CONFORMATIONAL DYNAMICS OF SUBSTITUTED N-ACETYL-N-PHENYLBENZYLAMINES. 1H-DNMR AND AM1-MO STUDY

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ABSTRACT

Activation parameters for the rotation around the methylene-nitrogen single bond found in a series of four 2,2´-disubstituted N-acetyl-N-phenylbenzylamines, dissolved in DMSO-d_6, were measured employing the temperature dependence of the 1H-NMR spectrum lineshape between 340 and 400 K. The results are : (I) 2 – [N-acetyl -N- (2-acetamidophenyl) aminomethyl]phenylacetate ΔG^r=79.9±2.0 kJ/mol (370K), ΔH^r=96.2±6.0 kJ/mol and ΔS^r=+45±20 J/Kmol; (II) 2 - [N – acetyl – N - (2-acetyloxybenzyl)amino]benzylacetate ΔG^r=82.0±2.0 kJ/mol (370K), ΔH^r=79.1±6.0 kcal/mol and ΔS^r=-8±20 J/Kmol; (III) 2 - [N – Acetyl – N – (2-nitrobenzyl)amino]benzylacetate ΔG^x=80.8±2.0 kJ/mol (380K), ΔH^r=60.7±6.0 kcal/mol and ΔS^r=-53±20 J/Kmol; (IV) 2-[N–Acetyl–N-(2-acetyloxybenzyl)amino]phenylacetate ΔG^r=77.0±2.0 kJ/mol (370K), ΔH^r=65.3±6.0 kJ/mol and ΔS^r=-32±20 J/Kmol. Substitution at positions 2 and 2´ with bulky groups appears to be essential to freeze the *gauche* structure at room temperature and consequently, the main contribution to the barrier arises from the steric hindrance between these two groups. Structure I shows an anomalous behavior, possibly due to the formation of a hydrogen bond between the NH at position 2´ and the solvent. This interaction increases $\Delta H\pi$ and freezes the rotation around the aryl-nitrogen bond, increasing ΔS^r.

KEYWORDS: Conformational Dynamics, 1H-NMR, N-AcetyPhenylbenzylamines, AM1-MO.

RESUMEN

Se evaluaron los parámetros de activación en torno al enlace nitrógeno - metileno de una serie de N-Acetil-N-fenilbencilaminas sustituidas en solución de DMSO-d_6, empleando la dependencia con la temperatura de la forma de la línea del espectro 1H-RMN, entre 340K y 400K. Los resultados son: (I) 2 – [N-acetil -N- (2-acetamidofenil) aminometil]fenilacetato ΔG^r=79.9±2.0 kJ/mol (370K), ΔH^r=96.2±6.0 kJ/mol and ΔS^r=+45±20 J/Kmol; (II) 2 - [N – acetil – N - (2-acetiloxibencil)amino]bencilacetato ΔG^r=82.0±2.0 kJ/mol (370K), ΔH^r=79.1±6.0 kcal/mol and ΔS^r=-8±20 J/Kmol; (III) 2 - [N – Acetil – N – (2-nitrobencil)amino]bencilacetate $\Delta G\pi$=80.8±2.0 kJ/mol (380K), ΔH^r=60.7±6.0 kcal/mol and $\Delta S\pi$=-53±20 J/Kmol; (IV) 2-[N–Acetil–N-(2-acetiloxibencil)amino]fenilacetato ΔG^r=77.0±2.0 kJ/mol (370K), ΔH^r=65.3±6.0 kJ/mol and ΔS^r=-32±20 J/Kmol. Sustitución en las posiciones 2 y 2´ con grupos voluminosos parecer ser esencial para congelar la estructura *gauche* a temperatura ambiente, y la mayor

contribución a la barrera proviene de interacciones estéricas entre estos dos grupos. La estructura I presenta un comportamiento anómalo, posiblemente debido a la formación de un puente de hidrógeno entre el grupo amino de la posición 2´y el solvente. Esta interacción aumenta $\Delta H^{\neq}$ y congela la rotación en torno al enlace N-aril, aumentando $\Delta S^{\neq}$.

