Ab initio calculations of the structure and conformations of 2,6-lutidine

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Summary. — *Ab initio* molecular orbital calculations at the SCF level have been utilized to determine the structure and the electronic and vibrational properties of 2,6-lutidine (2,6-dimethyl-pyridine) in the ground electronic state. Comparative calculations have been perfomed on the parent molecule pyridine. Structure predictions of both molecules are in good agreement with experimental data. The most stable rotamer of 2,6-lutidine has C_{2v} symmetry with one of the C-H bonds of both the methyl groups lying in the plane of the aromatic ring and pointing in the opposite direction with respect to the nitrogen atom. This is the result of the minimization of competiting forces deriving from steric hindrance and electronic stabilization. Vibrational frequencies and oscillator strengths of C-H stretching in the fundamental region have been calculated for both pyridine and the most stable rotamer of 2,6-lutidine and compared to IR data obtained in pure liquids. The potential energy profile of the C-H bond in and out of plane has been investigated up to five times the equilibrium distance. The trend of the potential curves confirms that the C-H bond lying in the plane has a higher dissociation energy than that of the in-plane bonds as observed in experiments on vibrational overtones.

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PACS 33.15.Hp – Barrier heights (internal rotation, rotational isomerism, conformational dynamics).
PACS 33.20.Ea – Infrared spectra.

1. – Introduction

The effects of steric hindrance and electronic charge distribution play the most important roles in determining the structure and the conformations of a molecule. Understanding how these forces act on the structure may aid in the comprehension of more complex properties such as, for example, bond reactivity.

In the recent past, many studies have been performed combining various spectroscopic methods and calculations on different types of molecules. Among them, a

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large number of studies concern conformational problems of methyl groups in aliphatic and aromatic compounds [1-9]. Methyl group behavior can resemble that of a free rotor but the barrier of the internal rotation can change dramatically depending on the molecule (local steric hindrance) and the phase (gas, liquid or solid). The lack of any straightforward correlation with steric effects makes the interaction between the methyl group and the rest of the molecule apparently specific [4]. The spectroscopic study of highly excited vibrational levels helped in understanding part of this problem. The local character of vibrational overtones (mainly of X-H bond stretching) makes them a good probe of small changes in the molecular structure [1, 3, 7, 9-14]. In addition working with optical frequencies to investigate effects due to processes occuring at lower frequencies (*e.g.*, internal rotations) provides a picture of an almost frozen system. If a conformation is slightly more stable than others, bands as many as the number of inequivalent C-H bonds will be observed in the spectra. Their intensity will be proportional to the number of equivalent C-H bonds and the frequency will provide the strength of the C-H bond affected by the local environment [3, 7, 11].

In a previous experimental work we have studied the vibrational spectra of C-H stretching of 2,6-lutidine (2,6-dimethyl-pyridine) up to the fifth overtone [7]. The results showed that in this molecule there is a strong evidence for the stabilization of a structure with one bond of both methyl groups in the ring plane and the other two in equivalent positions out of it [7]. This conclusion was derived from the observation that two bands with intensity in the ratio 2:1 appear in the spectra of the 3rd, 4th and 5th overtones. The same effect has been observed for analogous compounds [3, 11]. It was not possible to determine experimentally if the hydrogen in plane was pointing toward

