Internal Rotation of the *NN*-Dimethylamino-group in Aromatic and Heteroaromatic Systems

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The origin of the rotational barrier of the dimethylamino-group in several aromatic and heteroaromatic systems has been analysed by a comparison of the results of MO calculations and experimental energies. For most of the compounds considered theory predicts that the dimethylamino-group should be coplanar with the attached ring in the ground state, except in a few cases where steric effects are present. For *NN*-dimethylaniline nitrogen inversion was also studied for several conformations (different angles of rotation θ around the C–N bond) by *ab initio* MO calculations with a limited basis set. It was thus found that, while the pyramidal structure is stable both for the planar and perpendicular conformations, the ground state of the molecule should correspond to the fully planar conformation averaged over two rapidly equilibrating pyramidal structures. The rotational behaviour for the planar-averaged dimethylamino-group was calculated for several angles of rotation by different MO approaches, namely extended Hückel, CNDO/2, INDO, PCILO, and *ab initio* STO-3G. The different MO approaches provide qualitatively similar results with the planar conformation corresponding to the ground state, except extended Hückel which indicates the perpendicular conformation to be more stable. The π-bond order given by CNDO/2 shows a linear dependence on the experimental free-energy of activation (ΔG^*), and it appears that the resulting equation can be usefully employed for predicting the ΔG^* values for different systems. Even the energy differences, ΔE, are roughly proportional to the corresponding ΔG^* values, but the correlation is less satisfactory than that obtained with the π-bond order. Provisions of energy barriers with the above equations for a number of protonated and alkylated forms show that in molecules where conjugation is expected the barriers should increase. This has been verified experimentally in two molecules where measurements were made possible.

HINDERED rotation about the Ar–N bond in substituted anilines and *NN*-dimethylaniline derivatives is a well known phenomenon[1-4] and in some derivatives it has been revealed by a n.m.r. technique. The possibility of observing optical activity as a result of hindered rotation has also been explored.[5] The presence of *para*-substituents with electron-withdrawing characteristics increase the energy barriers for internal rotation[2] while *ortho*-disubstitution causes a decrease of ΔG^* and ΔH^* values: this last characteristic has been attributed to an increase in the energy content of the ground state which makes the energy difference for passing the transition state smaller.[2] Obviously these conclusions are based on the assumption that the ground state of these molecules, as regards the amino-group, is planar or nearly planar, while the transition state corresponds to a 90° rotation of the amino-group. Also in heterocyclic derivatives a number of examples of hindered rotation around the C–N bond of the dimethylamino-group have been reported: examples refer to pyridine,[6,7] pyrimidine,[7] and azole[8] derivatives.

In biomolecules such as derivatives of cytosine[9,10] and adenine[11] rotation of the dimethylamino- or methylamino-group is too fast on the n.m.r. time scale to be detected; however on passing to the hydrochlorides hindered rotation around the exocyclic C–N bond may be revealed.[9]

In nitrogen heteroaromatic molecules containing the amino-group (or alkylamino-derivatives) the protonation or *N*-alkylation of the ring nitrogen is important in determining the barrier to rotation around the *exo* C–N bond since, excluding steric effects at this stage, protonation of the ring should enhance the barrier to rotation with conjugation effects. Recent INDO calculations[12] confirm this point for 4-aminopyridine. In the aminopyridines and dimethylaminopyridines, protonation or *N*-alkylation should increase the barrier to rotation in *ortho*- and *para*-derivatives while this effect should be greatly reduced in the *meta*-compound.

