Nematic Phase Nuclear Magnetic Resonance, Ultrasonic Relaxation, and Theoretical *ab initio* Investigation of Internal Rotation in Pyridine-2-carbaldehyde

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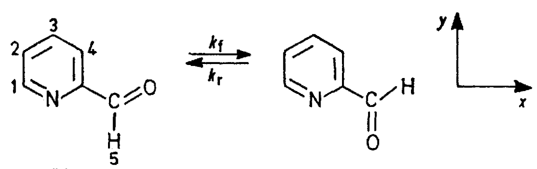
The 100 MHz ^{1}H n.m.r. spectrum of pyridine-2-carbaldehyde partially oriented in the nematic phase of a liquid crystalline solvent has been obtained and analysed. It has been shown that a conformational equilibrium is present and that the *N–O-trans*-form is the more stable (*ca.* 96%). The barrier height to *cis–trans*-interconversion in the pure liquid has been investigated by means of the ultrasonic relaxation technique and a value of 4.5 ± 0.3 kcal mol^{-1} has been found. The hindering internal potential has also been investigated by means of quantum mechanical calculations using the SCF–MO–LCAO *ab initio* method. The overall results have been compared with previous experimental findings and theoretical calculations.

N.M.R. spectroscopy in liquid crystalline solvents is a convenient method for the solution of conformational problems. The advantages and the limits of this technique have been discussed and tested in previous work.[1] In many cases, however, only the percentage of stable rotamers can be estimated, the height of the potential barrier being practically unobtainable or obtainable only with low accuracy.[2] On the other hand the ultrasonic relaxation technique has been successfully used for evaluating the height of the energy barrier between rotational isomers in cases where some previous estimation of rotamer populations was available.[3]

In this paper the results of a study of internal rotation in pyridine-2-carbaldehyde [(I) and (II)] † partially oriented in the nematic phase are given together with a determination of the *cis–trans*-barrier height by ultrasonic relaxation in the pure liquid.



(I) (II)

Moreover, in order to compare the experimental and theoretical results, we have performed *ab initio* quantum mechanical calculations, involving no empirical parameterisation, of the internal rotation potential. For a general discussion on the applicability of this method see, for example, ref. 4. In this paper the standard *ab initio* SCF–MO–LCAO method [5] has been used, building up the molecular wavefunction with the minimal STO-3G basis set.[6]

The overall results agree with previous experimental studies (see for example the accurate determination [7] of the long-range coupling constants in various solvents). As far as theoretical calculations are concerned, non-empirical methods give better agreement with the experimental findings than the semi-empirical ones.

RESULTS

The 100 MHz spectrum of pyridine-2-carbaldehyde obtained at room temperature in nematic Phase IV (Merck) as solvent, has been interpreted by means of an iterative computer program in terms of five chemical shifts and ten D_{ij} dipolar couplings, the indirect couplings being taken from the literature.[7] Negligible variations of these parameters were found when indirect couplings were included in the iteration procedure. Experimental and computer simulated spectra are given in Figure 1. The computed spectrum was obtained using the data reported in Table 1. As

TABLE 1

Dipolar couplings and chemical shifts (Hz) of the 100 MHz n.m.r. spectrum of pyridine-2-carbaldehyde partially oriented (20% mole) in nematic Phase IV. *J* Values were taken from ref. 7

$\nu_1 = -100.2 \pm 1$, $\nu_2 = 0$, $\nu_3 = -6.3 \pm 1$, $\nu_4 = -7.5 \pm 1$, $\nu_5 = -269.4 \pm 1$

D_{12}	-593.5 ± 0.8	D_{24}	-359.7 ± 1
D_{13}	-24.3 ± 0.3	D_{25}	-172.1 ± 0.8
D_{14}	-106.2 ± 0.4	D_{34}	$-2\,168.7 \pm 0.8$
D_{15}	-373.7 ± 0.6	D_{35}	-133.2 ± 0.9
D_{23}	-755.9 ± 1	D_{45}	-228.0 ± 0.2

Figure 1 shows a considerable difference in linewidth is exhibited by the central lines. Quadrupolar effects of the ^{14}N nucleus seems to be responsible for this differential linewidth.

