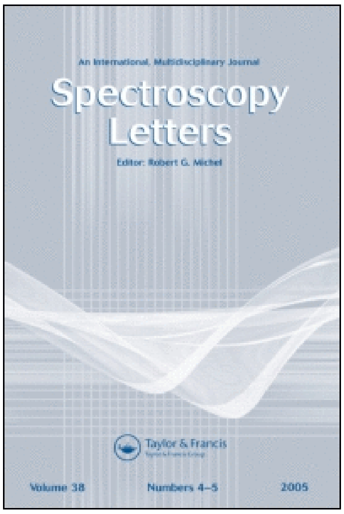

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Long Distance Electronic Effects on the Rotational Potential Barriers Around the $C_{aromatic}$-$C_{ethylenic}$ Bond

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LONG DISTANCE ELECTRONIC EFFECTS ON THE ROTATIONAL POTENTIAL BARRIERS AROUND THE $C_{aromatic}$-$C_{ethylenic}$ BOND

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Key Words: Rotational activation energies, AM1 M.O. calculations, aromatic carbonyl and styrene compounds, long distance electronic effects.

ABSTRACT. A systematic study of the rotational activation free energy around the $C_{aromatic}$-$C_{ethylenic}$ bond of *para*-substituted styrene systems is carried out in the present work from a quantum chemistry point of view.

Calculations of the rotational potential barriers in the AM1 approach are developed as function of the electron-donor groups localized on the aromatic ring. Based on these calculations and thermodynamical data, we predict changes in the activation free energy barriers due to the long distance electronic effects of the substituents in acetophenones, cinnamaldehydes and benzalketones according to the following equation:

$$\Delta G^{\neq}_{exp} = (2.41 \pm 0.16)\, V_{AM1} + 5.43 \pm 1.79, \text{ in kJmol}^{-1}.$$

Our results agree the experimental measurements registered up to date and the standard deviations are similar to experimental determinations.

INTRODUCTION

Rotational potential barriers around to the $C_{aromatic}$-$C_{ethylenic}$ bond is subject of broad interest in the characterization of the dynamic molecular structural behavior of several

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aromatic compounds.[1] However, due to the low activation free energy barriers, experimental determinations are actually complexes and hard to develop due to the low temperature conditions that it is necessary to reach. In general, NMR techniques have been broadly used in different molecular systems in liquid solutions,[2-5] but the main experimental problem are generally due to the solidification temperature of the solutions, before to reach the coalescence temperature of the NMR spectral shifts, and the low solubility in these low-melting solvents. Thus, styrene[1] as well as other similar systems present a very low π-barrier for measurements by dynamic NMR spectroscopy for which technique the practical limit is between 16 and 21 kJ/mol.

Due to the origin of the π-barrier is the loss of conjugation between the benzene and ethylene parts of the molecule when these become orthogonal, any substitution which enhances the conjugation should lead to a higher barrier.[1] By following, the long distance electronic effect due to the electron-donor groups can be used as modulators of the rotational energy barriers in this particular $C_{aromatic}$-$C_{ethylenic}$ bond. This assumption define in these kind of molecular systems the rotational potential barriers as mainly due to an internal electronic enthalpic interaction of the molecular structure. Therefore we have carried out a systematic calculation of the rotational activation barriers in the AM1 approach[6] (V_{AM1}) in *para*-substituted aromatic carbonyl and styrene compounds around the $C_{aromatic}$-$C_{ethylenic}$ bond. Up to date, M.O. calculations of semiempirical or *ab initio* nature do not describe well enough these kind of activation rotational barriers energies.[7,8] However, we have found that these V_{AM1} calculations give us good systematic results of activation free energy barriers ($\Delta G^{\neq}$).

In order to predict these $\Delta G^{\neq}_{calc}$, for *para*-substituted acetophenone, cinnamaldehyde and benzalketone series, we have used a linear function between the experimental rotational activation free energy ($\Delta G^{\neq}_{exp}$) and our V_{AM1} data in the *para*-substituted benzaldehyde series.

