technique for conformational and configurational analysis as deduced from the agreement (rms = 0.93 Hz) between calculated and experimental coupling constants in γ-butyrolactone rings.[39] The importance of taking into account the contribution of even the less stable conformers can be hardly overemphasized, in order to accurately reproduce experimental J's. As an indirect consequence of this work, the rule $J_{cis} > J_{trans}$ should be applied cautiously in five-membered rings. In several of the products studied herein the order is just the opposite ($J_{trans} > J_{cis}$); a strict application of the former rule may lead to erroneous configurational assignments, unless the final conclusion is supported by some other evidences, such as chemical proof, two-dimensional NMR spectra, etc.

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Registry No. 1, 96-48-0; **5c**, 99341-90-9; **5t**, 99341-89-6; **6c**, 103776-34-7; **6t**, 103776-35-8; **7c**, 24405-07-0; **7t**, 24405-08-1; **8c**, 10150-95-5; **8t**, 10150-96-6; **9c**, 103834-19-1; **9t**, 103834-20-4; **10cc**, 53155-68-3; **10tt**, 53155-65-0; **10ct**, 53155-66-1; **10tc**, 53155-67-2; **11cc**, 103834-21-5; **11tt**, 103834-22-6; **11ct**, 103834-23-7; **11tc**, 103834-24-8; **12cc**, 103834-25-9; **12tt**, 103834-26-0; **12ct**, 103834-27-1; **12tc**, 103834-28-2.

(39) The empirically generalized Karplus equation[12] was parameterized for cyclohexane derivatives. Consequently, a specific reparameterization for γ-butyrolactones would improve the agreement.
(40) Takahashi, N.; Suzuki, A.; Kimura, Y.; Miyamoto, S.; Tamura, S. *Tetrahedron Lett.* **1967**, *21*, 1961.

Molecular Mechanics Calculations on the C_{sp^3}–C_{sp^2} Rotation in the *N*,3,3-Trimethyl-2-phenyl-4-piperidone System

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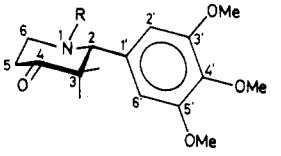
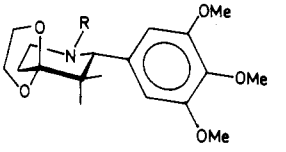
The rotational pathway of the phenyl ring in *N*,3,3-trimethyl-2-phenyl-4-piperidone has been determined by molecular mechanics calculations to be chair piperidone ⇌ twist-boat piperidone ⇌ phenyl rotation. The calculated barrier height for the process (ca. 63 kJ/mol) is in good agreement with the previously reported experimental value of 54 kJ/mol in a remotely substituted phenyl derivative determined by ^{1}H DNMR.

The restricted rotation around C_{sp^3}–C_{sp^2} bonds has been the subject of a number of studies.[1] However, not many examples can be found wherein the rotational barrier is high enough to be observed or measured by dynamic nuclear magnetic resonance spectroscopy techniques. Very recently we published[2] the synthesis and rotational barrier determination of one of the few examples: 1,3,3-trimethyl-2-(3,4,5-trimethoxyphenyl)-4-piperidone (1). The aryl group displays a rotational barrier of 54 kJ/mol as determined by ^{1}H NMR with $CDCl_3$ as solvent.[2] Rotational barriers of several other compounds (1·HCl, **2**, **2**·HCl, **3**, **3**·HCl, and **4**) were also studied, showing a great influence of the N-methyl group on the barrier height.[2]

Molecular mechanics (MM) calculations have recently emerged as a powerful technique[3] with wide application to conformational analysis and molecular dynamics. One of the MM applications to the latter is the study of rotational barriers. In this respect, a very complete study has been published[4] recently on the rotational pathways of phenylcyclohexane and bicyclohexane systems in which the importance of the gauche-progauche[4] (gp) and gauche-progauche-ortho[4] (gpo) interactions on the barrier heights for phenyl rotation was stated. The compound of



1 R=Me
2 R=H



3 R=H
4 R=Me

our study, 1, can present two gp interactions[4] in its rotational saddle point and, consequently, it can be expected

† Universidad Autónoma de Barcelona.
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(1) For a recent review, see: (a) Ōki, M. *Top. Stereochem.* **1983**, *14*, 1. (b) Ōki, M. *Applications of Dynamic NMR Spectroscopy* to Organic *Chemistry*; VCH Publishers Inc.; Deerfield Beach, FL, 1985.
(2) (a) Giralt, E.; Feliz, M.; Rubiralta, M.; Bosch, J. *J. Heterocycl. Chem.* **1984**, *21*, 715. (b) Rubiralta. M.; Feliz, M.; Jaime, C.; Giralt, E. *Tetrahedron*, in press.

