

Elucidating the Role of Aromatic Interactions in Rotational Barriers Involving Aromatic Systems

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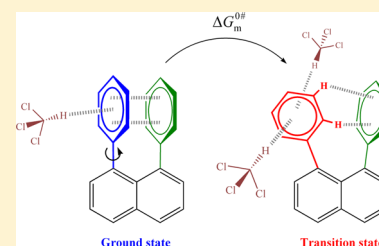
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Supporting Information

ABSTRACT: The measurement of aryl-naphthyl rotational barriers, ΔG_m^\ddagger , in various solvents for two substituted 1,8-diarylnaphthalenes by dynamic ^1H NMR showed that ΔG_m^\ddagger trends in aromatic systems can be fully rationalized only when considering the different types of aromatic interactions that can be established in the ground and transition states, namely, intramolecular interactions involving the aromatic rings and specific solvation interactions.



The pioneering work of Cozzi and co-workers^{1–3} on the measurement of rotational barriers in substituted 1,8-diarylnaphthalenes established a useful and ingenious way of experimentally evaluating aromatic interactions. The authors consistently observed an increase of the rotational barrier, ΔG_m^\ddagger , with the weaker electron-donating and stronger electron-withdrawing capabilities of the substituents, which was attributed to the accompanying decrease in the electrostatic $\pi\cdots\pi$ repulsion between the stacked aryl rings, thus stabilizing the ground state. However, in a recent work,⁴ we have experimentally quantified the gas phase aromatic interaction enthalpy between the two aryl rings in the ground state of various 1,8-diarylnaphthalenes. We found that the aromatic interaction enthalpy essentially increases with the ability of the aryl rings to establish dispersive interactions, and no correlation with the σ_{meta} or σ_{para} Hammett constants has been observed.⁴ This is an indication that for the trends in ΔG_m^\ddagger to be correctly rationalized additional sources of energetic differentiation must also be taken into account. The uppermost importance of dispersion in relation to electrostatics on aromatic interactions has also been advocated by other authors before.^{5–7} Herein the aryl-naphthyl rotational barriers, ΔG_m^\ddagger , in various solvents (CDCl_3 , $\text{THF}-d_8$, and CCl_4) were determined by dynamic ^1H NMR spectroscopy for 1,8-bis(3,4-dimethoxyphenyl)naphthalene (**1**) and *S,S'*-(naphthalen-1,8-diyl)bis(2-methoxybenzaldehyde) (**2**) (Figure 1). The experimental results were rationalized by evaluating individually each energetic contribution for ΔG_m^\ddagger : (1) the parallel-displaced intramolecular aromatic interaction in the ground state, evaluated on the basis of our previous experimental results;⁴ (2) the “T-shaped-like” intramolecular aromatic interaction in the transition state, evaluated by computational ab initio calculations; and (3) the

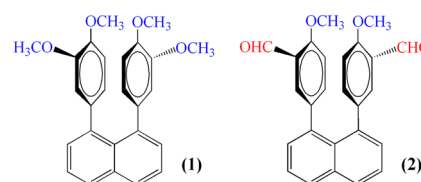


Figure 1. The two 1,8-diarylnaphthalenes studied herein.

specific solvation interactions both in the ground and transition states, evaluated by computational ab initio calculations.

The dynamic ^1H NMR results with respect to ΔG_m^\ddagger for the barrier to internal rotation about the aryl-naphthyl bond in **1** and **2** are summarized in Table 1. A mean value for ΔG_m^\ddagger , at $T = 298\text{ K}$, was considered, since the dependency on T within the

Table 1. Standard Molar Gibbs Energies of Activation, ΔG_m^\ddagger , at $T = 298\text{ K}^a$

compound		ΔG_m^\ddagger ($\text{kJ}\cdot\text{mol}^{-1}$)		
		CDCl_3	CCl_4^b	$\text{THF}-d_8$
1	<i>syn</i> → <i>anti</i>	64.3 ± 0.4	66.1 ± 0.3	64.1 ± 0.2
	<i>anti</i> → <i>syn</i>	66.3 ± 0.4	67.8 ± 0.3	65.0 ± 0.2
2	<i>syn</i> → <i>anti</i>	65.9 ± 0.2		66.3 ± 0.2
	<i>anti</i> → <i>syn</i>	68.9 ± 0.2		68.8 ± 0.2

^awith respect to the aryl-naphthyl barriers to internal rotation in the compounds studied, obtained by dynamic ^1H NMR in the selected solvents. ^b ΔG_m^\ddagger in CCl_4 could not be measured for **2** due to solubility issues.