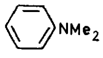
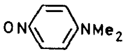
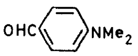
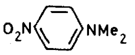
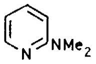
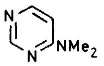
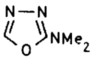
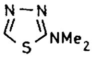
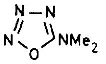
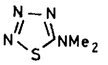
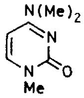
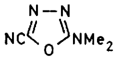
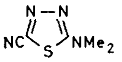
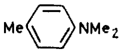
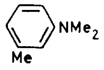
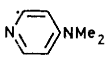
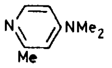
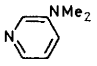
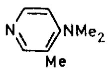
The aim of this paper is to examine the problem of internal rotation of the dimethylamino-group in aromatic and heteroaromatic systems by comparing thermodynamic activation parameters obtained experimentally with energy differences between ground and transition state evaluated by semi-empirical MO calculations and attempting to give a description of the molecular electronic characteristics which determine the barriers to rotation. The rotational behaviour in the *N*-protonated and *N*-alkylated forms relative to the free base of some dimethylaminopyridines will be also examined. Semi-empirical calculations will be employed to predict the activation parameters and to give a description of the rotational path in these systems.

RESULTS AND DISCUSSION

Neutral Molecules.—Several values of thermodynamic parameters relative to the rotation of the amino-group and *NN*-dimethylamino-group have been reported for a variety of organic compounds. It is thus possible to rationalize the behaviour of rotation of these groups as a function of the electronic structure of the molecules to which they are bonded and to the extent of conjugation effects which can contribute to the degree of double bond in the *exo* C–N bond. For a series of compounds selected from the literature and reported in Table 1, we have thus constructed the rotational path by plotting the total energy given by the CNDO/2 method[13] against the angle θ of rotation (planar conformation was assumed to correspond to $\theta = 0$). Standard geometries[14] were employed for the molecules studied. In Figure 1, for example, we give the diagram relative to the rotation of the dimethylamino-group in *NN*-dimethylaniline:

TABLE 1

Experimental free-energy of activation (ΔG^*), calculated (CNDO/2) energy barriers for rotation (ΔE), bond order (η), and calculated free-energy of activation according to equation (1) [$\Delta G^*_{\text{calc.}}(1)$] and equation (2) [$\Delta G^*_{\text{calc.}}(2)$]. All energy values in kJ mol^{-1}

Compound	ΔG^*	ΔE [a]	$\Delta G^*_{\text{calc.}}(1)$	$\Delta G^*_{\text{calc.}}(2)$	Calculated minimum conformation	$\eta_{\text{min.}}$	$\eta_{90°}$
(1) 	21.34 [b]	16.03	22.58	26.48	0°	0.3048	0.1857
(2) 	35.99 [b]	21.46	33.18	34.96	0°	0.3316	0.1932
(3) 	31.80 [b]	19.48	29.58	31.87	0°	0.3225	0.1906
(4) 	33.06 [b]	22.89	36.30	37.20	0	0.3396	0.1951
(5) 	31.80 [c]	25.11 22.47 [d]	27.52 31.12	40.66 36.54	15°	0.3173 0.3264 [e]	0.1920
(6) 	39.16 [f]	29.17 26.78 [d]	32.86 36.69	47.01 43.27	15°	0.3308 0.3405 [e]	0.1948
(7) 	$<$34.32 [g]	23.45	34.20	38.08	0°	0.3342	0.1983
(8) 	34.32 [g]	29.86	39.34	48.08	0°	0.3472	0.1902
(9) 	48.55 [g]	36.24	52.43	58.05	0°	0.3803	0.2019
(10) 	51.47 [g]	34.77	48.68	55.75	0°	0.3708	0.2022
(11) 	61.94 [g]	43.56 42.31 [d]	57.26 59.67	69.48 67.53	7°	0.3925 0.3986 [e]	0.2133
(12) 	42.69 [g]	25.73	38.20	41.63	0°	0.3443	0.2006
(13) 		31.14	43.06	50.08	0°	0.3566	0.1924
(14) 		14.90	20.56	24.72	0°	0.2997	0.1844
(15) 		16.24	23.29	25.37	0°	0.3066	0.1866
(16) 		22.43	30.64	35.03	0°	0.3252	0.1914
(17) 		23.31	31.91	36.41	0°	0.3284	0.1924
(18) 		15.11	17.87	25.05	0°	0.2929	0.1821
(19) 		82.42 (0—45°) 6.89 (45°—90°)	3.20 30.09 [h]		45°	0.2558 0.3238 [h]	

