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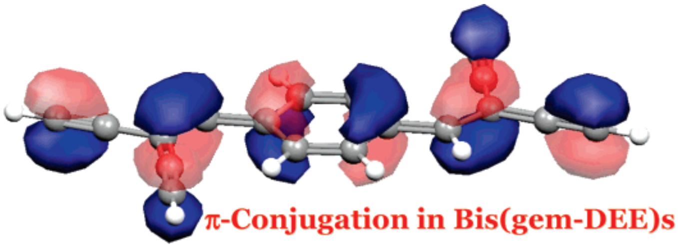
EDA Study of π-Conjugation in Tunable Bis(*gem*-diethynylethene) Fluorophores

Israel Fernández and Gernot Frenking*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein Strasse, D-35043 Marburg, Germany

frenking@chemie.uni-marburg.de

Received June 13, 2007



The strength of π-conjugation in a family of bis(*gem*-diethynylethene) fluorophores is estimated within the density functional theory framework using the energy decomposition analysis (EDA) method. The observed very good linear correlations between the calculated π-conjugation and the experimental values for the UV absorption and fluorescence emission for this series of compounds suggest that the values given by the EDA are useful for the interpretation and prediction of photochemical properties of the molecules. The calculated data predict that adequate modifications in the core moiety of the molecule such as π-donor substituents in the aromatic ring or in the periphery of the bis-enedyine unit like π-acceptor groups placed in the para position of the aryl substituent increase the total π-conjugation in the systems and thus provoke significant changes in both the absorption and emission spectra leading to large Stokes shifts. The effect of such substituents is quantitatively predicted by the EDA data.

Introduction

1,2-Diethynylethenes (DEEs) are important synthetic modules for the construction of conjugated systems in one, two, and three dimensions via acetylenic coupling reactions.[1] Thus, acetylenic scaffolding with suitable functionalized DEEs leads to π-conjugated oligomers with potential applications in the field of molecular materials.[2] For example, Kim and co-workers prepared, by two complementary Pd/Cu catalyzed cross-coupling methods, a new family of cross-conjugated bis-(*gem*-DEE)s as a promising class of tunable fluorophores.[3] The different chemical modifications in the core and periphery of the systems induce dramatic changes in their absorption and emission spectra, with the fluorescence colors spanning regions from indigo blue to reddish-orange. The different optical properties as well as the variation of the fluorescence quantum yield were explained in terms of the extension of the π-conjugation in these molecules.

Very recently, we suggested a theoretical method based on an energy decomposition analysis (EDA)[4] which provides a quantitative measure for the strength of conjugation and hyperconjugation in acyclic[5] and cyclic[6] compounds. One advantage of the method is that the calculated ΔE_π values, which are used to estimate the strength of π-conjugation, are a component of the EDA which together with the other energy components (for a description of the EDA see the method section) give the bond dissociation energy which is an observ-

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* To whom correspondence should be addressed.

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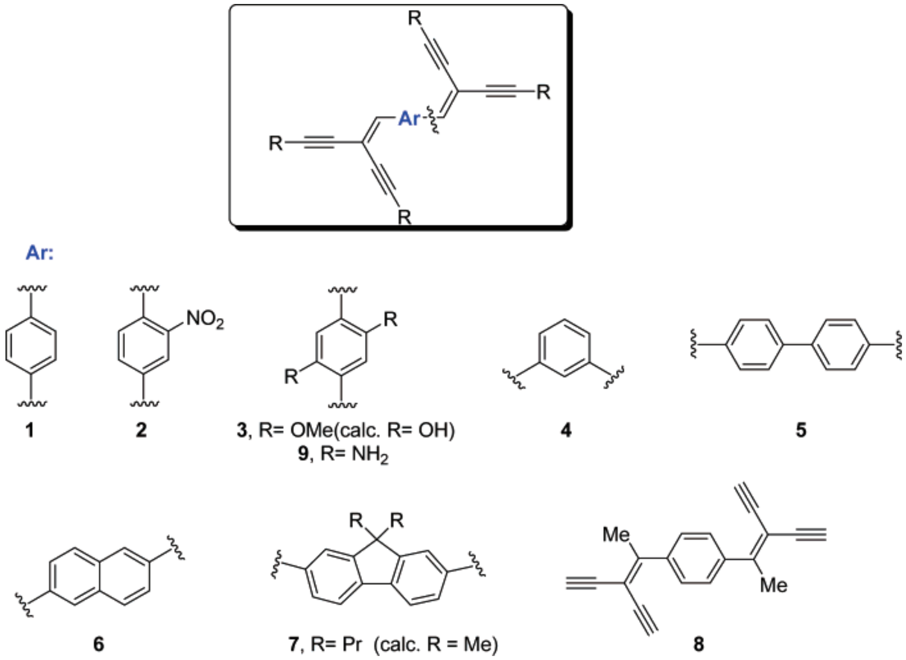