PALABRAS CLAVES: Dinámica Conformacional, ^{1}H-RMN, N-AcetyPhenylbenzylamines, AM1-MO

INTRODUCTION

Information concerning the intramolecular dynamics of organic compounds with several accessible minimum energy conformations is crucial to define their stereochemistry. This information may be very important to understand the molecular behavior, since the reactivity of different sites, and therefore the distribution of products, may be strongly influenced by the relative population of the several conformations accessible at a given temperature. On the other hand, a better knowledge of the potential energy surface along large amplitude molecular vibrations, may be useful information when defining force field parameters, commonly used in molecular mechanics and molecular dynamics potential functions.

NMR spectroscopy provides a very powerful technique to study the dynamics of different molecular processes in a wide range of timescales.[1-5] In particular, the lineshape of the NMR spectrum of systems with energy barriers between about 20 and 100 kJ/mol, is strongly dependent on temperature. This methodology, better known as Dynamic Nuclear Magnetic Resonance (DNMR),[6] has been employed with different nuclei to obtain activation parameters that characterize a variety of time dependent intramolecular processes, in different   phases.[7-15] In this work we have obtained $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, for the process of averaging the chemical shift of the methylene protons found in a series of 2,2´- disubstituted N-acetyl-N-phenylbenzylamines (see fig. 1), dissolved in DMSO-d$_6$. The nature of the observed dynamical process is explored using AM1 semi-empirical molecular orbital calculations.[16] The results are interpreted in terms of steric hindrance of the substituents at both *ortho* positions.
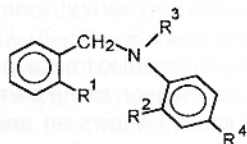
Molecule	R^1	R^2	R^3	R^4
I	-OCOCH$_3$	-NHOCOCH$_3$	-COCH3	-H
II	-OCOCH$_3$	-CH$_2$OCOCH$_3$	-COCH3	-H
III	-NO$_2$	-CH$_2$OCOCH$_3$	-COCH3	-H
IV	-OCOCH$_3$	-OCOCH$_3$	-COCH3	-H
V	-OCOCH$_3$	H	-COCH3	-CH$_3$
VI	H	-OCOCH3	-COCH3	-H
XVIII^a	H	-CH3	-COCH3	-H

Fig.1. Structure of the substituted N-acetyl-N-benzylanilines studied in this work. Molecule XVIII from ref.23 is also included.

^{a} Molecule studied in reference 23.

EXPERIMENTAL

NMR Spectra. Variable temperature ^{1}H-NMR spectra of all molecules in solution, (10 mg of solid in 0.5 ml of DMSO-d_6), from 290 K to 400 K, were obtained in a Bruker AVANCE DRX-300 spectrometer, equipped with a Bruker VT-2000 variable temperature unit. The readings of the VT unit were calibrated using a thermocouple and showed an uncertainty of ±0.5 K in the control of temperature. The lineshapes of the experimental spectra were calculated using the program DNMR5[17], compiled to run on a PC microcomputer. The temperature dependence of the chemical shifts in the slow exchange regime was employed to extrapolate the corresponding values for the input in the calculation of the exchange broadened spectra. The temperature dependence of the ratio between the linewidths of the peaks of interest and TMS, in the region of slow exchange, was used to estimate the value of T_2 at different temperatures.

Synthesis of N-Acetyl-N-Phenylbenzylamine Derivatives. All the studied molecules were prepared by a methodology described before,[18] which is briefly outlined here. An equimolar amount of the *ortho* substituted aldehyde was added dropwise to a stirred solution of the *ortho* substituted aniline in methanol. After 10 min of stirring at room temperature, the volume was reduced by evaporation under reduced pressure, to afford the corresponding imine in high yields. To a stirred suspension of the imine in methanol, sodium borohydride was added portionwise at room temperature. After 5 min., the solid imine dissolved to form a clear solution. The volume was reduced until a solid is formed. The product was filtered off and washed with methanol. This procedure gave the amine. A solution of the corresponding N-phenylbenzylamine in acetic anhydride was left at room temperature for 24 hours. The mixture was poured into ice-water, stirred for 4 h and neutralized with sodium hydrogen carbonate. The mixture was extracted with chloroform (3x25 mL) and the extract dried over sodium sulfate and the solvent evaporated *in vacuo*. The solid obtained was purified by column chromatography on silica gel.