[a] Difference between the minimum and 90° conformation. [b] Ref. 4. [c] Ref. 7. [d] Value relative to the difference between 0° and 90° conformation. [e] Value relative to the 0° conformation. [f] Ref. 6: the ΔG^* value was obtained by employing the experimental ΔH^* and ΔS^* (solvent Bu^tNH_2) and through the relation $\Delta G^* = \Delta H^* - T\Delta S^*$ at 213 K. [g] Ref. 8. [h] Referring to the planar conformation.

differences in calculated total energy are reported in the ordinate scale. The most stable conformation corresponds to the planar situation, the transition state to the perpendicular conformation. The energy barrier ΔE amounts to 16.03 kJ mol^{-1}, which should compare with an empirically extrapolated value of ΔG^* (free energy of activation) of 21.34 kJ mol^{-1}. The comparison with the experimental free-energy of activation, clearly not in line of having quantitative reproduction of the results, may be useful in comparing the trend of calculated results in respect to the experimental ones. A comparison between ΔE and ΔG^* values should hardly be affected by entropic considerations since barriers to internal rotation in the absence of *ortho*-groups [6] and with solvent effects minimized [6,9] should be, to a very good approximation, purely enthalpic.[15] Here the amino-group has been considered planar for the complete rotational cycle while experimental data [16] and theory [17,18] indicate that the bonds at the nitrogen atom in aromatic amines assume a pyramidal arrangement with a barrier to inversion through a planar transition state. For aniline the inversion barrier is smaller than the rotation barrier [18] and changes within a relatively small interval as a function of *para*-substituents.

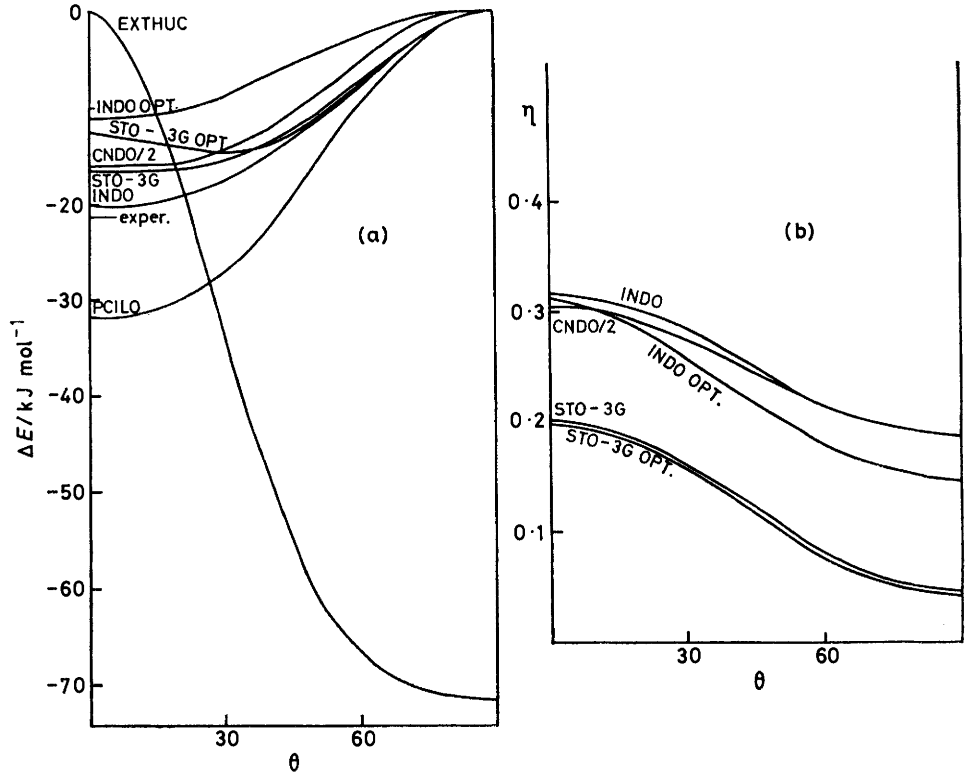
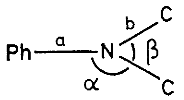


