# Through-Bond Interactions in Nonconjugated Dienes and Diones

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Abstract: Electron transmission spectroscopy is utilized to determine the vertical electron affinities associated with electron capture into the π^* orbitals of a series of nonconjugated dienes and diones. Those compounds in which the π groups are separated by three σ bonds show particularly large through-bond interactions resulting in inverted (i.e., π_-^* below π_+^*) ordering of the π^* orbitals.

The interactions between the π orbitals of the dienes **1–3** and between the lone-pair (n) orbitals of the corresponding diketones **4–6** have been studied[1] by utilizing photoelectron spectroscopy (PES) and theoretical calculations. PES yields the ionization potentials, which, according to Koopmans' theorem (KT),[2] may be associated with the negatives of the energies of the filled orbitals. These studies show that the splittings between the π_+ and π_- orbitals of **1–3** and between the n_+ and n_- lone-pair orbitals of **4–6** (where the "+" denotes the bonding combination and "−" the antibonding combination of the localized orbitals) increase along
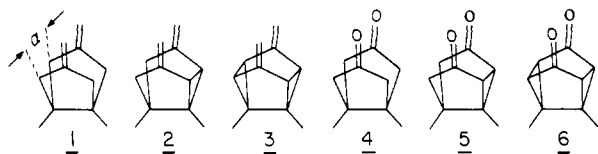
the sequence **1–3** and **4–6**, respectively. Due to overlapping of bands in the PE spectra, the π IP's of **4–6** have not been established. The π_+ orbital is more stable than the π_- orbital in **1**, and the reverse order is found for **2** and **3**. For the diones, the n_+ orbital was found to be more stable than the n_- orbital for all three compounds. The splittings between the filled π and n orbitals of **1–6** are primarily through-bond[3] in nature and derive from a strong interaction between these orbitals and those of the σ frame. In **2** and **3** the π_+ orbital interacts strongly with the symmetric Walsh orbital of the three-membered ring unit(s) and hence is destabilized. On the other hand, the interaction between π_- orbital and the σ frame remains essentially constant along the series **1**, **2**, and **3**. For the diketones **5** and **6** there is a strong interaction between n_- and the antisymmetric Walsh-type orbital of the three-membered ring unit(s), causing the splitting between n_- and n_+ to increase from **4** to **6**.

In the present study electron transmission spectroscopy (ETS)[4,5] is utilized to study the interactions in the unfilled π^* orbitals of **1–6**. ETS, in which one determines the energies at which molecules capture electrons to yield temporary anions, has proven well suited for characterizing through-bond and through-space interactions in unfilled orbitals.[6,7] In the format of ETS utilized here the derivative with respect to energy of the transmitted current is reported as a function of electron energy; hence the most probable attachment energies (AE) or vertical electron affinities (EA's) correspond to inflection points. The resolution of the spectrometer is better than 0.05 eV. Calibration of the energy scale is accomplished by admitting N_2 gas into the collision chamber and by reference to the $^2\Pi_g$ anion of N_2.

The ET spectra of compounds **1–3** are shown in Figure 1. Compounds **1** and **2** display single features near 1.38 and 1.55 eV, respectively, while **3** displays two features at 1.18 and 2.15 eV. For comparison we note that electron capture into the π^* orbital of ethylene occurs near 1.78 eV, and at somewhat higher

Table I. Experimental Electron Attachment Energies and Splittings between the π^* Orbitals of **1–6**

compd	exptl/AE's (eV)	exptl splitting[a]	calcd splitting[a]
1	1.38		0.19
2	1.55		−0.65
3	1.18, 2.15	−0.93	−1.70
4	0.45, 1.10[b]	0.65	0.20
5	0.54, 0.91	−0.37	−0.68
6	≤0, 1.37	≤−1.37	−1.80

[a] A positive splitting indicates that the π_-^* orbital is less stable than the π_+^* orbital, and a negative splitting indicates the opposite ordering. [b] In **4** there is also a peak at 0.75 eV. We have assumed that this peak is due to vibrational excitation and that the 1.1-eV peak is due to the second anion state.

energy in the alkyl-substituted ethylenes.[5] We believe that the appearance of only a single feature in the ET spectra of **1** and **2** indicates that the anion states derived from the π_+^* and π_-^* orbitals of these compounds occur at nearly the same energy.

