Cross-Hyperconjugation: An Unexplored Orbital Interaction between *π*-Conjugated and Saturated Molecular Segments**

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 π -Conjugation, which is the stabilizing interaction between local orbitals of π -symmetry at multiple bonds, is a core concept in chemistry. In the classical sense, a π -conjugated compound has a structure with alternating single and multiple (double and/or triple) bonds.^[1] However, this model is deceiving in its simplicity because conjugation also depends on the connectivity in the bond alternating path.^[2] Thus, π conjugation is divided into linear conjugation (vicinal connectivity), cross-conjugation (geminal connectivity), and



omniconjugation. The first provides a path for delocalization over, for example, a C=C double bond from one end to the other, the second provides strong delocalization paths only from the groups attached to the C=C bond but not between the groups, and the third is a branched system with all parts linearly conjugated.^[3]

Conjugative interaction is not limited to π -conjugated molecular segments but can also be found in σ -bonded species $(\sigma$ -conjugation)^[4] and between σ - and π -systems (hyperconjugation).^[5,6] Hyperconjugation can further be divided into

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1) positive, that is, donation of electron density from filled σ orbitals to empty π^* -orbitals; 2) negative, that is, interaction between π - or p_{π} -orbitals with σ^* -orbitals; and 3) neutral hyperconjugation, with no strong directional interaction.^[7]

The interaction between p_{π^-} or π - and σ -bond orbitals in a linear hyperconjugative connectivity is well-known and often found in charged species.^[8] However, the fusion of two neutral hyperconjugated paths to a cross-hyperconjugated molecule with geminal connectivity between the two paths should also be considered.^[9] This interaction would occur in species with two linearly π -conjugated fragments linked by an sp³ hybridized ER₂ unit (E = Group 14 element) that contributes with two localized orbitals of π -symmetry; a bonding pseudo- π and an antibonding pseudo- π^* (Figure 1). These orbitals must be symmetry-adapted combinations of either two E–R σ - or σ^* -bond orbitals, and in the C_2 point group they belong to the *b* irreducible representation.

We now report on a study of compounds that are suitable for probing the strength of such potential cross-hyperconjugation. Regular cross-conjugation has recently received increased attention in the fields of nano and materials sciences.^[10,11] Thus, if strongly cross-hyperconjugated compounds are realizable, they could serve as design alternatives



Figure 1. Qualitative molecular orbital diagram displaying both the pseudo- π and pseudo- π^* orbitals (*b*-symmetric) of H₂ER₂, and the inphase (*b*-symmetric) and out-of-phase (*a*-symmetric) fragment orbital combinations of the phenylacetylene frontier orbitals (HOMO and LUMO) of the phenylethynyl–phenylethynyl fragment.



to rigid and planar π -conjugated species. Owing to their nonrigid structure they should display higher solubilities than the latter compounds, a fact that can be beneficial from applications point of view. Cross-hyperconjugation would also expand the fundamental understanding of the conjugation phenomenon.

We first investigated bis(phenylethynyl)compounds **1–4**, where **2–4** are substituted at the central Si or C atom. By varying the substituents R from electron-releasing to electron-withdrawing, the energy levels of the pseudo- $\pi(ER_2)$ and pseudo- $\pi^*(ER_2)$ orbitals of the saturated segment are altered and brought closer to the frontier π -orbitals of the phenylethynyl arms (Figure 1). This should afford a varying degree of cross-hyperconjugation as a local filled pseudo- $\pi(ER_2)$ orbital is oriented similarly as a local filled π -bond orbital of a central C=C bond in a cross-conjugated compound. The outof-phase combination of the pseudo- $\pi(ER_2)$ and the *b*symmetric orbital on the phenylethynyl–phenylethynyl fragment leads to the highest occupied molecular orbital (HOMO) of the assembled molecule. The question then arises as to how extensive this interaction can become.



The heavier Group 14 elements are often found in studies on hyperconjugation, especially in charged species.^[12] Herein we show that they also provide opportunities for synthetically viable molecules by which the neutral cross-hyperconjugation strength can be varied. The ethynyl segments inserted between the phenyl and ER₂ groups were incorporated to minimize the steric interaction between the substituents on the E atom and the π -system, and thus, to safe-guard against poor orbital overlap as a result of conformational restrictions that originate from steric congestion.

