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Methylsalicylate: A Rotational Spectroscopy Study

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We report the free-jet rotational spectra of methylsalicylate, a molecule with a possible tautomeric and conformational equilibrium. In the ground electronic state, the molecule adopts a form stabilized by an intramolecular hydrogen bond between the phenolic hydrogen and the carbonylic oxygen, and this structure is characterized as the lowest-energy form by quantum chemical calculations. All rotational transitions are split because of the internal rotation of the methyl group, and the value of the barrier for this motion was determined to be $V_3 = 5.38$ kJ mol^{-1}.

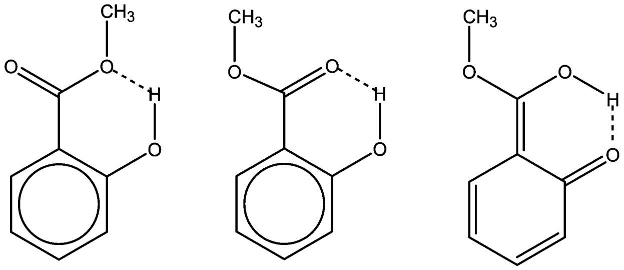
Introduction

Valuable information on tautomeric equilibria, present in many systems of chemical and biological interest, has been obtained by rotational spectroscopy. The rotational spectrum of malonaldeide[1] and acetylacetone,[2] for example, showed that each tautomeric equilibrium in the gas phase is shifted toward the enolic form and gave precise information on the potential energy barrier to the proton motion, which is different in the two cases. In malonaldeide, a potential energy barrier to proton transfer is present, whereas in acetylacetone, the ground state consists of a single minimum with C_{2v} symmetry.

Another case is 2-hydroxypiridine, which can be considered the prototype system for the study of the keto−enolic equilibrium present in more complex systems, for example, in the nucleobases. In 2-hydroxypyridine,[3−6] both the enolic and the ketonic forms were observed in the gas phase, and the energy of stabilization of 2-hydroxypyridine with respect to that of 2-pyridinone was determined from rotational spectroscopy as 0.32(3) kJ mol^{-1}.[6] In the related system 4-hydroxypyrimidine, the ketonic form is more stable, and this might indicate that the stability of the ketonic form with respect to the enolic form increases with the number of ring nitrogen atoms and with the number of OH units available to permute in ketonic groups.[7]

Methylsalicylate (MS) is another important molecule for which the keto−enolic equilibrium could play an important role. MS has been the subject of extensive study given that, with the explanation of its fluorescence spectrum, the foundations of what is known as the excited-state intramolecular proton transfer (ESIPT) mechanism were laid. Three plausible forms, represented in Chart 1 as I, **II**, and **III**, have been invoked in different studies to justify the spectroscopic behavior of the molecule. It is not possible to call the forms unequivocally ketonic or enolic because each one has a hydroxyl and ketonic group; nevertheless, the equilibrium between form **I** and **III** can surely be considered a tautomeric equilibrium between a ketonic and an enolic form.

CHART 1



II I III

Observed

Judging from the observed dual emission spectrum of MS, Weller, in his early work of 1956,[8] postulated that the absorption process from the ground-state form (**I**) was followed by intramolecular displacement of the proton in the electronically excited form (**III**) and subsequent radiative decay to the ground state.

Actually, the two emissions were found to originate from two different hydrogen-bonded conformations in the ground state. This conclusion was reached from experiments performed in the gas phase,[9,10] in solution,[10] and in supersonic jets,[11] and it was postulated that the more stable ground-state form has a hydrogen bond between the phenol and carbonyl group (I) whereas the less stable form has a hydrogen bond between the phenol and methoxyl group (**II**). In the latter work, an energy difference between the two forms, estimated from temperature-dependent measurements of the relative intensity of the transition bands, was reported as 10.5 kJ mol^{-1}.[11]

Although not responsible for the dual fluorescence of MS, a hydrogen-atom transfer process nevertheless seems to be re-