In order to obtain information on the molecular geometry, the basis equation linking the experimental D_{ij} values to the proton co-ordinates and molecular motional parameters [8] was used.

Assuming a rigid rotor model, H-1—H-4 form a rigid system and hence can be treated separately from the problem of internal rotation. The four dipolar couplings to the formyl proton can then be used to test models for internal

† Non-systematic numbering used for convenience.

[1] (*a*) P. Bucci and C. A. Veracini, *J. Chem. Phys.*, 1972, **56**, 1290; (*b*) L. Lunazzi, G. F. Pedulli, M. Tiecco, and C. A. Veracini, *J.C.S. Perkin II*, 1972, 755; (*c*) P. L. Barili, L. Lunazzi, and C. A. Veracini, *Mol. Phys.*, 1972, **24**, 673; (*d*) Lunazzi and C. A. Veracini, *J.C.S. Perkin II*, 1973, 1739.

[2] P. Bucci, M. Longeri, C. A. Veracini, and L. Lunazzi, *J. Amer. Chem. Soc.*, 1974, **96**, 1305.

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[8] L. C. Snyder, *J. Chem. Phys.*, 1965, **43**, 4041.

TABLE 2

Computed parameters (Hz) for various conformational models of pyridine-2-carbaldehyde

Parameter	Rigid part	Planar conformation	96% *trans* [a]	96.5% *trans* [b]
D_{12}	−593.49	−595.6	−593.7	−593.7
D_{13}	−24.3	−24.8	−24.4	−24.4
D_{14}	−106.2	−106.5	−106.4	−106.4
D_{15}		−364.2	−372.2	−372.3
D_{23}	−755.9	−757.5	−756.2	−756.3
D_{24}	−359.7	−360.0	−360.1	−359.9
D_{25}		−191.4	−173.1	−172.9
D_{34}	−2 168.7	−2 168.9	−2 168.9	−2 168.8
D_{35}		−155.4	−133.7	−133.6
D_{45}		−227.1	−228.6	−228.5
R.m.s. deviation	0.01	5.3	0.64	0.6
$C_{3z^2-r^2}$	−0.3350 ± 0.0002	−0.3354 ± 0.0006	−0.3349 ± 0.0003	−0.3350 ± 0.0003
$C_{x^2-y^2}$	0.1087 ± 0.0005	0.1086 ± 0.0005	0.1088 ± 0.0007	0.1087 ± 0.0006
C_{xy}	−0.1373 ± 0.0004	−0.1310 ± 0.0004	−0.1373 ± 0.0005	−0.1372 ± 0.0005

[a] First approximation (see text). [b] Second approximation (see text).

rotation. The following models were tested: (1) pure *trans*- and *cis*-isomers; (2) out-of-plane conformation at some angle θ; (3) conformational equilibrium with an intramolecular potential $V(\theta) = \sum_n V_n (1 - \cos n\,\theta)/2$ with a form suggested by theoretical calculations (see later).

Rigid Part of Molecule.—For the rigid part of the molecule six dipolar couplings are available to fix three constants of motions and three co-ordinates. For this purpose the computer program SHAPE [9] was used, assuming that the H-2—H-3 distance is equal to that of pyridine as determined by microwave measurements [10a] (2.483 Å) and varying the x and y co-ordinates of H-4 and the y co-ordinate of H-1. The calculated dipolar couplings and motional parameters are given in Table 2, while the best fit geometry is in Table 3. A different choice of the co-ordinates to be varied could be made giving, however, no substantial change in the final result.