FIGURE 1 Diagram of (a) the energy and (b) the π-bond order calculated by MO methods for *NN*-dimethylaniline as a function of the angle θ of rotation around the exocyclic C–N bond (θ = 0° corresponds to the planar structure)

The problem of inversion at nitrogen of the dimethylamino-group has been tentatively tackled by employing *ab initio* molecular orbital theory with the STO-3G minimal basis set [17] for *NN*-dimethylaniline. Calculations were performed by optimizing three geometrical parameters, namely *a*, α, β [see (A)] for each conformation. The energy of each conformation is given as a function of two parameters: (i) the dihedral angle θ between the CNC plane given by the sp^2 configuration at nitrogen and the CNC plane determined when a certain degree of distortion is introduced by proceeding along the inversion path; (ii) the angle of rotation ϕ of the dimethylamino-group around the exocyclic C–N bond. A map of the energy * as a function of θ and ϕ is reported in Figure 2, where a few sections are also presented for some constant θ and ϕ values. For $\theta = 0$, $\phi = 0$ corresponds (Figure 2b) to the whole dimethylamino-group lying in the same plane as the benzene ring and changes of ϕ indicate that the energy, after a small but still evident increase, falls to a minimum located at $\phi = 22°$, thereafter increasing suddenly for higher values of ϕ. This diagram shows that the most stable stereochemical arrangement for the conformation corresponding to $\theta = 0$ is that having the pyramidal disposition of bonds around the nitrogen atom: the energy corresponding to the inversion process is rather small, *ca.* 3 kJ mol^{-1}.



(A)

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* The map is obtained by a least-square analysis of calculated values with a tentative function: $E(\theta,\phi) = (a_0 + a_1\cos\phi + a_2\cos^2\phi + a_3\cos^3\phi) \times (b_0 + b_2\cos2\theta + b_4\cos4\theta)$.

The rotational behaviour for $\phi = 0$ shows a minimum at $\theta = 20°$ and a maximum at $\theta = 90°$ (Figure 2e) with an energy barrier of 16.42 kJ mol^{-1}: rotation should thus be a slower process than inversion. At $\theta = 20°$, corresponding to the energy minimum for the rotation of the planar dimethylamino-group, the behaviour of the energy as a function of ϕ is roughly parabolic with a minimum at $\phi = 0$ and no inversion minima. At different ϕ values rotation proceeds through higher energy barriers. When $\theta = 90°$, the inversion pattern shows a minimum at $\phi = 43°$ (Figure 2c) with an energy minimum lower than that corresponding to $\theta = 0$. In Figure 2d a section is also reported corresponding to $\theta = 45°$, where it is seen that no minimum exists for the inversion function at this rotational angle. Thus, even if the lower energy minima are those corresponding to the pyramidal arrangement of the perpendicular conformation, the energy content of the all-planar conformation rapidly inverting between two pyramidal minima is lower and thus this state should be the most populated. On the other hand experimental evidence suggests that the frozen conformation corresponds to an all-planar arrangement (probably rapidly inverting) as shown, for example, by derivative (2) and (3) of Table 1, which have non-equivalent methyl groups at low temperature.

