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Hindered rotational barriers in conjugated donor – acceptor substituted systems: calculations vs. experiments

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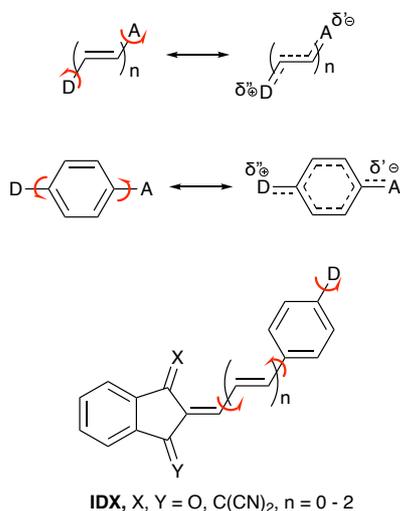
Quantum mechanical calculations of barriers to rotation within push-pull π -conjugated molecules involving strong electron donors (D) and acceptors (A) using the generally accepted approach fail to reproduce the experimental barriers determined by temperature-dependent NMR spectra. On the examples of seven derivatives of this type with substituents of varying electron donating and accepting strength, we find that determination of one of the rotational barriers, for instance, that of the acceptor substituent, requires not only the energy calculation of the respective transition state of this substituent, but also the transition state of the donor and the transition state involving both donor and acceptor substituents. Calculations of the rotation barriers using B3LYP and APFD functionals considering three transition states produce the results with mean absolute deviations from experimental 10 barriers of 0.28 – 0.19 kcal/mol depending on the basis set.

Introduction

Conjugated electron donor – acceptor substituted molecules, also known as push-pull π -conjugated molecules, represent an important class of organic compounds owing to the intramolecular through-bond charge transfer phenomenon giving rise to a variety of specific and practically useful properties. Thus, these derivatives are used as synthetic dyes

with light absorption in visible and NIR ranges, as active components of photochromic materials, nonlinear absorbing materials, organic light emitting diodes, sensors, and many other applications.¹

The properties of push-pull π -conjugated molecules depend on the electron donor (D), electron acceptor (A) strength and the ability of the conjugating bridge to participate in intramolecular charge transfer, in other words, on the contribution of the charge-separated mesomeric form into the electronic structure of such molecules, as shown in Scheme 1 for polyene systems and those involving an aromatic ring. Enhanced interaction between the D and A moieties gives rise to increasing molecular dipole moments, red shifts of the longest wavelength absorption band and, in particular, progressively shortening the D-bridge and A-bridge bonds. Indeed, if the D – A interaction is weak or not existent, the bonds D-bridge and A-bridge are essentially single and, in the absence of steric hindrance, allow almost unrestricted rotation of both the D and A moieties with respect to the molecular plane. In this case the molecular properties are mostly defined by the neutral mesomeric form, which contribution is close to unity. The increasing D – A interaction hinders the rotation and, in the case of considerable charge transfer, the contribution of the charge-separated mesomeric form is predominant, the barriers to rotation over the double bonds are high. The degree of charge transfer δ' toward the A moiety from the bridge and the D moiety is, in general, is not the same as the degree of charge transfer δ'' from the D moiety. The both deltas depend on the properties of D, A and the bridge, the latter compensates the charge difference between δ' and δ'' . The influence of the rotating and frozen D and A moieties on the NMR signal shapes is considerable and this feature makes variable-temperature (dynamic NMR, D-NMR) technique indispensable for determining the rotation barriers of the both D and A moieties



Scheme 1. Chemical structures of the push-pull derivatives with rotating electron donating D and accepting A substituents.

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in the range of about 4.5 – 23 kcal/mol, owing to the limitations of the S-NMR technique.²

To date, the barriers to internal rotation about the single bonds possessing partial double bond character (ΔG^\ddagger , activation barriers extrapolated to room temperature, ΔG_c^\ddagger , barriers at the coalescence temperature) have been determined using D-NMR with the precision of 0.15 – 0.5 kcal/mol for several organic compounds.^{2,3,4} A general notion is that the Density Functional Theory (DFT) based calculations reproduce the experimental barriers to rotation reasonably well⁴ and the calculation of the barrier to rotation of the acetyl group in *p*-dimethylaminoacetophenone is provided as one of the exercises in the last edition of the Gaussian software tutorial.⁵ However, in spite of the abundance of the experimental data on the barriers to rotation of the push-pull molecules,^{2,4,6} the calculations on these derivatives are mostly limited by relatively weak D and A couples (*p*-methoxy- and *p*-aminoacetophenones and benzaldehydes)^{7,8} and more complex tetrasubstituted push-pull ethylenes, for which the barrier to rotation was calculated for the elongated owing to the push-pull effect ethylene double bonds.^{9,10} To the best of our knowledge, no systematic studies in this important field have been undertaken. During our initial attempts to design new efficient chromophores for electro-optical applications, we used a series of known model compounds involving the 1,3-indandione accepting moiety (IDX in Scheme 1)^{11,12} and both ethylene and *p*-phenylene bridges, to determine the barriers to rotation using the D-NMR techniques. Photochromic conversions of a number of the IDX-type molecules^{13,14} also involve rotation over the partially double bonds, and correct estimation of the rotational barriers is important for designing effective photo-switchable molecules. The respective calculations using different DFT methods yielded, however, quite confusing results: the computed barriers for a number of derivatives severely overestimated the experimental values by about 1 – 3 kcal/mol and sometimes underestimated them by more than 1 kcal/mol. Whereas revealing a systematic trend in the deviation of the computed values from the experimental ones would be also acceptable, we failed to find any correlation between the derivative structures and the computational results and,

therefore, the utility of predictions on the properties of yet unknown compounds was doubtful.