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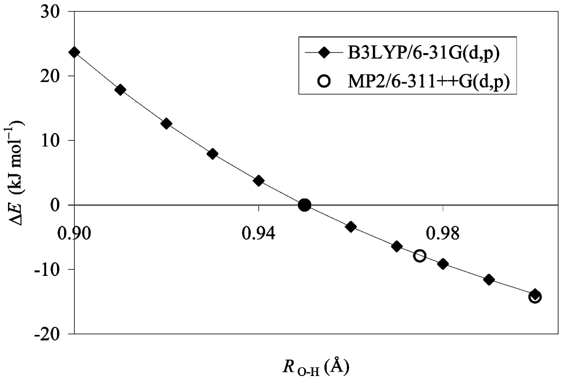


Figure 1. Calculated energy as a function of aliphatic O−H distance in structure III. ΔE is the difference with respect to the energy value at 0.95 Å calculated at the same level of theory. Absolute energy: $E_{\mathrm{B3LYP/6-31G(d,p)}} = -535.3412615$ hartrees, $E_{\mathrm{MP2/6-311++G(d,p)}} = -534.012116$ hartrees.

sponsible for the large Stokes shift between the absorption and emission spectra. The shift is attributed to an ultrafast change from excited form **I** to an excited tautomer **III**. The real-time dynamics of hydrogen-atom transfer in the electronic excited state of MS was studied by Zewail and co-workers with pico- and femtosecond depletion techniques.[12] The dynamics of the process was observed from the femtosecond range, where the formation of the hydrogen-transferred species takes place, up to the picosecond range where the species undergoes nonradiative decay that is strongly influenced by low-energy vibrational modes.

This picture was confirmed by the studies of Catalan and co-workers,[13,14] who calculated the potential energy surfaces for the ground and excited states of various 2-hydroxyenzoyl compounds and showed that radiationless transitions were responsible for the fact that emission from the excited keto form was never observed inducing the excited triplet state keto emission by external and internal heavy-atom perturbation.

From these studies, it is evident that the conformational equilibrium in the ground electronic state of MS and the low-frequency modes are essential in explaining the spectroscopic behavior of the molecule. In this article, we report the microwave free-jet spectrum of MS, and using experiment and theory, we explain the structural choices of the molecule.

Experimental Methods

The design of the Stark and pulse-modulated free-jet absorption millimeter-wave spectrometer used in this study has previously been described.[15,16] MS (purchased from Aldrich and used without further purification) was heated to about 95 °C as a stream of the carrier gas (Ar) at a pressure, P_0, of ca. 300 mbar was flowed over it. The mixture was then expanded to about 5×10^{-3} mbar through a continuous nozzle with a diameter of 0.35 mm. In this way, the concentration of MS in the mixture was estimated to be between 2% and 3%.

The deuterated species were formed by flowing the carrier gas over a sample of D_2O (99.9%, purchased from Cambridge Isotope Laboratories) at room temperature and subsequently over the heated MS sample.

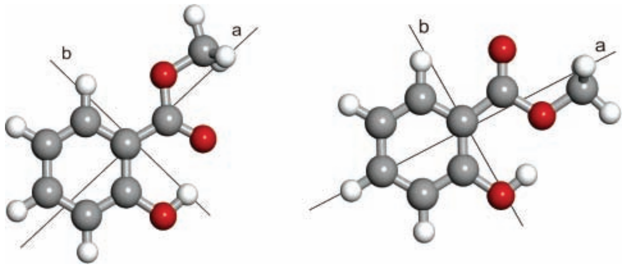
Results and Discussion

We performed preliminary quantum chemical calculations at the B3LYP/6-31G(d,p) and MP2/6-311++G(d,p) levels of approximation, in order to obtain information on the relative energies of different conformations and their geometries. The Gaussian 03 software package was used,[17] and the nature of all stationary points was verified by subsequent harmonic frequency calculations. The computations provided the rotational constants and the components of the dipole moment along the principal axes for the corresponding molecular geometries. All of these data, useful for microwave spectroscopy studies, are reported in Table 1, and the calculated geometries are provided as Supporting Information.

