π-Conjugation in donor-substituted cyanoethynylethenes: an EDA study†

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π-Conjugation in several donor-substituted cyanoethynylethenes was estimated using energy decomposition analysis (EDA); very good linear correlations between the ΔE_π values and experimental data are found.

Donor-substituted cyanoethynylethenes (CEEs) are a versatile class of modular building blocks for the construction of novel conjugated π-systems.[1] This family of donor–acceptor molecules combines the scaffolding capacity of tetraethynylethenes (TEEs) with the electron-accepting properties of tetracyanoethenes (TCNEs) and therefore they can function as electronic acceptor groups for nonlinear optical applications when substituted with dimethylanilino (DMA) donor groups.[2] CEEs are also more compact than TEE chromophores and can be sublimed without decomposition, thereby opening perspectives for opto-electronic device fabrication by ultra-thin film deposition.

The structural diversity of donor-substituted CEEs establishes them as suitable models for the study of π-conjugation and band gap tuning in strong charge-transfer chromophores. Thus, Diederich *et al.* proposed[1b] that the extent of π-conjugation in these systems can be experimentally estimated by means of different techniques such as X-ray crystallography, cyclic voltammetry, and NMR spectroscopy. The conjugation effectiveness was nicely revealed by large changes in the first oxidation and reduction potentials of CEEs with respect to the isolated donor and acceptor moieties as well as by the differences in the ^{13}C and ^{1}H NMR chemical shifts.

Recently we proposed a theoretical method where the strength of conjugation and hyperconjugation can be directly estimated with the help of an energy decomposition analysis (EDA).[3] The EDA makes it possible to 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 calculations were particularly helpful for addressing the recent controversy about the conjugation in diynes which was suggested to be zero because the energies for consecutive hydrogenation of the two triple bonds are nearly the same.[4] The EDA supported the suggestion[4c] that the partially hydrogenated alkynes are stabilized by hyperconjugation which makes the method of Kistiakowsky[5] for estimating the strength of conjugative interactions questionable.[4a,b] Our method was then successfully applied for the estimation of the extent of conjugation and hyperconjugation in acyclic[6a] and cyclic[6b] systems. It was also found that the π-conjugation values provided by the EDA given by the ΔE_π values correlate quite well with the experimentally derived Hammett (σ) and Hammett–Brown (σ^+ and σ^-) substituent constants in *meta* and *para* substituted benzylic cations and anions.[6c]

In this communication we wish to report on the application of the EDA method[7] to directly estimate the π-conjugation strength in several donor-substituted CEEs synthesized by Diederich *et al.*[1] and the correlation between the calculated ΔE_π values with experimental NMR and electrochemistry values.

The most important results of our analysis are gathered in Table 1 which gives the calculated ΔE_π values as well as selected NMR and electrochemistry data for donor-substituted CEEs. The geometries of compounds **1–8** were optimized with C_s symmetry constraints at the BP86/TZ2P level[8] and the resulting structures were used for the EDA in order to divide the orbital interactions into σ (a′) and π (a″) contributions. In all cases a C–C single bond connects the interacting fragments (*p*-ethynyl-*N*,*N*-dimethylanilino group and the corresponding cyanoethenyl fragment, see figures in Table 1), which are calculated for the EDA in the electronic doublet state with the unpaired electron in a formally sp or sp^2-hybridized orbital respectively, using the frozen geometry of the compound. We replaced the silyl protecting groups in compounds **2**, **3**, **5**, **7**, and **8** by hydrogens yielding the model compounds **2′**, **3′**, **5′**, **7′**, and **8′** since it is well-known that the deprotection of those groups results in a negligible shift in the UV/Vis spectra, indicating very small electronic differences between the silyl protected and deprotected compounds.[9]