For compound **3**, in which the anion states are well separated, the features in the ET spectra have widths of about 0.5 eV. The absence of vibrational structure indicates that electron detachment occurs in a time short compared to that associated with nuclear motion.[5] In the limit of very short lifetimes, the widths are governed by the autodetachment rate. For somewhat longer lifetimes, the features in the spectra correspond to the "smeared out" Franck–Condon envelopes. The single peak seen in the ET spectrum of **1** is about 0.4 eV broader than the individual peaks of **3**, consistent with the overlap of two states split by a few tenths of an eV. The feature in the ET spectrum of **2** is slightly broader than that in **1**. This could be the result of a larger splitting between the two anion states or to shorter lifetimes of the anion states of **2**. In general, changes in molecular structure which lower the symmetry cause a decrease in the lifetimes of temporary anions.[5]

The ET spectra of **4–6** are given in Figure 2. Compound **4** displays two well-defined features at 0.45 and 1.10 eV. In addition there is a weak feature at 0.75 eV, appearing as a shoulder on the 0.45-eV feature. The ET spectrum of compound **5** has a pronounced feature centered at 0.54 eV. The shape of this feature suggests that it arises from two anion states, one intense and near 0.5 eV and the other weak and near 0.9 eV. Compound **6** has a single feature at 1.37 eV, which is expected to correspond to

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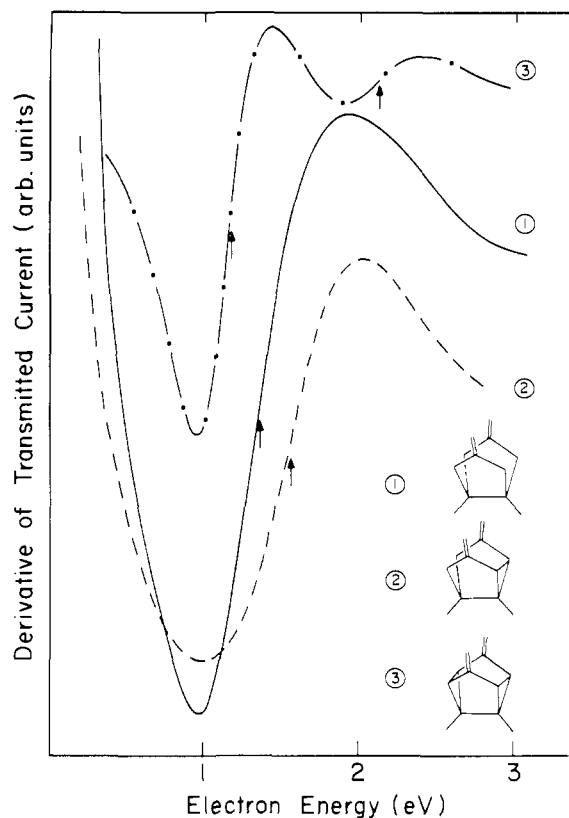(4) Sanche, L.; Schulz, G. J. *Phys. Rev.* **1968**, *A5*, 1672.
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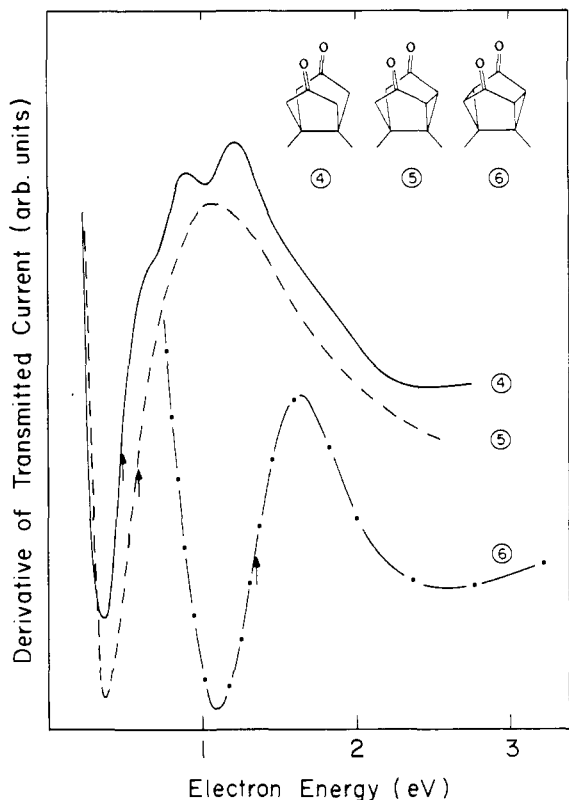(7) Burrow, P. D.; Jordan, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 5247 and references therein.

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Figure 1. Derivative of the transmitted current as a function of electron energy in **1**, **2**, and **3**. The vertical electron attachment energies are indicated by arrows.