0022-3263/86/1951-3951$01.50/0

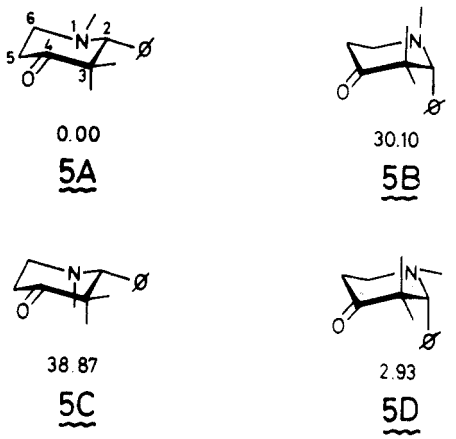


Figure 1. Four possible chair conformers of **5** (**5A**–**5D**), model for **1**, and their relative steric energies as calculated by MM2 (kJ/mol).

to have a very high barrier for the phenyl rotation in one of the chair conformers. However, the presence of a nitrogen atom in the α position relative to the carbon bearing the aryl group presents a difficulty in the study due to its ability to invert. Moreover, the presence of a carbonyl function in the six-membered ring substantially modifies the geometrical features in any conformation, thus, making it difficult to extend the conclusions reached by Ōsawa[4] to our compound, **1**.

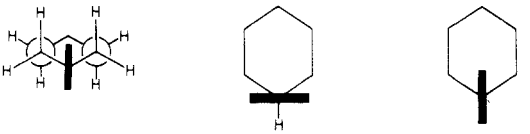
The importance of the N-methyl group on the barrier height has been clearly demonstrated,[2] but the course of the rotation remained unknown. The ensemble of factors influencing aryl rotation in 2-aryl-4-piperidone systems is too complex to be analyzed directly. Consequently, it seemed necessary to determine the pathway of the aryl rotation by MM calculations.

Results and Discussion

Computational Techniques. Allinger's latest force field (MM2[5]), within a somewhat modified version of MM2 program,[5b] was used throughout this work. The methoxy substituents on the aryl group are too far from the pivot bond to be considered in the rotational barrier study. Consequently, they were removed and the studied compound, **5**, was an analogue of **1** having a phenyl ring instead of a 3,4,5-trimethoxyphenyl ring. The phenyl ring was mechanically treated[6] and parameters for units containing phenyl ring carbon atoms were considered to be equal to those containing sp^2 (alkene) carbon atoms. Torsional energy surfaces were obtained by the usual two-bond drive techniue[7] at 10° steps. The exact location of saddle points was determined by using the BIGSTRN-3 program,[8] following Ōsawa's procedure[9] only for the lowest predicted barrier in twist-boat piperidone ring conformers and in all-chair conformers. The BIGSTRN-3 eigenvector distortion option was used to obtain the two minima interconnected by these saddle points.

Rotation in Chair Conformers. Compound **1** can exist in four chair conformations[2] which interconvert either through N inversion or rotation of the ring σ-bonds (see Figure 7 in ref 2 and Figure 1).

Phenylcyclohexane (**6**) is the parent compound of **1** and exists in an equatorial-parallel,[3a] **6-EP**, conformation rather than in an axial-perpendicular one, **6-AP'**. The experimental[10] conformational energy of the phenyl group in phenylcyclohexane is 11.99 kJ/mol, while MM2 calculations gave an energy difference of 15.30 kJ/mol for **6-AP'** – **6-EP**. The axial-parallel, **6-AP**, conformer was calculated to be 19.90 kJ/mol less stable than **6-EP**.