FIGURE 1. Experimentally investigated (R = Ph) and calculated (R = H) bis(*gem*-DEE)s **1**−**9**.

able quantity. Another advantage is that the EDA makes it possible to directly calculate the stabilization which arises from the mixing of occupied π orbitals with vacant π* orbitals in molecules without using an external reference system. The method was also successfully applied to estimate the strength of π-aromaticity in typical aromatic, homoaromatic, and antiaromatic compounds,[6a] and also in metallabenzenes[6b] by comparing the calculated ΔE_π values of the cyclic compounds with acyclic reference systems. It was found that the ΔE_π values of meta- and para-substituted benzylic cations and anions correlate very well with experimentally derived Hammett (σ) and Hammett−Brown (σ^+ and σ^-) substituent constants.[7] The calculations were particularly helpful for studying the strength of π-conjugation in donor-substituted cyanoethynylethenes (CEEs)[8] synthesized by Diederich and co-workers[9] which may serve as compounds for nonlinear optical applications.[10] The observed linear correlations between the ΔE_π values and various experimental data (^{13}C NMR chemical shifts and electrochemical potentials, which were proposed as indicators of the strength of π-conjugation) are further evidence that the calculated EDA values are reasonable and useful for interpreting and predicting the chemical properties of the molecule.

The good performance of the EDA encouraged us to apply the method to directly estimate the strength of π-conjugation in the bis(*gem*-DEE)s **1**−**8** (Figure 1) which have been synthesized by Kim et al.[3] and to analyze the correlation between the calculated ΔE_π values with experimental values of the absorption and emission spectra. The aim of this work is to answer the question if the trend of the experimentally measured spectra can be modeled and spectral values of unknown compounds may perhaps be predicted by the theoretical values of the strength of π conjugation.

Computational Methods

The geometries of the molecules were optimized at the gradient-corrected DFT level of theory using Becke's exchange functional[11] in conjunction with Perdew's correlation functional[12] (BP86). Uncontracted Slater-type orbitals (STOs) were employed as basis functions in SCF calculations.[13] Triple-ζ-quality basis sets were used, which were augmented by two sets of polarization functions, that is, p and d functions for the hydrogen atom and d and f functions for the other atoms. This level of theory is denoted as BP86/TZ2P. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[14] The calculations were carried out using the ADF(2003.1) program package.[15]

The binding interactions between the chosen fragments were analyzed by means of the energy decomposition analysis (EDA) of ADF,[4] which was developed by Ziegler and Rauk[16] following a similar procedure suggested by Morokuma.[17] EDA has proven to give important information about the nature of the bonding in main-group compounds and transition-metal complexes.[18] The focus of the bonding analysis is the instantaneous interaction energy, ΔE_{int},

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TABLE 1. Results of the Energy Decomposition Analysis at BP86/TZ2P for Compounds 1−9 Using Two Fragments As Shown in Figure 1 (Energy Values in kcal/mol)