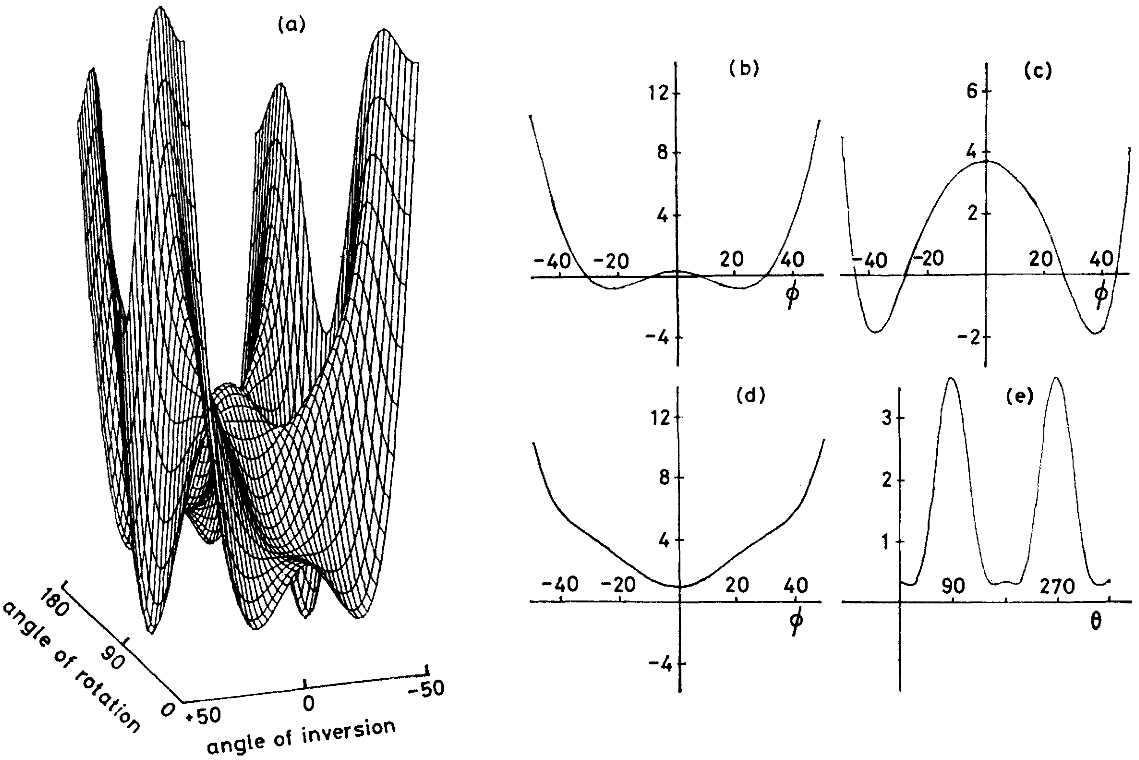

FIGURE 2 Total energy calculated by the *ab initio* STO-3G MO approach for *NN*-dimethylaniline; (*a*) diagram of the total energy as a function of the angle θ of rotation of the dimethylamino-group around the exocyclic C–N bond and of the angle ϕ of pyramidal inversion at nitrogen; (*b*), (*c*), and (*d*) planar sections of the full diagram obtained for values of θ corresponding in the order to 0, 90, and 45°; (*e*) planar section of the full diagram for $\phi = 0°$ (rotation of the planar dimethylamino-group)

The pyramidal structure at nitrogen seems thus to be preferred to the planar ground state at $\theta = 0$: the two pyramidal forms should be considered as rapidly inverting, which is equivalent to dealing with a nearly all-planar ground state. This conclusion could not hold for *ortho*-substituted compounds.

Since some doubts have been expressed about the handling of energy barriers and relative stabilities of conformers given by CNDO/2,[19] we have preliminarily tested the results of this method against those of other semi-empirical techniques for *NN*-dimethylaniline (see Figure 1). In the extended Hückel frame [20] (EHTHUC) the barrier turns out to be exceedingly high and the minimum is predicted at 90°; this is unacceptable on several grounds. The PCILO approximation [21] provides an energy diagram which resembles that obtained with CNDO/2: the barrier height is higher, exceeding even the experimental value. When the more sophisticated INDO [13] is employed, the behaviour of total energy is qualitatively similar to that given by CNDO/2, as shown in Figure 1, while the barrier height is still underestimated. An optimization of the geometry following the method suggested by Purcell and Zapata [22] in the INDO approximation does not significantly change the energy behaviour. With the *ab initio* minimal basis set STO-3G the optimization of the set of parameters a, b, α was performed. For the all-planar conformation a and b remain unchanged as 1.42 and 1.47 Å respectively and the angle α slightly increases from the initial 120 to 122.5°. For the perpendicular conformation (with the dimethylamino-group considered planar) a becomes slightly longer, 1.44 Å, while α is very near to 120°. In general it can thus be concluded that the standard geometrical parameters employed represent a reasonable approach to the 'real molecular geometry.'