6

MM2 calculations of the four chair conformers of **5** (**A**–**D**), the analogue of **1** (Figure 1), indicate the greatest stability of conformer **5A**, closely followed in energy by **5D** at only 2.97 kJ/mol. Conformers **5B** and **5C** are less stable, mainly due to the existence of Me/Me 1,3-diaxial interactions. Conformer **5D** is the mirror image of the **5A** epimer in C_2; thus, it should be ca. 19.90 kJ/mol less stable than **5A** because the methyl groups at N_1 and C_3 prevent the phenyl ring from adopting an axial-perpendicular conformation and force it to be axial-parallel.

For a better approach to the structure of **1** we studied the model compound 2-phenyl-4-piperidone (**7**). A conformational energy of 5.31 kJ/mol for the phenyl group was obtained, a value much smaller than that of **6** as a consequence of the absence of one axial hydrogen on C_4 and the greater flattening of the six-membered ring in **7** than in **6**. Moreover, **7** does not present two conformational energy minima for its axial conformer as is the case for **6**. However, only one energy minimum having an almost eclipsed conformation of the C_{sp^2}–C_{sp^2}–C_2–C_3 dihedral angle is obtained on rotation of the H–C_2–C_{sp^2}–C_{sp^2} dihedral angle, and a rotational barrier of 17.10 kJ/mol, as determined by the one-bond drive technique.

In spite of the difficulties in interpreting the small calculated energy difference between **5A** and **5D** (2.97 kJ/mol represents an **5A**/**5D** ratio of 77/23 at 25 °C), the high-field ^{1}H NMR spectrum of **1** in $CDCl_3$ as a solvent is in agreement with an almost exclusive predominance of a conformer equivalent to **5A**. The -CH_2CH_2- region of the spectrum was analyzed by simulation using the LAOCOON-3 program. After full optimization, the simulated and experimental spectrum were superimposable (rms error less than 0.15 Hz). The coupling constant between the 5-proR and 6-proS protons can be used as a conformational probe because of the large difference expected between coupling constants corresponding to trans-diaxial and trans-diequatorial dispositions. By comparison of the experimental J value (12.5 and 3.0 Hz for $J_{5proR-6proS}$ and $J_{6proR-5proS}$, respectively) with those calculated for each conformer (**1A**, $J_{5proR-6proS}$ = 13.2 and $J_{6proR-5proS}$ = 2.1 Hz; **1D**, $J_{5proR-6proS}$ = 1.6 and $J_{6proR-5proS}$ = 12.8 Hz) using the Karplus–Altona equation[11] and the optimized geometry for **5A** and **5D**, a population of 94% or 92% for conformer **1A** was calculated depending on which J value was used.

(3) (a) Allinger, N. L.; Burkert, U. *Molecular Mechanics, ACS.* Monograph 177, American Chemical Society: Washington, DC, 1982. (b) Ōsawa, E.; Musso, H. *Top. Stereochem.* **1982**, *13*, 117. (c) Ōsawa, E.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1. (d) Ermer, O. *Aspekte von Kraftfeldrechnungen*; Wolfgang Baur Verlag: Munchen, 1981.
(4) Jaime, C.; Ōsawa, E. *J. Mol. Struct.* **1985**, *126*, 363.
(5) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Allinger, N. L.; Yuh, Y. H. *QCPE* **1980**, *12*, 395.
(6) Allinger, N. L. *QCPE Bull.* **1983**, *3*, 32.
(7) Ōsawa, E. *J. Comput. Chem.* **1982**, *3*, 400.
(8) Mislow, K.; Nachbar, R., Jr. *QCPE*, to be submitted.
(9) Ivanov, P. M.; Ōsawa, E. *J. Comput. Chem.* **1984**, *5*, 307.
(10) Eliel, E. L.; Manoharan, M. *J. Org. Chem.* **1981**, *46*, 1959.
(11) (a) Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Bull. Soc. Chim. Belg.* **1980**, *89*, 125–131. (b) Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.