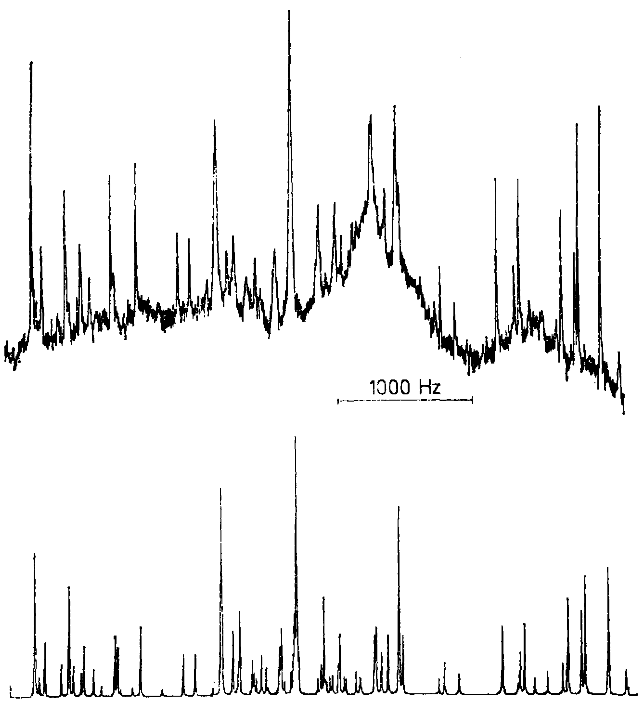

FIGURE 1 Experimental and computer simulated 100 MHz n.m.r. spectrum of pyridine-2-carbaldehyde partially oriented in a nematic solvent

(1) *Planar* cis *and* trans-*Conformers.*—The planar *cis*- and *trans*-models require three parameters of motion and it is possible to vary the x and y co-ordinates of the formyl proton to fit the four dipolar couplings to it. However, starting from both an approximate *cis*- or *trans*-structure, the program SHAPE converges to a nearly *trans*-geometry (Table 3). The best fit dipolar couplings and parameters of motion for this planar form are given in Table 2. It is seen that only the couplings to the formyl proton have a large deviation from the experimental values (the r.m.s. deviation for this structure is 5.3 Hz). In addition the co-ordinates of the formyl proton deviate appreciably from the values observed under the same experimental conditions for pyridine-2,6-dicarbaldehyde.[11] We can conclude that the conformation of the molecule is nearly *trans* (the r.m.s. deviation for the *cis*-structure was 936 Hz). However with this conformation alone it is not possible to obtain a good fit of the experimental couplings.

TABLE 3

Co-ordinates of the hydrogen atoms (in Å) for the rigid part and for the CHO proton in the NO-trans conformation for the various models (see text)

		x	y
H-1		−2.092 ± 0.003	0.203 ± 0.006
H-2		−2.129 ± 0.004	2.609 ± 0.003
H-3		0	3.882
H-4		2.149 ± 0.002	2.598 ± 0.006
H-5	*a*	2.271 ± 0.06	−0.790 ± 0.02
	b	2.125 ± 0.03	−1.187 ± 0.02
	c	2.093 ± 0.02	−1.20 ± 0.01

[a] Planar conformer. [b] Equilibrium of conformers (first approximation). [c] Conformer equilibrium with potential curve averaging.

(2) *Out-of-plane Conformations.*—Theoretical calculations clearly exclude non-planar conformations (see later). However, to study the out-of-plane conformations five constants of motion are required as there is no element of symmetry. Assuming that $C_{3z^2-r^2}$, $C_{x^2-y^2}$, and C_{xy} are those of the rigid part, the C_{xz} and C_{yz} constants have to be determined together with the geometrical parameters of the formyl

[9] P. Diehl, P. M. Henrichs, and W. Niederberger, *Mol. Phys.*, 1971, **20**, 139.

[10] (*a*) B. Bak, L. Hansen, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1958, **2**, 361; (*b*) F. Mönnig, H. Dreizler, and H. D. Rudolph, *Z. Naturforsch.*, 1965, **20a**, 1323; (*c*) R. W. Kilb, C. C. Lin, and E. B. Wilson, jun., *J. Chem. Phys.*, 1957, **26**, 1695.

