Some Aspects of Orbital Interactions through Bonds: Physical and Chemical Consequences

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In 1968 Hoffmann, Imamura, and Hehre reported calculations on diradical systems that led to the now classic conceptual dissection of orbital interactions into through-space and through-bond varieties.[1,2]

As the term implies orbital interactions through space result from the direct, spatial overlap of two interacting (basis) orbitals, ϕ_a and ϕ_b. For positive values of overlap between the basis orbitals, through space interactions always result in the bonding combination of orbitals (i.e., $a\phi_a + b\phi_b$) lying below the antibonding combination (i.e., $b\phi_a - a\phi_b$) in energy. This is called the natural sequence of orbitals.[3] Because the extent of the interaction[4] depends on the size of the overlap integral between the basis orbitals,[3] it follows that through-space interactions are negligible for interorbital separations greater than 3 Å.[1,2]

The unexpectedly large calculated interactions (ca. 1.5 eV) between the nitrogen nonbonding orbitals in Dabco (1) and pyrazine (2), notwithstanding the large
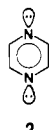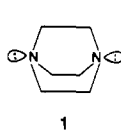

spatial separation of the N atoms in these molecules, together with the *inverted* sequence of these orbitals (vide infra), led to the concept of orbital interactions through bonds[1] in which orbitals interact as a result of their mutual mixing with the intervening σ framework. Thus, 1 and 2 are examples in which nitrogen non-bonding orbitals interact through three σ bonds.

A simple PMO-based model of orbital interactions through three bonds has been developed[1,2] and is illustrated in Figure 1 for the case of the interacting orbitals, n_1 and n_2, of 1,4-butanediyl. Firstly, symmetry-adapted combinations of n_1 and n_2 are formed: $n_+(S) = (n_1 + n_2)/2^{1/2}$ and $n_-(A) = (n_1 - n_2)/2^{1/2}$. The symmetries (A or S) of the orbitals are classified with respect to the C_2 axis which interchanges n_1 and n_2. The level ordering, n_+ below n_-, follows the natural sequence due to the presence of (weak) through-space interactions. Symmetry-allowed mixing of n_+ and n_- with respectively the $\sigma_{2,3}$ and $\sigma^*_{2,3}$ MOs of the central C2–C3 bond gives rise to through-bond interactions. This mixing leads to the most characteristic feature of orbital interactions through three bonds, namely, that an inverted sequence of orbitals results; i.e., the bonding (S)

level $(an_+ - b\sigma_{2,3})$ lies *above* the antibonding level $(cn_- + d\sigma^*_{2,3})$. This result is not dependent on the system having any symmetry. When n_1 and n_2 are nondegenerate, each may mix with both $\sigma_{2,3}$ and $\sigma^*_{2,3}$. However the nodal characteristics of the orbitals ensure that the $n_+,\sigma_{2,3}$ and $n_-,\sigma^*_{2,3}$ interactions are dominant, thereby leading to an inverted sequence.

Model calculations of Hoffmann et al. led to several important generalizations[1,2,5] concerning orbital interactions through n bonds of which three are relevant to this account: (1) The energy level ordering of the orbitals resulting from through-n-bonds interactions depends on the parity of the number, n, of the relaying σ bonds, being S below A[6] for even values of n and the reverse for odd values of n.[1] This *parity rule* predicts that interactions through space and through n bonds reinforce each other for even values of n but are mutually antagonistic for odd values of n. (2) The extent of orbital interactions through n bonds,[4] for a given value of n, depends on the geometry of the σ relay and is maximized for an all-trans arrangement of σ bonds.[1,2,7] For example, this trans effect predicts that interactions through four bonds should diminish along the series 3 (t-t^8 arrangement of σ bonds) > 4 (c-t^8) > 5 (c-c^8). (3)
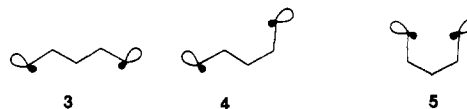
Extended Hückel calculations suggest that, in contrast to through-space effects, interactions through n bonds are attenuated slowly with increasing n and may be significant ($\Delta = 0.2$ eV[1,4]) for $n = 8$.

It is apparent from the two excellent reviews covering all aspects of orbital interactions through bonds up to 1974[2,5] that almost all of the numerous experimental studies have been focused on systems exhibiting interactions of the through-three-bond type, e.g., 1 and 2. Indeed, only a handful of experimental reports on orbital interactions extending over four or more bonds have appeared up to 1981. Consequently the three theoretically derived generalizations about orbital interactions through bonds mentioned above have received scarcely any experimental investigation, particularly with respect to the trans and attenuation effects.

