

## INTERNAL ROTATIONAL BARRIERS BY QUANTUM CHEMICAL METHODS. AROMATIC CARBONYL COMPOUNDS

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Internal rotational barriers of aromatic carbonyl compounds were calculated by means of semi-empirical quantum chemical methods such as AM1 and PM3. Rotational potential barriers in the AM1 approach ( $V_{AM1}$ ) follow the experimental rotational free energy of activation ( $\Delta G^\ddagger$ ) according to the linear relationship  $\Delta G^\ddagger$  ( $\text{kJ mol}^{-1}$ ) =  $(2.24 \pm 0.08) V_{AM1} + (7.79 \pm 0.84)$ . A standard deviation of  $1.08 \text{ kJ mol}^{-1}$  permit leads to a good method for calculations of internal rotational barriers in these aromatic series.

### INTRODUCTION

Barriers to internal rotation about the carbonyl-aromatic bonds in some *para*-substituted benzaldehydes and acetophenones have been extensively studied by both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.<sup>1-5</sup> Preliminary studies have been carried out to explain these rotational barriers by means of empirical molecular parameters in the Hammett approach.<sup>4</sup> However, the aim of these studies was to gain a deeper insight into the  $\pi$ -electron delocalization which is considered to be the main reason for this type of barrier. Several studies on this question have been reported over the last two decades.<sup>6-10</sup>

From a theoretical point of view, rotational barriers in molecular systems of intermediate or large size are so far not well described by *ab initio* or semi-empirical quantum chemical methods.<sup>8,9</sup> *Ab initio* potential barrier calculations have shown a poor performance in systematic studies on substituted aromatic carbonyl compounds<sup>8,9</sup> and also large amounts of computational time are involved in the calculations. In particular, *ab initio* calculations on benzaldehyde have determined rotational barriers that are highly dependent of the basis set chosen, the STO-3G results being in better agreement with experiment than other sophisticated basis set such as 6-31G, 6-31G\*, MP2/3-21G and MP2/6-31G\*,<sup>8</sup> mainly owing to a fortuitous cancellation of errors. Further, the same calculations, including electron correlation, have not improved the previous *ab initio* calculations.<sup>8,9</sup> However, in spite of these previous

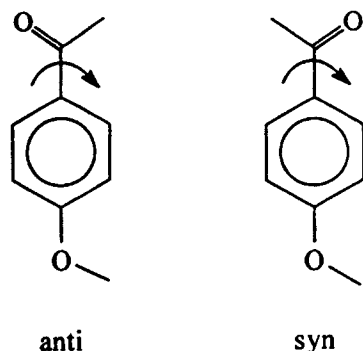
considerations, *ab initio* results for benzaldehyde,<sup>8</sup> and also other aromatic systems such as acetophenone,<sup>11,12</sup> agree with the expected conformational changes from a quasi-planar configuration in the ground state to a perpendicular configuration at the energy maximum potential barrier.

The main problem with the semi-empirical methods in the description of internal rotational potential barriers has been the repulsion forces for non-bonded atoms.<sup>13</sup> One of the best semi-empirical methods, widely used by chemists over the last 15 years, MNDO,<sup>14</sup> predicts erroneous geometrical conformations for benzaldehyde and nitrobenzene. Owing to the overestimation of the repulsion interactions between oxygen and the *ortho* hydrogen atoms, this method predicts stable structures with the nitro or carbonyl groups orthogonal to the aromatic ring.<sup>13</sup> This problem led to the modification of the core repulsion function in MNDO, improving this method as the new version AM1 (a reparametrized MNDO with modified core-core interaction terms).<sup>13</sup> Part of the improvement of AM1 over MNDO was due to the fact that a better minimum was found, which has a large effect on activation barriers. The correction of non-bonded repulsions is evident in the geometries of benzaldehydes and nitrobenzenes, both of which are correctly predicted to be planar by AM1.

Recently, a new optimization of the MNDO/AM1-type parameters has been developed,<sup>15</sup> the new version has been called PM3 (modified neglected of diatomic overlap, parametric method 3).

Based on both semi-empirical quantum chemical methods, in the present work we developed a systematic calculation of the AM1 and PM3 internal rotational

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Figure 1. Structures of *anti* and *syn* conformers

activation energy barriers ( $V_{AM1}$  and  $V_{PM3}$ , respectively) about of the benzene-to-carbonyl substituent bond (see Figure 1) of *para*-substituted benzaldehydes and *para*-substituted acetophenones. The intention was to establish a reliable method for internal rotational barrier energy calculations on this series of aromatic carbonyl compounds owing to the difficult experimental condi-

tions which are necessary when the rotational potential barriers are lower than  $20 \text{ kJ mol}^{-1}$ .