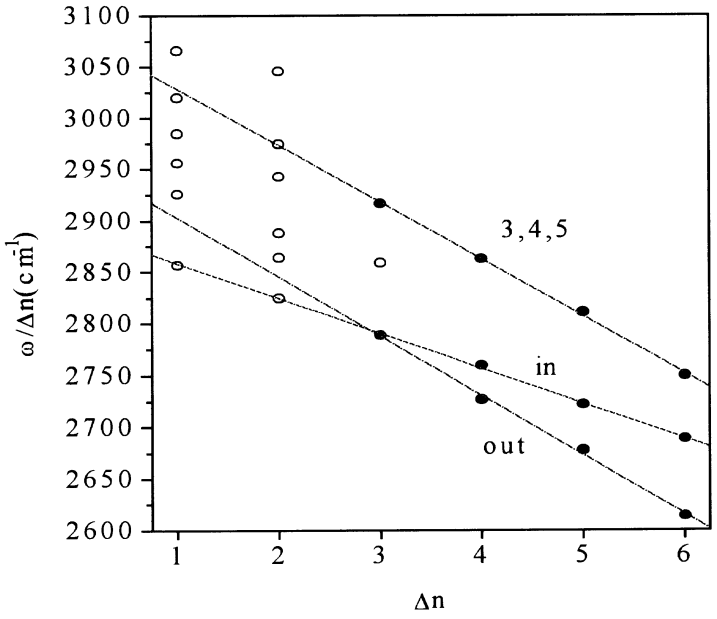

Fig. 1. – Plot of Morse progressions for 2,6-lutidine (data from ref. [7]). Experimental frequencies (circles) are reported as $\omega/\Delta n$ *vs.* Δn. Straight lines are fits of the pure local modes (full circles). The numbers 3, 4 and 5 refer to the aromatic C-H bonds in meta and para positions, *in* and *out* refer to the aliphatic C-H bonds in and out of the molecular plane.

the N atom or in the opposite direction. A second interesting result which stimulated the present study was that the C-H bond in the plane was less anharmonic than the other two bonds as observed from a plot of Morse progressions (see fig. 1). We have undertaken therefore an analysis of the structure and of electronic properties of 2,6-lutidine by means of *ab initio* calculations [12].

Ab initio calculations have demonstrated to be of big support in the interpretation of experimental results concerning conformational problems even in the case of toluene where the low energy barrier to rotation can be only roughly estimated [4]. We have tested different basis sets and calculated the barrier in the ground state for toluene, and 2,6-lutidine, the former to compare the accuracy of our calculations to that of others already reported in the literature [4]. We have been able to assign unambiguously the structure with the lowest conformation energy of 2,6-lutidine. In addition we have calculated the ground state vibrational modes in harmonic approximation of both the parent molecule pyridine and 2,6-lutidine in the most stable configuration. Finally the potential energy curve of the different C-H bonds of pyridine and 2,6-lutidine have been evaluated in a strict local picture by calculating the energy of the molecular structure with one of the C-H bonds stretched up to five times the bond equilibrium length. This allowed us to give an explanation to the experimental observation that the bond in the plane has a lower anharmonicity.

2. – Computational methods

Calculations of the molecular geometry of 2,6-lutidine and pyridine were carried out at the Hartree-Fock level utilizing the *ab initio* program HONDO [16] with STO-3G, 3-21G, 4-31G and DZV basis sets [15-18]. In the present case DZV basis set was chosen because it provided the optimum balance between accuracy and feasibility of calculations. To test the reliability of the calculation we undertook a calculation for toluene and compared the results to others previously reported [4]. In table I DZV geometrical parameters are reported together with the 6-31 G* results from ref. [4]. The DZV basis gives generally higher values for bond distances. However the maximum difference is less than 1% and the agreement is fairly good when the differences between rotamers are compared (last two columns of table I).

In common with previous calculations for toluene [4] we observed that the order of stability of the various rotamers changes when different basis sets are utilized. More sofisticated calculations are needed in order to reproduce correctly the very low value of the barrier (0.059 kJ/mol) [4]. On the contrary in methyl substituded pyridines barriers have generally higher energies: for example in 2-picoline (2-methyl pyridine) is 1.079 kJ/mol [19] in 2,6-lutidine the 3-fold barrier has been estimated to be 1.63 kJ/mol [20]. In the case of 2,6-lutidine, we verified a consistence of the results obtained with different basis sets. However we decided to utilize DZV basis for the rest of the calculation because it provided the lowest energy for the most stable rotamer. In addition we observed that calculated vibrational frequencies obtained with this basis set were the closest to the experimental ones (IR and Raman).