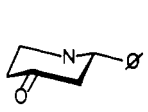
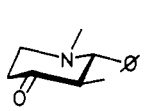
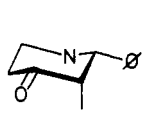
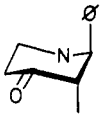
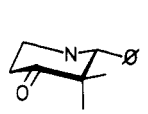
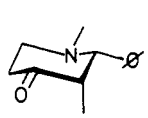
Compound	C_2-eq.	C_2-ax.	$\Delta H°$(kJ/mol)
5			2.93
7			5.31
8			8.44
9			3.22
10			5.52
11			2.72

Figure 2. $\Delta\Delta H°$ (kJ/mol) for the C_2 epimers having equatorial and axial phenyl rings in variously substituted 2-phenyl-4-piperidones, **5**, **7**, **8**, **9**, **10**, and 11 as calculated by MM2 program.

To explain the energy difference between **5A** and **5D**, MM2 calculations on 2-phenyl-4-piperidones with various degrees of substitution were carried out (Figure 2). The removal of the axial methyl on C_3 leads to *all-equatorial*-1,3-dimethyl-2-phenyl-4-piperidone (**8**) which has a $\Delta H°$ = 8.44 kJ/mol between the two epimers of the phenyl-bearing carbon atom. However, the removal of both equatorial methyls, from N and C_3, leads to 3-methyl-2-phenyl-4-piperidone (**9**), which in turn has a $\Delta\Delta H°$ = 3.22 kJ/mol for the corresponding epimers. If only one equatorial methyl group is removed, the energy difference obtained depends on which of the methyls it is. Thus, removing the N-methyl group leads to 3,3-dimethyl-2-phenyl-4-piperidone (**10**), for which a $\Delta\Delta H°$ = 5.52 kJ/mol for the two epimers under consideration is obtained. However, *N*,3-dimethyl-2-phenyl-4-piperidone, (**11**) shows a $\Delta\Delta H°$ value of only 2.72 kJ/mol. In summary, these MM2 results on variously substituted 2-phenyl-4-piperidones (Figure 2) seem to indicate that the reason for the small calculated energy difference between conformers **5A** and **5D** is the presence in the molecule of an axial C_3-methyl group[12] together with an axial C_2-phenyl group.

The phenyl rotation on the four possible chair conformers of **5**, **A**–**D**, was simulated by the usual one-bond drive technique under rigid rotation. The results are collected in Figure 3. The curve corresponding to conformer **5A** was not continuous. The location of this saddle point (type gp/gp)[4] was sought by several extensive two-bond drive mappings[13] around the zone corresponding to

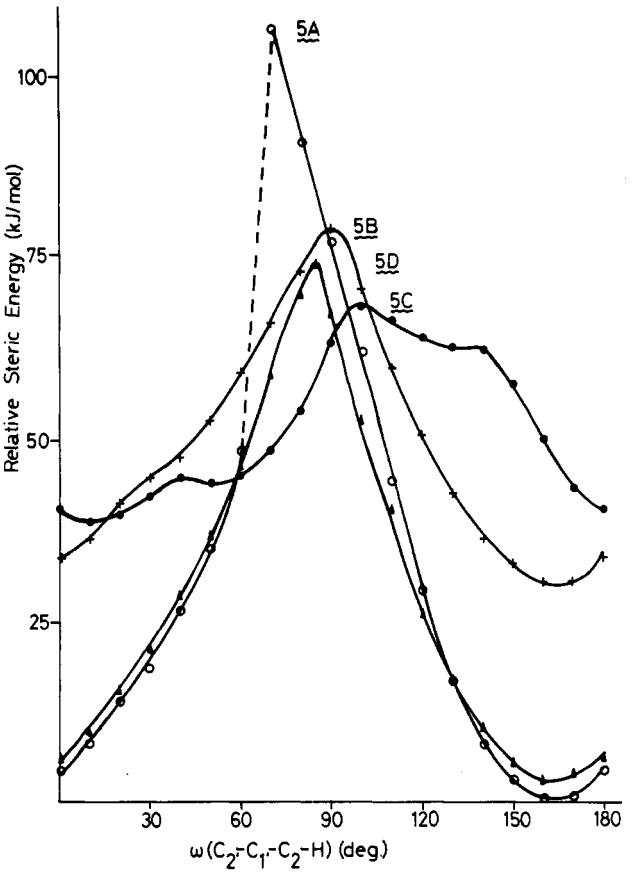


Figure 3. Relative steric energies (kJ/mol) for phenyl ring rotation in the four chair conformers of **5** (**5A**–5D) obtained by the one-bond drive technique.