(1) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.
(2) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.
(3) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936.
(4) The extent or magnitude of orbital interactions, Δ, may be defined as the energy gap separating the orbitals after interaction minus that gap separating them in the (theoretical) absence of such interaction.[2]
(5) Gleiter, R. *Angew. Chem.* **1974**, *86*, 770; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696.
(6) For those systems not having a symmetry element that interchanges the basis orbitals, the labels S and A are approximate and refer to an approximate interchange symmetry.
(7) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1976**, *98*, 4392.
(8) t = trans; c = cis.

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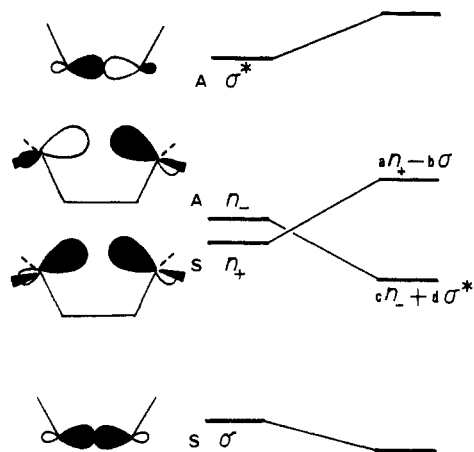
Figure 1. Interaction diagram for the diyl lobes and the C2–C3 bond of 1,4-butanediyl.

A similar dearth of experimental studies on the chemical consequencies of through-bond interactions is apparent upon perusal of the above-mentioned reviews,[2,5] many of them being in fact of a negative nature. Our interest in the physical and chemical consequencies of orbital interactions through space[9] and in bond-stretch isomerism[10] led us to undertake experimental studies of through-bond interactions with the explicit purpose of (1) testing the trans effect, (2) assessing the dependence of the extent of orbital interactions through n bonds on the value of n, and (3) developing a chemical probe for investigating through-bond effects. Our efforts along these lines, together with those of other investigators, form the basis of this Account.

Experimental Evidence for the Parity Rule

The parity rule for orbital interactions through n bonds has been satisfactorily verified for $n = 1$–4 mainly by photoelectron (PE) spectroscopy. This technique is unquestionably the most useful for investigating orbital interactions because it provides a direct estimate (through Koopmans' theorem) of MO energies.[11] Although PE spectroscopy cannot give directly the symmetries of the levels, these may often be deduced by using various ingenious techniques pioneered largely by Heilbronner and his co-workers and illustrated by the following examples.

Orbital Interactions through One Bond. 1,4-Cyclohexadiene (6) is the archetypal molecule in which π orbital interactions through 1 bond are operating. Extended Hückel calculations on planar 6 ($\omega = 180°$)
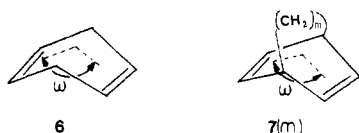
(9) (a) Paddon-Row, M. N.; Patney, H. K.; Brown, R. S. *Aust. J. Chem.* **1982**, *35*, 293. (b) Paddon-Row, M. N.; Lap, B. V.; Patney, H. K.; Warrener, R. N. *Ibid.* **1980**, *33*, 1493. (c) Oliver, M. J.; Patney, H. K.; Paddon-Row, M. N. *Ibid.* **1980**, *33*, 795. (d) Paddon-Row M. N.; Hartcher, R. *Ibid.* **1980**, *33*, 785. (e) Paddon-Row, M. N.; Patney, H. K.; Warrener, R. N. *J. Org. Chem.* **1979**, *44*, 3908.

(10) (a) Paddon-Row, M. N.; Radom, L.; Gregory, A. R. *J. Chem. Soc., Chem. Commun.* **1976**, 427. (b) Gregory, A. R.; Paddon-Row, M. N.; Radom, L.; Stohrer, W.-D. *Aust. J. Chem.* **1977**, *30*, 473.

(11) PES reviews: (a) Bock, H.; Ramsey, B. G. *Angew. Chem.* **1973**, *85*, 773; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 734. (b) Heilbronner, E.; Maier, J. P. "Electron Spectroscopy: Theory, Techniques and Applications"; Brundle, C. R.; Baker, A. D., Eds.; Academic Press: New York, 1977; Vol. 1.

