

Luminescent Molecules Hot Paper

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Broadening the Horizon of the Bell–Evans–Polanyi Principle towards Optically Triggered Structure Planarization

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Abstract: Finding a relationship between kinetics and thermodynamics may be difficult. However, semi-empirical rules exist to compensate for this shortcoming, among which the Bell-Evans-Polanyi (B-E-P) principle is an example for reactions involving bond breakage and reformation. We expand the B-E-P principle to a new territory by probing photoinduced structure planarization (PISP) of a series of dibenz-[b,f]azepine derivatives incorporating bent-to-planar and rotation motion. The latter involves twisting of the partial double bond character, thereby inducing a barrier that is substituent dependent at the para N-phenyl position. The transition-state structure and frequency data satisfy and broaden the **B-E-P** principle to PISP reactions without bond rearrangement. Together with dual emissions during PISP, this makes possible harnessing of the kinetics/thermodynamics relationship and hence ratiometric luminescence properties for excited-state structural transformations.

Introduction

In chemistry, discovering the correlation between kinetics and thermodynamics is of paramount importance but is not feasible in general. Nevertheless, theories, rules or principles exist to describe the correlation between the kinetics and thermodynamics of certain reactions.^[1-5] One elegant example is Marcus electron transfer theory in the weak electronic coupling region,^[3,6] where the relationship between the kinetics and thermodynamics relevant to internal and external reorganization can be formulated. As for reactions involving bond breakage and reformation, finding the relationship is very difficult or perhaps impossible in most instances. In this regard, one long-standing chemical theory is the Bell–Evans–Polanyi (*B-E-P*) principle.^[7,8] In an A–B + $C \rightarrow A + B - C$ bond breakage-formation reaction, the *B***-E**-*P* principle states that if the position and frequency of the transition state along the reaction coordinate are approximately the same within a family of derivatives, then the activation energy, ΔE_a , of the reaction is proportional to the enthalpy of the reaction, ΔH , expressed as^[7]

$$\Delta E_{\rm a} = E_0 + \alpha \Delta H$$

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 the author(s) of this article can be found under: https://doi.org/10.1002/anie.202015274. where E_0 is the intercept, and α is a value characteristic of the transition state along the reaction coordinate, which should be in the range of $0 \le \alpha < 1$. These lead to the conclusion that a decrease in the reaction barrier should increase the reaction exothermicity. While the **B**-**E**-**P** principle has been applied to a number of reactions involving bond rearrangement,^[9-14] the fundamental issue of whether the reaction parameters, e.g., transition-state structure and reactive frequency, meet the criteria is often overlooked.

In vet another instance, upon excitation, changes in the electron density distribution are induced, where structure relaxation becomes a ubiquitous phenomenon. Interestingly, despite wide studies on photoinduced structural transformation,^[15-23] probing the kinetics/thermodynamics relationship is very rare. One example is the study on the structural profile for the dinuclear platinum(II) complexes in the triplet manifold, where the **B-E-P** principle was qualitatively cited.^[22] In this study, we aim to expand the *B***-***E***-***P* principle to a new class of photoinduced structure planarization (PISP),^[24-26] with no rearrangement of chemical bonds. To open up this new research direction, we designed and synthesized a series of seven-membered heterocyclic π -conjugated molecules based on the dibenzo[b,f]azepine (DBA) core, forming N-phenyl DBA derivatives denoted PDBAs (Figure 1a). This platform is reminiscent of heteropine systems, nonplanar seven-membered rings such as oxepins and thiepins, [27-32] where dibenz [b, f] oxepin exhibited a large Stokes-shifted emission that was proposed to result from structural planarization. Chemically, this process is driven by a gain in aromaticity in the excited state, which is known as Baird's rule.^[27,33-36] In comparison. PDBAs offer the obvious advantage that their N substitution provides a versatile chemical handle for fine-tuning the reaction dynamics.

Comprehensive spectroscopic and dynamic analyses were used to establish a mechanism of the excited-state structural $R^* \rightarrow P^*$ transformation of **PDBAs**, which incorporates planarization of the core azepine accompanied by rotation (φ) of the *N*-phenyl moiety. The synergy of these two motions induces a barrier that can be simply envisaged as in Figure 1 b (vide infra). We then discovered such a transformation possessing similar transition-state structure and reactive frequency along the PISP pathway, satisfying the kinetics/ thermodynamics relationship declared by the *B-E-P* principle. This, together with the ratiometric dual emission during PISP, leads to bright prospects in harnessing excited-state structure planarization.

(1)

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Figure 1. a) Chemical structures and brief synthetic pathways to the target molecules. The red circle arrow represents an increase in the electron-donating strength. b) Illustration of the structural transformation for **PDBAs** in the excited state, where R*, T* and P* denote the starting structure, transition state and final structure, respectively, in the excited state.