Two stable forms of MS, corresponding to structures **I** and **II**, were found. These geometries are stabilized by an intramolecular hydrogen bond between the phenolic hydrogen and the ketonic (**I**) or methoxy (**II**) oxygen atom, as can be inferred from the calculated O−H···O distance of ca. 1.7 Å for both rotamers. Structure **III** seems not to be stable, and every energy minimization starting from this geometry always fell in the minimum corresponding to **I**. This is in agreement with the calculations on the ground state reported in ref 13, but assuming

TABLE 1: Calculated Spectroscopic Constants and Energies of the Two Conformations of MS

	I		II	
	B3LYP/6-31G(d,p)	MP2/6-311++G(d,p)	B3LYP/6-31G(d,p)	MP2/6-311++G(d,p)
A (MHz)	2168	2158	2258	2249
B (MHz)	829	830	827	828
C (MHz)	602	602	608	608
μ_a (D)[a]	−1.0	−1.1	−0.8	−0.9
μ_b (D)	2.3	2.4	−0.9	−0.57
ΔE (kJ mol^{-1})	0.0[b]	0.0[c]	16.06	10.38



[a] μ_c= 0 by symmetry. [b] Absolute energy = −535.3734333 hartrees. [c] Absolute energy = −534.0500547 hartrees.

that the quantum chemical program could be missing the minimum of the energy curve and desiring to calculate the spectroscopic constants related to this structure, we forced the program to compute the geometry and energy of structure **III** for different positions of the aliphatic hydroxyl hydrogen atom. In this way, we obtained the diagram in Figure 1, which reports the trend of the conformational energy with respect to the O−H distance. To compare the density functional and ab initio values, we normalized the energies to that calculated for an O−H distance of 0.95 Å with the same method. The diagram displays decreasing energy values with increasing distance and shows no minimum with either theoretical method.

The calculated energy difference between the two stable conformations is reported in Table 1. The two theoretical methods give slightly different results; the MP2 value is lower and in better agreement with the experimental result reported in ref 11 (10.5 kJ mol^{-1}). Using the MP2 value of the energy difference, we estimated that, at the temperature used prior to the expansion, the population of the high-energy conformation should be around 3% of the global minimum. Assuming that no conformational relaxation takes place during the supersonic expansion and taking into account the values of the dipole moment components, we should then expect that, for the μ_b rotational transitions, the intensity ratio between conformers II and **I** should be 1:500, whereas it should be 1:50 for the transitions involving the μ_a component. These numbers are estimated upper limits of the intensity of the rotational transitions originating from the less stable structure. Using the density functional results, we obtained a lower value.

Trial predictions of the rotational transitions were based on the rotational constants given in Table 1. The most intense predicted lines are μ_b R-type lines with rotational quantum numbers ranging from 14 to 27, whereas the μ_a R-type lines should be of very low intensity given that their rotational quantum numbers are above 40 in the scanned frequency range. If this picture is correct, we should then observe μ_b transitions arising from rotamer I, whereas the μ_a transitions and the absorption signals due to rotamer **II** will probably be beyond the sensitivity of our apparatus.

The first observed lines were indeed μ_b R-type transitions, which were measured for rotational quantum number J from 15 up to 27. Because of the internal rotation of the methyl group, all lines were split. They were observed as doublets (A and E components) or triplets (A, E$^+$, E$^-$)[16] for transitions involving levels that are degenerate in the near symmetric limit. All frequencies are reported in the Supporting Information.

A global fit to the absolute positions of all component lines was performed with the computer program XIAM,[19] which uses the combined axis method (CAM). A “rigid” limit set of rotational constants was determined, common to A and E sublevels. In addition, three quartic centrifugal distortion constants (A reduction and I^r representation),[20] the V_3 barrier, and the I_α moment of inertia of the methyl group were determined, whereas the angles $\angle ai$ and $\angle bi$ (which are the angles that the axis of rotation of the methyl group forms with the principal axes) were fixed to the values determined from the theoretical geometry. The spectroscopic constants obtained with this approach are reported in Table 2 for the normal and deuterated species.