compd	1	2	3	4	5	6	7	8	9
ΔE_{int}	−133.8	−134.0	−136.3	−131.5	−133.6	−133.2	−133.6	−127.7	−135.2
ΔE_{Pauli}	280.8	281.6	282.2	277.0	277.8	279.7	280.1	272.3	291.4
ΔE_{elstat}[a]	−177.4	−176.9	−177.5	−175.3	−176.0	−176.8	−177.4	−174.5	−181.3
	(42.8%)	(42.6%)	(42.4%)	(42.9%)	(42.8%)	(42.8%)	(42.9%)	(43.6%)	(42.5%)
ΔE_{Orb}[a]	−237.2	−238.6	−241.0	−233.2	−235.4	−236.0	−236.2	−225.6	−245.3
	(57.2%)	(57.4%)	(57.6%)	(57.1%)	(57.2%)	(57.2%)	(57.1%)	(56.4%)	(57.5%)
ΔE_{σ}[b]	−212.5	−214.1	−214.9	−210.9	−211.2	−211.8	−211.7	−203.5	−217.6
	(89.6%)	(89.7%)	(89.2%)	(90.4%)	(89.7%)	(89.7%)	(89.6%)	(90.2%)	(88.7%)
ΔE_{π}[b]	−24.67	−24.52	−26.11	−22.36	−24.20	−24.26	−24.54	−22.01	−27.68
	(10.4%)	(10.3%)	(10.8%)	(9.6%)	(10.3%)	(10.3%)	(10.4%)	(9.8%)	(11.3%)
r(C−C)[c]/Å	1.445	1.446	1.439	1.452	1.446	1.446	1.446	1.466	1.437

[a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}. [c] Calculated C−C distance between the fragments in the molecules.

of the bond, which is the energy difference between the molecule and the fragments in the electronic reference state and frozen geometry of the compound. The interaction energy can be divided into three main components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \qquad (1)$$

ΔE_{elstat} gives the electrostatic interaction energy between the fragments, which are calculated using the frozen electron density distribution of the fragments in the geometry of the molecules. The second term in eq 1, ΔE_{Pauli}, refers to the repulsive interactions between the fragments, which are caused by the fact that two electrons with the same spin cannot occupy the same region in space. ΔE_{Pauli} is calculated by enforcing the Kohn−Sham determinant on the superimposed fragments to obey the Pauli principle by antisymmetrization and renormalization. The stabilizing orbital interaction term, ΔE_{orb}, is calculated in the final step of the energy partitioning analysis when the Kohn−Sham orbitals relax to their optimal form. This term can be further partitioned into contributions by the orbitals belonging to different irreducible representations of the point group of the interacting system. The EDA calculations of the present molecules have been carried out using C_s symmetry. Thus, the contributions of the a′ orbitals to ΔE_{orb} give the strength of the σ interactions while the contributions of the a″ orbitals give the strength of the π interactions:

$$\Delta E_{orb} = \Delta E_{\sigma} + \Delta E_{\pi} \qquad (2)$$

Further details of the energy partitioning analysis can be found in the literature.[4,18]

Results and Discussion

Table 1 gives the EDA values for the measured compounds **1**−**8** and for the unknown molecule **9** (Figure 1). The geometries of compounds **1**−**9** were optimized with C_s symmetry constraints at the BP86/TZ2P level, and the resulting structures were used for the EDA in order to divide the orbital interactions into σ(a′) and π(a″) contributions. For computational reasons, we replaced the phenyl groups attached to the terminal triple bonds in the experimental compounds[3] by hydrogen atoms. We also substituted the OMe group of **3** by OH and the propyl groups of **7** by methyl groups. The EDA calculations have been carried out using two interacting fragments as shown on top of Figure 1, i.e., one 1,1-diethynylethenyl fragment and one 1,1-diethynylethenylaryl fragment in a doublet state where the unpaired electron is in a σ orbital, using the frozen geometry of the compound.

TABLE 2. Experimental Values and Theoretical Results for Compounds 1−9 at BP86/TZ2P

compd	λ_{abs}[a]	λ_{emis}[b]	ΔE_{π}[c]	r(C−C)[d]
1	416	475, 506	−24.67	1.445
2	413	560	−24.52	1.446
3	455	522, 549	−26.11	1.439
4	349	413, 431	−22.36	1.452
5	394	461, 490	−24.20	1.446
6	418	473, 498	−24.26	1.446
7	422	473, 501	−24.54	1.445
8	360	454, 471	−22.01	1.467
9			−27.68	1.437

[a] Wavelength (in nm) of the absorption maximum, taken from ref 3b. [b] Wavelength (in nm) of the emission maximum when excited at the absorption maximum, taken from ref 3b. [c] Calculated ΔE_{π} values from the EDA at BP86/TZ2P level (in kcal/mol). [d] C−C bond lengths (in Å) between the interacting fragments calculated at the BP86/TZ2P level.