### EXPERIMENTAL AND RESULTS

The molecular computational calculations were developed using the AM1 and PM3 versions with an Apollo 10000 workstation. The AM1 and PM3 calculations were carried out under complete molecular geometry relaxation. Good agreement between the experimental and AM1 bond lengths and bond angles was found for the set of molecular species under study, where the ground-state conformation is described by a planar ring-carbonyl group configuration. However, PM3 does not follow the same behaviour as AM1, since for the acetophenone series, except *p*-dimethylaminoacetophenone, this method describes the ground state as an out-of-plane molecular conformation (torsional angle between  $0$  and  $50^\circ$ ) and gives potential barriers lower than  $1.6 \text{ kJ mol}^{-1}$ .

In Table 1 we present the internal rotational barrier energies calculated by AM1 and PM3 for the ground-state conformers and those corresponding to the *syn* and *anti* conformers due to the methoxy substituent in the

Table 1.  $V_{AM1}$ ,  $V_{PM3}$  and experimental free energies ( $\Delta G^\ddagger$ ) of internal rotational barriers ( $\text{kJ mol}^{-1}$ ) in *para*- and *meta*-substituted aromatic carbonyl compounds

No.	Compound	This work						$\Delta G^\ddagger$	
		$V_{AM1}$	$V_{AM1}^{syn}$	$V_{AM1}^{anti}$	$V_{PM3}$	$V_{PM3}^{syn}$	$V_{PM3}^{anti}$	Value	Ref.
1	<i>p</i> -Nitroacetophenone	4.48			<sup>a</sup>			18.4	4
2	<i>p</i> -(Trifluoromethyl)acetophenone	5.21			<sup>a</sup>			19.7	4
3	<i>p</i> -Bromoacetophenone	6.25			<sup>a</sup>			22.6	4
4	Acetophenone	6.83			<sup>a</sup>			22.4	4
5	<i>p</i> -Chloroacetophenone	6.84			<sup>a</sup>			22.7	4
6	<i>p</i> -Methylacetophenone	7.33			<sup>a</sup>			24.7	4
7	<i>p</i> -Fluoroacetophenone	7.62			<sup>a</sup>			24.7	4
8	<i>p</i> -Nitrobenzaldehyde	8.43			<sup>a</sup>			27.7	4
9	<i>p</i> -Methoxyacetophenone	9.08	8.81	9.34	<sup>a</sup>			27.6	3
10	Terephthal dicarboxaldehyde	9.44			5.31			28.8	4
11	<i>p</i> -Cyanobenzaldehyde	9.79			5.56			28.5	4
12	<i>p</i> -(Trifluoromethyl)benzaldehyde	10.2			5.05			28.9	2
13	<i>p</i> -(Trifluoromethoxy)benzaldehyde	10.8			6.26			32.0	4
14	<i>p</i> -Dimethylaminoacetophenone	11.0			1.73			34.7	3
15	<i>p</i> -Chlorobenzaldehyde	11.1			6.61			32.3	2
16	Benzaldehyde	11.2			6.60			31.7	2
17	<i>p</i> -Isopropylbenzaldehyde	11.7			7.32			34.0	4
18	<i>p</i> -Fluorobenzaldehyde	12.0			6.85			33.6	4
19	<i>p</i> -Methylbenzaldehyde	12.4			7.04			34.1	4
20	<i>p</i> -Methoxybenzaldehyde	13.6	13.3	13.8	8.61	8.42	8.79	37.7	4
21	<i>p</i> -Dimethylaminobenzaldehyde	15.6			9.94			44.9	4
22	<i>m</i> -Fluorobenzaldehyde	10.1	9.80	10.4	5.72	5.50	5.94	30.7	5
23	<i>m</i> -Chlorobenzaldehyde	10.7	10.4	11.0	6.14	5.95	6.32	31.9	5
24	<i>m</i> -Bromobenzaldehyde	10.5	10.3	10.5	6.31	6.01	6.61	33.0	5
25	<i>m</i> -Methylbenzaldehyde	11.1	11.1	11.2	6.51	6.40	6.52	33.0	5

<sup>a</sup> PM3 gives anomalous rotational barriers lower than  $1.6 \text{ kJ mol}^{-1}$ .

*para* position. For the molecular series under study we have found the maximum energy barriers at  $90 \pm 1^\circ$  from the planar configuration, except for the molecular systems mentioned before calculated by the PM3 method.

For comparison, we collected experimental rotational barrier energies ( $\Delta G^\ddagger$ ) of the molecular systems under study determined by means of variable-temperature, preferably  $^{13}\text{C}$  NMR spectroscopy, which are normally within  $\pm 1 \text{ kJ mol}^{-1}$  in chlorofluorocarbon solvent mixtures.<sup>1-5</sup>

In order to appreciate the effect of the substituent structural factors on the rotational barrier energy, we compared experimental and theoretical parameters defined as energy barrier ratios ( $r_{\text{exp}}$  and  $r_t$ , respectively) of two molecular systems of the same carbonyl series. We chose the higher rotational energy barrier (*p*-dimethylamino substituent) and benzaldehyde (B) or acetophenone (A), according to

$$r_{\text{exp}} = [\Delta G^\ddagger(\text{B})/\Delta G^\ddagger(\text{pDMAB})]$$

and

$$r_t(\text{AM1}) = [V_{\text{AM1}}(\text{B})/V_{\text{AM1}}(\text{pDMAB})]$$

where, for benzaldehyde,  $r_{\text{exp}}$  is 0.706 and  $r_t(\text{AM1})$  is 0.718. The PM3 ratio [ $r_t(\text{PM3})$ ] is 0.664.