The value of the internal rotation barrier for MS (5.38 kJ mol^{-1}) must be compared to those found for other molecules containing the methoxy esteric group. For increasing complexity of the molecules, the values are as follows: methylformate,[21] 4.77 kJ mol^{-1}; methylacetate,[22] 5.08 kJ mol^{-1}; methylacrylate [$CH_2CHCO(OCH_3)$],[23] 5.104 kJ mol^{-1}. We can see that the V_3 barrier increases only slightly when the lateral chain to the methoxy group increases in complexity. The experimental value of V_3 is in the same range as those found for similar molecules, and it has the highest value according to the complexity of the group attached to the methoxy moiety. The theoretical values for V_3 calculated as a transition state for the rotation of the methyl group, namely, 3.22 kJ mol^{-1} [B3LYP/6-31G(d,p)] and 6.08 kJ mol^{-1} [MP2/6-311++G(d,p)], are comparable to the experimental data, although the difference is greater than 10% even for the better-performing MP2 method.

TABLE 2: Spectroscopic and Internal Rotation Parameters of the Normal and Monodeuterated Species of MS

	MS(OH)	MS(OD)
A (MHz)	2169.32(1)^a	2124.245(6)
B (MHz)	832.547(4)	832.40(4)
C (MHz)	604.223(5)	600.59(4)
Δ_J (Hz)^b	0.016(2)	[0.016]^c
Δ_{JK} (Hz)	0.037(4)	[0.037]^c
Δ_K (Hz)	0.123(7)	0.132(3)
V_3 (kJ mol^{-1})^d	5.38(2)	5.46(3)
I_α (uÅ^2)	3.23(1)	3.18(2)
$\angle ai$ (deg)	10.7^e	10.7^e
$\angle bi$ (deg)	79.3^e	79.3^e
N	142	92
σ (MHz)	0.04	0.04

[a] Errors in parentheses are expressed in units of the last digit. [b] δ_J, δ_K fixed to zero. [c] Fixed to the value of the parent species. [d] The theoretical value for V_3 is 3.22 kJ mol^{-1} [B3LYP/6-31G(d,p)] and 6.08 kJ mol^{-1}[MP2/6-311++G(d,p)]. [e] From the theoretical structure.

TABLE 3: Principal Axis System Coordinates (Å) of the Hydroxyl Hydrogen of MS (OH/D)^a

	experimental	calculated			
		I		II	
	r_s	B3LYP^b	MP2^c	B3LYP^b	MP2^c
a (Å)	±0.31(5)	−0.29	−0.27	−0.86	−0.85
b (Å)	±2.2241(7)	−2.21	−2.23	−1.90	−1.90

[a] $|c| = 0$ by symmetry. [b] B3LYP/6-31G(d,p). [c] MP2/6-311++G(d,p).

Using the experimentally determined value of the barrier, in a harmonic approximation, and neglecting the A−E splitting of the vibrational levels, we can estimate the fundamental frequency of 145 cm^{-1} for the internal rotation of the methyl group. This value might be useful for the vibrational assignment of MS given that the internal rotation of the methyl group has been called upon in explaining the low-energy vibrational progressions observed in the fluorescence spectrum of MS.[11]

The agreement between the experimental and calculated rotational constants (within 1%) and the estimated energy difference between the two rotamers of MS already indicate that the observed rotational spectrum should belong to the calculated global minimum structure, that is, structure I. An independent piece of evidence comes from the comparison of the substitution coordinates[24] of the hydroxyl hydrogen. They are reported in Table 3 together with the calculated Cartesian coordinates in the principal axis system of the two rotamers, and it can be easily seen that the experimental values are in agreement with those of rotamer I.

Conclusions

We observed the rotational spectrum of the global minimum structure of MS, which has an intramolecular hydrogen bond between the hydroxyl hydrogen atom and the ketonic oxygen

(I). The second rotamer of MS (**II**) was not detected, in agreement with its higher energy of stabilization.

A different tautomer with a carbonyl group inserted in the ring was also not observed, in agreement with previous investigations and with the results of theoretical calculations indicating that it is not a stable structure.

The value of the barrier to the internal rotation of the methyl group of MS is close to that of similar molecules, showing that the intramolecular hydrogen bond does not affect this barrier.

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Supporting Information Available: Calculated geometries of the two stable rotamers of MS (**I** and **II**) (Table 1s) and experimental transition frequencies (MHz) of MS (Table 2s). This material is available free of charge via the Internet at http://pubs.acs.org.

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