3. – Results and discussion

3'1. *Equilibrium conformation.* – The computed equilibrium structures of pyridine and 2,6-lutidine are reported in tables II and III, respectively. The structure of

TABLE I. – *Comparison of bond lengths* (Å) *and bond angles* (*degrees*) *for toluene calculated using* 6-31 G* (*from ref.* [4]) *and* DZV (*present work*) *basis sets. The definition of* (s-e) *and* (o) *is given in subsect.* **3**·1.

	6-31 G* T(s-e)	DZV T(s-e)	6-31 G* T(o)-T(s-e)	DZV T(o)-T(s-e)
C1-C2	1.3884	1.3973	− 0.0027	− 0.0021
C2-C3	1.3835	1.3932	+ 0.0019	+ 0.0018
C3-C4	1.3879	1.3968	− 0.0025	− 0.0018
C4-C5	1.3834	1.3931	+ 0.0023	+ 0.0021
C5-C6	1.3930	1.4013	− 0.0025	− 0.0019
C6-C1	1.3885	1.3885	+ 0.002	+ 0.0019
< C6C1C2	120.95	120.93	+ 0.01	0.01
< C1C2C3	120.17	120.22	+ 0.01	0
< C2C3C4	119.43	119.36	− 0.01	0
< C3C4C5	120.19	120.21	− 0.01	0.01
< C4C5C6	120.94	120.95	+ 0.02	− 0.01
< C5C6C1	118.32	118.33	− 0.02	0
C6-Cme (1)	1.5112	1.5155	+ 0.0003	− 0.0001
< C5C6Cme	120.41	120.41	− 0.42	+ 0.0042
< C1C6Cme	121.27	121.26	+ 0.86	− 0.0042
C1-H1	1.0766	1.0725	0	0.0003
C2-H2	1.0760	1.0719	− 0.0003	0
C3-H3	1.0755	1.0715	− 0.0002	0
C4-H4	1.0761	1.0719	− 0.0004	0
C5-H5	1.0772	1.0731	− 0.0006	− 0.0003
< H1C1C6	119.59	119.59	− 0.07	− 0.05
< H2C2C3	120.09	120.07	− 0.02	− 0.04
< H3C3C2	120.33	120.35	− 0.04	− 0.03
< H4C4C3	119.99	120.00	+ 0.08	+ 0.03
< H5C5C6	119.45	119.49	+ 0.07	+ 0.05
Cme-H1me	1.0835	1.0815	+ 0.0035	+ 0.0032
Cme-H2me	1.0861	1.0838	− 0.0018	− 0.0016
Cme-H3me	1.0861	1.0838	− 0.0018	− 0.0016
< H1meCmeC6	111.26	111.29	− 0.11	− 0.0046
< H2meCmeC6	111.18	111.05	+ 0.07	+ 0.0022
< H3meCmeC6	111.18	111.05	+ 0.07	+ 0.0022
< H1meCmeH2me	107.81	107.63	− 0.28	+ 0.0003
< H2meCmeH3me	107.43	107.59	+ 0.51	+ 0.004
< H2meCmeH1me	107.81	107.64	− 0.28	+ 0.0002

(1) Cme is the methyl carbon atom.

pyridine obtained in the present work is in good agreement with that derived experimentally and with the structure previously calculated [21, 22]. The lacking of electronic correlation results generally in shorter bond distances and, as a consequence, wider valence angles [15].

TABLE II. – *Optimized geometry and experimental bond lengths* (Å) *and bond angles* (*degrees*) *for pyridine.*

Parameter	Exp. ([1])	Calc.
N-C2	1.3402	1.3378
C2-C3	1.3945	1.3950
C3-C4	1.3944	1.3948
C2-H2	1.0843	1.0697
C3-H3	1.0805	1.0698
C4-H4	1.0773	1.0709
< C6NC2	116.83	118.80
< NC2C3	123.88	122.62
< C2C3C4	118.53	118.54
< C3C4C5	118.33	118.86
< NC2H2	115.88	116.30
< C4C3H3	121.30	121.28

(1) From ref. [2].