Table I
π Vertical Ionization Potentials, $I_v(\pi)$, of Dimethanonaphthalenes

compd	$I_v(\pi)$, eV	assignment	ref
10	8.08	π_-	21a
	9.34	π_+	
11	8.46	π_-	21a
	8.90	π_+	
12	8.48	π_-	20
	9.35	π_+	
13	8.60	π	21b
14	8.65	π	20
15	8.78	π	20
16	8.85	π	20
19	8.58	π_-	24
	8.90	π_+	

indicated the presence of extensive through-bond coupling of the π MOs, via the two methylene units,[12] with the π_+[13] (i.e., S) level lying above the π_-[13] (i.e., A) level.[14] The large observed $\Delta I_v(\pi)$ of 1.0 eV[15] for **6** is certainly consistent with the orbital interactions through 1 bond mechanism. The inverted sequence of π MOs in **6** was elegantly demonstrated by Heilbronner et al. through their PE spectral studies of the series **7**(m) $(m = 1$–4). For **7**(1), i.e., norbornadiene, the π MOs are known from experiment to interact predominantly through space and to follow the natural sequence, i.e., $\pi_->\pi_+$.[11b,16,17] Because the dihedral angle, ω, increases along the series **7**(m), through-space interactions, and therefore $\Delta I_v(\pi)$, should decrease regularly from **7**(1) to **7**(∞), the latter system being modeled by **6**. However, the $\Delta I_v(\pi)$'s were observed to go through a minimum, for **7**(3), and then increase again to **7**(∞) (i.e., **6**). This trend is best explained in terms of compensating influences of the π MOs interacting both through space and through one bond in **7**(m),[11b] the former being predominant for m < 3 and the latter becoming more important for larger values of m (through improved overlap with the polymethylene chain). The inverted sequence of π levels in **6** therefore follows.

Orbital Interactions through Three Bonds. The inverted sequence of levels resulting from interactions through three bonds has received extensive experimental support.[2,5,11b] PE spectral studies on configurational isomers have often enabled the level symmetries to be determined. For example, the larger $\Delta I_v(\pi)$ found for *anti*-**8** (0.97 eV) compared to the syn isomer **9** (0.36 eV) is consistent only with an inverted sequence of π levels in the former molecule.[18,19] The reduced
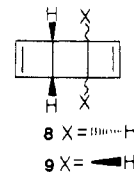
(12) In describing the orbital interactions through bonds in **6** in terms of the through-one-bond variety, each CH_2 unit is considered to act as a "one"-bond relay. The justification for this is that, on either side of the molecular plane, the π MOs overlap with the same CH bond.

(13) $\pi_+ = \pi + \pi$; $\pi_- = \pi - \pi$; $n_+ = n + n$; $n_- = n - n$.

(14) Hoffmann, R.; Heilbronner, E.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 706.

(15) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745.

(16) Heilbronner, E.; Martin, H.-D *Helv. Chim. Acta* **1972**, *55*, 1490.

(17) Heilbronner, E. *Isr. J. Chem.* **1972**, *10*, 143.

$\Delta I_v(\pi)$ for **9** is due to the presence of competing through-space interactions, which are of course absent in **8**. It was also deduced that the π level ordering in **9** was $\pi_+ > \pi_-$, i.e., that through-bond interactions predominated even in the syn isomer.[18a]

Orbital Interactions through Four or more Bonds. Direct experimental support for the cooperation of through-space orbital interactions and those occurring through four bonds came from the comparison of the PE spectra of the series of dimethanonaphthalenes **10–16**, the $I_v(\pi)$'s of which are given in
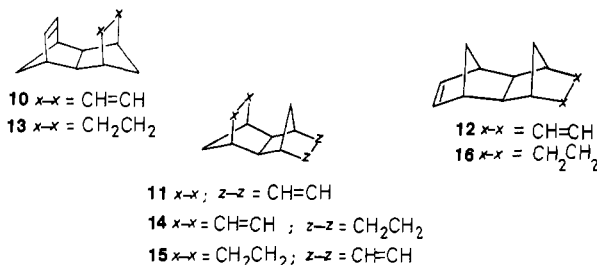
10 x–x = CH=CH
13 x–x = CH₂CH₂

11 x–x ; z–z = CH=CH
14 x–x = CH=CH ; z–z = CH₂CH₂
15 x–x = CH₂CH₂ ; z–z = CH=CH

12 x–x = CH=CH
16 x–x = CH₂CH₂

Table I. The large $\Delta I_v(\pi)$ value for **12**[20] is obviously the consequence of pure through-bond interactions. The corresponding $\Delta I_v(\pi)$ value for **10** is even larger[21] (1.26 eV) and has been attributed to the presence of reinforcing through-space interactions induced by the spatial proximity of the π bonds. The relative contributions of through-space and through-bond interactions to the total $\Delta I_v(\pi)$ of **10** were estimated to be 0.90 and 0.36 eV, respectively.[21b]