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experimental range (271–323 K) was found to be negligible for all cases. 2D NOESY experiments in CDCl_3 allowed differentiating between the *syn* and *anti* conformers of the compounds. The results suggest that the *anti* conformer is favored in a ratio of about 7:3 in **1** and 8:2 in **2**. The prevalence of the *anti* conformer was also verified for the other solvents in roughly the same molar ratio: 6:4 (**1**) and 7:3 (**2**) in $\text{THF-}d_8$ and 7:3 (**1**) in CCl_4 .

These results follow the rationale proposed by Cozzi and co-workers for similar substituted 1,8-diarylnaphthalenes,^{1–3} with the compound presenting more electron-donating groups ($-\text{OCH}_3$) showing the smaller $\Delta G_m^{0\ddagger}$. According to Cozzi this happens because greater electron donation to the ring increases the intramolecular electrostatic $\pi\cdots\pi$ repulsions and hence destabilizes the ground state.^{1–3} Nevertheless, as shown in our previous work, the gas phase intramolecular interaction in the ground state is more significantly enhanced by $-\text{OCH}_3$ substitution than by $-\text{CHO}$,⁴ thus contradicting Cozzi's argument. Since aryl-naphthyl conjugation is practically absent in 1-arylnaphthalenes,⁴ the homodesmotic reaction presented in Figure 2 is a good way of directly comparing the relative

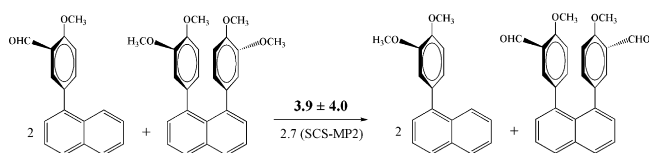


Figure 2. Gas phase homodesmotic reaction comparing the relative ground state stabilities of the compounds studied. Experimental, at $T = 298.15$ K (in bold) and SCS-MP2/cc-pVDZ values in kJ mol^{-1} .

ground state stabilities between **1** and **2** (experimental values of $\Delta_r H_m^0(\text{g})$, at $T = 298.15$ K, for all compounds were taken from ref 4). Both theoretical and experimental results indicate that the scenario of $-\text{CHO}$ leading to stronger intramolecular $\pi\cdots\pi$ interactions relative to $-\text{OCH}_3$ is highly unlikely.⁴ Generally, $\Delta_r S_m^0(\text{g})$ for a homodesmotic reaction is negligible compared to $\Delta_r H_m^0(\text{g})$, and particularly for the reaction presented in Figure 2 we may consider $\Delta_r H_m^0(\text{g}) \approx \Delta_r G_m^0(\text{g})$. These results clearly indicate that the observed decrease in $\Delta G_m^{0\ddagger}$ with the stronger electron-donating power of the substituents cannot be ascribed to the destabilization of the ground state (ignoring solvation). As it was shown,⁴ the $-\text{CHO}$ group has the effect of weakening the parallel displaced aromatic interaction in the ground state relative to the electron-donating $-\text{OCH}_3$ substituent, due mainly to its lower capability of enhancing dispersive interactions between the two aryl rings.

To explain the lower $\Delta G_m^{0\ddagger}$ observed for **1** in CDCl_3 and THF, other interactions must be considered as well, namely, the T-shaped aromatic interaction that can be established in the transition state and specific interactions with the solvent both in the ground and transition states. Figure 3 depicts the different interactions that can be considered as major contributions for $\Delta G_m^{0\ddagger}$ in 1,8-diarylnaphthalenes.