The comparison between these results indicates that, beside the EXTHUC method, which gives an incorrect description of the relative energy of conformers, techniques such as INDO and STO-3G give, in the case of the *NN*-dimethylamino-derivatives here studied, results which are qualitatively similar to those provided by CNDO/2 but are more time-consuming to obtain. We have thus retained only the results given by CNDO/2 method, since even if the height of the barriers is underestimated,[19a] this method provides a realistic description of electronic distribution of molecules with respect to other semi-empirical methods.[23] It is thus here employed to discuss the relative stability of ground and transition state of the systems under study.

In Figure 1b is shown the behaviour of π-bond order, η, relative to the C–N bond of *NN*-dimethylaniline as a function of the angle of rotation θ. The bond order is greater for the planar form of the molecule while it decreases progressively on going to the perpendicular conformation: this trend is common to the different MO methods employed. The values of η given by CNDO/2 for the molecules examined are reported in Table 1 for the minimum and 90° conformation. For planar conformations the values of η relative to different molecules differ sensibly, while they are close to each other for the perpendicular conformations. In the absence of steric effects, this quantity should be an indication of the stabilization of the ground and transition state. Consequently, if the energy of the transition state is not too different in the molecules examined, the η values relative to the planar conformation should be proportional to the energy of the barrier for internal rotation. The correlation between the experimental free energy of activation (ΔG^*) and η for the planar conformation is reported in Figure 3. Only selected molecules have been considered where it is believed that steric factors are minimized. The correlation of Figure 3, which can be considered satisfactory in view of the large number of molecules included and of the indetermination in experimental results, may be transformed in equation (1) by a least-squares analysis: this may be useful in predicting in similar systems approximate values of ΔG^* (within 3—4 kJ mol^{-1}) from calculated π-bond orders.* The calculated values are reported in Table 1 under the column $\Delta G^*_{\text{calc}}(1)$: a number of ΔG^* values for derivatives where these quantities cannot be experimentally determined for reasons of symmetry are also calculated together with those for systems not yet tackled experimentally. It is thus found that the calculated value for 3-dimethylaminopyridine is 18 kJ mol^{-1}, lower than that measured and calculated for 2-dimethylaminopyridine and even lower than that extrapolated for *NN*-dimethylaniline.[5]

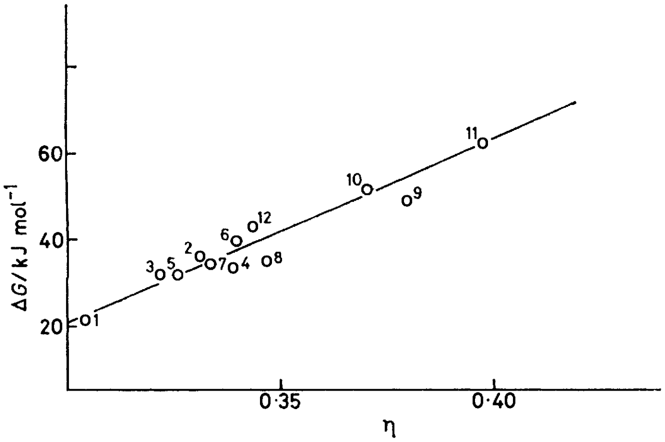

FIGURE 3 Correlation of the experimental free energies of activation (ΔG^*) for a number of conjugated dimethylamino-derivatives as a function of the π-bond order η for the C–N bond calculated by CNDO/2

$$\Delta G^* = 395.50\,(\pm 32.09)\eta - 97.97\,(\pm 11.16) \qquad (1)$$
Bravais–Pearson coefficient 0.97

