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Perspective

Perspective on "Benzynes, dehydroconjugated molecules, and the interaction of orbitals separated by a number of intervening σ bonds"

Hoffmann R, Imamura A, Hehre WJ (1968) J Am Chem Soc 90: 1499–1509

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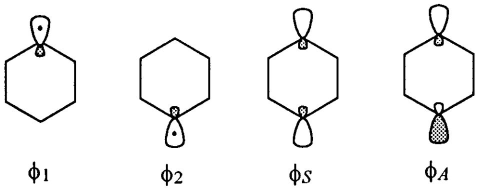
Abstract. This paper provides an overview of the title paper by Hoffmann, Imamura, and Hehre, and the impact this paper has had on the area of long-range intramolecular interactions. The author has made extensive use of the through-bond/through-space decomposition of Hoffmann et al. in his work on long-range interaction in bichromopheric molecules. In particular he has applied these ideas in analyzing electron transmission spectra of such molecules.

Key words: Through-bond interactions – Orbital ordering

Chemists have long been fascinated with interactions between remote functional groups. One of the most intriguing aspects of such interactions is that they can proceed directly via through-space (TS) coupling between the functional groups, or indirectly via orbitals of the intervening bridge. Through-bond (TB) coupling (although not specifically referred to as such) is the basis of the McConnell model [1] introduced in 1961, and which has proven to play a central role in electron-transfer theories. A systematic procedure for dissecting net interactions into their TB and TS components and for analyzing how the TB coupling depends on the number and relative orientation of the bonds of the intervening bridges, was first laid out in the pioneering paper of Hoffmann, Imamura, and Hehre (HIH) [2]. Although the HIH paper focused on the orbital interactions in benzynes and dehydroconjugated molecules, the strategies introduced therein have a much wider range of applicability [3–13].



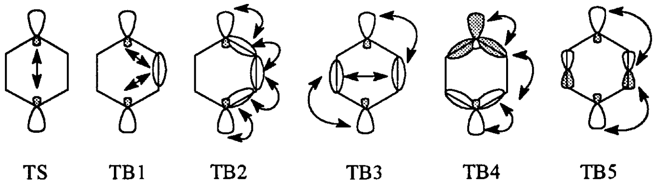
In reviewing the main contributions of the HIH paper, it will suffice to focus on one of the molecules, *p*-benzyne, considered in that study. *p*-Benzyne has two half-occupied localized lone-pair orbitals, ϕ_1 and ϕ_2, depicted in Scheme 1. These give rise to the symmetry-adapted molecular orbitals (MO)

$$\phi_S = \phi_1 + \phi_2$$

$$\phi_A = \phi_1 - \phi_2 \ ,$$

where S and A denote, respectively, the symmetric and antisymmetric combinations of the localized lone-pair orbitals, and ϕ_1 and ϕ_2 have been assumed to be orthogonal. Of primary interest is the splitting energy $\Delta E = \varepsilon_S - \varepsilon_A$, as this provides a measure of the coupling between the localized orbitals.

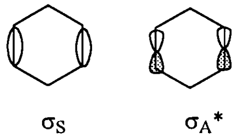
The major conceptual advance provided by HIH was the dissection of ΔE into TS and TB components. As defined by HIH, TS refers to the direct interaction between the localized ϕ_1 and ϕ_2 orbitals and TB to the indirect interaction via the intervening σ bonds. The TS interaction and a subset of the TB pathways for coupling the lone-pair orbitals of *p*-benzyne are shown in Scheme 2.



Note, in particular, that with the HIH definition, pathways TB1, TB3, TB4, and TB5, which involve interactions via σ orbitals not directly coupled to ϕ_1 or ϕ_2 or which skip over bonds, are classified as TB.

MO calculations on *p*-benzyne place the A orbital energetically below the S orbital, counter to one's expectations [2]. The TB/TS decomposition provides an explanation for this surprising result, namely that the TB interactions with the σ and σ^* orbitals of the bridge destabilize ϕ_S relative to ϕ_A and, moreover, that the TB interactions are sufficiently large so as to reverse the "natural", TS ordering of the A and S orbitals. HIH showed how this can be understood in terms of a perturbative treatment, describing the interactions of the symmetry-adapted ϕ_S and ϕ_A orbitals with the symmetry-adapted orbitals of the benzene "bridge".

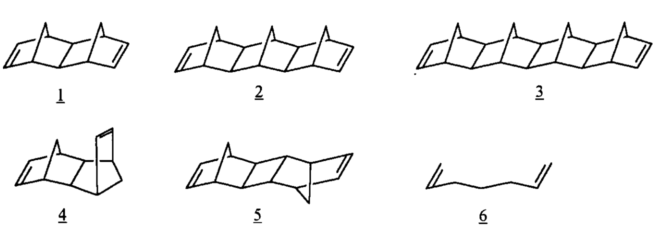
To simplify the analysis we consider the two symmetry-adapted bridge orbitals σ_S and σ^*_A shown in Scheme 3.