From the data in Table 1, it becomes obvious that the increase in the number of CN groups in molecules possessing one DMA group strongly enhances the strength of π-conjugation. In fact, the highest values of ΔE_π were found for compound **1** and compounds **2′** and **3′** (with three and two CN groups per DMA moiety, respectively) compared to compounds **7′** and **8′** (with only one CN group). This result is in very good agreement with the experimentally observed downfield shifts of the aryl carbons *ipso* and *meta* to the NMe$_2$ group in the corresponding ^{13}C NMR spectra and with the large shifts to more positive potentials in the cyclic voltammograms induced by the introduction of further cyano groups.[1b]

The calculated ΔE_π values allow us to predict the effectiveness of the different conjugative pathways in compounds **7** and **8**. It was pointed out by Moonen and Diederich that the interpretation of the corresponding UV/Vis spectra gives misleading indications of the strength of π-conjugation and therefore the generally accepted rule that stronger π-conjugation leads to a bathochromic shift in

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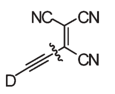
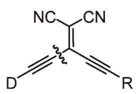
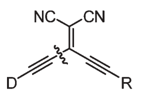
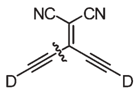
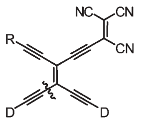
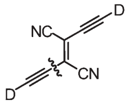
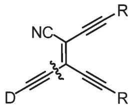
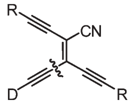
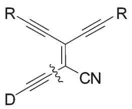
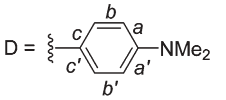
† Electronic supplementary information (ESI) available: Complete EDA Tables and Cartesian coordinates (in angstroms) and total energies (in a.u.) for compounds **1–10**. Plot of ΔE_π *versus* E^0. See DOI: 10.1039/b613671k

Table 1 Energy decomposition analysis (EDA) of donor-substituted CEEs at BP86/TZ2P

									
	1	**2**, R= ≡–$\mathrm{SiMe_3}$ **2'**, R= ≡–H	**3**, R = $\mathrm{SiMe_3}$ **3'**, R = H	**4**	**5**, R = $\mathrm{Si}^i\mathrm{Pr}_3$ **5'**, R = H	**6**	**(*E*)-7** R = $\mathrm{Si}^i\mathrm{Pr}_3$ **(*E*)-7'**, R=H	**(*Z*)-7** R = $\mathrm{Si}^i\mathrm{Pr}_3$ **(*Z*)-7'**, R=H	**8** R = $\mathrm{Si}^i\mathrm{Pr}_3$ **8'**, R = H
δ_{ipso}[a]	153.41	152.58	152.28	151.98	151.51	151.42	151.14	151.06	150.95
δ_{meta}[a]	136.38	135.58	135.37	135.03	134.49	133.93	133.95	133.79	133.37
E^{0}[b]	+0.79	—	+0.67	+0.63	—	+0.58	+0.56	+0.56	+0.52
ΔE_{π}[c]	−39.52	−35.62	−35.40	−31.29	−33.01	−31.95	−31.83	−31.21	−30.97
δr[d]	0.04201	0.03868	0.03854	0.03508	0.03691	0.03477	0.03526	0.03485	0.03447

[a] ^{13}C NMR chemical shifts (in ppm, 75 MHz, $\mathrm{CDCl_3}$), taken from ref. 1*b*. [b] Potential E^0 (in V), taken from ref. 1*b*. [c] Calculated ΔE_{π} values from the EDA at BP86/TZ2P level (in kcal mol^{-1}). [d] Calculated quinoid character: $\delta r = (((c + c')/2 - (b + b')/2) + ((a + a')/2 - (b + b')/2))/2$.



the UV/Vis spectrum is not always valid.[10] From the data in Table 1, it can be concluded that the *cis* donor–acceptor conjugation path in (*E*)-**7** is more effective than the *trans* path in (*Z*)-**7** and that the linear conjugation is more efficient than geminal cross-conjugation (ΔE_{π}: (*E*)-**7** > (*Z*)-**7** > **8**).[11] This is in agreement with the experimental NMR data while according to the NBO analysis by Lüthi *et al.*[12] geminal conjugation is predicted to be stronger than linear conjugation in non-donor substituted CEEs.[13]