Here we present our experimental and computational results on a series of simple push-pull derivatives **1** – **7** (Scheme 2) and propose an alternative approach for calculating the rotational barriers.

Experimental

All calculations were carried out using Gaussian 16 software.¹⁵ Geometry optimizations of the stationary structures were done using tight convergence criteria and Gaussian 16 defaults (in particular, integral=ultrafine). The relaxed potential energy surfaces (PES) for derivatives **3** and **4** were calculated by rotating the D and A substituents independently by 180°, step 5° (for **3**) and 90°, step 10° (for **4**) from the pre-optimized ground states for both molecules using opt=(modredundant, tight) keyword. The dihedral angle for rotating the dimethylamino group of **4** was determined as the angle between the two methyl groups and C3 and C5 carbon atoms of the benzene ring to avoid discontinuity of the surface. There was no difference in total electronic energies of the ground (GS) and transition states (TS) calculated for derivative **3** found by PES and calculated by Bery algorithm, this difference did not exceed 0.09 kcal/mol for **4**.

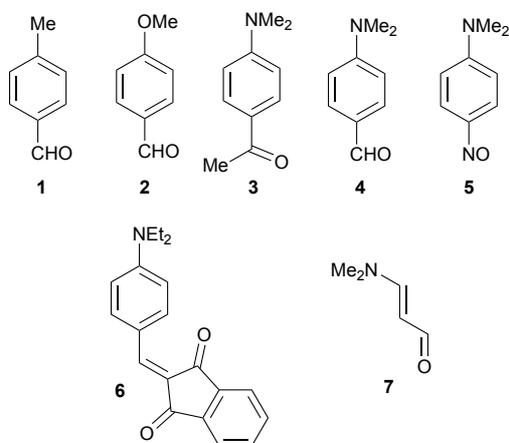
The transition state (TS) geometries and energies used for the barrier calculations were found using Bery algorithm. Harmonic frequency calculations at the same level verified achieving ground states (GS) (zero imaginary frequencies) and TS (one or two imaginary frequencies) and provided the estimates of the free energies *G*. All calculations were performed using the default self-consistent reaction field (SCRF) model. The highest barriers were selected in the cases when rotation of the substituents over 360° was found to involve two different minima or maxima for GS and TS (like in the case of *syn*- and *anti*- conformers of *p*-methoxybenzaldehyde **2**). We used MP2, DFT (B3LYP¹⁶, APFD¹⁷ and M062X¹⁸) and hybrid B2PLYPD¹⁹ theoretical levels with 6-311+G(2d,p), 6-311++G(2df,2p), aug-cc-pVDZ and aug-cc-pVTZ basis sets.

Variable temperature ¹H NMR spectra

Derivatives **5** and **7** were obtained from TCI Europe. Derivative **6** was prepared according to ref.²⁰ Variable temperature ¹H NMR spectra were recorded on the Bruker AMX-400 spectrometer at 400.1 MHz, in CD₂Cl₂ and toluene-d₈ in the temperature range 190-300 K for compounds **5** and **6**, and 280-320 K for compound **7**. The barriers to rotation were measured as the energy of activation at the coalescence temperature (*T_c*) for aromatic protons (derivatives **5** and **6**), and methyl groups (derivatives **5** and **7**). The rate constants of exchange *K_c* were obtained from equation:

$$K_c = \pi\Delta\nu/\sqrt{2}$$

and the barriers to rotation at the coalescence temperature *T_c* by substitution of the *K_c* values into modified Eyring equation³: $\Delta G^\ddagger = 4.57T_c\{9.97 + \log(T_c/\Delta\nu)\}$.



Scheme 2. Molecular structures of derivatives under investigation

Results and discussion

The series of push-pull derivatives **1** – **7**, selected for calculations, involves *p*-substituted benzenes **1** – **5**, for which the data on the barriers to rotation are available from the published results. Derivative **6** is a parent compound for the IDX-type series of push-pull derivatives. Derivative **7** is a simplest push-pull conjugated molecule involving the same electron acceptor (HC(O)-) and donor (Me₂N-) as **4**, but linked by the ethene bridge. The calculations of the barriers to rotation over the C-A and C-D bonds (denoted further as B_A and B_D) were carried out in the same solvent used in D-NMR experiments, except those for derivative **1** and B_D barriers for derivatives **3** and **4**, for which toluene was used as the solvent. The frequency jobs were done at the coalescence or room temperatures, when the latter were available (Table 1). For comparison with the calculated values, we selected the available experimental data, while avoiding, wherever possible, those obtained in the solvent mixtures and polar solvents that can interact with the solute specifically. We also carried out the experiments on derivatives **5** – **7** to perform the full line shape analysis. In addition, the considerable degree of charge transfer in both **5** and, especially, **7** can make these compound more sensitive to the solvent polarity. The two available experimental barrier B_D values for **7** ($\Delta G_c^\ddagger = 14.68$ kcal/mol at 291.9 K²¹ in 1,1-dichloroethylene and 15.6 kcal/mol at 305 K²² in dibromomethane) confirm that the difference in barriers in different solvents can be considerable.