The differences between maximum and minimum calculated total energy given by CNDO/2, ΔE, are always lower than the experimental ΔG^* values, as has generally been found for other systems.[19a] For the molecules where the full rotational path was calculated it is seen that the experimental ΔG^* and ΔE values are roughly proportional. A least-squares analysis of the data gives equation (2), which allows an estimate of ΔG^* values as an alternative to equation (1). The values calculated

$$\Delta G^* = 1.562\,(\pm 0.155)\Delta E + 1.445\,(\pm 3.15) \qquad (2)$$
Bravais–Pearson coefficient 0.97

with equation (2) are collected in Table 1 under the column $\Delta G^*_{\text{calc.}}(2)$. Comparison of the calculated values, where possible, shows that those obtained from equation (1) are closer to the experimental values than those obtained from equation (2), showing that the energy pattern of the molecule given by CNDO/2 is less satisfactory than the electronic description.

The presence of a methyl group *ortho* to the dimethylamino-group in compound (19) gives rise to considerable differences in the energy pattern calculated by CNDO/2: the maximum is found for the planar conformation and the minimum for an angle of rotation near 45°. The energy behaviour is similar in the CNDO/2 and PCILO approaches. By employing the π-bond order of the minimum conformation and equation (1) the resulting calculated ΔG^* is very small, while by employing the π-bond order of the planar conformation a value of 30.09 kJ mol^{-1} is obtained, 2 kJ mol^{-1} lower than the value obtained for compound (17). Unfortunately experimental results for these compounds are not known and neither could they be obtained in our experimental attempts. However, a decrease of a few kJ mol^{-1} in energy barriers of this kind is expected when an *ortho*-methyl group is present; an example of this behaviour is found in *ortho*-substituted benzaldehydes.[24]

Thus, besides the suspicion generated in general by

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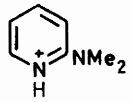
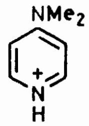
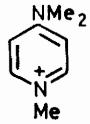
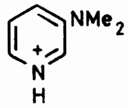
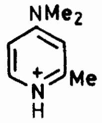
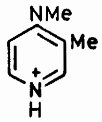
* The π-bond order has been calculated for a few molecules also in the *ab initio* STO-3G approach and the equation has a slope very near to that obtained by employing CNDO/2 results.

the employment of CNDO/2 energy values for conformational analysis,[25,26] the electronic description, *i.e.* π-bond orders, of the molecules examined may be handled with a higher degree of confidence. This conclusion has been reached also in our work [26] on internal rotation of the formyl and acetyl group in conjugated systems.

TABLE 2

Experimental free-energy of activation (ΔG^*), calculated (CNDO/2) energy barriers (ΔE), bond orders (η), and free-energy of activation [according to equations (1) and (2) reported in the text] for a number of protonated *NN*-dimethylaminopyridines. All energy values in kJ mol^{-1}

Compound	ΔE	$\Delta G^*_{\text{calc.}}(1)$	$\Delta G^*_{\text{calc.}}(2)$	η_{planar}	$\Delta G^*_{\text{exper.}}$ (298 K)
(5a) 	37.83 38.50 [a]	74.42 72.56 [a]	60.53 61.58 [a]	0.4359 0.4312 [a]	
(16a) 	51.35	85.46	81.65	0.4638	
(16b) 	47.37	79.17	75.43	0.4479	
(18a) 	22.73	40.49	36.95	0.3501	
(17a) 	50.30	83.40	80.01	0.4586	39.78 [b]
(19a) 	71.56 (40—0°) 21.15 (40—90°)	84.07 47.22 [a]	113.22 34.48 [a]	0.4603 0.3671 [a]	22.87 [c]

[a] Values corresponding to the energy minimum which falls for compound (5a) at 7° and for compound (19a) at 40°. [b] $\Delta S^* = 2.4$ J K^{-1} mol^{-1}, $\Delta H^* = 42.77$ kJ mol^{-1}, $T_c = 194.5$ K. [c] $\Delta S^* = 24.0$ J K^{-1} mol^{-1}, $\Delta H^* = 52.77$ kJ mol^{-1}, $T_c = 168$ K.