ω = 90°. However, all attempts to locate the saddle point were unsuccessful. The usual one-bond drive for conformers **5B**, **5C**, and **5D** gave quite smooth curves, and by analyzing them using the BIGSTRN-3 program,[8] the exact positions of the phenyl group rotation saddle points were located. The lowest energy pathway corresponds to rotation in the conformer **5C** ($\Delta H^{\ddagger}$ = 67.97 kJ/mol, approaching the experimentally obtained barrier for **1**, 54 kJ/mol) while the barriers in **5B** and **5D** are equal to 78.58 and 73.35 kJ/mol, respectively.

The rotational pathway of **5** should then be as follows: starting from conformer **5A**, N-inversion leads to **5C** and then the phenyl ring rotates. Nitrogen inversion cannot be calculated by any MM calculations, but the N-inversion in *N*-methyl-4-piperidone systems requires a $\Delta G^{\ddagger}$ = 35.95 kJ/mol.[14] The corresponding barrier for **5A** $\rightleftarrows$ **5C** should not be too much different and an almost free equilibrium between these two conformers can be expected at room temperature for **5**.

Rotation in Nonchair Conformers. Only those rotations carried out in chair conformers were considered in the previous section. However, it is not certain that any dynamic property of a given molecule will correspond to the most stable conformer, i.e., chair conformers in this case, because any other dynamic pathway going through less stable conformers, like twist-boats, may have lower global energetic requirements. Consequently, the phenyl group rotation was also studied in nonchair conformers.

The six twist-boat (TB) conformers corresponding to the **5A**–**5B** family and the other six corresponding to the **5C**–**5D** family are collected in Figures 4 and 5, respectively.

(12) The C_2-methyl group in 1,2,3,3-tetramethylpiperidine has an unusually small calculated preference for the equatorial position (2.5 kJ/mol), with no experimentally known counterpart. See: Profeta, S., Jr. Ph.D. Thesis, University of Georgia (cited in ref 3a, p 231).

(13) Dihedral angles driven were as follows: (a) ω_1 = 2–3–4–5 from 0° to −80° and ω_2 = sp^2–sp^2–2-H from 60° to 110° at 10° steps. (b) ω_1 = 2–1–6–5 from 50° to 80° and ω_2 = sp^2–sp^2–2-H from 60° to 110° at 10° steps. (c) ω_1 = 1–2–3–4 from 20° to 60° and ω_2 = sp^2–sp^2–2-H from 60° to 110° at 10° steps.

(14) Lehn, J. M.; Wagner, J. *J. Chem. Soc., Chem. Commun.* **1970**, 414. Quoted in Lambert, J. B. *Top. Stereochem.* **1971**, *6*, 19.

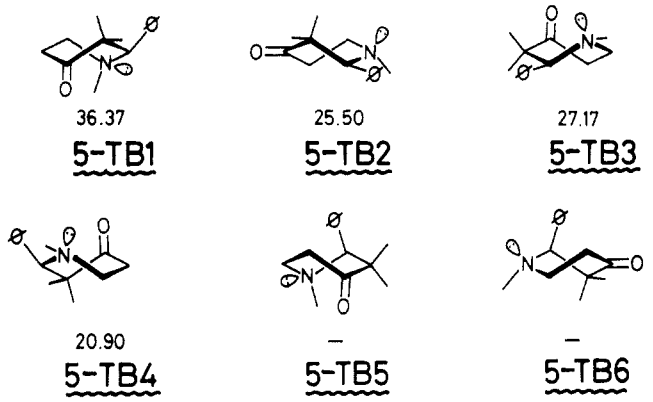


Figure 4. Six twist-boat conformers corresponding to the **5A–5B** family, **5-TB1** to **5-TB6**, as well as their steric energies relative to **5A** (kJ/mol).