Theoretical Method

The main problem of the semiempirical methods in the description of the internal rotational potential barriers has been the repulsion forces for non bonded atoms.[6] One of the widely used semiempirical methods in the last fifteen years, MNDO,[9] predicts erroneous geometrical conformations for benzaldehyde and nitrobenzene.[7] However we have used an improved version called AM1, based on the modification of the core repulsion function in MNDO (a reparametrized MNDO with modified core-core interaction terms[6]). Lately, a new method based on the MNDO/AM1-type parameters[10] called PM3

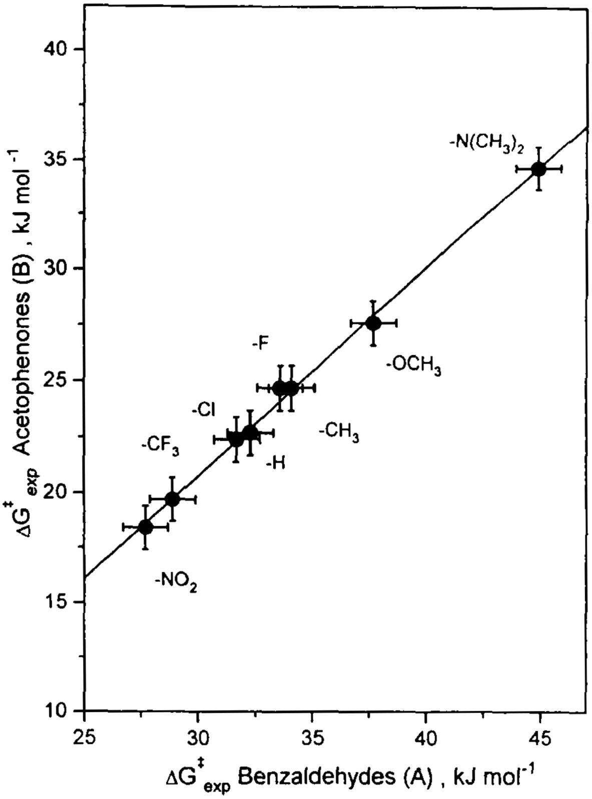

Figure 1. $\Delta G^{\neq}_{exp}$ Benzaldehydes (A) versus $\Delta G^{\neq}_{exp}$ Acetophenones (B) in kJ mol^{-1} (see Table 1).

(modified neglected of diatomic overlap, parametric method 3) has not resulted appropriate to these kind of studies.[11,12]

The molecular computational calculations have been developed in a Silicon Graphics 2000 workstation at the University of Chile. The AM1 calculations has been carried out under complete molecular geometry relaxation.

A Thermodynamics Model

If we consider that the rotational potential barriers for two similar isolated molecular systems such as benzaldehyde (B) and acetophenone (A) are mainly affected by the long

TABLE 1

AM1 rotational potential barriers (V_{AM1}), and experimental ($\Delta G^{\neq}_{exp}$) and calculated ($\Delta G^{\neq}_{calc}$) rotational activation free energies of *para*-substituted benzaldehydes, acetophenones, cinnamaldehydes and benzalketones (in kJ mol^{-1}).

Substituent	Benzaldehydes			Acetophenones			Cinnamaldehydes			Benzalketones	
	V_{AM1} ref. 11	$\Delta G^{\neq}_{calc}$ this work	$\Delta G^{\neq}_{exp}$ ref. 5	V_{AM1} ref. 11	$\Delta G^{\neq}_{calc}$ this work	$\Delta G^{\neq}_{exp}$ ref. 5	V_{AM1} this work	$\Delta G^{\neq}_{calc}$ this work	$\Delta G^{\neq}_{exp}$ ref. 1	V_{AM1} this work	$\Delta G^{\neq}_{calc}$ this work
$-NO_2$	8.43	25.8	27.7	4.48	16.2	18.4	6.13	20.2		6.11	20.2
-CHO	9.44	28.2	28.8								
-CN	9.79	29.0	28.5								
$-CF_3$	10.2	30.0	28.9(3)	5.21	18.0	19.7	6.46	21.0		6.19	20.4
$-OCF_3$	10.8	31.5	32.0								
-Br				6.25	20.5	22.6	6.98	22.3		6.89	22.0
-Cl	11.1	32.2	32.3(3)	6.84	21.9	22.7	7.39	23.2		7.19	22.8
-H	11.2	32.4	31.7(3)	6.83	21.9	22.4	7.59	23.7		7.35	23.1
-i-Pr	11.7	33.6	34.0								
-F	12.0	34.4	33.6	7.62	23.8	24.7	7.99	24.7		7.57	23.7
-OH							8.96	27.0		8.65	26.3
$-CH_3$	12.4	35.3	34.1	7.33	23.1	24.7	8.06	24.9		7.78	24.2
$-OCH_3$	13.6	38.2	37.7	9.08	27.3	27.6(14)	9.08	27.4	25.9	8.84	26.7
$-N(CH_3)_2$	15.6	43.0	44.9	11.0	31.9	34.7(14)	11.2	32.3	30.5	10.4	30.5