Results and Discussion

Synthesis and characterization. Figure 1 a depicts the series of *N*-substituted **DBA** derivatives probed in this study. Details of the synthetic route and characterization are presented in the Supporting Information. As shown in single-crystal X-ray diffraction analyses (Figure 2; Supporting Information, Table S1),^[37] all the **PDBAs** exhibit bent dibenzo[*b*,*f*]azepine structures with bay angles Θ_{s1} (defined

by the angle between the C(6)-C(7)-C(9) plane and the C(1)-C(6)-C(14) plane) of 21–28° and Θ_{s2} (defined by the angle between the C(1)-N-C(14) plane and the C(1)-C(6)-C(14) plane) of 47–57°. Moreover, the bending angle Θ_a (angle between the C(1)-C(3)-C(4) plane and the C(14)-C(12)-C(11)) of **PDBA** was recorded as 126°, while that of **DBA** was substantially greater at 144°, and the angle $\Theta_{\rm b}$ (the angle between the C(7)-C(8)-N plane and the line along N-C(15)) was 107° and 134° for PDBA and DBA, respectively. This difference can be attributed to the steric interactions between the N-substituted phenyl group and the dibenzazepine core. When the substituent was varied from an electron-donating group (-OMe) to an electron-withdrawing group (-CN), the bending angle Θ_a increased from 119° to 128°, and the angle Θ_b ranged from 92° to 117°. The N-C(15) bond length provides more direct evidence of this, as it decreases in the order of **PDBA-OMe** (1.421 Å) > **PDBA-Me** (1.404 Å) > **PDBA** (1.399 Å) >**PDBA-COMe** (1.391 Å) >**PDBA-CN** (1.385 Å) (Figure 2), presumably due to charge transfer from the N-phenyl nitrogen to the para substituent. The results thus indicate that both the nature of the azepine bending structure and the substituent substantially influence the conformation and molecular characteristics.

Photophysical properties. Figure 3 shows the absorption (in terms of the extinction coefficient, ε) and emission spectra of DBA (the control group) and the PDBAs in cyclohexane. The maxima of the lowest lying $(S_0 \rightarrow S_1)$ absorption bands of **DBA** and all **PDBAs** appear at approximately 350 nm and show small absorptivity. For example, the absorption molar extinction coefficient, ε , of **DBA** at 350 nm was measured to be $820 \pm 30 \text{ M}^{-1} \text{ cm}^{-1}$ (Table 1; Supporting Information, Figure S2). The N-phenyl-derivatized PDBAs show even weaker lowest lying absorption bands, with extinction coefficients of approximately 300-700 M⁻¹ cm⁻¹ at their maxima. This trend can be rationalized by the large separation between the electron densities of the HOMO and LUMO (vide infra), which are mainly located on the para-substituted N-phenyl moiety and the dibenzo- moiety, respectively, i.e., by the charge-transfer properties.^[38] This conclusion is also supported by the resulting solvatochromism of the initially prepared bent-structure emission (Figure S5).



Figure 2. Single-crystal structures of the studied molecules from two perspectives.

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Figure 3. Steady-state absorption (dashed lines) and photoluminescence (solid lines) spectra of a) **DBA**, b) **PDBA-OMe**, c) **PDBA-Me**, d) **PDBA**, e) **PDBA-COMe**, f) **PDBA-CN** and g) **MDBA** in cyclohexane (λ_{ex} =300 nm), and of h) **PDBAs** in solid film.

Table 1: Experimental and calculated optical characteristics for the target molecules in cyclohexane at room temperature.^[a]

Name	Absorption $S_0 \rightarrow S_1$		Emission $S_1 \rightarrow S_0$			Q.Y. [%] ^[b]	τ [ps] ^[c]	
	$\lambda_{abs} \text{ [nm]} \ (\varepsilon \ [\text{M}^{-1} \text{cm}^{-1}])^{[a]}$	$\lambda_{ m calc}$ $[nm]^{[a]}$	$f^{[a]}$	$\lambda_{_{em}}$ $[nm]^{[a]}$	λ_{calc} $[nm]^{[a]}$	$f^{[a]}$		
DBA	360	406	0.0326	666	733	0.0115	0.05	600 at 600 nm
	(821)							
MDBA	349	386	0.0380	556	636	0.0264	0.35	1100 at 550 nm
	(1209)							
PDBA-OMe	356	425	0.0001	498	621	0.0001	0.50	1600 at 460 nm
	(305)							
PDBA-Me	351	401	0.0001	482	548	0.0020	0.05	167 at 440 nm
	(395)			648	698	0.0150		183 at 660 nm
PDBA	348	388	0.0005	462	517	0.0062	0.03	56 at 440 nm
	(397)			642	696	0.0153		184 at 650 nm
PDBA-COMe	pprox 360	366	0.0020	451	480	0.0185	0.03	29 at 410 nm
	(472)			628	658	0.0164		225 at 660 nm
PDBA-CN	\approx 343	357	0.0026	434	470	0.0285	0.03	20 at 420 nm
	(735)			626	658	0.0184		200 at 650 nm

[a] Experimental lowest lying absorption (λ_{abs}), emission wavelengths (λ_{em}), calculated lowest lying absorption or emission wavelengths (λ_{calc}), molar extinction coefficient (ε), oscillator strengths (f). [b] Emission quantum yield (Q.Y.). The measurement was performed by using excitation at 370 nm for **DBA** and **MDBA**, and at 287 nm for **PDBA-OMe**, **PDBA-Me**, **PDBA**, **PDBA-COMe**, and **PDBA-CN**. [c] Decay time constants (τ).