In 2,6-lutidine two methyl groups can rotate independently thus originating several different rotamers. The structure of four of them is reported in table III. The orientation of a given C-H bond of the methyl group in 2,6-lutidine as well as in toluene may be described as an "in plane" eclipsed (e) with respect to the ring or "out of plane" staggered (s) (see fig. 2) [4]. Another particular position is that with one C-H bond orthogonal to ring plane (o). This configuration leads to two equivalent positions in the case of toluene but not in the case of 2,6 lutidine because of the asymmetry introduced in the molecule by the presence of a nitrogen atom. Therefore sign (+) and sign (–) are added to indicate the C-H bond above and below the ring plane, respectively.

The introduction of two methyl groups in 2 and 6 position leads to an increase of the N-C distance, as previously observed in monosubstituted pyridines [2]. As can be observed in table III, some changes in bond distances and angles also accompany rotation of the two methyl groups. In particular the angle $N\text{-}C_2\text{-}C_7$ becomes 1 degree smaller in the (e-s, s-e) rotamer (see definition in caption of fig. 2) thus increasing the hindrance to the rotation when the methyl group assumes this position (see fig. 3).

This conformation is also the most stable one (see fig. 4). It has a stabilization energy of 170.75 cm^{-1} (2.02 kJ/mol) in respect to the least stable (s-e, e-s) rotamer. This energy difference can be taken as an estimate of the energy barrier to rotation and is close to the observed one [20]. The relative energies of some conformers are reported in table IV.

The presence of the two methyl groups in 2 and 6 position stabilizes the pyridine ring as a consequence of an increased charge density: a nitrogen atom can better accomodate a higher π density. This effect changes with rotation (see table V). A maximum of the π electronic density on the N atom is calculated for the (e-s, s-e) rotamer. From these results it is possible to draw the conclusion that both steric effects and electronic density contribute to the stability of the (e-s, s-e) rotamer.

3˙2. *Ground state vibrational frequencies.* – In table VI the fundamental frequencies in the C-H stretching region of pyridine are compared to experimental

TABLE III. – *Optimized geometry for various rotamers of* 2,6-*lutidine.*

	(e-s, s-e)	(s-e, e-s)	(o(–), o(–))	(o(–), o(+))
N-C2	1.3405	1.3415	1.3411	1.3409
C2-C3	1.3985	1.3984	1.3984	1.3986
C4-C5	1.3932	1.3926	1.3929	1.3928
C5-C6	1.3932	1.3926	1.3928	1.393
C6-N	1.3985	1.3984	1.3986	1.3984
	1.3406	1.3415	1.3411	1.3411
C3-H3	1.0699	1.0706	1.0703	1.0702
C4-H4	1.0715	1.0716	1.0715	1.0715
C5-H5	1.0699	1.0706	1.0702	1.0703
C2-C7	1.5078	1.5094	1.5085	1.5084
C7-H7a	1.0821	1.0783	1.0843	1.0843
C7-H7b	1.0822	1.0837	1.0794	1.0795
C7-H7c	1.0812	1.0837	1.082	1.0818
C6-C8	1.5078	1.5094	1.5085	1.5082
C8-H8a	1.0821	1.0783	1.0843	1.0844
C8-H8b	1.0812	1.0837	1.0795	1.0795
C8-H8c	1.0822	1.0837	1.082	1.082
< C6NC2	120.73	120.64	120.7	120.68
< NC2C3	121.18	121.18	121.17	121.17
< C2C3C4	118.74	118.82	118.77	118.76
< C3C4C5	119.42	119.36	119.41	119.43
< C4C5C6	118.74	118.82	118.77	118.76
< C5C6N	121.18	121.18	121.17	121.18
< C2C3H3	120.25	120.14	120.22	120.22
< C3C4H4	120.29	120.32	120.29	120.29
< C4C5H5	121.01	121.04	121.01	121.02
< NC2C7	116.57	117.25	116.88	116.88
< NC6C8	116.57	117.25	116.88	116.88
< C2C7H7a	110.08	109.6	110.31	110.28
< C2C7H7b	110.09	110.99	109.84	109.88
< C2C7H7c	111.58	110.99	111.5	111.51
< H7aC7H7b	107.41	108.77	107.81	107.78
< H7aC7H7c	108.79	108.77	108.03	108.06
< H7bC7H7c	108.79	107.66	109.25	109.25
< C6C8H8a	110.08	109.6	110.31	110.28
< C6C8H8b	11.58	110.99	109.83	109.89
< C6C8H8c	110.47	110.99	111.49	111.49
< H8aC8H8b	108.79	108.77	107.81	107.8
< H8aC8H8c	107.42	108.77	108.03	108.03
< H8bC8H8c	108.12	107.66	109.25	109.25