Table 1. Experimental barriers to rotation over the C-A and C-D bonds and conditions for derivatives **1** – **7**.

Comp	ΔG^\ddagger (kcal/mol)	Temp (K)	Solvent	Ref.
1	8.5	165.5 ^a	CH ₂ Cl ₂ / CH ₂ =CHCl	23
2	9.4	198 ^a	toluene _{dB}	24
3	8.5 7.2 ^b	181 ^a 133	toluene _{dB} toluene _{dB} / CH ₂ =CHCl	24 25
4	10.7 7.8 ^b	205-212.5 ^a 133	CD ₂ Cl ₂ toluene _{dB} / CH ₂ =CHCl	23, 26 25
5	12.3 9.9 ^b	298 201 ^a	toluene _{dB} toluene _{dB}	This work - " -
6	10.2	298	CD ₂ Cl ₂	- " -
7	15.0 ^b	298	toluene _{dB}	- " -

^a Coalescence temperature.

^b C-D bond.

Our initial calculations of the barriers (B) were done according to the protocol described on the example of derivative **3**,⁵

assuming $\Delta G^\ddagger = B = G_{TS} - G_{GS}$. This approach is referred in the following discussion as the one-state approximation. Thus, it

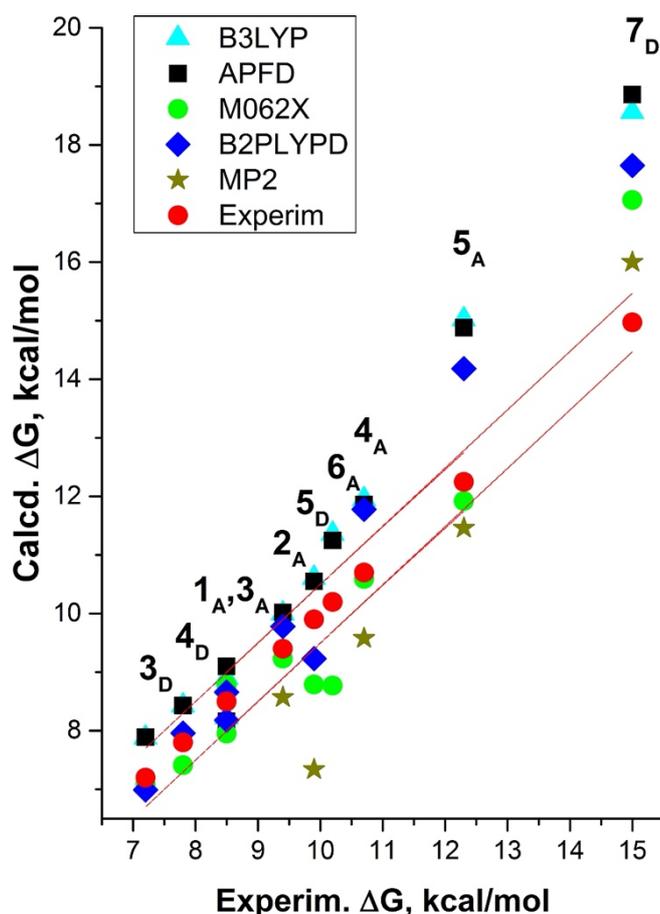


Figure 1. Calculated (6-311++G(2df,2p) basis set) $\Delta G_{A(D)}^\ddagger = B_{A(D)} = G_{TS} - G_{GS}$ (one-state approximation) vs. experimental $\Delta G_{A(D)}^\ddagger$ (red circles, +/- 0.5 kcal/mol denoted by dashed red lines).

does not take into account the interaction between already rotating substituent and yet frozen substituent occurring under the experimental conditions of determining the barrier to rotation of the latter. Although in the recent review⁴ it was noted that the barriers computed at the DFT level using the total energies without the ZPE correction provide usually good fit with the experimental ΔG^\ddagger values, we preferred to introduce the thermodynamic corrections and compare the free energies, as the above notion might be not valid in the case of push-pull derivatives. We employed the popular B3LYP functional recommended in⁴, APFD used in book⁵ and M062X functional parametrized to reproduce, in particular, the thermodynamic and kinetic data and frequently used for calculations of the push-pull derivatives^{8,27-30}. Although the MP2 and B2PLYPD levels are not practical for computations on larger molecular systems, we also used both for a number of molecules to see if these methods provide better fit with the experiment.

Quantum mechanical calculations using one-state approximation

For comparison of the computational results with the experimental, we assume that the deviation of +/- 0.5 kcal/mol is acceptable considering that the experiments were done using different techniques in different laboratories and, in some cases in a mixture of solvents. A summary of the results on derivatives **1** – **7** using the 6-311++G(2df,2p) basis set is presented in Figure 1. Further increase of the basis set did not noticeably change the resulting barrier energies.

