextic force field of a molecule like CO<sub>2</sub> determined using ab initio techniques

should be accurate and thus can help to resolve existing uncertainties in the experimental anharmonic force fields of CO<sub>2</sub>.<sup>10-12</sup>

Carbon dioxide has been thoroughly studied by several experimental groups.<sup>10-18</sup> It is one of those few molecules for which the complete force field through sixth order has been determined experimentally.<sup>10,11</sup> By comparing the available sextic (and quartic) experimental force fields (see Table III), one has to conclude that, partly due to the fact that different procedures were used to derive these force fields, deviations of unacceptable magnitude exist in these fields. It was hoped that a high-level theoretical study could result in anharmonic force constants whose accuracy allows improvement of the anharmonic force field of CO<sub>2</sub>.

Due to its highly symmetric geometric structure and the relative simplicity of its electronic structure, CO<sub>2</sub> is a good candidate for theoretical studies as well. Thus, it is surprising to see that the first attempt<sup>19</sup> to calculate the complete anharmonic force field (through fourth order) of CO<sub>2</sub> by means of ab initio calculations was published only in 1990.<sup>3</sup> In that paper the highest-quality quartic force fields of CO<sub>2</sub> were determined at the TZ2P SCF and TZ2P CISD levels using the respective theoretical optimized geometries as references. The agreement between experiment and theory was impressive but may be not as good as one would like to see. Part of the deviations was thought to be connected to the choice of the reference geometry, since there were sizable differences between the theoretical and experimental  $r_e(\text{C}=\text{O})$  bond lengths. Thus, in this study the reference geometry was elected to correspond to the best experimental estimate of  $r_e(\text{C}=\text{O})$ <sup>12,14</sup> to improve the quality of the theoretical force constants.<sup>4,5</sup>

To calculate the sextic force field of a molecule using ab initio methods, one would desirably have a program which calculates the analytic sixth derivatives of the electronic energy with respect