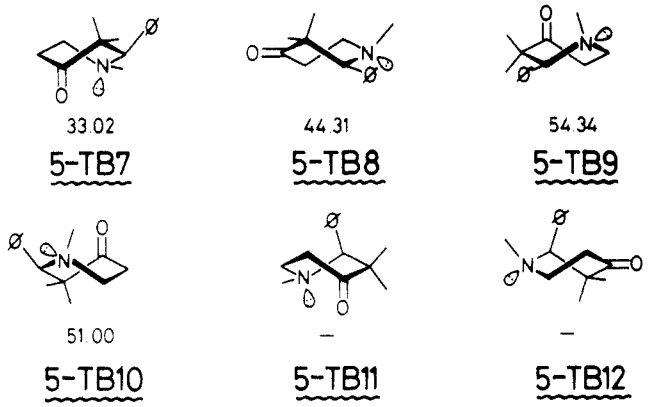


Figure 5. Six twist-boat conformers corresponding to the **5C–5D** family, **5-TB7** to **5-TB12**, as well as their steric energies relative to **5A** (kJ/mol).

It is noteworthy that all TB conformers having the phenyl ring in a pseudoaxial position do not exist as energy minima under the MM2 force field. All attempts to obtain the minimized structures for **5-TB5**, **5-TB6**, **5-TB11**, and **5-TB12** lead to different TB conformers. Those TB conformers having the N-methyl group in a pseudoaxial position were highly unstable, probably due to the nonbonded interactions between the methyl group and the C_4 carbonyl (see **5-TB1**, **5-TB5**, **5-TB9**, and **5-TB10**). The most stable TB conformer within each family has the phenyl ring in an isoclinal position and the N-lone pair facing the carbonyl group on C_4 (**5-TB4** and **5-TB7**).

Once all existing TB conformers of **5** were obtained, the phenyl group rotation was studied. In a first step, the one-bond drive technique was applied under the rigid rotation option in the MM2 program for all TB conformers (**5-TB1** to **5-TB4**, and **5-TB7** to **5-TB10**). Only the calculated barrier heights for the rotation under **5-TB1** and **5-TB9** (63.11 and 67.29 kJ/mol, respectively) approached the experimental[2] value (54 kJ/mol). These conformers have the phenyl group in a pseudoequatorial position but it is flanked by one methyl group and one lone pair, a situation similar to that found in **5C**, producing a saddle point of the gp/p type.[4] Conformers **5-TB3** and **5-TB7** produce very high barriers[15] (180.15 and 185.17 kJ/mol, respectively) as might be expected from their saddle point conformations: phenyl rings in a pseudoequatorial position surrounded by two methyl groups in a biphenyl-like disposition. Two conformers, **5-TB2** and **5-TB10**, gave nonsmooth curves[16] and their phenyl rotation lead to different TB conformers (**5-TB1** and **5-TB9** or **5-TB7**, respectively) due to the high energy processes required. Conformer **5-TB4** lead to a rotational barrier of 84.43 kJ/mol, and that in **5-TB7** presented a large $\Delta H^{\ddagger}$ value (100.73 kJ/mol) changing the conformation while rotating (leading to **5-TB8**).

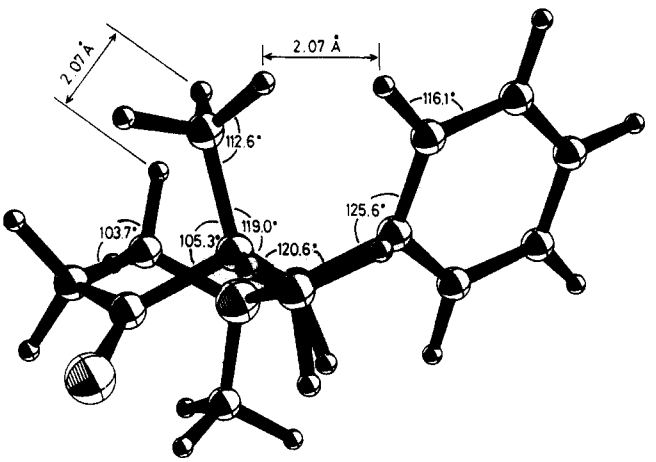


Figure 6. ORTEP[17] representation of the T1 saddle point containing the main geometrical features, as obtained by the BIGSTRN-3[8] program.