DBA was previously reported to be nonemissive at room temperature.^[39] However, in this study, **DBA** was found to exhibit a weak orange-red, vibronic progressive emission with a maximum at approximately 600 nm in various solvents (Figure 3a; Figure S5). This emission feature was previously unrecognized, perhaps due to its anomalously large Stokes shift of $> \approx 10000$ cm⁻¹ in the red region. Such a large Stokesshifted emission even in nonpolar solvents, together with the the normal emission with charge-transfer behavior of **PDBA-OMe**. Dual fluorescence emission bands were observed for the rest **PDBAs** (Figure 3). In terms of the peak wavelength and solvent polarity dependence, the short emission wavelength band (the F_1 band) shows spectral features and charge-transfer trends similar to those of the band of **PDBA-OMe**, while the long wavelength red emission band (the F_2 band) is nearly solvent polarity independent and hence similar to the

polarity

vibronic spectral feature, suggests

that **DBA** undergoes planarization in the excited state to restore the

All the **PDBAs** exhibit absorption profiles similar to that of **DBA**. In sharp contrast, however, depending on the substituent, they exhibit diverse emission characteristics very distinct from those of **DBA** (Figure 3). Compared to the vibronic progressive 600 nm emission of **DBA**, the emission of **PDBA-OME** is drastically blue-shifted to 500 nm in cyclohexane, which is mirrored by the lowest lying absorption spectrum. Moreover, unlike the solvent

independence of the

600 nm emission band of **DBA**,

the PDBA-OMe emission exhibits

pronounced solvatochromism, as it

is redshifted from 500 nm in cyclo-

hexane to 550 nm in THF (Figure S5). These results demonstrate

aromaticity.



red **DBA** emission band. Importantly, in solid thin film form, all the **PDBAs** exhibit only an F_1 band (Figures S6 and S7).

The observation of the F₁ band only for **PDBA-OMe** and dual emission for the other PDBAs suggests that the electronic properties of the para substituent play a key role in fine-tuning the barrier and hence altering the structural relaxation dynamics. When the para substituent is switched from an electron-donating group to an electron-withdrawing group, the F_2/F_1 emission intensity ratio appears to increase in the order of PDBA-OMe < PDBA-Me < PDBA < PDBA-**COMe** < **PDBA-CN**. The presence of only the F₁ band for PDBA-OMe implies that the reaction barrier and/or energetics are high, prohibiting PISP. Conversely, the control compound, DBA with no N-phenyl ring to induce steric hindrance shows the opposite case of a negligible barrier for PISP, giving solely F₂ emission. Chemically, introducing a bulky group homogenously distributed through the space so that the azepine will be always hindered during planarization would be intriguing. Accordingly, the azepine may be locked at a specific bending angle rather than undergoing a planar configuration. To prove this viewpoint, we synthesized N-methyl-substituted DBA, namely, MDBA (Figure 1b), in which the methyl group induces a steric hindrance that is independent of its rotation. As shown in Figure 3g, **MDBA** exhibits a 550 nm emission band that is between F_1 $(\approx 440 \text{ nm})$ and F_2 ($\approx 600 \text{ nm}$) band, affirming the proposal.

Time-resolved emission spectroscopy. For **DBA**, when monitoring the F_2 emission in the range of 600 to 650 nm, the

time-correlated single-photon counting (for TCSPC, see the Supporting Information) results show single exponential decay dynamics with a lifetime of 576 ps (Figure 4a). We then performed a fluorescence upconversion experiment by monitoring at 500 nm, which is supposed to be in the region of F_1 emission where the steady-state intensity is obscured due to its fast relaxation to F_2 . The results shown in the inset of Figure 4a reveal a fast decay time constant of 3.9 ps. The fast structural planarization of **DBA** can be attributed to the lack of steric hindrance during PISP. For **PDBA-OMe**, which exhibits solely F_1 emission, the time-resolved studies reveal a single exponential decay time of as long as 1.6 ns (Figure 4b). The results imply prohibition of structural relaxation for **PDBA-OMe** within its lifespan in the excited state.