Initially we sat out to match the HOMO energy ($\varepsilon_{\rm HOMO}$) of phenylacetylene with the pseudo- $\pi(ER_2)$ orbitals of various H₂ER₂ molecules (in all cases HOMO). Calculations using M062X/6-311G + (2d,p)//B3LYP/6-311G(d) hybrid meta density functional theory $(DFT)^{[13-16]}$ reveal that ε_{HOMO} of phenylacetylene $(-7.96 \,\mathrm{eV})$ and 2-methylpropene (-8.25 eV), corresponding to fragments of 1, differ by less than 0.3 eV (for computational details, see Supporting Information). The pseudo- $\pi(ER_2)$ of H₂Si(SiMe₃)₂ is even closer (-7.98 eV), while the analogous orbitals of H₂SiMe₂ (-9.99 eV) and H₂CMe₂ (-10.49 eV) are deeper down. With two trifluoromethyl groups at silicon, leading to $H_2Si(CF_3)_2$, $\varepsilon_{\text{HOMO}}$ is -11.58 eV. Thus, bis(trimethylsilyl)bis(phenylethynyl)silane (2) should show strong cross-hyperconjugation, and we therefore synthesized 1 and 2, both reported earlier^[17,18] (for details see Supporting Information).

The UV absorption spectra of 1 and 2 reveal similar spectral features (Figure 2), with the first absorption shoulders at 298 (1) and 281 nm (2), respectively, corresponding to



Figure 2. UV absorption spectra of solutions of 1 and 2 in cyclohexane.

excitation energies of 4.17 and 4.42 eV. The second and third absorptions are found at 274 (1) and 265 nm (2), and at 261 (1) and 253 nm (2), respectively.

Evaluations of conjugation based on features in UV spectra should however be carried with caution.^[19] Thus, to further elucidate the similarities the compounds were studied by cyclic voltammetry as well as by DFT calculations, with geometries optimized at B3LYP/6-311G(d) and M062X/6-311G(d) levels and vertical excitations obtained at these geometries by time-dependent DFT (TD-DFT) at TD-M062X/6-311 + G(2d,p) level.^[20]

The calculations reveal that the analogies persist to the frontier orbitals of 1 and 2. For example, in the HOMO there is significant orbital density on the Si(SiMe₃)₂ moiety of 2 aligned in a cross-conjugated manner, similar as on the C= CMe₂ segment of 1 (Figure 3). With regard to orbital energies, $\varepsilon_{\text{HOMO}}$ of **2** is within 0.3 eV from that of **1** (1: -6.87, **2**: -7.13 eV). The *a*-symmetric HOMO-1 orbitals are nearly isoenergetic (1: -7.78, 2: -7.81 eV) and display strong resemblance which stem from the *a* orbital symmetry imposing a nodal plane bisecting the ER₂ and C=CMe₂ moieties. With regard to the lowest and second lowest unoccupied molecular orbitals (LUMO and LUMO + 1), they are clearly analogous in the two compounds, yet in 2 they are isoenergetic but split by 0.70 eV in 1. The splitting reflects the overlap of the in-phase combination of the LUMO of the phenylethynyl-phenylethynyl fragment with the $\pi^*(C=CMe_2)$ of **1** versus the pseudo- $\pi^*(Si(SiMe_3)_2)$ of **2**. It also reflects the distance between the closest two sp-hybridized C atoms of the phenylethynyl arms (2.412 vs. 2.986 Å in 1 and 2) and thus the local bonding overlap. This clearly leads to a lower LUMO in 1 than in 2. With TD-M062X/6-311 + G(2d,p)//B3LYP/6-311G(d) the first transitions in 1 and 2 are 298.9 nm (4.28 eV) and 269.0 nm (4.60 eV), respectively. However, the transitions are to states of opposite symmetries $(2^{1}A vs.)$ 1¹B, Table 1), and this repeats for the second transitions, which are to 1^{1} B in **1** and 2^{1} A in **2**. Thus, the similarity in the UV absorption spectra of the two compounds is deceiving, as the seemingly analogous transitions involve different excitations.



Figure 3. Frontier orbitals of 1 and 2 at the M062X/6-311 + G(2d,p)// B3LYP/6-311G(d) level.