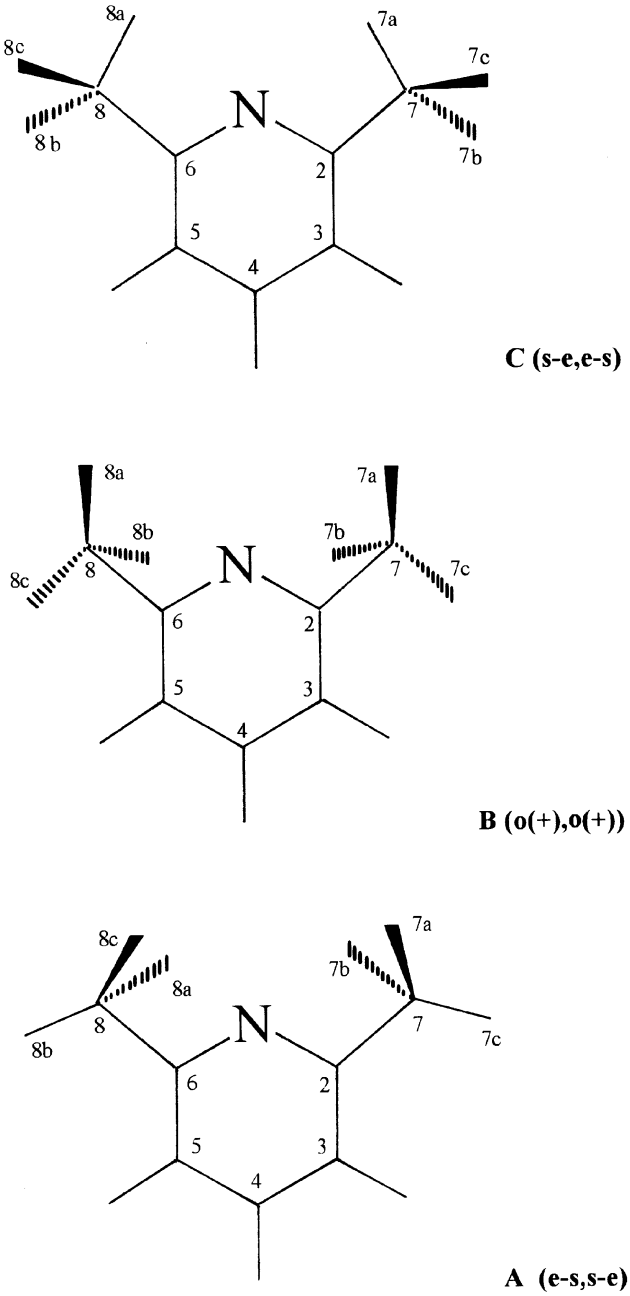

Fig. 2. – Methyl groups in 2,6-lutidine in three different positions. In conformer A, starting from the left, an eclipsed (e) bond is found followed by two identical staggered (s) bonds (e-s). The opposite situation is found for the second methyl group (s-e). In conformer B two bonds are orthogonal (o) to the ring plane and both lie on the same side (o (+) - o (+)).