Cationic Compounds.—Protonation or alkylation and, in general, transformations of cationic pyridine species should enhance the barrier to internal rotation of the dimethylamino-group.

An experimental study of the cationic species of compounds (5), (17), (18), and (19) has been carried out. Only for compounds (17a) and (19a) was it possible to observe temperature-dependent spectra: the singlet of *N*-methyl protons changed to a pair of slightly broad signals at low temperature, and thus the thermodynamic parameters were obtained by an analysis of line-shapes [15] at different temperatures. The experimental values are reported in Table 2. The barrier to rotation is higher in compound (17a) than in (19a), as expected on the basis of the conclusions reached for free bases having an *ortho*-methyl group and from the calculated values reported in Table 2: for compound (19a) the results refer to the minimum calculated conformation. As regards the protonation effect on the energy barrier, it is unfortunately not possible to carry out a direct comparison between free and protonated forms but a survey of the results indicate that protonation should increase the barrier in compound (17) by *ca.* 7—8 kJ mol^{-1}. The calculated values of ΔG^* reported in Table 2 show that for the cations the energy barriers should always be higher than in the corresponding free bases: this effect is produced both by protonation and *N*-methylation, as indicated for compounds (16a) and (16b). A comparison of experimental and calculated values of ΔG^* shows that the calculated values appear largely overestimated. For 4-aminopyridine the same conclusion was reached [13] by employing the INDO approach. Further, the π-bond order does seem to be overestimated, since equation (1) which rationalizes the behaviour of the free bases does not give satisfactory results when applied to their cations. The same situation holds for the π-bond orders obtained in the *ab initio* STO-3G approach. Probably the fact that polar solvents are also employed has an influence on the energy barriers experimentally determined. The cation should, in fact, be solvated and the positive charge tends to diffuse in the solvent: both the degree of double bond in the exocyclic C–N bond and the energy barrier should be consequently lowered.

EXPERIMENTAL

Derivatives (5), (16), (18), and (19) were prepared according to previously reported procedures.[27,28] Compound (17) was obtained [28] (as a colourless oil, b.p. 150—152 °C, 16 mmHg) from 2-picoline. The methiodide (16b) was prepared in good yield (90%) by addition of equimolecular amounts of methyl iodide to a 1M-solution of derivative (16) in benzene at room temperature. After 1 h the crystalline product was collected, washed with benzene, and recrystallized; it had m.p. 248—249 °C.* The compound, dissolved in $(CD_3)_2SO$ showed two singlets (δ 3.20 and 3.95, intensity 2 : 1) corresponding to the form methylated at the ring nitrogen. Unfortunately it could not be employed for low-temperature studies owing to solubility problems.

Protonated forms were obtained by adding trifluoroacetic acid to solutions of the free bases in $[^2H_6]$acetone, $CHCl_2F$, CCl_2F_2 or in a mixture of the two last-named solvents: ^1H n.m.r. spectra confirm that the site of protonation is the nitrogen atom of the ring, as found also for the aminopyridines.[29] The n.m.r. spectra were recorded by employing a JEOL-C60-HL spectrometer equipped with a variable-temperature unit. The best separation in the methyl peaks at low temperature was obtained by employing *ca.* 0.25M-solutions of the free bases in $[^2H_6]$acetone for compound (17a) and in CCl_2F_2 for compound (19a) and by adding trifluoroacetic acid in slight molar excess relative to the compound. Temperature calibration was carried out by employing a thermocouple in a dummy tube.

All calculations were performed on a Cyber 76 CDC computer equipped with a plotting unit.

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* All new compounds gave satisfactory elemental analysis (C, H), the results of which together with mass spectral data have been treated as a Supplementary publication (SUP No. 22487 (3 pp.). See Notice to Authors No. 7, *J.C.S. Perkin II*, 1978, Index issue.

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