Figure 2. Derivative of the transmitted current as a function of electron energy of **4**, **5**, and **6**. The vertical electron attachment energies are indicated by arrows.

the excited-state anion, with the ground-state anion being either stable or close to 0 eV. This follows from comparison of the trends in **1–3** with those in **4–6** and from the fact that the π^* orbital of formaldehyde is nearly 1 eV more stable than that of ethylene.[5]
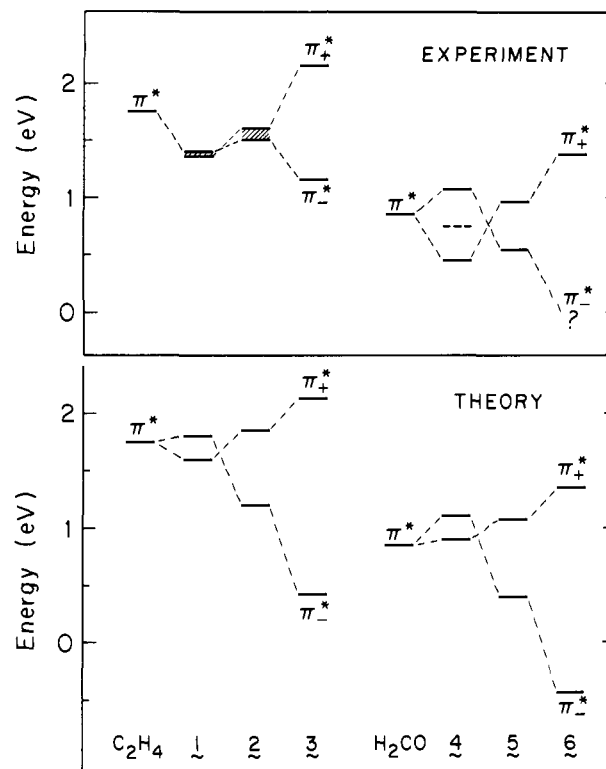

Figure 3. Correlation diagram comparing the relative energies of the anion states of compounds **1–6**. The upper portion of the correlation diagram utilizes the vertical attachment energies measured here. The bottom portion is derived from the orbital energies derived from STO-3G calculations as described in the text.

To aid in the interpretation of the spectra we performed STO-3G calculations[8] on the neutral molecules, equating the negatives of the energies of the unfilled orbitals with the EA's. Although the absolute EA's obtained in this manner are not meaningful, our experience has been that the *relative* values for related molecules correlate fairly well with the *relative* experimental values. For **4–6** MNDO optimized geometries were employed, while for **1–3**, the geometries were generated by modifying those of the corresponding ketones. The theoretical EA's of **1–3** are corrected by the amount required to bring the STO-3G EA of ethylene into agreement with the experimental EA, and the theoretical EA's for **4–6** are corrected by the amount needed to bring the STO-3G EA for formaldehyde into agreement with the experimental value. The experimental and calculated EA's of **1–6** are summarized in Table I and in the correlation diagram presented in Figure 3.

The calculations indicate that the π_+^* orbital is more stable than the π_-^* orbital for compounds **1** and **4** but that the π^* orbitals have the opposite ordering in the other four compounds. They also show that the trends in the π^* orbitals are mirrored in the filled π-orbital space; that is, in **1** and **4** the π_+ orbital is more stable than the π_- orbital, whereas the opposite is true for **2**, **3**, **5**, and **6**. The splitting between the π_-^* and π_+^* orbitals is predicted to be only about 0.2 eV for **1** and **4** and to be much greater in the other compounds. The small splitting predicted between the π_-^* and π_+^* orbitals of the bicyclic systems **1** and **4** indicates that in these compounds the through-space interaction between the two π fragments is small and also that the π_-^* and π_+^* orbitals interact to nearly the same extent with the σ frame.

Introduction of one or two additional σ bonds as in the tricyclic (**2**, **5**) or tetracyclic (**3**, **6**) systems causes a reduction of the average

(8) The STO-3G calculations were performed with the GAUSSIAN 83 program developed by W. Hehre and co-workers at the University of California, Irvine: DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hout, R. F., Jr.; Pietro, W. J.; Blurock, E. A.; Hehre, W. J., to be submitted for publication to the Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.
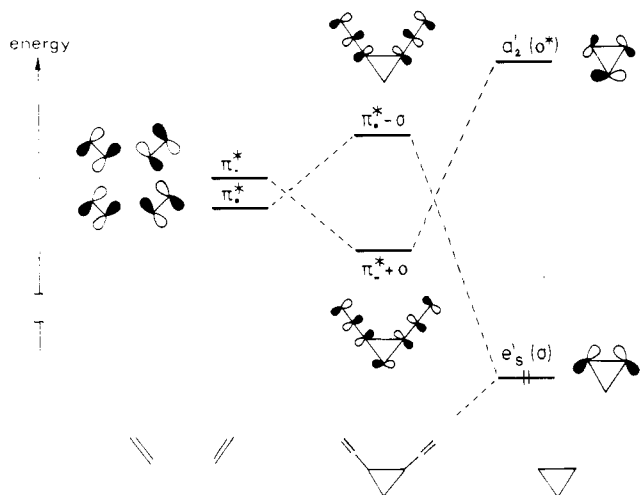
Figure 4. Schematic interaction diagram between the two linear combinations of the π^* orbitals in **2**, **3** and **5**, **6** with the corresponding Walsh orbitals of the three-membered ring fragment(s).