TABLE IV. – HF/DZV *relative energies* (cm^{-1}) *of different rotamers of* 2,6-*lutidine.*

Rotamer	(s-e, e-s)	(s-e, o)	(s-e, s-e)	(o, e-s)	(o(–), o(–))
Rotation (1)	0, 0	0, 30	0, 60	30, 0	30, 90
ΔE	0	− 52.81	− 101.88	− 52.81	− 86.05

Rotamer	(o(+), o(–))	(o, s-e)	(e-s, e-s)	(e-s, o)	(e-s, s-e)
Rotation (1)	90, 90	30, 60	60, 0	60, 30	60, 60
ΔE	− 92.26	− 134.37	− 101.88	− 134, 37	− 170.75

(1) Counterclockwise rotation (degrees).

values. Force constants and consequently frequencies are higher because of the lacking of electronic correlation [15, 16]. Therefore a factor of 0.89 has been utilized to rescale the calculated to the experimental values [9, 23]. The general agreement between scaled and experimental frequencies is good. On the contrary there is not a complete correspondence between calculated and experimental intensities. This is mainly due to the fact that in the experimental spectra in the C-H stretching region there are also combination bands which can modify the intensity distribution.

The same correction factor has been utilized to calculate the ground state frequencies of C-H stretching in 2,6-lutidine. In table VII the assignment is reported.

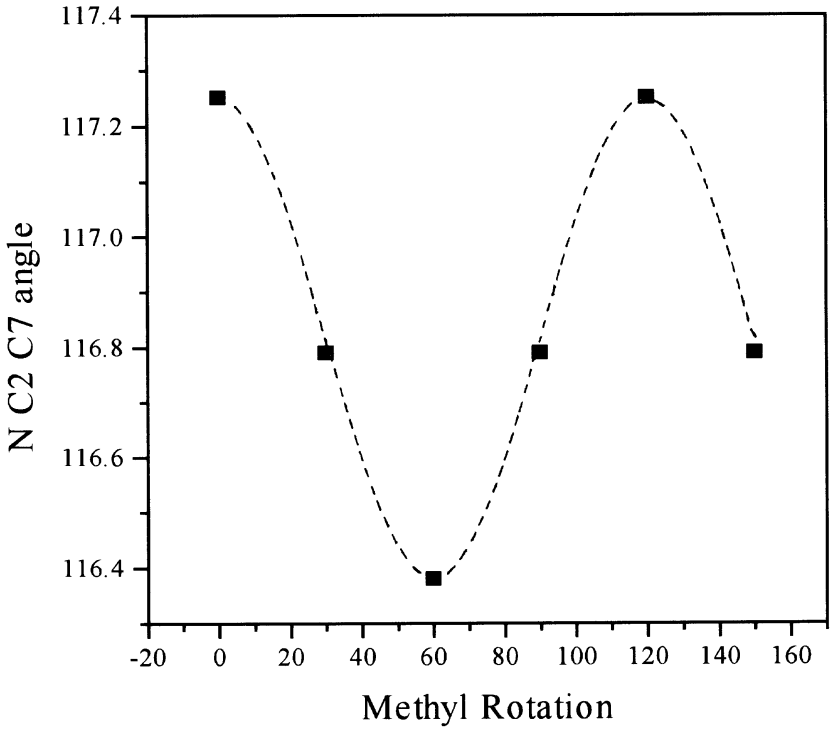

Fig. 3. – The variation of N-C2-C7 angle with the rotation of the methyl group. The conformer at 0° corresponds to the one with the methyl group with one C-H bond in the plane and ponting toward the N atom. Full squares are calculated values. The dashed line is a guide for the eyes.

TABLE V. – π *Mulliken population data for different rotamers of* 2,6-*lutidine and pyridine.*

Rotamer	N	C2	C3	C4	C5	C6
s-e, e-s	1.18273	0.90460	1.07142	0.92112	1.07142	0.90460
o(–), o(+)	1.18323	0.89844	1.07503	0.91852	1.07503	0.89844
o(+), o(+)	1.18339	0.89839	1.07494	0.91877	1.07494	0.89839
e-s, s-e	1.18338	0.89406	1.07830	0.91667	1.07830	0.89406
pyridine	1.14062	0.92513	1.03515	0.93883	1.03515	0.92513

TABLE VI. – *Fundamental* C-H *stretching frequencies* (cm^{-1}) *of pyridine.*

Simmetry	Frequency (cm^{-1})			Intensity (1)	
	calc.	corr.	exp. (2)	calc.	exp.
A_1	3404	3030	3026	0.08	—
A_1	3425	3048	3033	0.14	0.3
B_1	3405	3030	3026	0.11	0.8
B_1	3425	3048	3053	1	0.7
B_1	3450	3070	3079	0.28	1

(1) Normalized to the most intense peak.
(2) Data obtained from pure liquid samples (present work).