The calculated B_A and B_D values using all methods give satisfactory results only when the experimental ΔG^\ddagger are below 9.5 kcal/mol. For the derivatives with higher experimental barriers, both B3LYP and APFD functionals give similar numbers overestimating the experimental values progressively up to 3 – 3.5 kcal/mol for derivative **7**, not depending considerably on the basis set (see Tables 1S – 2S and Figures 1S, 2S, ESI). Similar results were obtained by the hybrid B2PLYPD method, although the overestimation for **7** is smaller (about 2.7 kcal/mol, Figure 1). A very good fit is observed in the case of the M062X functional for derivatives **1** – **4** and **5** (B_A). At the same time, this model chemistry *underestimates* the barriers for **5** (B_D) and **6** (by 1.4 kcal/mol) and *overestimates* the barrier for **7** (by 2.1 kcal/mol). For the whole set of compounds, the mean absolute deviations from experiment (MAD) calculated for 10 barriers to rotation (derivatives **1** – **7**) using B3LYP and APFD do not depend considerably on the basis set and are 0.9 – 0.8 and 0.55 kcal/mol for M062X. MP2 barriers are lower than experimental for all compounds and higher for **7**.

The systematic overestimation of the rotational barriers by the well-established methods (B3LYP, APFD and B2PLYPD) indicates that the very approach equating the barrier energy to the difference between the energies of a single transition state and ground states ($\Delta G^\ddagger = G_{TS} - G_{GS}$) is too simplistic and should not be applied in the cases of strong interaction between the D and A moieties within push-pull conjugated molecules. In our opinion, at least three transition states should be considered for the molecular systems involving two conjugated rotating moieties interacting with each other through the conjugating bridge. These states, TS_A , TS_D and TS_{DA} , are considered within the proposed approach referred further as three-state approximation

Quantum mechanical calculations using three-state approximation

Let us consider the influence of the rotating moiety over the bond possessing the lowest barrier to rotation on the examples of derivatives **2** and **4**, for which, according to both experiments and calculations, the lowest barriers to rotation correspond to the D group. The calculated barrier energies are schematically presented in Figure 2. Under the condition of rotating D substituents, D-bridge-A conjugation (GS \rightarrow TS_D) is broken, whereas the A substituent remains conjugated with the bridge. Under the conditions A substituent is rotating, the D substituents are already rotating. Therefore, for A substituent

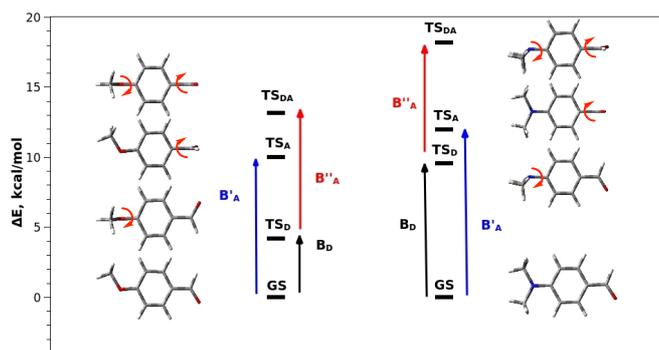


Figure 2. Calculated transition state energies TS and two extreme barriers to rotation B'_A and B''_A calculated for **2** and **4**.

there are two extreme cases with regards to the rotating D substituents: at the moment when the D substituents are passing the ground state conformation (GS \rightarrow TS_A) and at the

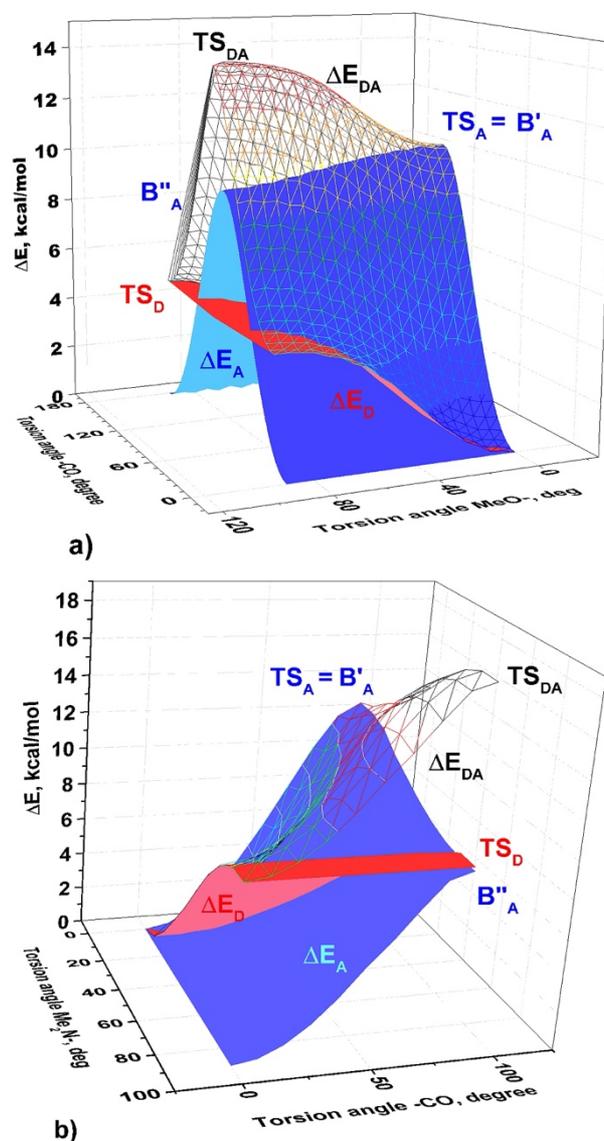


Figure 3. Total relative electronic energy surface ΔE_{tot} for derivative **2** (a) and **4** (b) (mesh surfaces) and their components ΔE_D (red surfaces) and ΔE_A (blue surfaces) (B3LYP/aug-cc-pVDZ model chemistry)