RESULTS AND DISCUSSION

Figure 2 shows the room temperature ^{1}H-NMR spectrum of molecule III in $CDCl_3$. In the region between 4.0 and 6.0 ppm the resonance peaks of both methylene groups appear. It can be seen that the four aliphatic protons, in the two methylenes, are all non-equivalent. This is conclusive evidence for the existence of a frozen structure in the NMR timescale. The protons of the methylene bonded to the nitrogen atom, common to all the structures, display the greatest chemical shift difference in the absence of exchange: 260 Hz. The methylene protons in substituent R^2 present a chemical shift difference of 40 Hz. Similar values were observed for the other molecules. Figure 3 shows the temperature dependence of the ^{1}H-NMR spectrum of molecule III in the region of interest, along with the DNMR5 lineshape calculation. The observed phenomenon indicates the existence of one or more intramolecular dynamic processes that average the chemical environment of the two protons at each methylene group. The experimental spectra were satisfactorily calculated on the assumption of an AB ⇔ BA exchange for structures I and IV, and an ABCD ⇔ DCBA exchange for molecules II and III. Particularly interesting to note is the fact that in the lineshape calculation of molecules II and III, only one rate constant is sufficient to account for the observed dynamic process, even though there exist two different sites of exchange. This observation indicates that either the averaging of the chemical shift of both methylenes occurs at the same rate and simultaneously, evidencing the existence of only one dynamic process, or both methylenes average their environment through two different processes with the same activation energy. Since significant structural differences exists between both methylene groups, the latter situation seems very unlikely. Therefore, we are inclined to believe that only one dynamic process is responsible for the averaging of both methylene groups in structures II and III, and possibly the same coordinate corresponds to the dynamics observed in structures I and IV. However we can not determine this from our data. Activation parameters for each molecule were extracted from the temperature dependence of the first order rate constant. $\Delta G^{\neq}$ was calculated using Eyring´s equation and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were extracted from the usual plot of $\ln(k/T)$ vs. $1/T$.[19] At least 10 rate constants were measured for each molecule at different temperatures in the region of intermediate exchange. Figure 4 shows the Eyring plot of molecule II, a typical set of data. These results are listed in table I and will be discussed later.
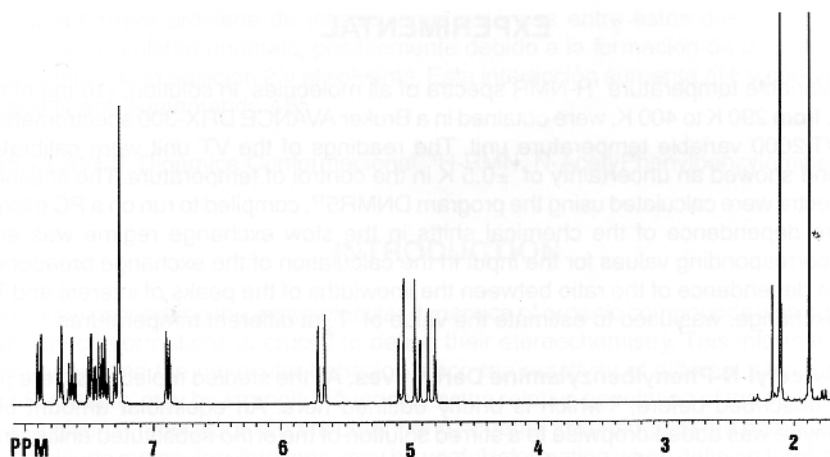
Fig.2. 300 MHz ¹H–NMR spectrum of 2 - [N – acetyl – N – (2-nitrobenzyl)amine]benzylacetate (molecule III) in CDCl₃ solution at 300 K. The signals at about 2 ppm arise from the methyl groups, in the region between 4 and 6 ppm the signals from the methylene protons appear, and between 6.5 and 8 ppm the aromatics and solvent signals appear. The region between 4 and 6 ppm clearly shows the non-equivalence of the four methylene protons, evidencing a frozen structure in the NMR time scale.
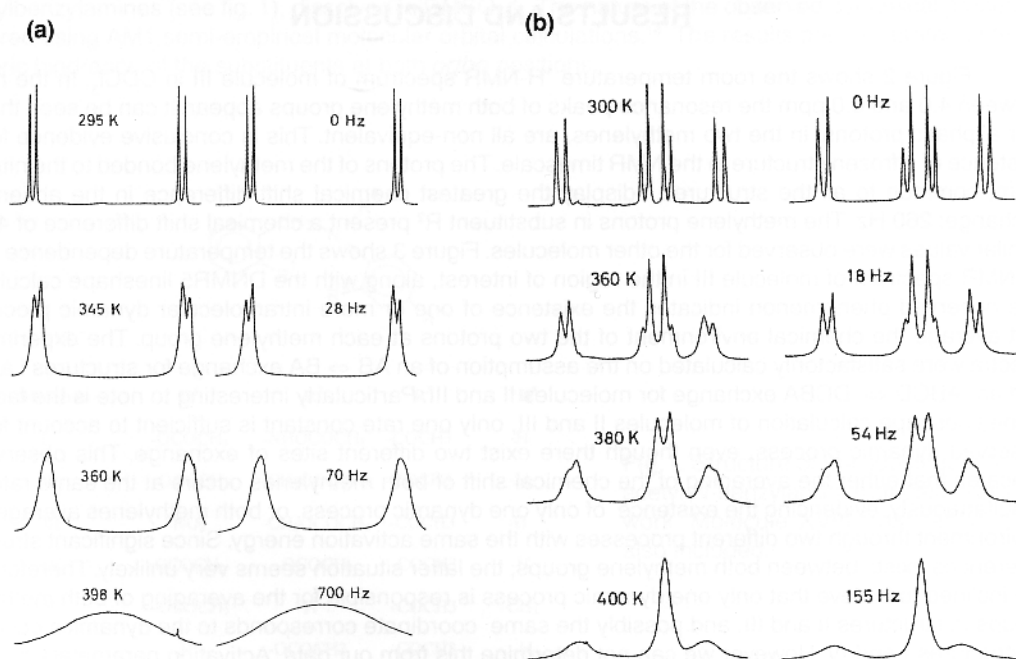