We next probed those **PDBAs** showing dual emission. Figure 4c depicts the kinetic profiles for the F_1 and F_2 emission bands of **PDBA**, while the time-resolved profiles for the other **PDBAs** are displayed in Figure S17. All pertinent kinetic data are listed in Table S11. Using **PDBA** as an example, upon monitoring the F_1 band emission at, e.g., 440 nm, the time-resolved measurements reveal a single exponential decay time constant of 56 ± 8.0 ps. This time constant, within the experimental error, matches the rise component of 58 ± 8 ps of the F_2 emission monitored at 660 nm (Figure 4c; Table S11). Similarly, **PDBA-Me**, **PDBA-COMe** and **PDBA-CN** all show good correlations in which the decay time constants of their F_1 band are the same as the rise time constants of their F_2 band (Figure S17).



Figure 4. Emission kinetic profiles of a) **DBA**, b) **PDBA-OMe** and c) **PDBA** in cyclohexane. The monitored emission wavelength is shown in the inset. Inset of (a) presents fast decay dynamics monitored at 500 nm measured within 20 ps. d) Temporal spectral evolution of **PDBA** and its 2D plot (inset) in cyclohexane at 298 K. e) Temperature-dependent relaxation kinetics of **PDBA** monitored at the F_1 band (460 nm) from 258 K to 298 K in methylcyclohexane. Inset: plot of $\ln k_{obs}$ v.s. 1 K^{-1} ; λ_{ex} : 287 nm.

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The data listed in Table S11 provide strong evidence that the rate constant of the structural transformation, k_{t} , which is deduced from $k_t = 1/\tau_{decay}$ of the F₁ bands increases in the order of **PDBA-Me** $(0.60 \times 10^{10} \text{ s}^{-1}) < \text{PDBA} (1.79 \times 10^{10} \text{ s}^{-1})$ < **PDBA-COMe** $(4.17 \times 10^{10} \text{ s}^{-1})$ < **PDBA-CN** $(5.56 \times 10^{10} \text{ s}^{-1})$ 10^{10} s^{-1}). Realizing that **PDBAs** all possess an *N*-phenyl group, the kinetic trend cannot be rationalized simply by the differences in the steric hindrance imposed by the N-phenyl group. Alternatively, the increase in the reaction rate correlates well with the electron-withdrawing ability of the substituents, which deceases in the order of -CN > -COMe >-H > -Me. This trend also fits with the strongest electrondonating group, -OMe, in PDBA-OMe, where the barrier appears to be too high to undergo structural relaxation during the lifespan of the F_1 emission (1.6 ns). Using **PDBA** as a prototype, we then scanned the time-resolved emission wavelength throughout the entire visible region and plotted the emission temporal evolution in cyclohexane. The results shown in Figure 4d clearly indicate that the decrease in the F_1 emission band is accompanied by an increase in the F₂ emission at 600 nm, affirming the $R^* \rightarrow P^*$, i.e., precursor \rightarrow successor, type of structural transformation.

The temperature-dependent kinetic study for **PDBA** depicted in Figure 4e clearly show that as the temperature decreases, the decay time constant of the emission monitored at the F_1 band (e.g., 450 nm) increases. Assuming that the decay of the F_1 emission is dominated by the structural relaxation rate k_t , the plot of $\ln k_t (=1/\tau_{obs})$) versus 1/T(K) gives a straight line (see inset of Figure 4e), and the slope renders a value of 2.49 kcalmol⁻¹ for the activation energy $\Delta E_a(exp.)$ (exp. stands for experimental data to distinguish it from the $\Delta E_a(calc.)$ obtained from calculations (vide infra)). A similar approach provides $\Delta E_a(calc.)$ values of 3.23 kcal mol⁻¹, 2.16 kcalmol⁻¹ and 1.86 kcalmol⁻¹ for **PDBA-Me**, **PDBA-COMe** and **PDBA-CN**, respectively (Table 2; Figures S31 and S32).

General theoretical approach. To rationalize the above structure-reaction relationship, computational studies were carried out (Supporting Information). The calculated absorption and emission data are listed in Table 1, the gaps in terms of wavelength are compatible with the onset of both the steady-state absorption and emission spectra. In particular, the calculated oscillator strength (*f*) for the lowest lying transition is small, supporting the experimentally observed small extinction coefficient of <1000 M⁻¹ cm⁻¹ for the S₀ \rightarrow S₁ peak wavelength (vide supra). The optimized ground state

Table 2: Experimentally obtained frequency factor v, $\Delta E_a(exp.)$, calculated energy barrier $\Delta E_a(calc.)$ and calculated energy difference ($\Delta E_{P^a,R^a}$) for the $R^* \rightarrow P^*$ structural transformation of **PDBAs.**

Name	Excited state (S1) planarization					
	$\nu [s^{-1}]$	$\Delta E_{a} \ (exp.)^{[a]}$	ΔE_{a} (calc.) ^[a]	$\Delta E_{P^{\star}-R^{\star}}^{[a]}$		
PDBA-OMe	-	-	9.15	2.61		
PDBA-Me	$1.52(\pm 0.31) \times 10^{12}$	3.23	5.67	-1.49		
PDBA	$1.17(\pm 0.16) \times 10^{12}$	2.49	4.55	-2.85		
PDBA-COMe	$1.23(\pm 0.46) \times 10^{12}$	2.16	3.41	-3.69		
PDBA-CN	$1.31(\pm 0.17) \times 10^{12}$	1.86	3.22	-4.10		

[a] Units kcal/mol.