moment when the dihedral angles between the D substituents and the bridge are close to 90° ($TS_D \rightarrow TS_{DA}$). Obviously, the barriers calculated using the one-state approximation correspond to the $GS \rightarrow TS_A$ case, denoted as B'_A , and the $TS_D \rightarrow TS_{DA}$ case, denoted as B''_A in Figure 2 remains completely neglected in the frame of the one-state approximation. The calculated B'_A values include thus an overhead: the energy of breaking conjugation of a push-pull molecule, conjugation in which is already broken by rotating D substituent, and the stronger is the conjugation, the larger is the overhead.

The total relative electronic energy scans (ΔE_{tot} in kcal/mol, $E_{GS} = 0$) for **2** and **4** shown in Figure 3a,b provide more details. Expectedly, the minima on the ΔE_{tot} surfaces for both compounds correspond to the conformation in which the D substituents are conjugated to the *p*-phenylene bridge. These saddle points ($\Delta E_{tot} = TS_A$) for **2** and **4** represent the barriers to rotation traditionally determined in the frame of the one-state approximation (rotation of the $-C=O$ group of the charge-separated mesomeric form). Progressive rotation of D substituents gives rise to the increase in ΔE_{tot} energy and the maxima on the $\Delta E_{tot} = TS_{DA}$ surfaces correspond to the orthogonal conformation of both D and A substituents (rotation of the neutral non-conjugated mesomeric form). Rotation of D substituents while keeping the accepting $-C=O$ group conjugated to the bridge, provides the surfaces corresponding to ΔE_D (red surfaces) and the difference of $\Delta E_{tot} - \Delta E_D$ presents the variations in ΔE_A (blue surfaces). The minima on the ΔE_A surfaces coincide with the maxima on the $\Delta E_{tot} = TS_{DA}$ and $\Delta E_D = TS_D$ surfaces for both derivatives **2** and **4**. The minimum on ΔE_A surface of **4** is deeper than ΔE_A of **2**. Further analysis of both surfaces can be simplified by considering the 2-D projections of the surface maxima ΔE_{tot} and ΔE_A vs. variation at the rotation angles of D group from 0° to 90° (Figure 4).

The effect of rotation of the $-OMe$ group (D, the lowest barrier) in derivative **2** is as follows: as the dihedral angle of the $-OMe$ group goes from nearly 0° (conjugated D, as in polar mesomeric form) to 90° (non-conjugated D, as in neutral mesomeric form), the total energy increases from TS_A to TS_{DA} (black curve) and the TS_A barrier decreases from B'_A to B''_A , from 10.55 to 9.45 kcal/mol (Figure 4a). The experimentally measured barrier to rotation B_A should then fall in between these two extremes, with its exact position determined by the relative contributions of each of the two extreme conformations of D.

Indeed, assuming $B_A = (B'_A + B''_A)/2$ considerably improves the calculated barriers for the whole set of derivatives. This simple assumption can be refined taking into account that the degree of charge transfer between D and A (Scheme 1) can be within the limits of 0 (no charge transfer) and 1 (full charge transfer). Let us designate as δ_A the ratio TS_D/TS_{DA} (in terms of Fig. 2) characterizing the contribution of the polar mesomeric form into the molecular electronic structure (in terms of Scheme 1, full possible charge transfer to A in a conjugated conformation), corresponding to the calculated A rotation barrier B'_A . Then the contribution of the non-conjugated form (free rotation, no charge transfer) can be expressed as $(1-\delta_A)$ with the corresponding barrier B''_A , and the total barrier value as:

$$B_A = \delta_A \cdot B'_A + (1-\delta_A) \cdot B''_A \quad (1)$$

The calculated δ_A value for derivative **2** is 0.33 (using the non ZPE-corrected electronic energies) and, therefore, B_A can be calculated as $0.33B'_A + 0.67B''_A = 9.81$ kcal/mol (the green horizontal line in Figure 4a). Using the respective values of free energy (Table 4S, ESI), we arrive to $B_A = \Delta G^\ddagger_c = 9.28$ kcal/mol in a good agreement with experiment (Table 1). It is worth of noting that the calculated values δ_A are almost independent of the tested model chemistries, using free energies, we obtain δ_A of 0.31 – 0.32 by all methods including M062X and MP2.

The respective 2-D projection for derivative **4** (Figure 4b) shows similar features with steeper barrier curves reflecting stronger electron donating ability of the $-NMe_2$ group. The main difference from derivative **2** is that the barrier to rotation of the D substituent is higher than B''_A so that we cannot state now

