A Simple Variational Method for Quantitative Assessment of "Through-space" and "Through-bond" Interactions

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A simple method is described for separating "through-space" from "through-bond" interactions. The method is applied to 1,4-cyclohexadiene, 2,5-dihydrofuran, 2,5-dihydrothiophene, and 2,5-dihydropyrrole.

It was recently shown [1–9] that the π orbital "localization" procedure of Baird [10, *] and a variant [9, 11, *] of it are very useful for a quantitative treatment of several fundamental problems (as e. g. orbital interactions, aromaticity, inductive and conjugative effects or conformational forces) in theoretical organic chemistry. In this communication we proceed to study the potentiality of the method for a quantitative assessment [12] of "through-space" and "through-bond" interactions [13, 14, **].

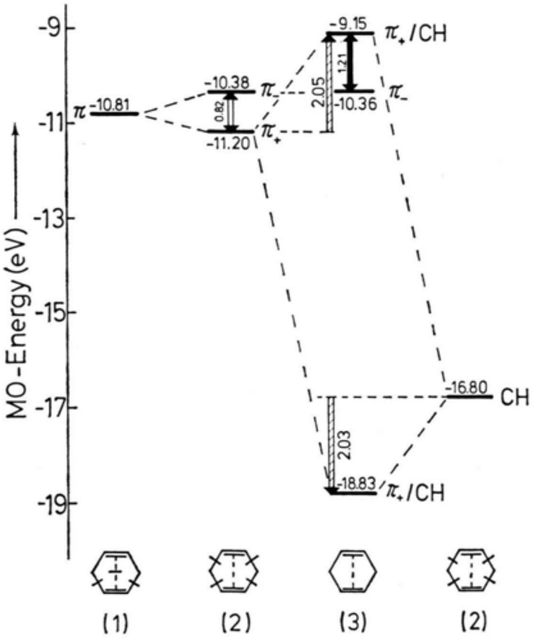

Fig. 1. Calculated interaction diagram for 1,4-cyclohexadiene using the CNDO/S method. The basis orbital energy, the "through-space" (◀═▶), "through-bond" (▨▶) and total (◀━▶) effects are evaluated on the base of the two individual π decoupled models (1) and (2) and the fully coupled case (3). For details see text.

To this end, we choose the well-known 1,4-cyclohexadiene case [12, 15–17] (Figure 1). Here, three models, (1) to (3), are considered: (1) means complete π conjugative decoupling of one double bond from the rest of the molecule, (2) means π isolation of both double bonds from the methylene groups, and (3) refers to a usual full π coupled calculation. With (1) we interrupt both "through-space" and "through-bond" interactions, with (2) we cut off the "through-bond" but retain the "through-space" process, and with (3) both events remain intact.

In the actual calculation the planar geometry [18–21] of 1,4-cyclohexadiene was taken and the CNDO/S (MINDO/2) method used. We obtain a "through-space" splitting of 0.82 (0.59) eV, a "through-bond" destabilization of the π_+ orbital of 2.05 (1.84) eV so that the predicted orbital sequence for 1,4-cyclohexadiene is π_+/π_- and the energy difference between both orbitals 1.21 (1.21) eV [+]. It is gratifying to note that these values agree well with the MINDO/2 results ("through-space" splitting $= 0.66$ eV, "through-bond" destabilization of the π_+ orbital $= 1.86$ eV, energy difference between π_+ and $\pi_- = 1.20$ eV) of Heilbronner and Schmelzer [12]. These authors obtained their results on the base of a rather different and seemingly more complicated perturbational approach. The present variational method is simple and easy to apply.

To check the consistancy of the method we considered an additional model [*] (4) which admits "through-bond" but excludes "through-space" interaction. In this case the π_+/CH orbital is destabilized by 0.31 eV and the π_- orbital stabilized by 0.41 eV relative to case (3) in harmony with what is expected from (2). This result of near additivity of effects corroborates the method used.

The method was further applied to the question of "through-space" interaction in 2,5-dihydrofuran [22], 2,5-dihydrothiophene [23], and 2,5-dihydropyrrole [++]. Taking the π lone pair orbital on the heteroatom as an indicator we obtained as percentage [‡] "through-space" interactions in this series: 19%, 20%, and 83%, respectively. Thus, for 2,5-dihydropyrrole, "through-space" interaction may be relevant.

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[*] In the Baird method π orbital localization on a selected molecular subunit is accomplished by setting the SCF matrix elements between any π atomic orbital of this subunit and any π atomic orbital of the molecular remainder zero. Instead of this full decoupling our variant method allows us to set individually selected matrix elements zero so that individual interactions (as e. g. here the "through-space" interaction) can be selectively investigated.

[**] Current usage equates "through-space" interactions with "homoconjugative" or "transannular" interactions and "through-bond" interactions with "hyperconjugative" interactions.

[+] The measured separation between the two π ionization events is 1.0 eV; see Reference [15].

[++] Taken to be planar and the nitrogen atom sp^2 hybridized.

[‡] Referred to the calculated "through-bond" interaction.

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