 (S_0) structures with the corresponding frontier molecular orbital contours for the HOMO and LUMO of DBA, PDBA-OMe, PDBA and PDBA-CN are depicted in Figure 5. Similar structure/frontier orbital properties were obtained for PDBA-Me and PDBA-COMe (Figure S26). Similar to the X-ray crystal structures, the ground-state optimized structures, defined as R (Figure 5), for DBA and the PDBAs all exhibit a bent structure for the core dibenz [b, f] azepine moiety with a bending angle Θ_a of 126–143°. Frontier orbital analyses of DBA and PDBAs in the R form indicate that the lowest lying excited state for DBA and PDBAs mainly involves a HOMO \rightarrow LUMO transition, which is solely attributed to the $\pi \to \pi^*$ character (Figure 5). For **DBA**, HOMO is on the dibenzo[b, f] azepine moiety, while LUMO is located at the dibenzo- moiety. For PDBAs, HOMO is mainly on the outer N-phenyl ring, while LUMO is located at the dibenzo- moiety. In addition, the natural transition orbitals (NTOs) were also applied to analyze the $S_0 \rightarrow S_1$ transition, which were in line with the results from the frontier molecular orbital contours (Figure S27).^[40,41] The spatially charge-separated HOMO and LUMO result in the weak transition dipole and hence small absorption extinction coefficient, consistent with the experimental observations.

Upon optimizing the S_1 state of **DBA**, a substantial difference is that the bending angle Θ_a changes from 143° in R to nearly planar (180°). The results indicate that the original structure of **DBA** (R) cannot maintain the proximal bending angle but spontaneously relaxes to a planar configuration with a negligible barrier. In contrast, all PDBAs appear to encounter an appreciable barrier along the structural relaxation pathway and localize at a bent structure R* position under free geometry optimization (Figure 5). For this case, the N-phenyl group is expected to be the key factor in introducing a barrier along the potential energy surface (PES) of the structural transformation. We also analyzed the changes in aromaticity after PISP for all PDBAs by using the harmonic oscillator model of aromaticity (for HOMA, see the Supporting Information).^[32,41] The results clearly indicate that **PDBAs** with $4n \pi$ electrons possess a bent-shaped azepine core in the ground state and undergo a structural planarization process in the excited state (Figure S28), obeying Baird's rule.^[33]

B-E-P principle extended to PISP of PDBAs. The reaction PES was then plotted as a function of bending angle $\Theta_{\rm a}$ and the angle φ that represents the rotation of the Nphenyl group, generating the 3D plots shown in Figure 5 for PDBAs (Figures S26 and S30a,b). In the ground state, all the PDBAs show a global minimum, which increases the potential energy en route to planarization. In the S_1 state, the plot of the PES along Θ_a and φ shows an appreciable barrier ΔE_a (calc.); i.e., a saddle point is calculated for all PDBAs along the corresponding structural transition pathway from R* to P*. These data, together with the calculated difference in energy between the reactant and product in the excited state, $\Delta E_{\mathbf{P}^*\cdot\mathbf{R}^*}$, and experimental data of the barrier $\Delta E_{a}(\exp)$ derived from the temperature-dependent kinetics, are listed in Table 2. Note that ΔE_a (calc.) for **PDBA-OMe** was calculated to be as large as 9.15 kcal mol⁻¹, prohibiting structural relaxation of R* in the excited state.

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Figure 5. Optimized structures and corresponding frontier molecular orbital contours of a) DBA, b) PDBA-OMe, c) PDBA, and d) PDBA-CN in the S_0 and S_1 states. The R conformer represents the optimized conformer in the ground state. R* represents the local minimum of the bent conformer, and P* is the global minimum of the planar conformer in the S_1 state after structural transformation. e) The bending angle Θ_a and rotation angle φ (see text for definition) for PDBA. Optimized conformations and potential energy surfaces of f) PDBA-OMe, g) PDBA and h) PDBA-CN in the S_0 and S_1 states.