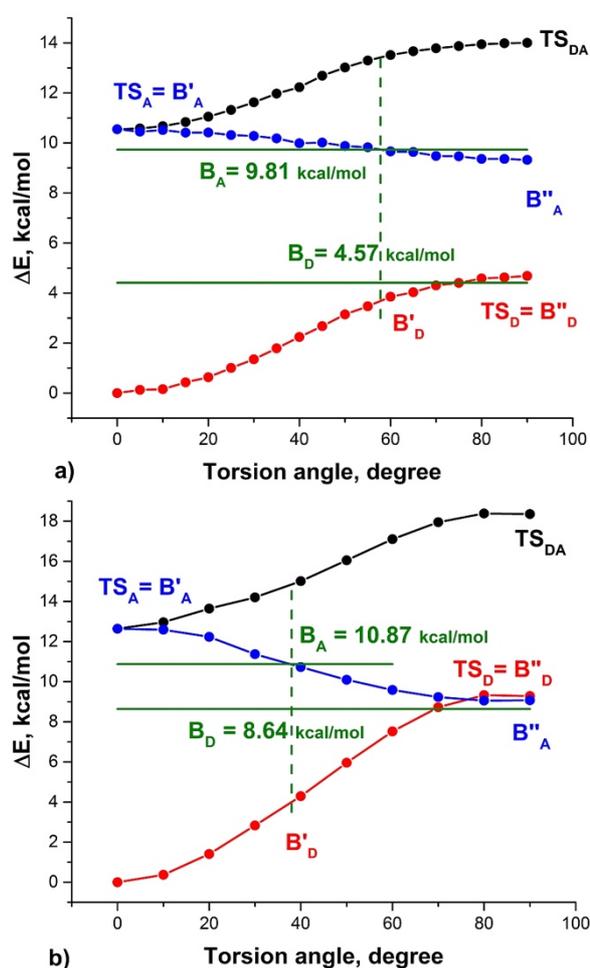


Figure 4. 2-D projections of the surface maxima variation of ΔE_{tot} (black curves), ΔE_A (blue curves) upon rotation of D substituents (red curves) from Figure 3: a) derivative **2**, b) derivative **4**. (B3LYP/aug-cc-pVDZ model chemistry).

that its rotation is independent of rotation of A substituent in the range of the dihedral angles close to TS_D . Therefore, B_D is not equal to TS_D , as it is for derivative **2** and we need to introduce B'_D and B''_D components and find their relative contributions in analogy to B_A .

Using the same approach as described above, we determine δ_A as $TS_D/TS_{DA} = 0.51$ (from ΔE calculations) and 0.52 (from ΔG calculation), the latter value varies between 0.51 and 0.53, except for MP2 ($\delta_A = 0.45$). Using $B'_A = 12.54$ and $B''_A = 7.55$ kcal/mol, we arrive to $B_A = 10.87$ kcal/mol (shown as the green horizontal line in Figure 4b). The maximal contribution of the polar structure B'_D can be determined by first applying $\delta_A = 0.51$ (green dashed vertical line in Figure 4b), since ΔE_D is higher than B''_A only in the vicinity of TS_D and δ_D cannot be larger than δ_A . The contribution of the neutral free rotating form reaches unity at TS_D and, therefore, $0.51 < \delta_D < 1$. Defining δ_D as TS_A/TS_{DA} , we obtain $\delta_D = 0.59^{\ddagger}$ and $B_D = 0.59B'_D + 0.41B''_D = 8.64$ kcal/mol. Using the free energy calculation results, $B_A = 10.27$ kcal/mol at 208 K and $B_D = 7.52$ kcal/mol at 133 K (B3LYP/aug-cc-pVDZ model chemistry). A larger basis set improves the both calculated barriers: $B_A = 10.36$ kcal/mol at 208 K and $B_D = 7.83$ kcal/mol at 133 K (B3LYP/6-311++G(2df,2p) model chemistry), but the values of δ are again practically independent of the calculation levels.

The above scheme is applicable also for derivative **2**, although the TS_D for this compound is lower than TS_A at any dihedral angle of the -OMe group as shown in Figure 4a. In this case, according to this scheme, the calculated $TS_D = 4.68$ and $B_D = 4.57$ kcal/mol, $\delta_D = 0.69$. For derivative **1** involving a weakest electron donor, $TS_D = 0.07$ and $B_D = 0.07$ kcal/mol, $\delta_D = 0.99$.

The proposed barriers estimation scheme eliminates the necessity of computing and analyzing full surfaces and requires only optimization of three transition states corresponding to two conjugated rotors. Using δ_A and δ_D also takes into account the degree of curvature of variations of ΔE_A and ΔE_D (see Figure 3S in ESI). It works well for derivatives **1**, **2**, **4**, **5** with $TS_D < TS_A$. For derivatives **6** and **7** with $TS_A < TS_D$, it works equally well, requiring just replacing the indices A for D in the expression (1). The general equation (2) used for calculating the higher barriers $TS_{A(D)}$ and (3) for the lower barriers $TS_{D(A)}$ are:

$$\delta_{A(D)} = TS_{D(A)}/TS_{DA}, B_{A(D)} = \delta_{A(D)}B'_{A(D)} + (1-\delta_{A(D)})B''_{A(D)} \quad (2)$$

$$\delta_{D(A)} = B_{A(D)}/TS_{DA}, B_{D(A)} = \delta_{D(A)}B'_{D(A)} + (1-\delta_{D(A)})B''_{D(A)} \quad (3)$$

The largest $\delta = 0.66$, corresponding to the largest contribution of the polar conjugated mesomeric form, was found for derivative **7**. For this derivative, $B'_D = 18.28$ and $B''_D = 10.05$ kcal/mol (from free energies at RT) affording $B_D = \Delta G^{\ddagger} = 14.96$ kcal/mol, in excellent agreement with the experiment.