From the above results, the ability of the EDA to directly estimate the π-conjugation strength in donor-substituted CEEs is clearly proven. Therefore, a high correlation between the calculated ΔE_{π} values and the experimental data used to qualitatively estimate the conjugation in these systems should exist. In fact, when we plot the ^{13}C NMR chemical shifts of the aryl carbons *ipso* and *meta* to the $\mathrm{NMe_2}$ group *versus* the calculated ΔE_{π} values from the EDA, very good linear relationships (Fig. 1: δ_{ipso} *vs.* ΔE_{π}, correlation coefficient of 0.99 and standard deviation of 0.43; Fig. 2: δ_{meta} *vs.* ΔE_{π}, correlation coefficient of 0.98 and standard deviation of 0.62) were found between both parameters with the notable exception of compound **4**. We also found a linear correlation between the ΔE_{π} values and the first oxidation potentials (E^0 values) from the cyclic voltammograms (correlation coefficient of 0.99 and standard deviation of 0.45; see Fig. 1S in Supporting Information).

To check our method and to compare the π-conjugation strengths in different conjugating donor–acceptor systems, we also carried out an EDA for compounds **9** and **10**, where the cyano groups are replaced by a (*p*-nitrophenyl)ethynyl substituent (Table 2). According to the data in Tables 1 and 2, it becomes clear that the cyano group is a stronger electron acceptor than the (*p*-nitrophenyl)ethynyl unit since the π-conjugation strength given by ΔE_{π} is higher in cyano-compounds **7'** and **8'** compared to **9** and **10**, respectively. This result is in good agreement with the experimental findings.[10] The higher ΔE_{π} values of compounds **9a,b** with respect to **10**, which are in agreement with the more downfield shifted δ_{ipso} ^{13}C NMR chemical shifts, support the conclusion that the linear donor–acceptor conjugation path is more efficient than cross conjugation. The ΔE_{π} values indicate that π-conjugation in the *trans* isomer **9a** should be stronger than in the *cis* isomer **9b** which does not agree with the δ_{ipso} values (Table 2) but the difference between the latter is very small (0.07 ppm).

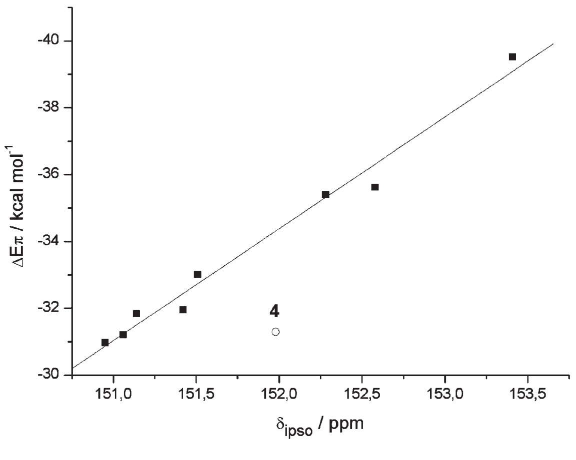


Fig. 1 Plot of the ΔE_{π} values *versus* the ^{13}C NMR chemical shift of the aryl carbon *ipso* to the $\mathrm{NMe_2}$ group.