distance between the π systems from 520 pm (estimated for **1** and **4**) to 460 pm (**5**)[b] and 430 pm (**6**)[9] as well as a strong discrimination in the interaction between the two linear combinations of the π^* orbitals with the σ frame. The interactions responsible for the through-bond (TB) mixing are depicted in Figure 4. The destabilization of the π_+^* orbital is due to the interaction with the occupied symmetric Walsh orbital (e_s') of the three-membered ring fragment(s). The π_-^* orbital is stabilized by interaction with a low-lying unfilled Walsh orbital (a_2') of the three-membered ring fragment(s). These interactions are sufficiently large to cause an inversion of the order of the π^* orbitals (i.e., π_-^* below π_+^*). On the left-hand side of this figure we show the two linear combinations π_+^* and π_-^* resulting from a purely spatial interaction between the two fragments, while on the right we have indicated the occupied Walsh orbital e_s' and the unoccupied linear combination a_2' of the three-membered ring(s). The resulting interaction between these orbitals is indicated in the center of Figure 4.

The splitting calculated between the π_+^* and π_-^* orbitals of **2** is the mean of those calculated for **1** and **3**, and the splitting calculated between the π_+^* and π_-^* orbitals of **5** is the mean of those calculated in **4** and **6**. This is precisely what would be expected if the interactions in **1** and **4** are of the 4-σ TB variety, those in **3** and **6** are predominantly 3-σ TB, and those in **2** and **5** are due to both 3-σ and 4-σ TB interactions.

Although the STO-3G/KT approximation is quite successful for accounting for the trends in the relative energies of the cation states of **1–6** (i.e., the π IP's of **1–3** and the lone-pair IP's of **4–6**), it is less successful for the anion states. In particular, the splittings calculated for **2**, **3**, and **5** are significantly larger than those observed experimentally. Presumably, this is also the case for **6**, for which the first anion state is not observed because it is bound. The "corrected" STO-3G calculations predict that the ground-state anion of **6** is bound by 0.45 eV.

A possible explanation for the inadequacy of the STO-3G/KT procedure for the EA's of **2**, **3**, **5**, and **6** is that through-space

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(9) Irngartinger, H.; Jähne, G.; Gleiter, R., to be published.

interactions are also important in the anions of these species. In these compounds through-space interactions would operate counter to the through-bond interactions and would tend to decrease the splittings between the anion states. Previous studies have shown that through-space (TS) interactions are more important in anion states than in cation states[7] and that the STO-3G minimal basis set is inadequate for describing the long-range through-space interactions in temporary anions. Another possible limitation of the STO-3G basis set for these compounds is that an accurate description of the orbitals of the cyclopropane rings requires more flexible (e.g., 6-31G*) basis sets.

In constructing the correlation diagram given in Figure 3 we have assumed that the weak 0.9 shoulder on the main peak in the ET spectrum of **5** and the feature near 1.1 eV in the ET spectrum of **4** correspond to the second anion states of these compounds. The latter assignment in particular is open to question since the ET spectrum of **4** has two other peaks at 0.45 and 0.75 eV. Our analysis assumed that the 0.75-eV peak is due to vibrational excitation in the ground-state anion. The overlap between the first two features in the ET spectrum of **4** precludes determining the splitting to better than 0.05 eV. Hence the upper feature could correspond to excitation of the CO stretch. Another possible interpretation of the structure in the ET spectrum of **4** is that the two anion states are nearly degerate and that the feature near 1.1 eV is vibronic in nature. We note that an "extra" feature, attributed to vibronic structure arising from a pseudo-Jahn-Teller coupling of the two nearly degerate electronic states, appears in the ET spectra of the alkyl-substituted benzenes.[11]

Conclusions

Using ETS and ab initio calculations we have studied the interactions between the π^* orbitals of the nonconjugated dienes and diones **1–6**. The interactions of the localized π^* orbitals with the σ and σ^* framework orbitals are responsible for the stabilization of the LUMO's of those compounds relative to those of ethylene and formaldehyde and for the sizable splittings between the π_+^* and π_-^* orbitals of **3**, **5**, and **6**. In the compounds with 3-bond links between the unsaturated moieties, the ordering of both the π and π^* orbitals is inverted from that expected based on TS interactions. In compounds **3** and **6**, with two 3-bond linkages, the π_-^* orbitals are strongly stabilized and the π_+^* orbitals somewhat destabilized relative to the corresponding orbitals of ethylene and formaldehyde. Through-bond coupling dominates the interactions between the π^* orbitals in all six compounds studied. Through-space interactions appear to be negligible in **1** and **3** but appear to play a small role in the other four compounds.

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(11) Burrow, P. D.; Jordan, K. D., unpublished results.