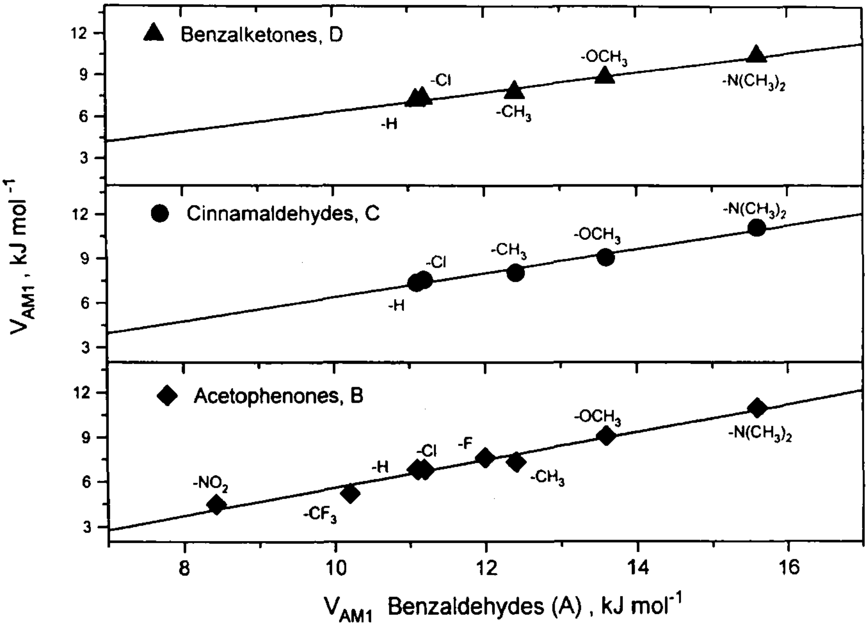

Figure 2. AM1 rotational potential barriers (V_{AM1}) of *para*-substituted acetophenones, cinnamaldehydes and benzalketones versus benzaldehydes in kJ mol^{-1} (see Table 1).

distance electronic effect of the *electron-donor para*-substituent (Y) through the π-molecular orbitals channel involved in the $C_{aromatic}$-$C_{ethylenic}$ bond, we can expect that these rotational activation enthalpies of both molecular series follow a linear relationship given by: $\Delta H^{\neq}_{A}(Y) = a\ \Delta H^{\neq}_{B}(Y) + b$, where a and b are constants.

According to the Gibbs energy: $\Delta G^{\neq}_{A}(Y) = \Delta H^{\neq}_{A}(Y) - T\Delta S^{\neq}_{A}(Y)$, and since $\Delta S^{\neq}_{A}(Y) \cong \Delta S^{\neq}_{B}(Y)$, we will have: $\Delta G^{\neq}_{A}(Y) = a\ \Delta G^{\neq}_{B}(Y) + b'$, where b' is a constant at the same temperature. From experimental $\Delta G^{\neq}$ energies of benzaldehyde and acetophenone series obtained from literature data,[5] we have found a linear behavior given by a regression coefficient (r) of 0.998 and a slope of 0.94 ± 0.07 (see Figure 1). This result enforce our assumption about the internal enthalpic term as the main contribution to the rotational activation free energies. In addition, for this kind of aromatic carbonyl compounds, some scarce measurements of rotational activation entropies ($\Delta S^{\neq}$) in chlorofluorocarbon solvents [5] present experimental data as lower than 6 J mol^{-1} K^{-1}.