Table 1: The first two excitations of **1–4** from UV absorption spectroscopy and the corresponding vertical excitations as calculated with TD-M062X/6-311+G(2d,p)//B3LYP/6-311G(d).^[a]

		Transition 1 nm (eV), state sym.	Transition 2 nm (eV), state sym.
1	exp.	298 (4.16)	274 (4.53)
	comp.	289.9 (4.28), 2 ¹ A	268.2 (4.62), 1 ¹ B
2	exp.	281 (4.41)	265 (4.68)
	comp.	269.0 (4.61), 1 ¹ B	265.1 (4.68), 2 ¹ A
3	exp.	261 (4.75)	249 (4.98)
	comp.	250.6 (4.95), 1 ¹ B	250.1 (4.96), 2 ¹ A
4	exp.	253 (4.91)	241 (5.15)
	comp.	241.6 (5.13), 1 ¹ B	239.1 (5.18), 2 ¹ B

[a] All transitions are visible, with calculated oscillator strengths above 0.20. For **4**, there are four forbidden transitions between the first and second visible excitation.

To determine whether other bis(phenylethynyl)silanes and methanes display similar features as 2, we synthesized 3 and 4 with ER₂ as SiMe₂ and CMe₂.^[21] Compared to 2, their first UV absorptions are hypsochromically shifted to 261 (3) and 253 nm (4), respectively, corresponding to raises in energy by 0.34 and 0.49 eV (Figure 4). The TD-M062X calculations reproduce the blue-shift as the first excitation of 4, a HOMO \rightarrow LUMO transition leading to the 1¹B state, is found at 241.6 nm (5.13 eV). However, in 3 the lowest transition is calculated at 250.6 nm (4.95 eV) and it is much more complex. Also, the contribution of the pseudo- π (ER₂) orbital to the HOMOs of 3 and 4 is negligible, indicating that 3 and 4 are much less cross-hyperconjugated than 2. Locking



Figure 4. UV absorption spectra of solutions of 1-4 in cyclohexane.

the molecules to planar $C_{2\nu}$ symmetric structures so as to optimize the orbital overlap gives more orbital density at the ER₂ segment in **3'** and **4'** (Figure 5), but brings only little change in the calculated first excitation energies.



Figure 5. The HOMOs of the optimal C_2 -symmetric **3** and **4** and the planar $C_{2\nu}$ -symmetric **3'** and **4'** calculated at the M062X/6-311 + G-(2d,p)//B3LYP/6-311G(d) level.

Further than UV spectroscopy, electrochemically determined redox potentials can provide substantial information on the nature of the frontier orbitals of **1–4**. Thus, the compounds were investigated by means of cyclic voltammetry (CV), and the anodic scans of the CVs of **1**, **2**, **3**, and **4** (Figure 6) feature electrochemically irreversible oxidative processes at 1.17, 1.22, 1.92, and 1.83 V vs. Fc^+/Fc^0 , respectively. It is thus apparent that compounds **1** and **2** are oxidized at similar potentials, while the oxidations of **3** and **4** are anodically shifted by more than 600 mV. These findings strongly support the results obtained in the UV analysis as well as the DFT calculations in that the HOMOs of **1** and **2** are considerably higher in energy compared to those of **3** and **4**.

The calculated geometries also reveal that **2** is more related to **1** than is **3** and **4**, as the C2-C1-C1'-C2' dihedral angle Θ involving the inner *ortho*- and the *ipso*-C atoms of the phenyl groups (Table 2), which measures the out-of-plane rotation of the phenyl groups and thus reflects the linear π -





Figure 6. Cyclic voltammograms (anodic scans) of **1–4** (1 mm solutions in CH₃CN) containing 0.1 m NBu₄PF₆ versus Fc⁺/Fc⁰, $\nu = 100 \text{ mV s}^{-1}$. * Fc⁺/Fc⁰ couple as internal standard.