Figure 6 shows the plots of $\Delta E_a(\exp.)$ and $\Delta E_a(calc.)$ (kinetics) versus $\Delta E_{P^*.R^*}$ (thermodynamics). Evidently, $\Delta E_a(\exp.)$ and $\Delta E_a(calc.)$ show the same trend that decreasing the electron-donating ability of the substituent on the phenyl ring decreases the barrier, which decreases in the order of -OMe > -Me > -H > -COMe > -CN. Moreover, both plots of $\Delta E_a(\exp.)$ and $\Delta E_a(calc.)$ versus $\Delta E_{P^*.R^*}$ (Figure 6) reveal straight lines, showing a consistent trend that lowering ΔE_a gives a more negative value of $\Delta E_{P^*.R^*}$. This result is reminiscent of the **B-E-P** principle^[7,8] expressed in Equa-



Figure 6. Dependence of the energy barrier on the energy difference between R* and P*. Plot of $\Delta E_a(\text{calc.})$ (blue •) and $\Delta E_a(\text{exp.})$ (orange •) versus $\Delta E_{\text{P*},\text{R*}}$ and fit from Equation (2).

tion (1). Assuming that the difference in ΔPV (*P*: pressure, *V*: volume) is negligible in the intramolecular structural transformation, we take data of ΔE_a (calc.) versus $\Delta E_{P^*-R^*}$ (Figure 6, upper plot) and fit them with Equation (2).

$$\Delta E_{\rm a}({\rm calc.}) = E_0 + \alpha \Delta E_{\rm P*-R} *$$
⁽²⁾

The best linear fit gives E_0 and α of 6.89 kcalmol⁻¹ and 0.89, respectively. Additionally, we also fit the experimentally resolved $\Delta E_a(\exp)$ as a function of $\Delta E_{P^*.R^*}$ (Figure 6, lower plot), rendering E_0 and α of 3.98 kcalmol⁻¹ and 0.51, respectively. Despite the difference in values, both results fulfil the criterion of $0 \le \alpha < 1$ for the *B***-***E***-***P* principle.

Fundamentally, the **B-E-P** principle relies on a stringent condition in that the structure of the transition state and its frequency along the reaction coordinate have to be similar among the family of target PDBAs. We then mark out the coordinates of the transition state in terms of Θ_a , φ and ΔE_a in the 3D plot shown in Figure 7, where the energy barrier ΔE_a , bending angle Θ_a and rotation angle φ have been previously defined and the PES is taken from the plots shown in Figure 5 f-h (Figure S30) for PDBAs along the steepest slope from T* to R*. The energy of R* for all **PDBAs** is set to zero. In Figure 7, except for **PDBA-OMe**, $\Delta E_a(exp.)$ is applied for all PDBAs to reflect the real experiment. According to Figure 7, the bending angle Θ_a and rotation angle φ in the studied PDBAs are all located around 151-152° and 40-50°. From the viewpoint of bending angle Θ_a and rotation angle φ , the structures of the transition state are thus more or less the same for all PDBAs.



Figure 7. Computed **PDBA** bending angle Θ_a from R* to T* and then to P*. The coordinates of T* are marked by (Θ_a , φ , $\Delta E_a(exp.)$) except for **PDBA-OMe**, where $\Delta E_a(calc.)$ is applied.

Experimentally, we can also obtain the frequency factor ν from the Arrhenius-type kinetics, expressed as

$$\ln k(T) = \ln v - \frac{\Delta E_a(\exp.)}{RT}$$
(3)

by extrapolation of the fitted $\ln k(T)$ versus 1/T (see **PDBA** in Figure 4e). The deduced frequencies listed in Table 2 clearly indicate that ν lies within a narrow interval of $1.17 \times 10^{12} \text{ s}^{-1}$ – $1.52 \times 10^{12} \text{ s}^{-1}$ for all **PDBAs**. Therefore, both transition-state structure and frequency factor for the **PDBA** family meet the criteria set by the *B-E-P* principle, rationalizing the linear relationship between $\Delta E_a(\exp)$ and $\Delta E_{P^*R^*}$ for the **PDBA** family. Similar trends should be obtained upon using the calculated ΔE_a (calc.). This result thus extends the *B-E-P* principle to a structural relaxation/planarization that virtually does not involve any bond breakage or reformation.

Origin of the substituent-induced barrier. Finally, insights into the origin of the barrier and the substituent effect are discussed. During structural relaxation, the interplay between the bent-to-planar motion of the core and the twisting of the N-phenyl group must be strong, creating steric hindrance during PISP. This, together with the charge-transfer property from N-phenyl to the core dibenz[b, f] azepine moiety in the R* state (Figure 5), suggests that the properties of the N-C(15) bond, which is the twisting axis of the N-phenyl ring, play a key role in controlling the barrier of the reaction (Figure 1 b). The calculated N-C(15) bond lengths for R* are in the range of 1.348 Å to 1.379 Å for all PDBAs, indicating that N-C (15) has a partial double bond character. This can be rationalized by the excited-state N-phenyl (donor) \rightarrow dibenz-[b,f] azepine (acceptor) charge transfer that increases the N-C(15) bond order. Increasing the electron-donating ability of the para substituent of the N-phenyl moiety enhances the charge transfer and hence increases the N-C(15) double bond character.