These are singled out because they interact especially strongly with ϕ_S and ϕ_A (due to the interactions with the back lobes of the lone-pair orbitals. Specifically σ_S mixes with ϕ_S destabilizing the latter, while σ^*_A mixes with ϕ_A stabilizing the latter. This results in an inverted ordering of the "mixed" lone-pair orbitals as shown in Fig. 1. Of course, a quantitative prediction of the ϕ_S/ϕ_A splitting requires inclusion of the other possible TB coupling pathways. The relevenacy of the orbital splittings for the singlet/triplet gaps in *p*-benzyne and other aryl biradicals is discussed in a recent paper of Squires and Cramer [14].

The HIH paper also made important contributions to our understanding of how the electronic coupling depends on the length and conformation of the bridge. Specifically, it was shown why the relative energy of the S and A orbitals depends on whether there is an odd or even number of carbon–carbon linkages in a bridge, and why the coupling is generally greater through bridges with all-trans orientation of the carbon–carbon σ bonds. The TB coupling model is also able to account for the inverted ordering of the π MOs ($\pi_A < \pi_S$) in 1,4-cyclohexadiene and a wide range of other hydrocarbrons [3, 15]. In the case of 1,4-cyclohexadiene, the TB coupling proceeds via the bridging methylene groups.

The ideas laid down in the HIH paper have also proven pivotal for analyzing the interactions responsible for long-range electronic coupling in bichromophoric systems such as **1–5** shown in Scheme 4 [8–13].



For example, both MO calculations and experiment (photoelectron spectra) reveal that the splitting between the π orbitals of **4** is much smaller than that in **1** (0.44 versus 0.87 eV) [16, 17]. This is understandable in terms of the greater effectiveness of all-trans bridges at relaying the coupling as discussed by HIH (sometimes referred to as the "all-trans" effect [2, 3, 4, 7]. Also, the HIH analysis explains the "inverted" ($\pi_A < \pi_S$) ordering of the π orbitals of **5**.

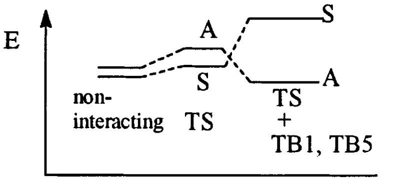
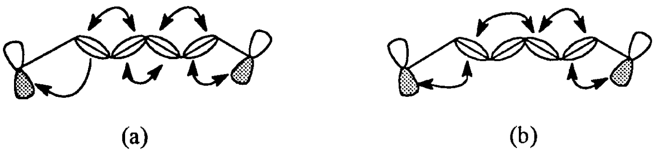


Fig. 1. Energies of the ϕ_S, and ϕ_A, orbitals of *p*-benzyne, in the absence of interactions, with through-space (*TS*) coupling only, and with both TS and through-bond (*TB*) TB1 + TB5 coupling

There has been immense interest in understanding how electronic couplings fall off with increasing bridge length, for example, along the sequence of molecules **1**, **2**, and **3**. MO calculations on this series of molecules and other bichromophoric species show that both the π_S, π_A and π^*_S, π^*_A splittings fall off nearly exponentially with the length of the bridge [9–11, 19, 20]. Although, this is consistent with the predictions of the McConnell model [1], which includes only nearest-neighbor interactions, the strong coupling through the bridges in fact derives from pathways that skip over bonds [9–13, 19, 20]. This conclusion is based on an analysis in which the net TB coupling is dissected into contributions due to individual pathways, very much in the spirit of HIH.

Scheme 5 shows the nearest-neighbor pathway **a** and a non-nearest-neighbor pathway **b** for a six-bond bridge. Although the contribution of **b** to the π_S, π_A splitting is indeed smaller than that of **a**, this is compensated by the fact that there are multiple pathways that skip over bonds. Moreover, the number of pathways that involve "bond-skipping" grows rapidly with increasing chain length [9, 11].



Recent theoretical studies have also elucidated the role of constructive/destructive interference between various TB coupling pathways [12, 21]. For example, it has been shown that the smaller π_S, π_A splitting in **1** compared to **6** is due to the destructive interference between pathways that jump between two parallel bridges in the former [12, 21]. The theoretical analysis leading to this conclusion is a natural extension of the perturbative approach presented by HIH.

Although the examples discussed previously focused on systems in which the chromophores are covalently bonded to the bridge, it has been demonstrated that TB coupling can be sizable through noncovalently linked bridge units, for example, the model system comprising two ethylene molecules separated by *n* methane molecules in van der Waals contact [9, 20]. This implies that solvent molecules can be very effective at relaying electronic coupling. Not surprisingly, several research groups have been designing bichromophoric systems which allow testing of this idea [22, 23].

In summary, the pioneering paper of HIH not only provided a conceptual and computational framework for dissecting electronic coupling between remote functional groups into TB and TS components, but also a qualitative understanding of how the TB coupling depends on the number and orientation of the σ-bond linkages. Moreover, the perturbative approach used by HIH forms the basis of modern theoretical studies of the contributions of various TB pathways to the net coupling in D–B–A and other bichromophoric systems.

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