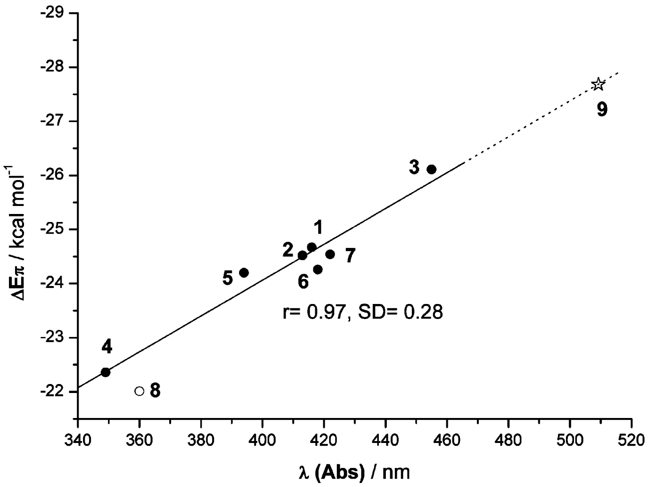


FIGURE 2. Plot of the ΔE_{π} values versus the wavelength of the absorption maxima for compounds **1**−**9**.

The EDA results for **1**−**9** exhibit rather uniform values for the interaction energies between 131 and 136 kcal/mol except for **8** which has a slightly smaller value $\Delta E_{int} = -127.7$ kcal/mol. The C−C bond between the two fragments has a somewhat stronger contribution from the orbital interactions than from the electrostatic term ΔE_{elstat}. The breakdown of ΔE_{orb} into the σ and π contributions shows that the covalent interactions come mainly (∼90%) from ΔE_{σ}. The values for ΔE_{π} are much smaller (22−27 kcal/mol) than the other energy terms and they show little variation among the compounds **1**−**9**. Note that the C−C distances between the interacting fragments correlate with the ΔE_{π} values. Compound **9** has the shortest bond length and the largest ΔE_{π} value while **8** has the smallest ΔE_{π} value and the

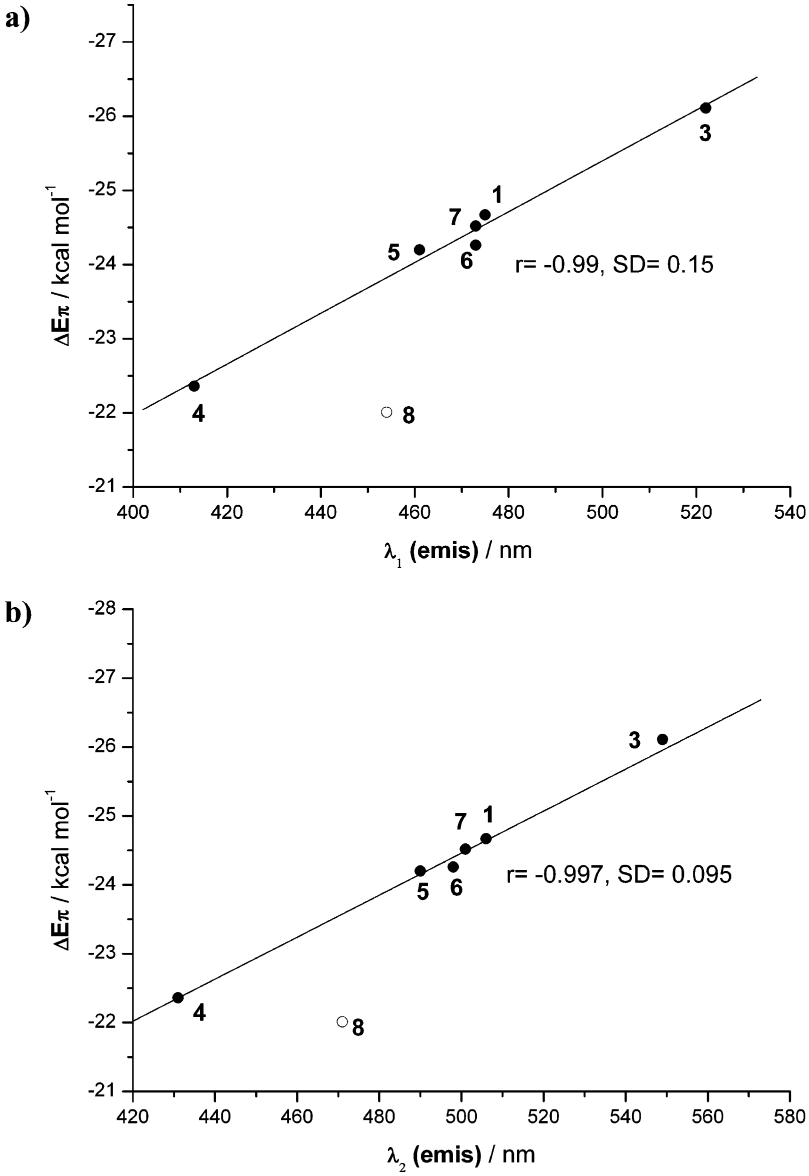
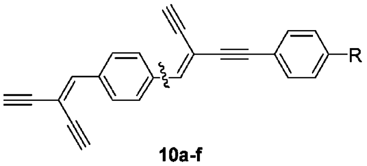