Table 2: Dihedral angle Θ and essential CC bond lengths calculated at B3LYP/6-311G(d) (normal) and M062X/6-311G(d) (*italics*) levels.^[a]

Molecule, sym.		Θ[°]	<i>r</i> _{C≡C} [Å]	r _{C-C(Ph)} [Å]	$\Delta r_{\rm cc}({\rm Ph})$ [Å]
1	<i>C</i> ₂	10.7	1.210	1.423	1.394–1.407
2	C ₂	49.6	1.218	1.425	1.390–1.406
	C_1	44.6	1.213/1.213	1.431/1.431	1.388–1.400
3	<i>C</i> ₂	89.3	1.215	1.426	1.390–1.406
4	<i>C</i> ₂	84.5	1.208	1.428	1.390–1.406
5	<i>C</i> ₂	49.7	1.214	1.423	1.389–1.406
6	<i>C</i> ₂	0.0	1.230	1.433	1.399–1.414
	C_1	0.0	1.226/1.226	1.438/1.438	1.395–1.406
7	<i>C</i> ₂	8.2	1.210	1.426	1.390–1.407
	C_1	8.2	1.210	1.427	1.390–1.407
8	<i>C</i> ₂	0.0	1.226	1.433	1.399–1.415
	C_1	2.3	1.223/1.223	1.437/1.437	1.395–1.408
9	<i>C</i> ₂	54.2	1.203	1.426	1.390–1.405

[a] Θ denotes the C2-C1-C1'-C2' dihedral angle involving the inner *ortho*and the *ipso*-C atoms of the phenyl groups, $\Delta r_{cc}(Ph)$ denotes the C–C bond length range of the Ph groups. Here, only values of species with bulky R=SiMe₃ or SnMe₃ are given with both B3LYP and M062X; for the full table see the Supporting Information.

conjugation/hyperconjugation strengths between the phenylethynyl arms and either the C=CMe₂ or ER₂ segments, has values with B3LYP of 10.7° (1), 49.6° (2), 89.3° (3), and 84.5° (4), respectively. Interestingly, the dihedral angle of 2 is even smaller with M062X, a dispersion corrected DFT method suitable to handle steric congestion such as between the two SiMe₃ groups of 2. On the other hand, no significant differences are seen in analogous CC bond distances of these compounds, even not when comparing the regularly cross-conjugated 1 with 3 and 4 (Table 2). The same holds for experimentally determined NMR chemical shifts, as there are no significant differences in the aromatic region of 1 when compared to those of 2–4.

We also computed how cross-hyperconjugation varies with atom E and a wider set of substituents R. For E = Si, a span in the excitation energies is provided by $R = CF_3$ (5) and SnMe₃ (6) giving a wavelength (energy) range for the first visible excitation of 249.6–276.3 nm (4.49–4.97 eV). Here, compound 6 was calculated at TD-M062X/LANL2DZdp// B3LYP/LANL2DZdp level,^[22] and the first excitation of 2 at



this level is 270.4 nm (4.58 eV). With E as C and R as either SiMe₃ (7), SnMe₃ (8), or CF₃ (9) excitations at 264.3 nm (4.69 eV), 286.5 nm (4.33 eV), and 235.0 nm (5.28 eV) are found. Thus, the computations reveal possibilities for wider tuning of the first transition when E = C than when E = Si, and compound 8 is the best cross-hyperconjugated analogue of 1. Yet, an important difference between 1 and the cross-hyperconjugated species, excluding 6,^[23] is that the first transition in 1 is to the 2¹A state, whereas in 2–5 and 7–9 it is to the 1¹B state.

A striking geometry feature of **6–8** is that these species are either planar $C_{2\nu}$ -symmetric (**6** and **8**, Table 2), or nearly so (**7**), supporting strong cross-hyperconjugation. It is also notable that the C=C triple bonds in **6** and **8** are notably elongated when compared to **1**. From the calculated lowest excitation energies and the geometries, it is thus apparent that cross-hyperconjugation strength can be tuned through choice of element E and substituents R, in a similar manner as found earlier for the hyperconjugative donor and acceptor abilities of C–X σ -bonds.^[24] In our species, electropositive R groups raise the energy of the pseudo- π (ER₂) orbital as well as polarize the E–R σ -bond electron density towards the E atom.

In conclusion, through a series of easily accessible and persistent compounds we have shown that a properly substituted ER₂ segment has similar effect on the electronic and optical properties of a molecule when inserted between two linearly π -conjugated segments as a C=C double bond with geminal connectivity. This cross-hyperconjugation provides new design motifs for compounds with applications in nano and materials sciences. A next question is now whether omnihyperconjugated molecules can also be designed.

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