The influence of substituents in the transition state is better rationalized in terms of the T-shaped structure of the benzene dimer. The importance of considering aromatic T-shaped interactions in the transition state for explaining the trends in $\Delta G_m^{0\ddagger}$ has also been pointed out before by Sinnokrot and Sherrill.⁶ As observed by various authors, substituent effects on this structure are more related with their electron-donating or -withdrawing capabilities.^{5,6,8} The general consensus is that T-

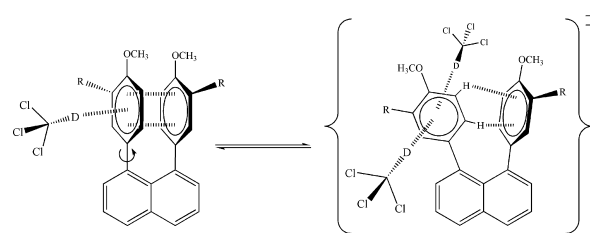


Figure 3. Possible interactions in the ground and transition states of 1,8-diarylnaphthalenes in CDCl_3 ; for the ones studied herein $R = \text{OCH}_3$ (**1**), CHO (**2**). For THF and CCl_4 analogous pictures can be drawn.

shaped aromatic interactions are enhanced by those changes that lead to increased δ^- of the aromatic π system or increased δ^+ of the interacting H atom. Therefore electron-withdrawing groups, EWGs, in the H-acceptor species weaken the interaction, while in the H-donor species they strengthen it. Electron-donating groups, EDGs, show the opposite trend. In regard to the role of the solvent it is well-known that chloroform establishes significant $\text{C-H}\cdots\pi$ interactions with aromatics.^{9–13} The general picture that emerges from those studies is that EDGs in benzene enhance the $\text{C-H}\cdots\pi$ interaction, since they make the aromatic system more electron-rich and thus increase the electrostatic interaction with the δ^+ hydrogen of the H-donor species. In the transition state the two π faces of the rotating ring are able to interact with the solvent, while in the ground state only one π face is available. Hence, solvation should stabilize more significantly the transition state of **1** relative to its ground state and contribute to a decrease of $\Delta G_m^{0\ddagger}$ relative to that of **2**. This reasoning is supported by the fact that for **1** $\Delta G_m^{0\ddagger}$ increases in CCl_4 , a solvent that cannot establish $\text{C-H}\cdots\pi$ interactions and thus is less able to stabilize the transition state relative to the ground state. However, in $\text{THF-}d_8$ the $\Delta G_m^{0\ddagger}$ values are very similar to those observed in CDCl_3 , the main difference arising due to the smaller energetic preference for the *anti* conformer in THF. This is consistent with the present picture if the $\text{aryl}\cdots\text{THF}$ interactions are similar in strength to the $\text{aryl}\cdots\text{CDCl}_3$ ones. As it will be shown this was in fact observed in our computational study. According to the rationale above, $\Delta G_m^{0\ddagger}$ for 1,8-diarylnaphthalenes can be schematically represented as depicted in Figure 4 and given by eq 1:

$$\Delta G_m^{0\ddagger} = K - \Delta G_{\text{solv}}(\text{GS}) - \Delta G_{\pi-\pi}(\text{GS}) + \Delta G_{\text{solv}}(\text{TS}) + \Delta G_{\pi-\pi}(\text{TS}) \quad (1)$$

where GS and TS stand for ground state and transition state, respectively, “solv” denotes the contributions from solvation, “ $\pi-\pi$ ” the contributions from the intramolecular aromatic interactions between the two aryl rings, and K represents a constant contribution for $\Delta G_m^{0\ddagger}$ in these systems, which is related with the intrinsic energetic cost for bond torsion.