Fig.3. Temperature dependence of the ¹H-NMR spectrum of (a) 2-[N–Acetyl–N-(2-acetyloxybenzyl)amino]phenylacetate (molecule IV) and (b) 2 - [N – Acetyl – N – (2-nitrobenzyl)amine]benzylacetate (molecule III) in solution of DMSO-d₆, in the region of interest. DNMR5 calculated spectra are also shown.
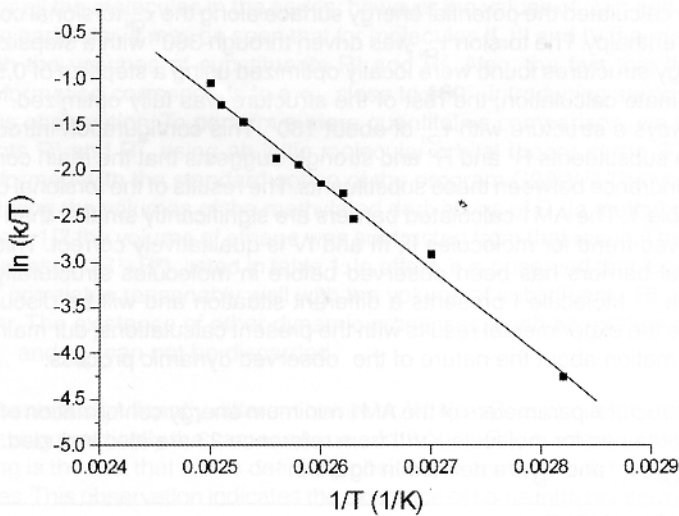
Fig.4. Plot of ln (k/T) vs. 1/T of 2 - [N – acetyl – N - (2-acetyloxybenzyl)amine]benzylacetate (molecule II). ΔH^* and ΔS^* are calculated from the slope and the intercept, respectively.