The PE spectral studies of α-, β-, and γ-dicarbonyls have provided valuable data on interactions between oxygen lone pairs through three, four, and five bonds, respectively.[22] In general the parity rule was found to be obeyed by acyclic dicarbonyl compounds. Interestingly for cyclic compounds in which the carbonyl groups are coaxial, the parity rule appears to be violated. Thus for 2,2,4,4-tetramethyl-1,3-cyclobutanedione, in which the lone pairs interact through *four* bonds, the level ordering was found to be n₊ > n₋,[13,22a,c] whereas for 1,4-benzoquinone, in which the lone pair interactions extend over *five* bonds, the levels follow the *natural* sequence, i.e., n₋ > n₊.[13,22] However it should be pointed out that the σ-bond relays in these two diones are *cyclic* and the shapes and sequence of the σ MOs are often different from those of their acyclic counterparts which were used for deducing the parity rule.[1] Thus reconciliation of experiment and theory is brought about if the appropriate σ MOs of cyclobutane and cyclohexane are used in the treatment of the 1,3-cyclobutanedione and p-benzoquinone, respectively.[22c]

Experimental Evidence for the Attenuation and Trans Effects

The only detailed study of the dependence of through-bond orbital interactions on the number, n, of relaying σ bonds has been provided by Heilbronner and his co-workers. They measured the σ–lone pair splitting energies, $\Delta I_v(\sigma)$, for a series of diiodopolyacetylenes, **17**(m) (m = 0–3).[23] As expected[1] ln $\Delta I_v(\sigma)$ was found

I–(C≡C)ₘ–I

17 (m)

18 (m)
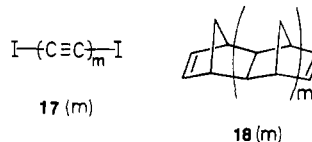
to be a linear function of n and that, for the series **17**(m), orbital interactions are negligible for n = 7.

We are studying π orbital interactions in the series of "norbornylogues", **18**(m), of which norbornadiene (m = 0), **12** (m = 1), and **19** (m = 2) are the first members. The $\Delta I_v(\pi)$'s for **12** and **19** are 0.87[20] and 0.32[24] eV,

19

20
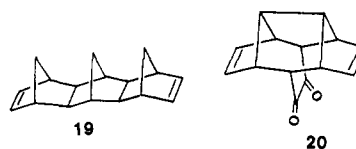
respectively (Table I). The splitting of the π levels in **12** is the largest value so far reported that is due exclusively to orbital interactions through four σ bonds. A large $\Delta I_v(\pi)$ value of 0.85 eV has been reported for **20**,[25] but this is probably due, in part, to the presence of reinforcing through-space interactions between the diene and carbonyl MOs. The $\Delta I_v(\pi)$ value for **19** represents the first demonstration of orbitals interacting through *six* bonds and is surprisingly large. It would seem, albeit from our limited data, that orbital interactions are attenuated more slowly along the series **18**(m) compared with the series **17**(m). Assuming a linear dependence of ln $\Delta I_v(\pi)$ on n for **18**(m), we predict that $\Delta I_v(\pi)$ for orbitals interacting over eight bonds should be ca. 0.1 eV. We are currently synthesizing **18**(3) in order to test this prediction.

Electronic absorption spectra of bichromophoric molecules have also revealed valuable insights into orbital interactions through bonds.[26,27] Thus the observed σ-coupled transition in the UV spectrum of the *trans*-6-thiadecalin **21** has been attributed to orbital interactions through five bonds.[27] This result is consistent with the trans rule in that the relevant orbitals of the chromophores in **21** overlap with the antiperiplanar set of σ bonds. The absence of a σ-coupled transition in the UV spectrum of the cis isomer **22** is probably due to the lack of an antiperiplanar arrange-

(18) (a) Gleiter, R.; Heilbronner, E.: Hekman, M.; Martin, H.-D. *Chem. Ber.* **1973**, *106*, 28. (b) Bodor, N.; Chen, B. H.; Worley, S. D. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *4*, 65. (c) Spanget-Larsen, J.; Gleiter, R.; Paquette, L. A.; Carmody, M. J.; Degenhardt, C. R. *Theor. Chim. Acta*, **1978**, *50*, 145.

(19) These splittings are larger, 1.16 eV for **8** and 0.78 eV for **9**, if the assignments of ref 18b and 18c are accepted.

(20) Paddon-Row, M. N.; Patney, H. K.; Brown, R. S.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5575.

(21) (a) Martin, H.-D.; Schweisinger, R. *Chem. Ber.* **1974**, *107*, 3143. (b) Prinzbach, H.; Sedelmeier, G.; Martin, H.-D. *Angew Chem., Int. Ed. Engl.* **1977**, *16*, 103.

(22) (a) Cowan, D. O.; Gleiter, R.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 401. (b) Dougherty, D.; McGlynn, S. P. *J. Am. Chem. Soc.* **1977**, *99*, 3234. (c) Dougherty, D.; Brint, P.; McGlynn, S. P. *Ibid.* **1978**, *100*, 5597 and references therein.