[11] P. L. Barili, M. Longeri, and C. A. Veracini, *Mol. Phys.*, 1974, **28**, 1101.

proton from the four dipolar couplings. Therefore the model can be tested only by assuming bond lengths and angles for the formyl group and rotating this group at various dihedral angles θ. A good starting point seemed to be the geometry of pyridine-2,6-dicarbaldehyde previously determined in the same solvent.[11] Starting from *trans*-position ($\theta = 0°$) the r.m.s. deviation increases with increasing values of θ. In another model the formyl group was considered to undergo a fast exchange between two positions above and below the pyridine ring ($+\theta$ and $-\theta$) retaining only three parameters of motion. Even in this model, however, the r.m.s. deviation increases as soon as θ increases from its value of zero in the *trans*-planar position.

(3) *Conformational Equilibrium.*—This situation is supported both from the conclusions of previous work in isotropic solution [7] and theoretical calculations. We used two levels of approximations to text this situation retaining only the three parameters of motion obtained from the rigid part. In a first attempt, the dipolar couplings to the formyl proton were averaged over the two conformers (I) and (II).[1] This approximation naturally depends on the form of the intramolecular potential and on the barrier height in particular. In the framework of this approximation the experimental couplings are reproduced (r.m.s. deviation 0.6 Hz) with a weight of 96% for the *trans*-conformer. The calculated couplings and parameters of motion are given in Table 2, the co-ordinates of the formyl proton in the *trans*-position in Table 3.

In a following step we used, for the rotating system, a potential function of the form (1) to obtain the averaged values of the dipolar couplings. In this calculation we

$$V(\theta) = \sum_{n=1}^{3} V_n\,(1-\cos n\theta)/2 \qquad (1)$$

assumed that the formyl group rotates rigidly around the C–C bond and the probability distribution with respect to

TABLE 4

Parameters of the intramolecular potential curve (cm^{-1})

	Computed from best fit of the dipolar couplings	Extracted from theoretical intramolecular potential
V_1	550 ± 30	795
V_2	2 230 ± 50	2 142
V_3	245 ± 30	84
V_4		−44

the dihedral angle was calculated by solving the Schrödinger equation for the rotor. The wave function was expanded in the harmonic series retaining the first 25 terms. The rotational angular probability was subsequently obtained by weighting with a Boltzmann distribution the first 40 rotational states. The co-ordinates of the formyl proton were varied and a reduced moment of inertia of 8.9 amu Å^2 was employed.[12] These calculations were performed with a suitable computer program (COSMO) and the values of V_1, V_2, and V_3 best fitting the experimental D_{ij} were obtained. The re-calculated D_{ij} and constants of motion are given in Table 2 while the co-ordinates of the formyl proton are in Table 3. Table 4 reports the V_1, V_2, and V_3 parameters obtained in this procedure. The weight of the *trans*-form calculated with the potential curve (dashed line in Figure 3) is 96.5 ± 0.2%, corresponding to ΔG^0_{300} −2.0 kcal mol^{-1} for *cis–trans*-interconversion in nematic Phase IV.

It can be shown [13] that the absorption of a sound wave travelling through a medium containing a chemical system at equilibrium is given by equation (2) where B is the contribution from classical absorption, f_{ci} is linked to the ith relaxation time by $1/\tau_i = 2\pi f_{ci}$, A_i is a constant characteristic of the ith relaxation process; α and f are the two experimental quantities measured, *i.e.* the absorption coefficient and the frequency of the sound wave.