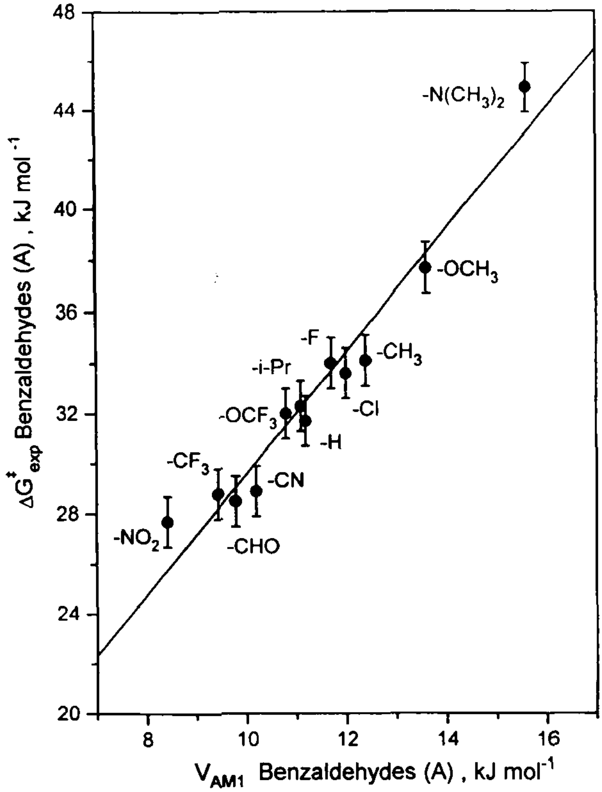

Figure 3. Experimental rotational activation free energies $\Delta G^{\ne}_{exp}$ of *para*-substituted benzaldehydes versus the calculated AM1 rotational potential barriers (V_{AM1}) in kJ mol^{-1} (see Table 1).

RESULTS AND DISCUSSION

In Table 1 we present the V_{AM1} calculations for each molecular series. In all cases we have found a good agreement between experimental and AM1 bond lengths and bond angles.[12] Furthermore, the ground state conformation is described by a planar configuration and the maximum energy barriers were found at 90° ± 1° respect to the planar configuration. We have compared the V_{AM1} for acetophenones, cinnamaldehydes and benzalketones respect to benzaldehydes and we have observed that all them follow a similar linear behavior (see Figure 2). This singular pattern determine a same kind of electronic effect on the $C_{aromatic}$- $C_{ethylenic}$ bond, i.e., the internal rotational potential barriers are mainly regulated by the long distance π-electronic effect of the *para*-substituents under without steric or specific interaction regime. Thus, after plot the $\Delta G^{\neq}_{exp}$ versus the calculated V_{AM1} of benzaldehydes (see Figure 3), we have found the following linear correlation (s.d. = 1.12 and r = 0.975):

$$\Delta G^{\neq}_{exp}(B) = 2.41 \pm 0.16\, V_{AM1}(B) + 5.43 \pm 1.79, \quad \text{in kJmol}^{-1} \qquad (1)$$

This equation is well followed by every one of the electron-donor substituent, including some medium and strong electron-acceptor groups such as -CN, -CHO and $-NO_2$. These scale factors permit us to determine the theoretical $\Delta G^{\neq}_{calc}$ for the aromatic carbonyl series under study as can be seen in Table 1. For comparison we have collected different experimental $\Delta G^{\neq}_{exp}$ determined up to date. These data have been determined preferably by ^{13}C -NMR spectroscopy, which are normally within ± 1kJ mol^{-1} in chlorofluorocarbons solvent mixtures.[3,5,13,14] In general we appreciate a good agreement between experimental and our calculated data, and the standard deviation (s.d.) result to be similar or lower than the own experimental measurements.

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