(23) (a) Heilbronner, E.; Hornung, V.; Kloster-Jensen, E. *Helv. Chim. Acta* **1970**, *53*, 331. (b) Heilbronner, E.; Hornung, V.; Maier, J. P.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1974**, *96*, 4252. (c) Bieri, G.; Heilbronner, E.; Jones, T. B.; Kloster-Jensen, E.; Maier, J. P. *Phys. Scr.* **1977**, *16*, 202.

(24) Paddon-Row, M. N.; Patney, H. K.; Jorgensen, F. S. *J. Chem. Soc. Chem. Commun.* submitted.

(25) Bartetzko, R.; Gleiter, R.; Muthard, J. L.; Paquette, L. A. *J. Am. Chem. Soc.*, **1978**, *100*, 5589.

(26) (a) Cookson, R. C.; Henstock, J.; Hudec, J. *J. Am. Chem. Soc.* **1966**, *88*, 1060. (b) Hudec; J. *Chem. Commun.* **1970**, 829. (c) Dekkers, A. W. J. D.; Verhoeven J. W.; Speckamp, W. N. *Tetrahedron* **1973**, *29*, 1691. (d) Pasman, P.; Verhoeven, J. W.; de Boer, Th. J. *Tetrahedron* **1976**, *32*, 2827.

(27) (a) Pasman, P.; Verhoeven, J. W.; de Boer, Th. J. *Tetrahedron Lett.* **1977**, 207. (b) Pasman, P. "Through-bond Charge-transfer Interactions", Dissertation, University of Amsterdam (October 1980).

21 X = ⅲ‴·H
22 X = ◄■H
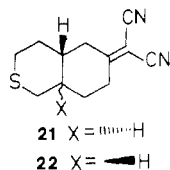
ment of σ bonds in this molecule.[27]

The estimated decrease in the magnitude of the π orbital interactions through four bonds along the series 12 (0.87 eV[20]) > 11 (0.44 eV[21]) > 10 (0.36 eV[21]) is consistent with the trans rule since the alignments of the σ bonds are t-t (for 12), c-t (for 11), and c-c (for 10).

Finally long-range NMR[28] and ESR[29] coupling constants are maximized with an (extended) "W" arrangement of relaying σ bonds, which is, of course, another manifestation of the trans rule.

A Simple General Model of OITB

On comparing 16 with 12, or 15 and 14 with 11, we were surprised to find that the π_+ MO of the diene is significantly more stable than that of the monoene(s) (Table I). According to the currently accepted model of orbital interactions through bonds,[1,2] the level lowering is a result of the mixing of π_+ with the LU-σ^*-MO. However, this mixing is much too weak to account for the large observed depression of π_+ (the depression effect), a conclusion that has been cogently presented for the case of orbitals interacting through three bonds.[7] We have presented a simple model of orbital interactions through bonds that explains not only the depression effect without invoking π,σ^* mixing but also the parity and trans rules.[20]

The essential features of our model are as follows:[20] (1) The most important contribution toward orbital interactions through bonds is the mixing of the π_+ and π_- basis combinations of a diene with the HO-σ-MO and SHO-σ-MO.[30,31] (2) The π_+ and π_- levels *together with that of the π basis of the corresponding monoene* are all raised through mixing with the σ MOs but by *different* amounts.[32] (3) The shapes and symmetries of the HO-σ-MO and the SHO-σ-MO of a system having n σ bonds are readily obtained by using the "C" approximation[33] since they then resemble those of the π MOs of a polyene having n conjugated double bonds. In this approximation the CC σ MOs are formed as linear combinations of sp³ hybrids (all CH bonds are ignored) using the Hückel treatment: i.e., the resonance integrals are β between orbitals of a C–C bond and $k\beta$ ($k < 1$) between orbitals on the same atom as shown by 23. All vicinal interactions are ignored. (4) The π,σ

23
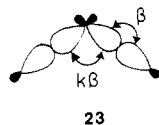
(28) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon: New York, 1969, Chapter 4-4.

(29) (a) King, F. W. *Chem. Rev.* **1976**, *76*, 157. (b) Ohsaku, M.; Murata, H.; Imamura, A.; Hirao, K. *Tetrahedron* **1980**, *36*, 177.

(30) SHO-σ-MO: second highest occupied σ MO.