FIGURE 3. (a) Plot of the ΔE_{π} values versus the wavelength of the first emission maxima λ_1 for compounds **1** and **3**−**8**. (b) Plot of the ΔE_{π} values versus the wavelength of the second emission maxima λ_2 for compounds **1** and **3**−**8**.

longest C−C bond. The crucial question is whether the trend of the ΔE_{π} values which are rather minor contributions to the total binding interactions correlates with the experimental values for the absorption and emission spectra of the compounds. Such a correlation may not be expected because the absorption and emission spectra arise from electronic excitation and relaxation processes which involve excited states that are not considered in the EDA.

The most important experimental and theoretical results for the correlation analysis are shown in Table 2 which gives the calculated ΔE_{π} values as well as optical experimental data of the absorption and emission maxima for bis-(*gem*-DEE)s. The data in Table 2 show that the lowest value for ΔE_{π} is found for compound **4**, which lacks extensive π-conjugation because of the meta linkage. The theoretical finding agrees with the measured absorption wavelength which is the lowest of the entire series. The largest values for the strength of π conjugation were calculated for compounds **3** and **9**, which have two electron-donor groups in the aromatic ring. These results are not surprising if we take into account the well-known electron acceptor nature of the DEE moiety.[8,9] Figure 2 displays a graphical correlation between the calculated ΔE_{π} data and the experimental λ_{abs} values for the absorption wavelength which are ascribed to $\pi-\pi^*$ transitions.[3] There is a very good linear correlation between the experimental and theoretical values of compounds **1**−**7** which exhibits a correlation coefficient of 0.97 and a standard deviation of 0.28. The notable exception from the linear correlation is compound **8**. We think that the deviation of the latter species from the good correlation is due to a steric effect of the methyl groups with the *o*-hydrogen atoms of the phenyl ring which provokes that **8** does not possess a planar equilibrium structure. Geometry optimizations of **1**−**9** without symmetry constraint gave equilibrium geometries which deviate only slightly from the C_s form except for **8**. The energy minimum structure of **8** has a twisted geometry which is 3.45 kcal/mol lower in energy than the C_s form. The good correlation between the ΔE_{π} data and the experimental λ_{abs} values for **1**−**7** puts some trust into the theoretically predicted λ_{abs} value for **9**

TABLE 3. Results of the Energy Decomposition Analysis at BP86/TZ2P (Energy Values in kcal/mol)