We did not observe any relevant change in the frequencies for different rotamers. The normal mode coefficients of the C_{2v} structure have been used to determine the assignments. From such coefficients we observe that none of the C-H stretching normal coordinates involves preminently the in-plane bond. Therefore the spectrum of the foundamental is not sensitive to the stabilization of a particular rotamer.

3·3. *The* C-H *stretching potential.* – In a strict local picture, the C-H stretching potential can be estimated by calculating the energy of the molecular structure starting from the optimized equilibrium geometry and varying the bond distance with the remaining degrees of freedom kept frozen. In this case no optimization cycle is performed. In this way we were able to estimate the form of the potential curve and to extrapolate the dissociation energy. As previously observed [15] such a calculation becomes less precise because at the Hartree-Fock level the electrons must occupy the same spatial orbital. When the atoms are completely separated the symmetric combination and the antisymmetric one become equivalent. A SCF wavefunction is constrained to be only one configuration. To bypass this limitation we have fitted the calculated points obtained by stretching the bond up to five times the equilibrium length to a Morse potential of the form

$$V = E_d[1 - \exp[-a(r - r_e)]]^2, \tag{1}$$

where E_d is the dissociation energy and a^{-1} is a measure of the width of the potential well. The best fit values have been compared to those obtained in our previous study on

TABLE VII. – *Fundamental C-H stretching frequencies* (cm^{-1}) *of* 2,6-*lutidine.*

Simmetry	Frequency (cm^{-1})			Intensity (1)	
	calc.	corr.	exp. (2)	calc.	exp.
A_1	3210	2857	2855	0.3196	0.33
A_1	3286	2925	2923	0.9369	1
A_1	3304	2940	2956	0.5909	0.79
A_1	3407	3032	—	0.0014	—
A_1	3442	3063	3066	0.5009	0.60
B_1	3209	2857	2855	1	—
B_1	3286	2925	—	0	—
B_1	3304	2940	2985	0.6562	0.61
B_1	3412	3032	3020	0.5224	0.24

(1) Normalized to the most intense peak.
(2) Data obtained from pure liquid samples (present work).

vibrational overtones [7]. Although the entire procedure which leads to the estimate of the dissociation energy has low accuracy, the calculation predicts that the in-plane bond is less anharmonic and has a higher dissociation energy than that of the out-of-plane bond as was observed experimentally (see table VIII).

From the analysis of π Mulliken populations as a function of bond lengthening it is apparent that a stretching of the in-plane bond increases the charge on the nitrogen atom giving rise to a more stable situation in comparison to that of a stretching of the out-of-plane C-H (see table IX). From our results we can conclude that the different behaviour of the two types of bond is mainly dominated by electronic distribution rather than by steric hindrance.

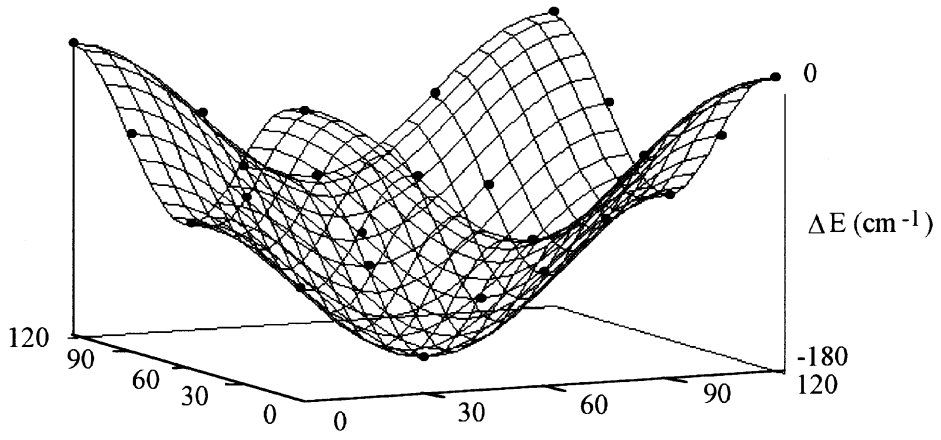

Fig. 4. – Three dimensional plot of the relative energy of different rotamers. Full circles correspond to the calculated values reported in table IV.