(31) This aspect of the model is certainly not new: it has been used by PE spectroscopists, particularly by Heilbronner's group,[11b] for years! (32) Gleiter has also discussed this point.[18c]

(33) (a) Sandorfy, C.; Daudel, R. C. *C. R. Hebd. Seances Acad. Sci.* **1954**, *238*, 93. (b) Sandorfy, C. *Can. J. Chem.* **1955**, *33*, 1337. (c) Herndon, W. C. *Prog. Phys. Org. Chem.* **1972**, *9*, 99. (d) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 957.
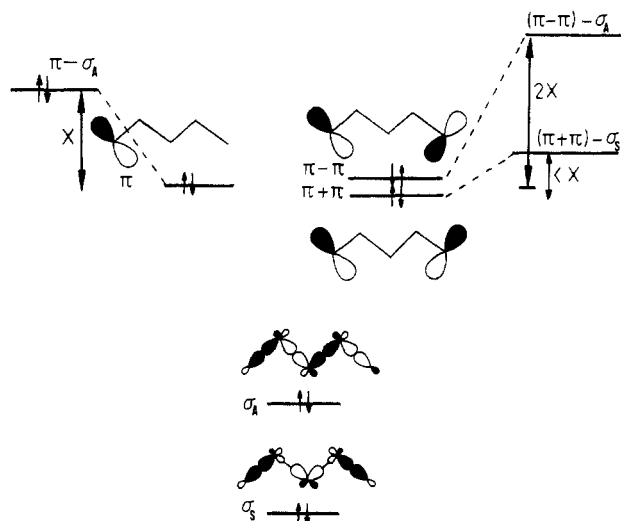

Figure 2. Schematic representation of σ–π mixing in 12 and 16. The π and top two σ orbitals before interaction are given in the middle. (Left) π (basis)–HO-σ-MO mixing. (Right) mixing of $\pi \pm \pi$ with HO-σ-MO and SHO-σ-MO.

Table II
Coefficients of AO_3 (See 24) in the HOMO and SHOMO of a Linear System of n σ Bonds (k of $k\beta = 0.7^{33d}$)

n	HOMO	SHOMO
2	0.40	0.58
3	0.45	0.18
4	0.42	0.10
6	0.35	0.26
8	0.29	0.29

mixing occurs principally through overlap of the π MO with that part of the σ MO which is contributed by the atomic orbital on the carbon adjacent to the π bond (AO_3), as shown by the thick arrows in 24.
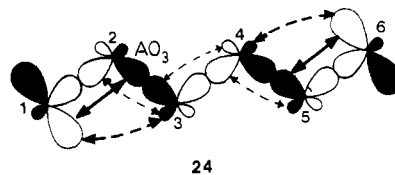

24

Figure 2 illustrates the application of the model to orbital interactions through four bonds, between a π orbital and a planar σ framework. The π basis orbital of the monoene and those (π_+ and π_-) of the diene are initially degenerate. An important feature of the model is the raising of the π basis orbital of the monoene, by an amount x, through its mixing with HO-σ-MO (there are no symmetry restrictions to this mixing). It is easily shown[20] that the normalized π_- combination in the diene is raised by *twice the amount*, $2x$, through its mixing with the antisymmetric HO-σ-MO. In contrast the normalized π_+ combination is only marginally raised ($<x$) through mixing with the symmetric SHO-σ-MO. The large difference between the respective interactions of π_- and π_+ with HO-σ-MO and SHO-σ-MO is because the HO-σ-MO level and the coefficient of AO_3 of HO-σ-MO are greater than those of the SHO-σ-MO (see Table II for the coefficients of AO_3). The PE spectrum of 12[20] nicely supports the above analysis: while the first π band is broad, indicating substantial σ,π mixing, the second π band is quite sharp, implying that ionization arises from a more nearly localized π MO.[34]

The origin of the depression effect observed in orbitals interacting through n bonds ($n = 3^{18}$ and 4^{20}) is therefore seen to be caused by the *raising* of the π (or lone pair) basis level through mixing with the HO-σ-MO and not through the *lowering* of a symmetry-adapted combination, π_+ or π_-, through mixing with LU-σ^*-MO. The model also suggests that the extent of through bond interactions is *due largely to the mixing of the appropriate symmetry-adapted pair of orbitals with the HO-σ-MO*. These conclusions appear to be general because, with the exception of $n = 2$, the coefficient of AO_3 in the HO-σ-MO is larger than that in the SHO-σ-MO (Table II). The data of Table II for the case of $n = 2$ suggest that the SHO-σ-MO could be the more important "mixer" than the HO-σ-MO. It is pleasing to note that more refined, SCF MO, calculations on norbornadiene, 7(1), fully support this prediction.[3] Thus it was estimated that the π_+ level was raised more than the π_- level, through mixing with the CC σ MOs of the six-membered ring, although the final ordering followed the natural sequence because of the dominant contribution of through-space interactions.