10a-f

compd	R = H, **10a**	R = Cl, **10b**	R = C≡CH, **10c**	R = CN, **10d**	R = CHO, **10e**	R = NO$_2$, **10f**
ΔE_{int}	−134.4	−134.5	−134.6	−134.8	−134.8	−135.1
$\Delta E_{\mathrm{Pauli}}$	286.2	285.1	286.2	284.4	286.0	284.9
$\Delta E_{\mathrm{elstat}}{}^{a}$	−180.2	−179.6	−180.2	−178.8	−179.7	−179.0
	(42.8%)	(42.8%)	(42.8%)	(42.7%)	(42.7%)	(42.6%)
$\Delta E_{\mathrm{Orb}}{}^{a}$	−240.3	−240.0	−240.6	−240.4	−241.1	−241.0
	(57.2%)	(57.2%)	(57.2%)	(57.3%)	(57.3%)	(57.4%)
$\Delta E_{\sigma}{}^{b}$	−214.8	−214.4	−214.8	−214.3	−215.0	−214.6
	(89.4%)	(89.3%)	(89.3%)	(89.2%)	(89.2%)	(89.1%)
$\Delta E_{\pi}{}^{b}$	−25.57	−25.67	−25.81	−26.07	−26.12	−26.34
	(10.6%)	(10.7%)	(10.7%)	(10.8%)	(10.8%)	(10.9%)

[a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$. [b] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}.

which according to the calculated ΔE_{π} value should have $\lambda_{\mathrm{abs}} = \sim 510$ nm. Thus, we can conclude that the presence of a π-electron donor substituent in the aromatic ring of the bis(*gem*-diethynylethene) compounds enhances the π-conjugation in these systems and therefore leads to higher values of the wavelength of the absorption maxima.

We also analyzed the correlation between the calculated strength of the π conjugation and the experimental emission spectra of **1**−**8** which show two strong emission bands in the visible region except **2** for which only one emission band was observed.[3] Figure 3 shows a graphical display of the correlation between the ΔE_{π} values and the emission bands with the smaller $\lambda_{\mathrm{emis}}(1)$ values (Figure 3a) and the larger $\lambda_{\mathrm{emis}}(2)$ values (Figure 3b). The correlation between the two sets of data using the experimental values for **1**, **3**−**7** is very good ($\lambda_{\mathrm{emis}}(1)$ vs ΔE_{π}, correlation coefficient of 0.990 and standard deviation of 0.150; $\lambda_{\mathrm{emis}}(2)$ vs ΔE_{π}, correlation coefficient of 0.997 and standard deviation of 0.095). The experimental values for **8** are again outliers which can be explained with the twisted equilibrium geometry of the compound. The experimental value for the sole emission emission band of **2** $\lambda_{\mathrm{emis}} = 560$ nm deserves to be discussed. The calculated ΔE_{π} value for **2** (−24.52 kcal/mol) does not correlate at all with the experimental value when one uses the correlation line from either part a or b of Figure 3. Inspection of the experimental data given in Table 2 strongly suggests that the wavelength of the emission spectrum of **2** does not come from the same type of π relaxation process as for the other compounds. For example, the λ_{abs} and $\lambda_{\mathrm{emis}}(1)$ values of **3** are shifted by a similar amount to higher wavenumbers with respect to **1**. By contrast, compound **2** has a slightly smaller λ_{abs} value than **1** but the $\lambda_{\mathrm{emis}}(1)$ value of the former is much higher than that of the latter.

TABLE 4. Experimentally Derived Substituents Constants and EDA Results for Compounds 10a−f at BP86/TZ2P

compd	$\sigma_{\mathrm{p}}{}^{+\,a}$	$\Delta E_{\pi}{}^{b}$
10a, R = H	0.00	−25.57
10b, R = Cl	0.11	−25.67
10c, R = C≡CH	0.18	−25.81
10d, R = CN	0.66	−26.07
10e, R = CHO	0.73	−26.12
10f, R = NO$_2$	0.79	−26.34

[a] Hammett−Brown substituent constants taken from ref 19. [b] Calculated ΔE_{π} values from the EDA at BP86/TZ2P level (in kcal/mol).