The above discussion can be visualized by plotting the N-C(15) bond distance as a function of the Hammett constant $(\sigma_p)^{[42]}$ of the added substituent, shown in Figure S34a.^[43,44] The results show that when the electrondonating ability of the substituent increases (smaller $\sigma_{\rm p}$), the N-C(15) double bond character also increases. As a result, the N-C(15) bond distances are calculated to decrease in the order of PDBA-CN > PDBA-COMe > PDBA > PDBA-Me > **PDBA-OMe** (Table S20), which follows the trend of σ_p in the order of -CN (0.66) > PDBA-COMe (0.50) > PDBA (0.00) > PDBA-Me (-0.17) > PDBA-OMe (-0.27). PDBA-**OMe** has the shortest N-C(15) bond, which is explained by its substituent having the strongest donating ability and hence the strongest charge transfer among all the PDBAs. A greater double bond character of the N-C(15) bond makes twisting of the N-phenyl moiety more difficult, consistent with PDBA-**OMe** having the largest ΔE_a .

Conclusion

In summary, the PISP of dibenzazepine (DBA) and its Nphenyl derivatives (i.e., the PDBA family) has been studied in a comprehensive manner. The results indicate a slower relaxation rate upon increasing the electron-donating ability of the substituent, giving substituent-dependent F_2/F_1 ratiometric emission. The relationship between the reaction barrier and thermodynamics can be well described by the Bell-Evans-Polanyi principle and is rationalized by the twisting of the N-phenyl group during the planarization to avoid the steric effect. While the occurrence of excited-state charge transfer from the N-phenyl group to the dibenzazepine core gives the N-C(15) bond a partial double bond character, the twisting of the N-phenyl moiety along the N-C(15) bond induces a barrier, and the barrier height thus depends on the electron-donating/withdrawing properties on the para substituent on the N-phenyl group. On reaching the transition state, the downhill PES to P* is driven by a stabilization in aromaticity, which is subject to similar frequencies along the reaction coordinate for the PDBA family. The correlation thus broadens the horizon of the Bell-Evans-Polanyi principle towards optically triggered structure planarization.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: azepine · Bell–Evans–Polanyi principle · dual emission · excited-state aromaticity · photoinduced structural planarization

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- [1] J. N. Brønsted, Chem. Rev. 1928, 5, 231-338.
- [2] L. P. Hammett, J. Am. Chem. Soc. 1937, 59, 96-103.
- [3] R. A. Marcus, Rev. Mod. Phys. 1993, 65, 599-610.
- [4] F. A. Carey, R. J. Sundberg, Advanced Organic Chemistry, Part A, Springer, Berlin, 2007, pp. 285–344.
- [5] R. Vinu, L. J. Broadbelt, Annu. Rev. Chem. Biomol. 2012, 3, 29– 54.
- [6] R. A. Marcus, J. Phys. Chem. 1968, 72, 891-899.
- [7] R. P. Bell, Proc. R. Soc. London Ser. A 1936, 154, 414-429.
- [8] M. G. Evans, M. Polanyi, Trans. Faraday Soc. 1938, 34, 11-24.
- [9] I. V. Alabugin, M. Manoharan, B. Breiner, F. D. Lewis, J. Am. Chem. Soc. 2003, 125, 9329–9342.
- [10] G. G. Wubbels, Tetrahedron Lett. 2015, 56, 1716–1719.
- [11] K. Lee, G. H. Gu, C. A. Mullen, A. A. Boateng, D. G. Vlachos, *ChemSusChem* 2015, 8, 315–322.
- [12] R. Papadakis, H. Ottosson, Chem. Soc. Rev. 2015, 44, 6472– 6493.
- [13] S. Hamatani, D. Kitagawa, T. Nakahama, S. Kobatake, *Tetrahedron Lett.* **2020**, *61*, 151968–151972.
- [14] T. Nakahama, D. Kitagawa, S. Kobatake, J. Phys. Chem. C 2019, 123, 31212–31218.
- [15] S. Saito in *Molecular Technology, Vol. 3* (Eds.: H. Yamamoto, T. Kato), Wiley-VCH, Weinheim, **2019**, pp. 17–52.
- [16] Z. Zhang, Y.-S. Wu, K.-C. Tang, C.-L. Chen, J.-W. Ho, J. Su, H. Tian, P.-T. Chou, J. Am. Chem. Soc. 2015, 137, 8509–8520.
- [17] Z. R. Grabowski, K. Rotkiewicz, Chem. Rev. 2003, 103, 3899– 4031.
- [18] H. V. Humeniuk, A. Rosspeintner, G. Licari, V. Kilin, L. Bonacina, E. Vauthey, N. Sakai, S. Matile, *Angew. Chem. Int. Ed.* **2018**, *57*, 10559–10563; *Angew. Chem.* **2018**, *130*, 10719–10723.
- [19] Z. Zhou, D.-G. Chen, M. L. Saha, H. Wang, X. Li, P.-T. Chou, P. J. Stang, J. Am. Chem. Soc. 2019, 141, 5535-5543.
- [20] M. Iwamura, H. Watanabe, K. Ishii, S. Takeuchi, T. Tahara, J. Am. Chem. Soc. 2011, 133, 7728–7736.
- [21] L. X. Chen, W. J. H. Jäger, G. Jennings, D. J. Gosztola, A. Munkholm, J. P. Hessler, *Science* 2001, 292, 262–264.
- [22] C. Zhou, Y. Tian, Z. Yuan, M. Han, J. Wang, L. Zhu, M. S. Tameh, C. Huang, B. Ma, *Angew. Chem. Int. Ed.* **2015**, *54*, 9591 – 9595; *Angew. Chem.* **2015**, *127*, 9727 – 9731.
- [23] M. Chaaban, Y.-C. Chi, M. Worku, C. Zhou, H. Lin, S. Lee, A. Ben-Akacha, X. Lin, C. Huang, B. Ma, *Inorg. Chem.* 2020, 59, 13109–13116.
- [24] Y. Chen, D.-G. Chen, Y.-A. Chen, C.-H. Wu, K.-H. Chang, F.-Y. Meng, M.-C. Chen, J.-A. Lin, C.-Y. Huang, J. Su, H. Tian, P.-T. Chou, *Chem. Eur. J.* **2019**, 25, 16755–16764.