Table I. Experimental and theoretical activation parameters obtained in this work. The experimental errors are ± 2.0 kJ/mol for ΔG^*, ± 6.0 kJ/mol for ΔH^*, and ± 20 J/K mol for ΔS^*. The STO-3G estimated volumes of R^1 and R^2 were added, $(R^1 + R^2)$, and the results are also listed.

| MOLECULE	I	II	III	IV
ΔG^* (kJ/mol)	79.9(370K)	82.0(370K)	80.8(380K)	77.0(370K)
ΔH^* (kJ/mol)	96.2	79.1	60.7	65.3
ΔS^* (J/Kmol)	+45	-8	-53	-32
AM1 Barrier (kJ/mol)	24.3	28.0	23.4	24.3
Volume(R^1+R^2) (cm³/mol)	67	65	57	52

More detail about the nature of the observed dynamics has been obtained using AM1 semi-empirical molecular orbital calculations. The calculations were performed in the absence of solvent with the MOPAC program, v.6.0, compiled to run on a PC microcomputer.[20] We have explored the AM1 potential energy surface of these molecules exhaustively. The conformation of these structures can be well described by specifying the values of at least six torsion angles, namely the torsion around the central C-N bond, τ_{CN}, two torsion angles to define the orientation of both rings, $\tau_{\phi 1}$ and $\tau_{\phi 2}$, and three torsional coordinates to define the orientation of substituents R^1, R^2, and R^3. We have performed minimum energy calculations for a variety of initial trial structures and found at least 12 minimum energy conformations, located up to 25 kJ/mol above the best minimum. One common feature present in all these structures is the value of the τ_{CN} torsion angle, around ± 75°, and the values of the torsion angles that define the orientation of the rings, $\tau_{\phi 1}$ and $\tau_{\phi 2}$, both around ± 100°. The structure corresponding to the best minimum energy conformation found for molecule II appears in figure 5, and table II shows the calculated values of the three main torsion angles that define the minimum energy conformations of the basic common structure, τ_{CN}, $\tau_{\phi 1}$ and $\tau_{\phi 2}$. As observed in figure 5 the rings are nearly co-planar to each other and this plane is nearly perpendicular to the central C-N bond, while the τ_{CN} torsion angle is -75°. Variations in the relative orientation of the substituents account for a variety of conformations, but since the observed dynamics seems to involves rotation of both methylene groups simultaneously, we did not explore this region of the potential energy surface in detail. Instead, observation of figure 5 strongly suggests that rotation around the τ_{CN} torsional

coordinate represents a plausible mechanism that involves both methylene groups simultaneously. Therefore, we have calculated the potential energy surface along the τ_{CN} torsional coordinate and obtained the AM1 activation enthalpy. The torsion τ_{CN} was driven through 360° with a stepsize of 5°. The maximum and minimum energy structures found were locally optimized using a stepsize of 0.5°. At every step along the torsional coordinate calculation, the rest of the structure was fully optimized. The maximum energy conformation is always a structure with τ_{CN} of about 160°. This configuration introduces important steric hindrance between substituents R^1 and R^2 and strongly suggests that the main component of the barrier arises from steric hindrance between these substituents. The results of the torsional coordinate calculations are also listed in table 1. The AM1 calculated barriers are significantly smaller than the experimental $\Delta H^{\neq}$, however the observed trend for molecules II, III and IV is qualitatively correct. This behavior of the AM1 calculated rotational barriers has been observed before in molecules structurally similar to the series studied in this work.[21] Molecule I presents a different situation and will be discussed later. We do not expect to reproduce the experimental results with the present calculations; our main purpose is to provide more detailed information about the nature of the observed dynamic process.

Table II. Selected structural parameters of the AM1 minimum energy conformation of the studied molecules Calculated values obtained for molecule XVIII from reference 23 are also included. . The torsional angles corresponding to τ_{CN}, $\tau_{\phi1}$ and $\tau_{\phi2}$ are defined in figure 5.