The model also clarifies other salient features of OITB:[20] (1) The parity rule automatically follows from the model because the HO-σ-MO is S for odd n and A for even n. An identical derivation of this rule has been independently reported by Verhoeven and Pasman.[35] (2) The trans rule follows from the property that the HO-σ-MO contains the most out-of-phase combinations of σ bonds, as shown by 24, and that for an all-trans, planar, arrangement of σ bonds the vicinal σ,σ interactions, shown by feint dashed lines in 24, are all antibonding. With OIT-5-B as an example the π_+ MO resembles 24 after mixing with the HO-σ-MO of an all-trans σ framework. The principal π-allylic antibonding interactions are indicated by heavy lines and the two π-homoallylic antibonding interactions by bold dashed lines. It should be apparent from 24 that the π_+ level is maximized through mixing with an all-trans planar conformation of σ bonds. Any deviations from this conformation will weaken the vicinal σ,σ antibonding interactions, thereby reducing both π_+ level and the extent of through-bond interactions. Planar cis arrangements of σ bonds markedly reduce through-bond interactions because cis vicinal σ,σ interactions are now bonding; e.g., the overlap between σ_{23} and σ_{45} of 24 is bonding when the dihedral angle C2-C3-C4-C5 = 0°.

Although our model satisfactorily explains some of the mysteries of orbital interactions through bonds, it is, nevertheless, crude and qualitative.[49] More rigorous treatments of these interactions, which are also more quantitative, have been developed by the Weinhold[7,36] and Heilbronner[3,37] groups.

The Chemical Consequences of Orbital Interactions through Bonds

Until recently there has been a dearth of examples of the chemical consequences of orbitals interacting through bonds,[2,5,38] perhaps the best known being the

Table III
Rate Enhancement Factors $k_D{}^E$ for the Birch Reduction[h] of Double Bonds in Some Substrates Relative to the Specified Reference Compound

substrate	ref	metal	$k_D{}^E$
7(1)	N[a]	Li	$10^{5\ c,d}$
25	N[a]	Li	140^e
25	N[a]	Na	169^f
25	N[a]	Na/C[b]	206^f
26	N[a]	Li	78^e
11	14	Li	26^f
12	16	Li	$18^{d,f}$
27	14	Li	96^g
28	16	Li	2900^g
29	14	Li	3^g
30	14	Li	3.5^g
31	14	Li	5^g
14	N[a]	Li	5.8^e
16	N[a]	Li	0.6^f

[a] N = Norbornene. [b] C = cryptand [2.2.2]. [c] Reference 9d. [d] A statistical factor of 2 has been applied. [e] Reference 38. [f] H. K. Patney and M. N. Paddon-Row, unpublished data. [g] Reference 47. [h] *tert*-Butyl alcohol was the proton source in each case.

Grob-type fragmentation reactions of, for example, 4-substituted quinuclidines[39a] that are almost certainly the result of N lone pairs interacting through three bonds.[39b] The remaining few examples of through-bond interactions affecting chemical reactivity have been reviewed.[38] Perhaps surprisingly some molecules whose physical properties are markedly affected by through-bond effects show no evidence of these interactions in their chemical reactions. Thus Dabco (1) and pyrazine (2) show no evidence of any "α-effect" or enhanced basicity.[40]

The Birch Reduction as a Probe

We felt that the Birch reduction[41] should be an excellent chemical probe for through-bond interactions, given its demonstrated sensitivity to through-space effects. For example, it has been found that nonconjugated double bonds, which are normally unresponsive toward the Birch reduction,[41] are rapidly reduced when they are constrained to lie in close proximity to another double bond or aromatic ring. Thus, norbornadiene[9d,42] and related compounds[9d,42] are reduced some 10^5 times faster than norbornene (Table III) and almost as rapidly as lithium benzoate![9d] These enormous rate enhancements are easily understood in terms of the currently accepted mechanism of the Birch reduction.[38,41,43] The observed rate constant, k_o, for the reduction is given by the product $k_o = Kk_H$, where K is the equilibrium constant for the formation of the anion radical of the substrate and k_H is the rate constant for the protonation of this species. Therefore interactions between the π^* levels, which result in a lowering of the LUMO level,

(34) For another illustration of this argument, see: Gleiter, R.; Gubernator, K.; Grimme, W. *J. Org. Chem.* 1981, 46, 1247.

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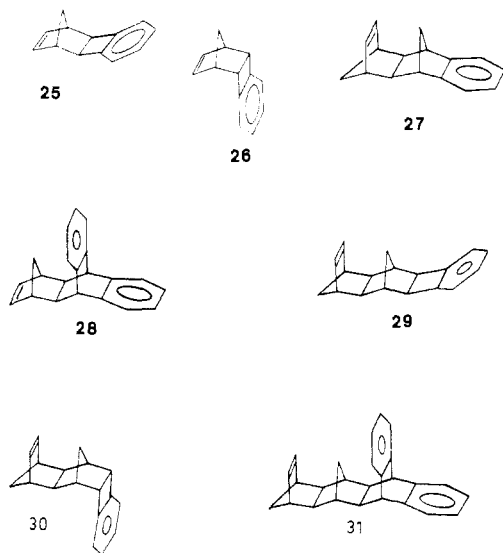
(41) Birch, A. J.; Subba Rao, G. *Adv. Org. Chem.* 1972, 8, 1.