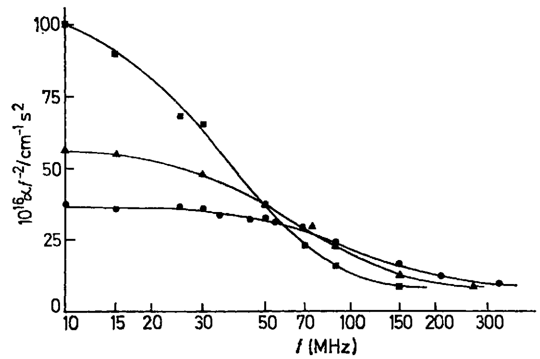

FIGURE 2 Plot of $10^{16}\,\alpha/f^2$ against frequency (MHz) for pyridine-2-carbaldehyde at: ● 44°; ▲ 25°; ■ 5.5°

$$\alpha/f^2 = B + \sum_{i=1}^{n} \frac{A_i}{1 + (f/f_{ci})^2} \qquad (2)$$

The results of our measurements in the frequency range 10—330 MHz were fitted to equation (2) for a single relaxation time; the very good fit obtained supports this assumption, and the relaxation process was attributed to *trans–cis*-isomerization, as in the case of analagous molecules.[14,15] The results, together with the curves calculated by a least squares method at the temperatures studied, are given in Figure 2, the parameters of relaxation equation being summarized in Table 5.

TABLE 5

Relaxation parameters for the *cis–trans*-isomerization of pyridine-2-carbaldehyde

Temperature (°C)	$10^{16}A/cm^{-1}\,s^2$	$10^{16}B/cm^{-1}\,s^2$	f_c/MHz	$\Delta H^{\ddagger}_{cis \rightarrow trans}$/kcal mol^{-1}	$\Delta S^{\ddagger}_{cis \rightarrow trans}$/cal K^{-1} mol^{-1}
5.5	103.6 ± 2.1	4.6 ± 0.6	32.9 ± 0.7		
25.0	51.3 ± 1.0	6.1 ± 0.5	62.9 ± 1.2	4.5 ± 0.3	−4.4 ± 1
44.0	30.3 ± 1.2	7.5 ± 1.1	100.6 ± 3.1		

The relaxation time for the *trans–cis*-isomerization is given by $1/\tau = k_f + k_r$, where k_f and k_r are the kinetic constants for the forward and reverse reaction respectively. Substitution of k_f by K_{eq}/k_r and insertion in the Eyring equation

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[13] M. Eigen and L. De Maeyer in 'Technique of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 1953, 2nd edn., vol. VIII, part II.

[14] M. S. de Groot and J. Lamb, *Proc. Roy. Soc.*, 1967, *A*, **242**, 36.

[15] R. A. Pethrick and E. Wyn-Jones, *J. Chem. Soc. (A)*, 1969 713.

gives (3) where k, h, and R are the Boltzmann, Planck, and

$$f_c = \frac{1}{2\pi}(1 + K_{eq})\frac{kT}{h} e^{\Delta S_r\ddagger/R} e^{-\Delta H_r\ddagger/RT} \qquad (3)$$

gas constants, and $\Delta S_r^\ddagger$ and $\Delta H_r^\ddagger$ are the entropy and enthalpy of activation for the reverse reaction. Assuming K_{eq} is independent of temperature and taking for it the value of 4/96 (from the n.m.r. results), the following values are obtained from the slope and intercept of $\ln f_c/T$ against $1/T$ respectively: $\Delta H_r^\ddagger = 4.5 \pm 0.3$ kcal mol^{-1} and $\Delta S_r^\ddagger = -5 \pm 1$ cal mol^{-1} K^{-1}.

For the quantum mechanical evaluation of the internal rotation potential of pyridine-2-carbaldehyde, we have performed *ab initio* SCF–MO–LCGO (STO-3G) computations for five conformations of the formyl group, the dihedral angle θ being equal to 0, 45, 90, 135, and 180° respectively (θ = 0° for the *N–O-trans*-rotamer). The internal rotation was performed by keeping bond lengths and angles fixed to their microwave values [10] and the corresponding proton geometry is very near the n.m.r. best fit reported in Table 3.

energy (retaining only the first three terms) gives a *trans*-population of 97.8% at 300 K, corresponding to a value of −2.2 kcal mol^{-1} for ΔG^0_{300} for the *cis–trans*-rotameric equilibrium in the vapour phase.