Derivative **3**, however, is an exception. Since calculated using B3LYP and APFD functionals $B'_A \approx B'_D$ and $B''_A \approx B''_D \approx B''_D$ (Table 6S, ESI) selecting the lower barrier is hardly possible and we apply no correction and use the one-state approximation. This case will be discussed in detail in the next section.

Although this approach should be valid for estimating the barriers using total energies, ZPE-corrected energies and free energies, we find that using free energies provides the best fit with the D-NMR results (Figure 5). The barriers calculated using B3LYP and APFD functionals are very similar and gave MADs of 0.28 (6-311+G2d,p), 0.26 (aug-cc-pVDZ) and 0.19 kcal/mol (6-311++G(2df,2p)). M062X functional afforded MAD of 0.63 kcal/mol. For more details see Figures 4S and 5S, ESI.

Scope and limitations of three-state approximation

Actually, derivatives **2** – **7** involve more than two electronically interacting rotating groups: three for derivative **2** (Me-O, MeO-

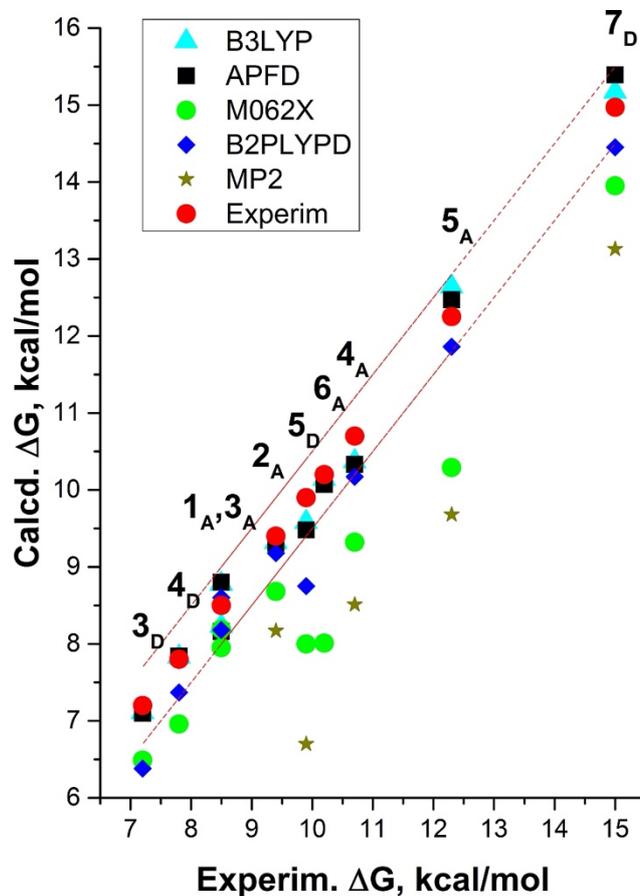


Figure 5. Calculated (6-311++G(2df,2p) basis set) $\Delta G^{\ddagger}_{A(D)} = B_{A(D)} \neq TS_{AD}$ (three-state approximation) vs. experimental $\Delta G^{\ddagger}_{A(D)}$ (red line) for derivatives **1** – **7**.

C and C-C(O)), five for **3** (two Me-N, Me₂N-C, Me-C(O) and MeCO-C), etc. Is it possible to neglect their influence and consider only three transition states for two rotors? The case of derivative **3** is instructive and deserves a more detailed analysis. The experimental barrier to rotation of the -C(O)CH₃ group in **3** is 8.5 kcal/mol at $T_c = 181$ K, lower than the -C(O)H barriers determined for **2** and **4** (9.4 and 10.7 kcal/mol, respectively, Table 1). As already mentioned, this molecule involves five rotating groups, of which two Me-N and Me-C(O) possess relatively low barriers to rotation of the Me group. Neglecting the influence of Me-N rotation is justified, since the NMR experiments showed that N,N-dimethyl-4-nitrosoaniline (**5**) and its *p*-mono-methylamino analog have practically the same barriers to rotation of the -N=O group (see the discussion in³² and references therein). The weak, if any, effect of replacing the Me- group by hydrogen at the amino group can be rationalized by the insignificant interaction of the weak electron donating Me group with the strong electron donating amino group (D->D-bridge-A vs. D-bridge-A). At the same time, the difference between the experimental barriers of the acetyl group in **3** and the carbonyl group in **4**, the molecules sharing the same bridge

and the D group, is relatively large: 2.2 kcal/mol. This strong effect can be rationalized by the stronger interaction of the Me group with the accepting carbonyl group weakening the accepting ability of the acetyl group (D->A-bridge-D vs. A-bridge-D).

Calculations of the barriers for derivative **3** were carried out using B3LYP and APFD functionals (6-311++G(2df,2p) basis set) in toluene, the frequency at 181 K for TS_A and 133 K for TS_D providing practically the same TS_A and TS_D at the coalescence temperature of the acetyl group signal (181K). The differences between TS_A and TS_D amount to 0.07 kcal/mol (B3LYP) and 0.03 kcal/mol (APFD), the three-state approximation cannot formally be used and the calculated B_A = TS_A are 8.23 kcal/mol (B3LYP) and 8.16 kcal/mol (APFD) were accepted (Table 6S, ESI). A larger difference between TS_A and TS_D resulted from calculations of the barrier for the Me₂N- group at 133 K and using the three-state approximation scheme provided B_D = 7.1 by both functionals (Table 10S, ESI).