TORSION ANGLE (degrees) MOLECULE	τ_{CN}	$\tau_{\phi1}$	$\tau_{\phi2}$
I	-82	-102	-94
II	-75	-102	-94
III	-74	-118	-96
IV	-75	-102	-72
V	136	- 58	-98
VI	132	- 85	-65
XVIII[a]	147	113	-101

[a] Molecule studied in ref. 23.
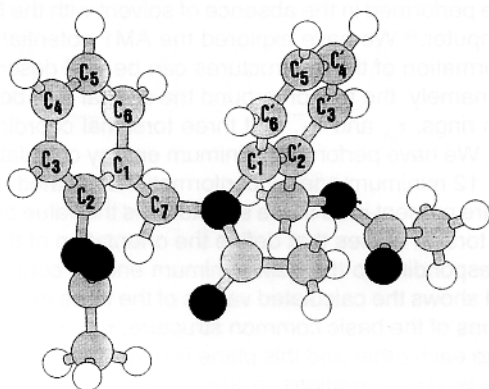
$$\tau_{CN} = C_1\text{-}C_7\text{-}N_1\text{-}C_1{'}$$
$$\tau_{\phi_I} = N_1\text{-}C_7\text{-}C_1\text{-}C_2$$
$$\tau_{\phi_2} = C_2{'}\text{-}C_1{'}\text{-}N_1\text{-}C_7$$

Fig.5. AM1 minimum energy conformation of 2 - [N – acetyl – N - (2-acetyloxybenzyl)amino]benzylacetate (molecule II). The definition of the torsional coordinates of interest is also shown. AM1 calculated structural parameters for the minimum energy conformation of the studied molecules appear in table 2.

Inspection of table I reveals that, within experimental error, the measured values of ΔG^* are practically the same for all the molecules in the series; however the values of ΔH^* and ΔS^* differ from one molecule to another. In particular, it may be seen that for molecules II, III and IV the measured ΔH^* values seem to correlate with the volumes of substituents R^1 and R^2. Also, the fact that the geometry of the maximum energy conformation corresponds to a τ_{CN} close to 160°, introducing steric hindrance between R^1 and R^2, support this observation. To perform a more quantitative comparison, we have calculated the volumes of substituents R^1 and R^2, using ab-initio molecular orbital theory at the STO-3G level. These calculations were performed with the standard option of the program G98W.[22] The volumes of R^1 and R^2 were estimated calculating the volumes of the methylated derivatives of R, (a methyl group instead of the aromatic ring), and then, 1/2 the volume of ethane was subtracted from that result. The volumes of R^1 and R^2 were added and the result, (R^1+R^2), listed in table 1. In effect, it is observed that for molecules II, III and IV the measured ΔH^* correlates reasonably well with the volume of substituents R^1 and R^2, and with the AM1 calculated barrier. The existence of other dynamic processes, such as rotation around τ_{CN} followed by rotations around $\tau_{\phi 1}$ and $\tau_{\phi 2}$, can not be discarded.

Molecule I presents a significantly different behavior. While ΔG^* is about the same as for molecule II, and despite both having practically the same volume sum of (R^1+R^2), it shows a ΔH^* which is 17 kJ/mol higher. More interesting is the fact that ΔS^* is definitely positive, in contrast with the negative values found in all the other structures. This observation indicates the existence of some intra or intermolecular interaction, which either stabilize the ground state of I by 17 kJ/mol or destabilizes the corresponding transition state by the same amount of energy. Considering that structure I has a secondary amino group and judging from the amount of energy involved, it is very likely that the NH group of structure I forms an hydrogen bond with the solvent. This interaction could stabilize the frozen structure by an additional 17 kJ/mol, increasing ΔH^* by the same amount. We discard the possibility of an intramolecular hydrogen bond, because in the process of exploring the potential energy surface of this molecule, a minimum energy structure with the proper geometry to favor the interaction between the NH group of R^2 and the C=O moiety of R^1, could not be found. This intermolecular H-bond also allows to rationalize the observed high value of ΔS^* for molecule I, as compared to the other members of the series. When structure I is hydrogen bonded to the solvent, the rotation around the bond between the aromatic ring and the nitrogen atom of R^2 is frozen. When it rotates, as a consequence of heating, the hydrogen bond is destroyed at the expense of an extra 17 kJ/mol. At the transition state the torsional coordinate around the aryl-N bond of R^2 should be more free to rotate than when it is forming a H-bond with the solvent. This effectively increases the density of states in the transition state as compared to the minimum energy conformation, increasing the entropy of activation.