DISCUSSION

The results for the conformational preference of pyridine-2-carbaldehyde are qualitatively consistent with previous experiments,[16] all showing that the *N–O-trans*-rotamer greatly prevails in the *trans–cis*-conformational equilibrium. The agreement is particularly good with a recent conformational study by means of accurate determination of long-range coupling constants,[7] showing that the amount of *trans*-conformer in the equilibrium ranges from 90 to 100%, depending mainly on the polarity of solvent used. An essentially *trans*-conformation (*ca.* 96%) is also in agreement with the totally *trans–trans*-conformation found for pyridine-2,6-dicarbaldehyde partially oriented in the same nematogen (nematic Phase IV).[11] As far as the determination of intramolecular potential is concerned, it can be observed that while the sum ($V_1 + V_3$), giving the energy difference between the two potential curve minima, can be determined with reasonable accuracy, the determination of the potential barrier is subject to relatively high uncertainty.

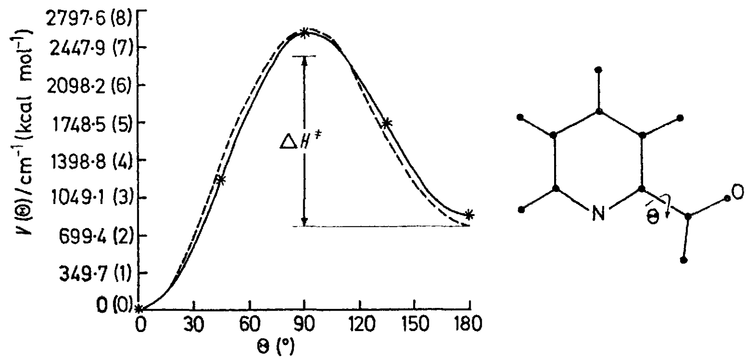

FIGURE 3 Potential energy for intramolecular rotation *versus* the dihedral angle in pyridine-2-carbaldehyde. —— *ab initio* results; – – – –, experimental from best fit of dipolar couplings. The ultrasonic evaluation of the *cis–trans*-barrier, $\Delta H^\ddagger$, in the pure liquid is also displayed

The minimum energy conformation is the *trans* (θ = 0°), with a total energy of −354.86331 a.u. A secondary minimum is also present for θ = 180° (*cis*-conformer) with an energy of 2.5 kcal mol^{-1} with respect to the absolute *trans*-minimum. The computed barrier for *cis–trans*-interconversion, corresponding to the orthogonal conformation (θ = 90°), is equal to 4.9 kcal mol^{-1}.

By fitting the computed values of the potential energy by an analytical function of the torsional angle θ of the form (4)

$$V(\theta) = \sum_{n=1}^{4} V_n (1 - \cos n\theta)/2 \qquad (4)$$

the values reported in Table 4 for the four parameters have been obtained, and the potential energy as a function of the dihedral angle is shown in Figure 3 (solid line). The harmonic force constant for the torsional motion [equation (5)]

$$\tfrac{1}{2} V^* = \tfrac{1}{2}(V_1 + 4V_2 + 9V_3 + 16V_4) \qquad (5)$$

is equal to 13.5 kcal mol^{-1} and to 14.5 kcal mol^{-1} on deleting the V_4 term.

The resolution of the Schrödinger equation for the hindered rotor in the field of the above computed potential

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However, the results show that even if the use of n.m.r. spectroscopy of partially oriented molecules in cases in which an internal motion is present cannot give the highly accurate geometrical data obtainable for rigid molecules (because of the increased number of parameters to be determined), nevertheless a satisfactory knowledge of conformational preferences is given, and the internal rotational potential curve of Figure 3 is in good agreement with the theoretical one.