The question of what difference between TS_A and TS_D is meaningful for selecting between the one- and three-state approximation persists as calculations on different model chemistries produce different results. The answer may be obtained from calculating the respective surface and analyzing the areas where TS_A and TS_D overlap. However, the confusing results may stem from the neglect of the low barriers such as the barrier of the Me- groups in the Me-C(O) group. A straightforward way to solve the problem with derivative **3** is to consider this molecule as a molecule involving three rotors. We have successfully tested the m-state approximation for derivatives IDX, n = 1, 2 (Scheme 1) and will report the results elsewhere. However, the number of states 'm' to be considered rapidly increases with the increasing number of rotors in the molecule making such calculations quite expensive. Therefore, we applied the three-state approximation after fixing the Me group in its rotational transition state TS_{Me} to obtain the initial models for transition states TS_D, TS_A and TS_{DA} and re-optimizing each of the state to saddle points of orders 2 and 3. The TS_A

increased by 1.3 – 1.7 kcal/mol and, applying the three-state approximation, we obtained the barriers B_A practically the same as the uncorrected values B_A = TS_A produced by the one-state approximation (Figure 6) (Table 8S, ESI). We conclude that the three-state approximation is not very sensitive to rotation within the substituents when the barriers are relatively low, probably as a result of error cancellations.

Since we assumed that coefficients δ and (1 - δ) estimate the contributions of the polar and the neutral mesomeric forms into the average conformation of the push-pull derivatives involving the rotating D and A substituents, these coefficients can be useful for estimating dipole moments of such molecules as well. The experimental dipole moments were determined at room temperature above the coalescence temperatures of derivatives **1**, **2**, **4** and **5**, *i.e.*, under conditions when both D and A substituents are rotating. Indeed, we find that the dipole moments calculated (B3LYP/6-311++G(2df,2p) in toluene using a rough approximation neglecting contribution of D substituents: $\mu = \mu_{GS} \delta_A + \mu_{TSDA} (1 - \delta_A)$. provides good fit with the experimental values (Table 2).

Calculations of dipole moments using the three-state approximation impose stricter requirements on the basis sets. This issue will be discussed in detail elsewhere.

Table 2. Dipole moments (in D) calculated for the GS (μ_{1S}) and using three-state approximation (μ_{3S}), B3LYP/6-311++G(2df,2p), in toluene and experimental dipole moments in benzene at 25°C.

Compd	μ_{1S}	μ_{3S}	μ_{exper}	Ref.
1	4.77	3.77	3.33	33, p. 286
2	5.56	4.06	3.88	-"- p. 287
4	8.11	5.76	5.58	-"-p. 331
5	9.92	6.75	6.9	-"- p. 294

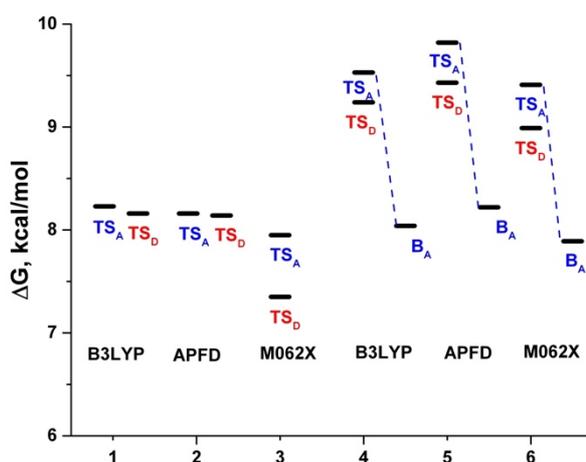


Figure 6. 1 – 3: Barriers to rotation TS_A= B_A of the acetyl group Me-CO- calculated for **3** using the one-state approximation; 4 – 6: barriers to rotation B_A calculated for **3**, involving the Me group of Me-C(O) in rotational transition state TS_{Me}, using the three-state approximation.

Conclusions

Calculations of barriers to hindered rotation that stem from charge transfer interaction between electron donating and electron accepting substituents *via* the conjugating bridge (D - bridge - A) necessitate consideration of at least three transition states: TS_D, TS_A and TS_{DA}, especially when the barriers exceed 9.5 kcal/mol. Using the three-state approximation enables predicting the barriers to rotation and electronic structures of yet unknown molecular systems involving strong electron donors and acceptors. The degree of intramolecular charge transfer can be evaluated by using δ and (1- δ) coefficients, which relevance is corroborated by the reasonable prediction of the dipole moments of push-pull derivatives.

Although we found that using M062X functional can give good results for 1,4-substituted benzene derivatives using the one-state approximation, it fails in other cases. The failures can stem from the special parametrization of this functional.¹⁸ Both B3LYP and APFD functionals gave very good fit for derivatives involving both moderate and large degree of charge transfer

using the three-state approximation. Using aug-cc-pVDZ basis set with these functionals can be recommended for predicting the barriers for rotation of large push-pull conjugated systems.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Note that if δ_A can be associated with δ' (Scheme 1), $(1-\delta_D)$ is the analog of δ'' when TS_D is the lower barrier; When TS_A is the lower barrier, δ_D is the analog of δ'' and $(1-\delta_A)$ corresponds to δ' .

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