The T-shaped aromatic interactions in the TS and the specific solvation interactions were evaluated by computing the interaction energy, ΔE_{int} for various representative 1:1 complexes, at the SCS-MP2/cc-pVDZ¹⁴ and CCSD(T)/CBS levels of theory. To test the accuracy of the SCS-MP2/cc-pVDZ method, a trial calculation was performed for the benzene/chloroform dimer, for which ΔE_{int} was found to be -21.8 kJ mol^{-1} , in perfect agreement with the reported experimental value of -21.8 kJ mol^{-1} .¹³ Counterpoise correction for BSSE was found to significantly underestimate

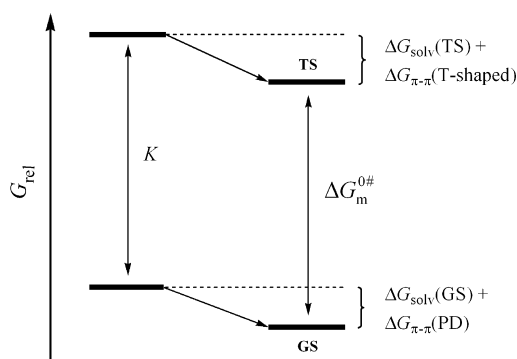


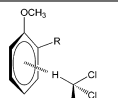
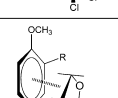
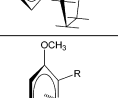
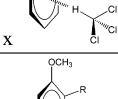
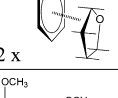
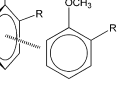
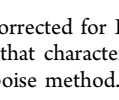


Figure 4. Relative Gibbs energy, G_{rel} , diagram showing each individual contribution for $\Delta G_m^{0\ddagger}$ in 1,8-diarylnaphthalenes.

the interaction, $\Delta E_{int}(BSSE) = -12.6 \text{ kJ mol}^{-1}$, and thus all SCS-MP2 calculations were carried out neglecting BSSE.¹⁵ Energy differences between similar complexes are expected to be well reproduced by SCS-MP2/cc-pVDZ.^{4,5} It was found that the MP2/cc-pVTZ method yields results in very nice agreement with the ones obtained by CCSD(T)/CBS (both were corrected for BSSE by the counterpoise method). Hence, for the T-shaped complexes that simulate the intramolecular interactions in the TS the full CCSD(T)/CBS calculations were not performed. Table 2 presents the results of ΔE_{int} for the relevant aromatic molecular complexes.

Energetic contributions arising from the bulk solvent were assumed as minor effects for differentiation in $\Delta G_m^{0\ddagger}$ and thus were not considered herein. As depicted in Table 2 all interactions are relatively strong and hence cannot be neglected. In the TS all interactions contribute to a more pronounced decrease of $\Delta G_m^{0\ddagger}$ for the compound bearing more electron-donating substituents, **1**. On the contrary, for the same

“electron-rich” compound, all interactions in the GS (including the parallel displaced aromatic interaction) contribute to a more pronounced increase of $\Delta G_m^{0\ddagger}$. This peculiar behavior arises because all aromatic interactions considered here are stronger for the compound bearing more EDGs. The trend in $\Delta G_m^{0\ddagger}$ in solution will therefore be ruled by the relative magnitude of these interactions. Taking into account the results published by Cozzi and co-workers,^{1–3} one may conclude that the overall contribution of interactions in the TS is more important than in the GS since $\Delta G_m^{0\ddagger}$ is lower for compounds presenting substituents with more electron-donating characteristics. Moreover, since the contributions in the GS and TS go in opposite directions and tend to dilute each other, the K term prevails, and this may explain the relative small differences observed among $\Delta G_m^{0\ddagger}$ in various 1,8-diarylnaphthalenes.^{1–3} As mentioned before, the magnitude of the aryl interactions with CHCl_3 and THF are very similar at the CCSD(T)/CBS level, thus supporting the results obtained by ^1H NMR. Furthermore, the difference in $\Delta G_m^{0\ddagger}$ between compounds **1** and **2** is slightly higher in THF than in CDCl_3 , which is nicely followed by the slightly higher differences in ΔE_{int} between $\text{R} = \text{OCH}_3$ and $\text{R} = \text{CHO}$, obtained for the aryl...THF interactions. However, one must be aware that the influence of solvation in $\Delta G_m^{0\ddagger}$ will be diluted to some extent due to (1) enthalpic/entropic compensation – stronger interactions lead to higher organization of solvent molecules around the solute and (2) molecular dynamics – TS species exist for very short times and the optimal rearrangement of solvent molecules around the newly formed molecular geometry may not be allowed, diminishing the stabilization brought about by solvation in the TS. Hence, these effects will contribute for leveling the differences in $\Delta G_m^{0\ddagger}$.