A similar correspondence can be found for acetophenone and *p*-dimethylaminoacetophenone, 0.646 and 0.621, respectively, whereas PM3 follows an anomalous behaviour in these acetophenones (see Table 1). A comparison of these  $r_{\text{exp}}$  and  $r_t(\text{AM1})$  ratios permit

the conclusion that the internal rotational barriers are strongly dependent on the enthalpic factors since entropic factors in pDMAB with respect to the B are not large enough to differentiate the experimental ratio  $r_{\text{exp}}$  from the theoretical ratio  $r_t$ , this last ratio involving only internal molecular interactions.

Few thermodynamic data are available for these carbonyl aromatic systems. However, based on the activation entropy ( $\Delta S^\ddagger$ ) reported<sup>4</sup> for *p*-methylbenzaldehyde ( $5 \text{ J mol}^{-1} \text{ K}^{-1}$ ), *p*-methoxybenzaldehyde ( $6 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and *p*-dimethylaminobenzaldehyde ( $7 \text{ J mol}^{-1} \text{ K}^{-1}$ ), a low contribution of  $\Delta S^\ddagger$  can be expected to the activation free energy ( $\Delta G^\ddagger$ ) for internal rotation. Therefore, we made a direct comparison between the experimental  $\Delta G^\ddagger$  and the  $V_{\text{AM1}}$  parameters. Figure 2 shows a linear correlation of  $\Delta G^\ddagger$  vs  $V_{\text{AM1}}$  for the aromatic carbonyl series under study. This linear behaviour describes well the experimental  $\Delta G^\ddagger$  data over a broad range of  $V_{\text{AM1}}$  potential barrier energies. Equation (1) shows the reported trend:

$$\Delta G^\ddagger (\text{kJ mol}^{-1}) = (2.24 \pm 0.08) V_{\text{AM1}} + (7.79 \pm 0.84) \quad (1)$$

where we have introduced some *meta*-substituted benzaldehydes, which show a similar behaviour to benzaldehyde without introducing a significant change in the linear correlation. A standard deviation of  $1.08 \text{ kJ mol}^{-1}$  in equation (1) shows that there is very good consistency with the barriers obtained from NMR studies, normally within  $1.0 \text{ kJ mol}^{-1}$ .

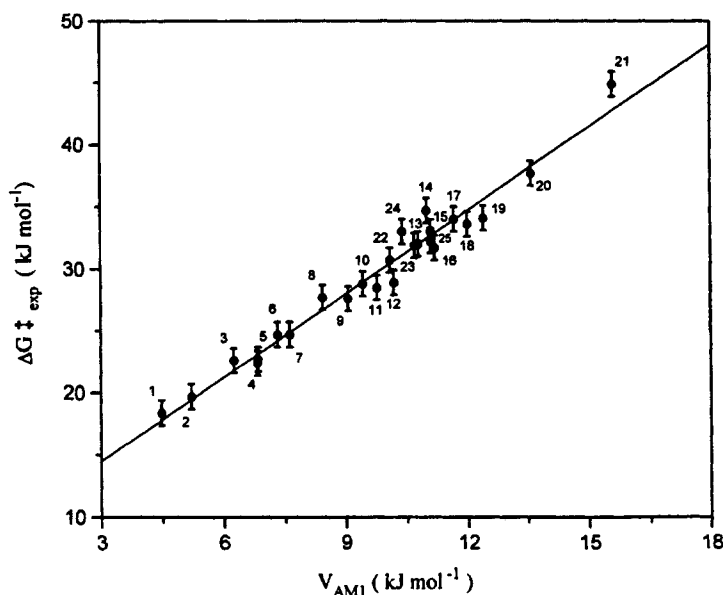


Figure 2. Rotational activation free energy ( $\Delta G^\ddagger$ ) vs AM1 rotational barriers ( $V_{\text{AM1}}$ ) for aromatic carbonyl compounds. Numbers represent compounds in Table 1.

In conclusion, the AM1 calculations cannot describe good absolute data for internal rotational energy barriers ( $V_{AM1}$ ), but we have found that these  $V_{AM1}$  correlate satisfactorily the experimental  $\Delta G^\ddagger$  data in these two series of aromatic carbonyl compounds. Unfortunately, PM3 calculations do not follow the same behaviour.

The study of the molecular orbital structural factors on the internal rotational barriers are currently under study in order to analyse the effect of the charge-transfer process from electron-donor to carbonyl groups on these potential barriers.

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