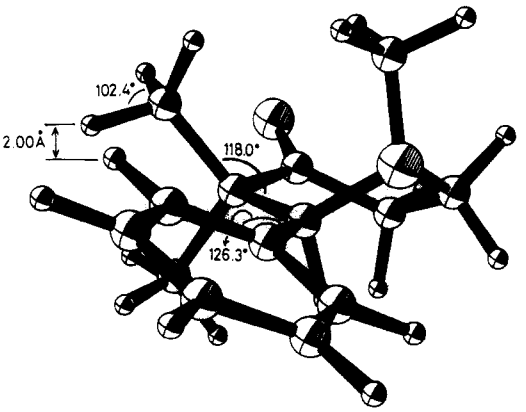


Figure 7. ORTEP[17] representation of the T2 saddle point containing the main geometrical features, as obtained by the BIGSTRN-3[8] program.

In a second step, a complete analysis was undertaken of the structure corresponding to the saddle points, T1 and T2, for phenyl rotation in **5-TB1** and **5-TB9** conformers, respectively. Their relative steric energies could be properly calculated (62.99 kJ/mol for T1 and 67.17 kJ/mol for T2; values relative to conformer **5A**), as well as their geometry, using the BIGSTRN-3[8] program. Figure 6 shows an ORTEP[17] representation of T1 and Figure 7 that of T2.

A detailed analysis of the T1 geometry reveals the presence of severe nonbonded H/H interactions between one of the ortho hydrogens of the phenyl ring and the methyl hydrogens of the C_3-methyl group cis with respect to the aromatic ring. Since the 4-piperidone ring is in a TB conformation, there is also a flag-pole nonbonded H/H interaction between the pseudoaxial C_3-methyl group and the C_6-hydrogen atom. These two interactions greatly disturb both the bond angles (Figure 6) and lengths around the pivot bond and the pseudoaxial C_3-methyl group. A

(15) Their hypothetical rotational saddle points would have been of the gp/gp type.[4]

(16) The hypothetical rotational saddle points for **5-TB2** and **5-TB10** would have been of the gp/gp and p/gp types,[4] respectively.

(17) Johnson, C. K. ORTEP-II, Oak Ridge National Laboratory Report, ORNL-5138, 1976.

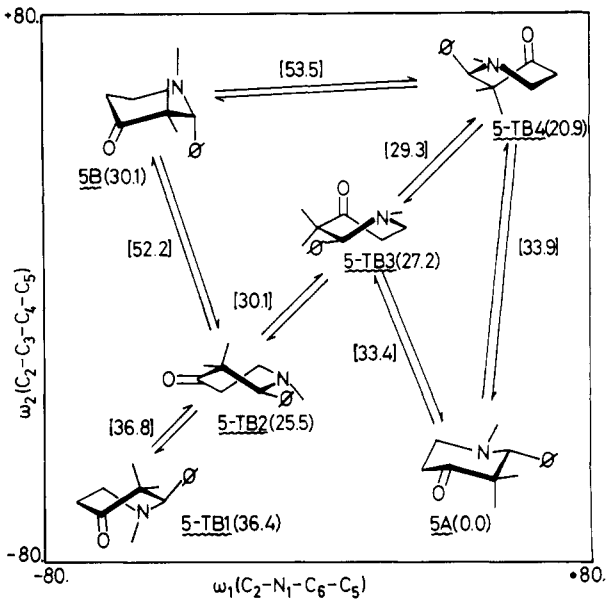


Figure 8. Schematic representation of an MM2 calculated torsional energy surface for the **5A** ⇌ **5B** interconversion process. Values within parentheses are relative steric energies for the several conformers, while those within brackets are the best estimates for the corresponding saddle points.