Table 2. Interaction Energies, ΔE_{int}^a

	Complex	$\Delta E_{int} / \text{kJ}\cdot\text{mol}^{-1}$		
		SCS-MP2/ cc-pVDZ	MP2/ cc-pVTZ *	CCSD(T)/ CBS *
Ground state	 R = OCH ₃	–26.9	–31.8	–31.5
	 R = CHO	–23.4	–28.0	–27.6
	 R = OCH ₃	–36.6	–29.2	–29.6
	 R = CHO	–28.3	–24.4	–25.2
Transition state	 R = OCH ₃	–53.8	–63.6	–63.0
	2 x  R = CHO	–46.8	–56.0	–55.2
	 R = OCH ₃	–73.2	–58.4	–59.2
	2 x  R = CHO	–56.6	–48.8	–50.4
	 R = OCH ₃	–29.9	–28.3	---
	R = CHO	–22.1	–22.6	---

^aCalculated at the SCS-MP2/cc-pVDZ (uncorrected for BSSE), MP2/cc-pVTZ (corrected for BSSE), and CCSD(T)/CBS (corrected for BSSE) levels of theory for the aromatic complexes that characterize the ground and transition states in the 1,8-diarylnaphthalenes studied. *Interaction energies corrected for BSSE by the counterpoise method.

Considering all independent contributions referred to above, the difference in $\Delta G_m^{0\ddagger}$, $\Delta\Delta G_m^{0\ddagger}$, observed between two 1,8-diarylnaphthalenes can be approximated as

$$\Delta\Delta G_m^{0\ddagger} \approx \Delta\Delta H(\text{GS}) + \Delta\Delta E(\text{TS}) + \Delta\Delta E(\text{solvation}) \quad (2)$$

where $\Delta\Delta H(\text{GS})$ denotes the energetic distinction between the two compounds in the GS, $\Delta\Delta E(\text{TS})$ the energetic distinction in the TS, and $\Delta\Delta E(\text{solvation})$ the energy difference brought about by solvation in the GS and TS. On dealing with relative quantities the entropic contributions for $\Delta\Delta G_m^{0\ddagger}$ can be neglected, since they tend to cancel out and are of relatively small magnitude compared to the enthalpic contributions in these systems. Although the contributions of solvation and intramolecular interactions in the GS can be directly evaluated, the T-shaped interaction in the TS is harder to characterize correctly, since the real orientation of the rings in the TS cannot be so easily reproduced by simple computational calculations. Although it is only approximate eq 2 correctly predicts a smaller $\Delta\Delta G_m^{0\ddagger}$ for **1** in both CDCl_3 and $\text{THF-}d_8$, as well as a slightly higher $\Delta\Delta G_m^{0\ddagger}$ in THF.

For the correct rationalization of internal rotation in aromatic systems the different types of aromatic interactions in the ground and transition states, including those related to solvation, must be considered. Recent studies on similar molecular systems do indicate that trends in $\Delta\Delta G_m^{0\ddagger}$ shall not be so simple as it was previously thought.^{16,17} In these systems the different molecular geometries change the interaction profiles with the solvent, thus altering and/or diluting/enhancing the direction of its influence. The reasoning presented herein shall be of great assistance for the elucidation of the factors ruling internal rotation. More generally, this work contributes for the understanding of how aromatic interactions influence dynamic molecular processes.