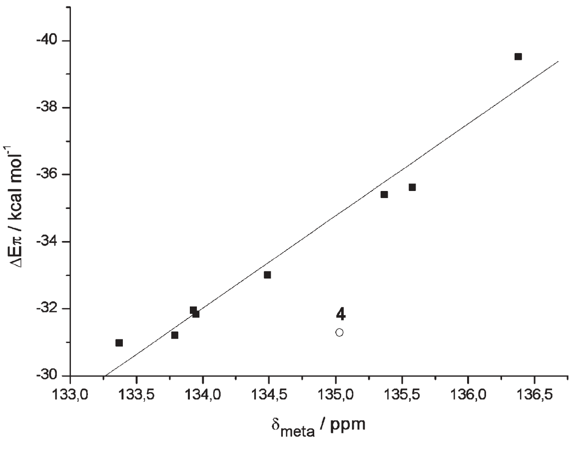
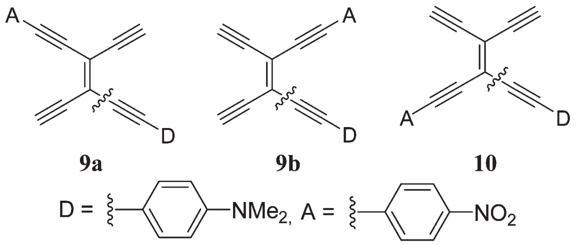


Fig. 2 Plot of the ΔE_{π} values *versus* the ^{13}C NMR chemical shift of the aryl carbon *meta* to the $\mathrm{NMe_2}$ group.

Table 2 EDA results of compounds **9**, **10** at BP86/TZ2P level



	9a	**9b**	**10**
δ_{ipso}[a]	150.69	150.76	150.60
ΔE_π[b]	−31.37	−30.96	−29.08
δr[c]	0.03477	0.03491	0.03315

[a] ^{13}C NMR chemical shifts (in ppm, 75 MHz, $CDCl_3$); N. N. P. Moonen, F. Diederich, personal communication. [b] Calculated ΔE_π values from the EDA at BP86/TZ2P level (in kcal mol^{-1}). [c] Calculated quinoid character δr (see footnote *d* of Table 1).

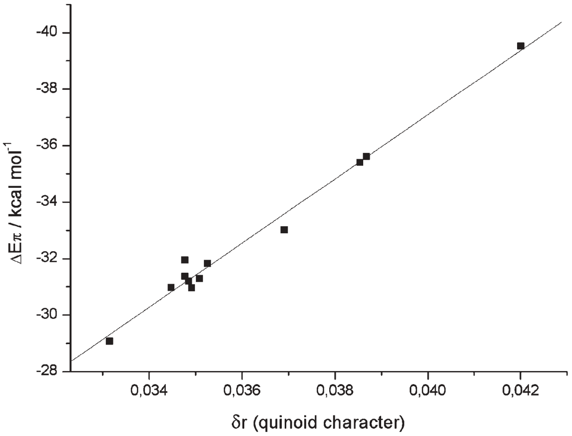


Fig. 3 Plot of the ΔE_π values *versus* the δr quinoid character.

Finally, we also considered the calculated bond alternation in the DMA rings of cyano and *p*-nitrophenylethynyl-ethenes as an indicator of the π-conjugation strength (Tables 1 and 2). The bond alternation in the DMA moiety shows the amount of charge-transfer from the donor to the acceptor group and can be expressed by the quinoid character δr of the aryl ring (for definition,[14] see footnote of Table 1). In benzene, the δr value equals 0, whereas values between 0.08 and 0.10 are found in fully quinoid rings. As can be readily seen from the data in Tables 1 and 2, the trend in δr values is very similar to the trend found in the EDA data. Thus, a very good linear relationship (correlation coefficient of 0.99 and standard deviation of 0.36) between both scales exists (Fig. 3). It is noteworthy that the δr value of compound **4** fits very well into the correlation with ΔE_π while the chemical shift values of **4** did not (Figs. 1 and 2). It might be worthwhile to reexamine the NMR data for **4**.

In summary, the EDA method is clearly useful to estimate the strength of the intrinsic π-conjugation of donor-substituted CEEs. The linear correlations between the ΔE_π values and various experimental data (^{13}C NMR chemical shifts and electrochemical potentials) which exhibit surprisingly high correlation coefficients suggest that the calculated values given by the EDA are reasonable for interpreting the chemical properties of the molecule. They may even be used to semi-quantitatively predict experimental values for hitherto unknown donor–acceptor systems.

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