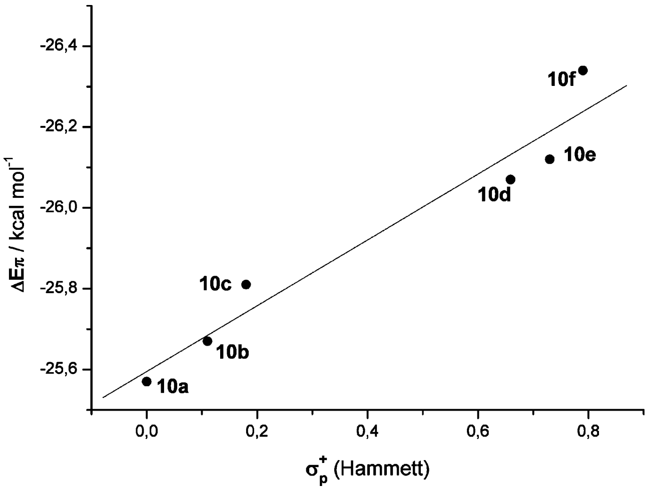


FIGURE 4. Plot of the ΔE_{π} values versus the Hammett−Brown $\sigma_{\mathrm{p}}{}^{+}$ substituent constants for compounds **10a**−**f**.

We extended the work to further unknown bis(*gem*-DEE) compounds by studying the effect of a para-substituted phenyl group attached to the terminal triple bond on the total π conjugation. The presence of a good π-acceptor should enhance the acceptor capacity of the DEE moiety leading to a more extended conjugation. The EDA results for compounds **10a**−**f** are given in Table 3. The variation of the para substituent R yields only small changes of the data for the energy terms. In particular, the ΔE_{π} values have only a span of 0.77 kcal/mol between **10a** ($\Delta E_{\pi} = -25.57$ kcal/mol) and **10f** ($\Delta E_{\pi} = -26.34$ kcal/mol). Despite that, we predict the presence of π-acceptor groups slightly enhance the π-conjugation in this series of fluorophores. In a previous study, we reported about an excellent correlation between ΔE_{π} values and Hammett−Brown "through-resonance" substituent constants.[7] Table 4 shows the calculated ΔE_{π} values of **10a**−**f** and Hammett−Brown $\sigma_{\mathrm{p}}{}^{+}$ parameters which were taken from the literature.[19] Figure 4 displays a graphical correlation between the values for ΔE_{π} and $\sigma_{\mathrm{p}}{}^{+}$. It becomes obvious that there is a linear correlation between the two sets of data (σ_p^+ vs ΔE_π, correlation coefficient of 0.97 and standard deviation of 0.08). It should be interesting to measure the absorption and emission spectra of **10a−f** in order to test the theoretically predicted trend which suggests that **10f** should exhibit absorption and emission maxima with the largest wavenumbers. Moreover, the latter results further support that Hammett parameters are indeed good measures for the π-conjugation strength which can be directly quantified with the EDA method as reported previously.[7]

Conclusions

The most important and somewhat unexpected conclusion from this work is that there is a very good linear correlation between the calculated strength of the π conjugation and the experimental values for the absorption and emission spectra of the bis(*gem*-diethynylethene) fluorophores **1−7**. The good correlation is surprising because the ΔE_π values are a measure of the π conjugation of the molecules in their ground state while the measure spectral lines arise from electronic excited states. The deviation between the absorption line of **8** and the ΔE_π value is explained with the twisted geometry of the molecule which indicates the limitation of the correlation. The very poor correlation between the maximum of the fluorescence spectrum of **2** and the ΔE_π value suggests that the electronic relaxation of the latter compounds is not a simple $\pi^* \rightarrow \pi$ process as it is for the other compounds. Furthermore, adequate modifications in the core moiety of the molecule (for instance, π-donor substituents in the aromatic ring) or in the periphery of the bis-enedyine unit (π-acceptor groups placed in para position of the aryl substituent) should increase the total π-conjugation in the systems and thus, provoke dramatic changes in both the absorption and emission spectra leading to large Stokes shifts. The extent of the latter may be estimated with the EDA prior to experiment.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. Excellent service by the Hochschulrechenzentrum of the Philipps-Universität Marburg is gratefully acknowledged. Further computer time was provided by the HLRS Stuttgart and HHLRZ Darmstadt. I.F. also acknowledges the Ministerio de Educación y Ciencia (Spain) for a postdoctoral fellowship.

Supporting Information Available: Cartesian coordinates (in Å) and total energies (in au, noncorrected zero-point vibrational energies included) of all of the stationary points discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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