EXPERIMENTAL SECTION

The two compounds studied were synthesized and purified as previously reported.¹⁸ ^1H NMR spectra at various temperatures for **1** and **2** were acquired in CDCl_3 , CCl_4 , and $\text{THF-}d_8$. 2D NOESY spectra for **1** and **2** were acquired in CDCl_3 . The chemical shifts (δ) are reported in ppm values. The existence of *syn/anti* isomerism in **1** and **2** enables the measurement of rate constants, k , with respect to internal rotation, by dynamic ^1H NMR. For each temperature, T , line shape analysis was performed on the basis of the following equation:¹⁹

$$g(\nu) = N \frac{(1 + \tau\Delta_{1/2}^0)P + QR}{4\pi^2 P^2 + R^2} \quad (3)$$

where N is a normalization constant, and P , Q , and R are given by the equations

$$P = (0.25\Delta_{1/2}^0 - \nu^2 + 0.25(\Delta\nu^0)^2)\tau + \frac{\Delta_{1/2}^0}{4\pi} \quad (4)$$

$$Q = (-\nu - 0.5(p_{\text{syn}} - p_{\text{anti}})\Delta\nu^0)\tau \quad (5)$$

$$R = 0.5(p_{\text{syn}} - p_{\text{anti}})\Delta\nu^0 - \nu(1 + 2\pi\tau\Delta_{1/2}^0) \quad (6)$$

where τ is the average lifetime, ν is the variable frequency (in Hz), p_{syn} and p_{anti} are the equilibrium populations of the two conformers, and $\Delta_{1/2}^0$ and $\Delta\nu^0$ are, respectively, the width at half height and peak separation in the absence of exchange. The $-\text{OCH}_3$ protons of **1** and the $-\text{OCH}_3$ and $-\text{CHO}$ protons of **2** have distinct chemical shifts in the *syn* and *anti* isomers and are thus the best choices for following the temperature-dependent spectral changes. The value of τ for each T is obtained by fitting eq 3 to the observed spectrum by the least-squares

method. The rate constants, k , are obtained by using the relation $k(T) = 1/\tau(T)$. For each T the barrier to internal rotation, $\Delta G_m^{0\ddagger}$, is then calculated according to the Eyring equation:¹⁹

$$\Delta G_m^{0\ddagger} = RT \left[23.76 - \ln\left(\frac{k}{T}\right) \right] \quad (7)$$

where R is the gas constant and k represents the rate constants relative to the *syn/anti* interconversions in the compounds studied.

All theoretical calculations were performed using the Gaussian 03 software package.²⁰ The full geometry optimizations of isolated monomers and aryl...aryl, aryl... CHCl_3 , and aryl...THF dimers were carried out at the MP2/cc-pVDZ level of theory without symmetry restrictions. The spin-component-scaled MP2 approach (SCS-MP2)¹⁴ using the cc-pVDZ basis set was used for the calculation of BSSE uncorrected interaction energies. Interaction energies corrected for BSSE by the counterpoise method¹⁵ were calculated at the CCSD(T)/CBS level of theory (CBS = Complete Basis-Set). Single point counterpoise calculations were performed on the MP2/cc-pVDZ optimized geometries of each dimer at the MP2 level using the Dunning's correlation consistent basis sets (cc-pVXZ, where X = D, T, Q)^{21,22} and at the CCSD(T)/cc-pVDZ level. Extrapolation to the MP2 interaction energies at the basis-set limit, $\Delta E_{\text{int}}(\text{MP2/CBS})$, was performed as suggested by Feller,²³ fitting the calculated interaction energies, ΔE_{int} , to the equation $\Delta E_{\text{int}} = \Delta E_{\text{int}}(\text{MP2/CBS}) + a \exp(-bX)$, where $X = 2$ for cc-pVDZ, 3 for cc-pVTZ, and 4 for cc-pVQZ, and $\Delta E_{\text{int}}(\text{MP2/CBS})$, a and b are the fitting parameters.^{10,24} The CCSD(T)/CBS interaction energies were then calculated according to the equation $\Delta E_{\text{int}}(\text{CCSD(T)/CBS}) = \Delta E_{\text{int}}(\text{MP2/CBS}) + \{\Delta E_{\text{int}}(\text{CCSD(T)/cc-pVDZ}) - \Delta E_{\text{int}}(\text{MP2/cc-pVDZ})\}$. In the computational calculations CHCl_3 was used to model CDCl_3 and THF to model $\text{THF-}d_8$.

The detailed experimental and computational results are available as Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Detailed dynamic ^1H NMR, NOESY, and computational results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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