- [25] D.-G. Chen, Y. Chen, C.-H. Wu, Y.-A. Chen, M.-C. Chen, J.-A. Lin, C.-Y. Huang, J. Su, H. Tian, P.-T. Chou, *Angew. Chem. Int. Ed.* **2019**, *58*, 13297–13301; *Angew. Chem.* **2019**, *131*, 13431– 13435.
- [26] Z. Zhang, C.-L. Chen, Y.-A. Chen, Y.-C. Wei, J. Su, H. Tian, P.-T. Chou, Angew. Chem. Int. Ed. 2018, 57, 9880–9884; Angew. Chem. 2018, 130, 10028–10032.
- [27] D. Shukla, P. Wan, J. Am. Chem. Soc. 1993, 115, 2990-2991.
- [28] M. L. G. Borst, R. E. Bulo, C. W. Winkel, D. J. Gibney, A. W. Ehlers, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* 2005, *127*, 5800–5801.
- [29] V. Lyaskovskyy, R. J. A. van Dijk-Moes, S. Burck, W. I. Dzik, M. Lutz, A. W. Ehlers, J. C. Slootweg, B. de Bruin, K. Lammertsma, *Organometallics* **2013**, *32*, 363–373.
- [30] I. Kawashima, H. Imoto, M. Ishida, H. Furuta, S. Yamamoto, M. Mitsuishi, S. Tanaka, T. Fujii, K. Naka, *Angew. Chem. Int. Ed.* **2019**, *58*, 11686–11690; *Angew. Chem.* **2019**, *131*, 11812–11816.
- [31] K. Padberg, J. D. R. Ascherl, F. Hampel, M. Kivala, *Chem. Eur. J.* 2020, 26, 3474–3478.
- [32] J. Toldo, O. E. Bakouri, M. Solà, P.-O. Norrby, H. Ottosson, *ChemPlusChem* 2019, 84, 712–721.
- [33] N. C. Baird, J. Am. Chem. Soc. 1972, 94, 4941-4948.
- [34] P. B. Karadakov, J. Phys. Chem. A 2008, 112, 7303-7309.
- [35] M. Rosenberg, C. Dahlstrand, K. Kilsa, H. Ottosson, *Chem. Rev.* 2014, 114, 5379-5425.
- [36] P. B. Karadakov, P. Hearnshaw, K. E. Horner, J. Org. Chem. 2016, 81, 11346-11352.
- [37] M. P. Sadashiva, B. H. Doreswamy, Basappa, K. S. Rangappa, M. A. Sridhar, J. Shashidhara Prasad, J. Chem. Crystallogr. 2005, 35, 171–175.
- [38] D.-G. Chen, T.-C. Lin, Y.-A. Chen, Y.-H. Chen, T.-C. Lin, Y.-T. Chen, P.-T. Chou, J. Phys. Chem. C 2018, 122, 12215-12221.
- [39] C. García, R. Oyola, L. Piñero, D. Hernández, R. Arce, J. Phys. Chem. B 2008, 112, 168–178.
- [40] R. L. Martin, J. Chem. Phys. 2003, 118, 4775-4777.
- [41] T. Lu, F. Chen, J. Comput. Chem. 2012, 33, 580-592.
- [42] C. Hansch, A. Leo, R. W. Taft, Chem. Rev. 1991, 91, 165-195.
- [43] M. W. H. Hoorens, M. Medved, A. D. Laurent, M. D. Donato, S. Fanetti, L. Slappendel, M. Hilbers, B. L. Feringa, W. J. Buma, W. Szymanski, *Nat. Commun.* **2019**, *10*, 2390–2400.
- [44] R. Ghosh, Phys. Chem. Chem. Phys. 2018, 20, 6347-6353.

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