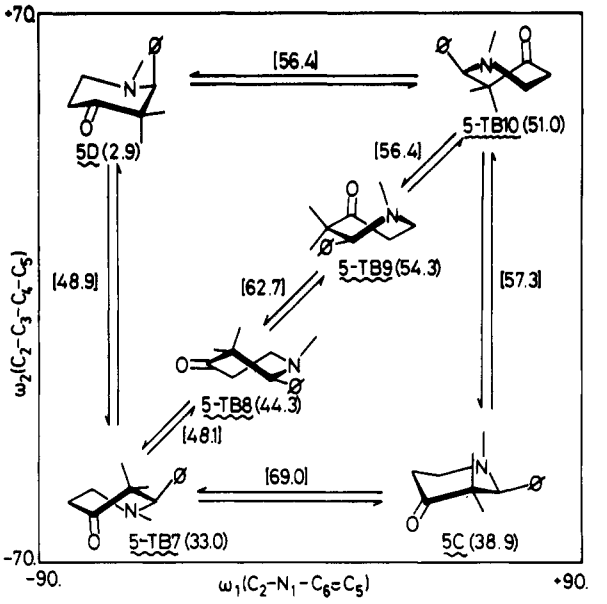


Figure 9. Schematic representation of an MM2 calculated torsional energy surface for the **5C** ⇌ **5D** interconversion process. Values within parentheses are relative steric energies for the several connformers, while those within brackets are the best estimates for the corresponding saddle points.

similar analysis of the T2 geometry also shows strong nonbonded H/H interactions between an ortho hydrogen and the C_3-methyl cis to the aromatic ring (in isoclinal position) producing distortions in the bond angles (Figure 7) and lengths around that region as well.

From all these computational results we can deduce that the aromatic ring rotation seems to occur in the **5-TB1** conformer, because in it the lower rotational barrier is produced (62.99 kJ/mol compared to 67.17 kJ/mol for **5-TB9** to 68.13 kJ/mol for **5C**).

Torsional Energy Surface for the 5A ⇌ 5-TB1 Process. In the previous section it has been established that the most probable phenyl ring rotational pathway involves conformations **5A**, **5-TB1**, and T1. This conclusion was reached by considering the rotation in various chair or TB conformers, but consideration has not yet been given to the barrier height for the **5A** ⇌ **5-TB1** process. In this section we present the results of the MM2 calculations of the torsional energy surfaces for that process.

A torsional energy surface corresponding to the **5A** ⇌ **5B** interconversion was obtained by the two-bond drive technique.[7] Dihedral angles driven were $\omega_1 = C_2$–N_1–C_6–C_5 and $\omega_2 = C_2$–C_3–C_4–C_5 from ±80° to ∓80° at 10° steps. A schematic representation of these results is given in Figure 8. From this torsional energy surface it can be concluded that conformer **5A** can be converted easily into conformer **5-TB1** by crossing a barrier of 36.78 kJ/mol corresponding to the pseudorotation between **5-TB2** and **5-TB1**. Although not all the possibilities for the dynamic **5A** ⇌ **5-TB1** process have been explored, we can discern one pathway (shown in Figure 8) which requires a low enthalpy of activation (ca. 37 kJ/mol). consequently (and according to MM2 calculations) we conclude that the conversion of **5A** into **5-TB1** is energetically not the limiting step for the rotation of the aryl group.

A completely equivalent study carried out on the **5C** ⇌ **5-TB9** process[18] (Figure 9) also allows us to confirm its viability, although in this case the barriers are slightly higher (the lowest found was 48.90 kJ/mol.

Conclusions

Molecular mechanics calculations on **5**, an analogue of 1,3,3-trimethy-2-(3,4,5-trimethoxyphenyl)-4-piperidone (**1**) have been used to determine its most probable rotational pathway. MM2 calculations agree with experimental observations in considering the conformer having N-methyl and C_2-phenyl groups in equatorial positions, conformer **5A**, as the most stable. The phenyl ring rotation has been studied in chair and nonchair conformations; MM2 results on **5** suggest the most likely pathway involves chair ⇌ twist-boat ⇌ phenyl rotation, i.e., **1A** ⇌ **1-TB1** ⇌ T1, with a calculated $\Delta H^{\ddagger}$ = 62.99 kJ/mol, a value close to that experimentally determined for **1** (54 kJ/mol by ^{1}H DNMR[2]).

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(18) The torsional energy surface was obtained by the two-bond drive technique. Dihedral angles driven were ω_1 = 2-1-6-5 and ω_2 = 2-3-4-5 from +90° to -90° and from -70° to +70°, respectively, at 10° steps.