More than 30 years ago, the temperature dependence of the ^{1}H-NMR spectra of a series of 20 substituted anilides, structurally related to the molecules of this work, were investigated.[23,24] Those authors examined mostly structures with voluminous substituents at positions R^2 and R^3. They followed the dynamics studying the AB⇌BA exchange pattern observed for the benzylic methylene group, and attributed this non-equivalence to rotational isomerism around the aryl-nitrogen bond. In view of the similarity of this series with our structures and the differences in the nature of the observed dynamic processes, we have explored the AM1 minimum energy conformations around the central C-N bond of molecule XVIII from reference 23. This molecule presents a minimum energy conformation with $\tau_{CN}=147°$. A more recent DNMR study of 1,2-diaryl derivatives of 1,1,2,2-tetrachloroethane, shows that the *trans* conformation around the central C-C bond, is always preferred over the *gauche*;[21] however no substituents were introduced in the *ortho* positions of the aromatic rings. The unsubstituted basic structure $(R^1=R^2=H)$ presents at least two AM1 minimum energy conformations around the central C-N bond, one with $\tau_{CN} = 131°$ (*trans*), and the other, 0.25 kJ/mol higher, with $\tau_{CN} = 13°$ (*gauche*). The first conformation possibly minimizes the steric hindrance between the substituents around the central C-N bond, whereas the second is probably stabilized by interactions between the aromatic rings.[25]

The conformation around the central C-N bond appears to be essential for the type of motion that the aromatic rings of these molecules can experience. For instance, if R^2 and R^3 are bulky groups, the torsion angle τ_{CN} is greater than about 130º and the aromatic rings might rotate independently around torsion angles $\tau_{\phi 1}$ and $\tau_{\phi 2}$. Therefore, the observed dynamics corresponds to rotation around $\tau_{\phi 2}$, as in refs. 23 and 24. Besides, if R^1, R^2 and R^3 are bulky groups, the value of τ_{CN} is only about 80° and the molecule adopts a conformation with the aromatic ring planes nearly parallel to each other and close to perpendicular

to the central C-N bond. In this conformation it is not possible to rotate the aromatic rings independently and the observed dynamics involves rotation around the central C-N bond. The relative stability of these two conformations and therefore the nature of the observed dynamics seems to depend on the volume and position of the substituents in the aromatic rings. For our series, we found that the AM1 minimum energy conformation presents a τ_{CN} torsional angle of about -75°, introducing serious hindrance to the rotation of the aromatic rings. Values of τ_{CN} close to 160° correspond to a maximum in the potential energy surface, probably due to the steric hindrance introduced by the two bulky *ortho* substituents. In this case, the observed dynamics should correspond to rotation around τ_{CN}. To support this hypothesis we have prepared molecules V and VI and measured their room temperature ^{1}H-NMR spectra. In molecule V the substituent R^2 of structure IV is replaced by a proton and a single peak is observed for the methylene signal, evidencing free rotation around $\tau_{\phi2}$. On the other hand, in molecule VI the substituent R^1 of structure IV is replaced by a proton. As expected, the spectrum of this molecule shows an AB pattern for the methylene group; however the limiting chemical shift difference in the absence of exchange is only 50 Hz, significantly smaller than the values observed for structures I to IV. This strongly suggests that the minimum energy conformation of molecule VI is significantly different from the conformation of molecules I to IV. The dynamic process that could be observed raising the temperature of VI corresponds to rotation around $\tau_{\phi2}$.

Finally, we have found that the minimum energy conformation as well as the conformational dynamics experienced by these molecules largely depends on the volume and position of the substituents in the aromatic rings. In particular, bulky substituents at positions R^1, R^2 and R^3 favor the *gauche* conformation, with $\tau_{CN} < 90°$, freezing the rotations around $\tau_{\phi1}$ and $\tau_{\phi2}$. Consequently, the observed dynamics involves rotation around the central C-N bond. On the other hand, unsubstituted or partially substituted derivatives favor the *trans* conformations, with $\tau_{CN} > 130°$, and the dynamics observed, if there are bulky groups at R^2 and R^3, corresponds to rotational isomerism around $\tau_{\phi2}$.

ACKNOWLEDGEMENTS

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