TABLE VIII. – *Morse parameters for different* C-H *bonds.*

	Calc.		Exp. (1)	
	a(Å^{-1})	E_d(10^4 cm^{-1})	a(Å^{-1})	E_d(10^4 cm^{-1})
Pyridine				
C2-H2	1.21 ± 0.04	7.97 ± 0.14	1.75	4.27
C3-H3	1.21 ± 0.03	8.00 ± 0.12	1.75	4.41
C4-H4	1.19 ± 0.04	8.00 ± 0.14	—	—
2,6-lutidine (e-s, s-e)				
C7-H7c (2)	1.16 ± 0.04	7.60 ± 0.15	1.43	6.23
C7-H7a (2)	1.21 ± 0.04	7.30 ± 0.14	1.86	3.96

(1) From ref. [7].
(2) Defined according to fig. 2.

TABLE IX. – π *Mulliken population of* 2,6-*lutidine in configuration* (e-s, s-e) as a function of C-H *bond length.*

Bond length (Å)					
C7-H7a (1)	1.0822	1.6233	2.1644	3.2466	5.411
N	1.18338	1.17057	1.15447	1.13686	1.14221
C2	0.89406	0.90469	0.92559	0.9561	0.96242
C3	1.07830	1.07131	1.05773	1.02877	1.00531
C4	0.91667	0.9201	0.92577	0.93454	0.94032
C5	1.07830	1.06976	1.05473	1.02735	1.00984
C6	0.89406	0.89664	0.90062	0.90411	0.90046
C7-H7c	1.0812	1.6218	2.1624	3.2436	5.406
N	1.18338	1.18885	1.19245	1.19389	1.1923
C2	0.89406	0.93983	0.93983	0.96306	0.95373
C3	1.07830	1.03912	1.03912	1.02612	1.04562
C4	0.91667	0.91913	0.91913	0.916	0.91017
C5	1.07830	1.06517	1.06517	1.05578	1.05555
C6	0.89406	0.89882	0.89882	0.89919	0.89469
C4-H4	1.0715	1.60715	2.15	3.2145	5.3575
N	1.18338	1.18167	1.17843	1.17549	1.18561
C2	0.89406	0.89889	0.90224	0.90287	0.89789
C3	1.07830	1.0818	1.0844	1.0848	1.09589
C4	0.91667	0.9037	0.89719	0.90061	0.89814
C5	1.07830	1.08181	1.0844	1.0848	1.09589
C6	0.89406	0.89889	0.90224	0.90287	0.89789

(1) Defined according to fig. 2A.

4. – Conclusions

We have utilized *ab initio* molecular orbital calculations to investigate the structure and the electronic and vibrational properties of pyridine and 2,6-lutidine in the ground state. We have studied in details the conformations of 2,6-lutidine. The most stable rotamer of this molecule has C_{2v} symmetry with one of the C-H bonds of both the methyl groups lying in the plane of the aromatic ring and pointing in the opposite direction with respect to the nitrogen atom. This is the result of the minimization of steric hindrance and electronic stabilization. Vibrational frequencies and oscillator strengths of C-H stretching in the fundamental region have been calculated for both pyridine and the most stable rotamer of 2,6-lutidine and compared to experiments in the pure liquids. Finally, the potential energy curve of the C-H stretching has been investigated for the different rotamers. We demonstrate that the C-H bond lying in the plane has a higher dissociation energy, as is expected from experimental results on vibrational overtones due to a more stable electronic distribution.

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