For the potential barrier determined by means of the ultrasonic technique a value for *cis–trans*-barrier of 4.5 kcal mol^{-1} compares quite well both with the experimental n.m.r. curve (*ca.* 5.2 kcal mol^{-1}) and theoretical non-empirical results.

Nevertheless some caution must be recommended in such comparisons, as the three reported results are obtained in different media. The difference between the two experimental phases are probably not important for the aim of the present study, but the solvent effect may play a significant role by passing from the vapour to the liquid crystal.

For the evaluation of the solvent effect, the classical reaction-field model gives good results for many solutes.[17] However, besides the general limitations of the theory,[17] such a method seems to depend somewhat on the dipolar and quadrupolar parameters used. In fact, for *cis–trans*-equilibrium, from ΔG^0_{300} (nematic) = 2.0 kcal mol^{-1}, and by assuming a value of 5.5 for the dielectric constant of the liquid crystal, the value of ΔG^0_{300} (vapour) ranges from −4.8 to −6.8 kcal mol^{-1}.* Higher values, as much as −8.0 kcal mol^{-1}, can be obtained from n.m.r. data in other solvents.[7] Therefore this experimental determination of ΔG^0 (vapour) cannot be regarded as conclusive. Nevertheless our theoretical value, −2.2 kcal mol^{-1}, seems to be an underestimate.

The reliability of the present *ab initio* calculations may be also checked with respect to far-i.r. data for the vapour.[12] From this comparison, it may be deduced that the STO-3G minimal basis set seems to exaggerate the barrier heights. In fact, for pyridine-2-carbaldehyde, the theoretical value of the harmonic force constant, 13.5 kcal mol^{-1}, must be compared with the experimental one of 9.3 kcal mol^{-1} (average value for the *trans*- and *cis*-conformers). This feature, which is common to several *ab initio* computations of force constants, is mainly due to an overestimation of the V_2 term, which is the most important for the barrier value, and therefore of the conjugation effects. Also for benzaldehyde the STO-3G barrier is too high, 6.6 *versus* 4.7 kcal mol^{-1}.[18]

The use of more extended basis sets and/or the geometry relaxation is necessary for a complete quantitative determination of the internal rotational potential in pyridine-2-carbaldehyde. The present STO-3G results with fixed geometry can be considered of semi-quantitative level and may be used for comparison purposes, thus representing a reasonable compromise between the accuracy of the results and the necessary amount of computational effort.

To finish, we append a few words on some semi-empirical calculations. The INDO results [7,19] are substantially wrong: the barrier is not present and the energy difference between the *trans*- and *cis*-conformers is small. Also the PCILO method [20] give an incorrect answer: the *ortho*-barrier is present, perhaps slightly underestimated (3.7 kcal mol^{-1}), but the *trans*- and *cis*-minima are equivalent from an energy point of view.

EXPERIMENTAL

Pyridine-2-carbaldehyde (Fluka) was fractionally distilled under nitrogen immediately before use.

The 100 MHz spectrum (JEOL PS 100 spectrometer) of a 20% mole solution in Merck Licrystal Phase IV [21] was recorded in the frequency sweep mode with external lock. The spectrum was interpreted by means of the LACOONOR program iterating 50 lines with a final r.m.s. deviation of 1.5 Hz.

Measurements of the sound absorption coefficient, α, were performed by the pulse technique on samples of pure liquid in the frequency range 10—330 MHz. The apparatus consisted of the Matec model 6 000 ultrasonic generator and receiver, and the 700 series radio frequency plug-in for the generation and detection of ultrasonic pulses at the appropriate frequency, and of the model 1235B MATEC pulse amplitude monitor for the continuous measurement of the relative attenuation of the echo's amplitude at various path lengths. The mechanical part and the vessel were constructed following Andreae *et al.*[22]

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* These computations refer to different choices of parameters,[7] and also to the use of the STO-3G dipole moments in the dipolar term (μ_{trans} 2.48; μ_{cis} 3.77 D).

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