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(43) (a) Krapcho, A. P.; Bothner-By, A. A. *J. Am. Chem. Soc.* 1959, 81, 3658. (b) Krapcho, A. P.; Nadel, M. E. *J. Am. Chem. Soc.* 1964, 86, 1096.

are expected to increase the magnitude of K, and this is reflected in an enhanced value of k_o.[9d,38] This expectation is substantiated by the observation of a larger splitting of the π^* levels of norbornadiene resulting in a lower LUMO level compared to norbornene[44] and by the observation of a linear relationship between ln k_o and the (extended Hückel) calculated LUMO level for a variety of molecules structurally related to norbornadiene.[9d,38]

Reassured thus, we studied the Birch reduction of the series 11, 12, 25–31 in which the unsaturated sites are separated by three (25, 26), four (11, 12, 27, 28), five (29, 30), and six (31) σ bonds. We reasoned that through-

bond interactions between the π^* LUMOs of the unsaturated sites should be manifested in an enhanced rate of reduction of the *double bond* relative to an appropriate model system in which such interactions are absent.

When Na is used as the reducing metal, product studies of the reduction of 25 and 28 revealed that $k_D/k_A = 2.1$ and 10, respectively (k_D and k_A are the rate constants for reduction of the double bond and aromatic ring, respectively).[45] The relative rates of reduction of these and other compounds using Li were obtained through the competition method. The relative k_D values were readily extracted from the rate and product distribution data, and these were used to calculate the enhancement factors, k_D^E, shown in Table III.

The k_D^E values in Table III are reasonably impressive and could reflect the presence of π^* MOs interacting through bonds in the compounds studied. The double bond in the *exo*-methanobiphenylene, 25, is reduced 140 times more rapidly than that in norbornene. Steric and strain effects cannot account for this rate enhancement since the double bonds in 25 and norbornene are in structurally similar environments. Inductive effects were also ruled out on the grounds that k_D^E for *anti*-7-methoxynorbornene is only 11 (relative to norbornene). Therefore the k_D^E value for 25 should be less than 11 if inductive effects alone were operating (phenyl is a weaker −I group than methoxyl).[38] Because of the known sensitivity of the Birch reduction to the effects

of ion pairing between the anion radical of the substrate and the counterion,[43a] it is essential to determine to what extent the k_D^E values shown in Table III are also dependent on ion pairing. Preliminary studies on 25 reveal that k_D^E increases with decreasing degree of ion pairing (cf. Na vs. Li as reducing metal, Table III). In fact when ion pairing is eliminated, by carrying out the reduction with Na in the presence of the potent sequestering agent cryptand [2.2.2], the k_D^E value for 25 is now 206![46]

In light of the above discussion we believe that π^* MO interactions through three bonds are responsible for the observed enhanced rate of double bond reduction of 25. Extended Hückel (EH) and INDO calculations on 25 support this view in that they reveal extensive mixing of the π^* MO of the double bond with the second LUMO of the aromatic ring.[38] The smaller k_D^E value for *endo*-26 compared with that for *exo*-25 is then nicely explained in terms of the presence of competing through-space interactions in this system.[38]

Turning to the through-four-bond candidates, we see that the k_D^E values for 27 and 28 are 96 and 2900, respectively. These results appear to constitute the first reported examples of the chemical consequences of orbitals interacting through four bonds.[47] The presence of an additional interacting (through-four-bond) aromatic ring in 28 would naturally enhance the double-bond reactivity of this compound compared with that of 27. The k_D^E values for 11 and 12 may also be interpreted in terms of through-four-bond interactions involving the π^* MOs of the double bonds. Ab initio MO calculations support this explanation in that they reveal a splitting of 0.54 eV between the π^* levels of 11, which results in a LUMO level ca. 0.3 eV lower than that of 14.[46] The result for 12 is puzzling because its k_D^E value is slightly less than that for the isomeric 11 whereas application of the trans rule and the results of ab initio MO calculations predict enhanced reactivity of 12 compared with 11. Clearly factors in addition to OITB are affecting the k_D^E values of these compounds, but their identification must await further investigation.

The results for 29–31 are more equivocal. The k_D^E values for these compounds are too small to be attributed to any specific cause. However it should be noted that model ab initio calculations indicate that orbitals interacting through six bonds and any chemical consequences arising from such interactions should be very small.[46]

σ **Assistance.** Verhoeven[35,48] has suggested that the observed modulation of reactivity of many intramolecular reactions may be explained in terms of the interplay of through-space and through-bond effects operating in the transition states of these reactions. Application of the principles of through-bond and through-space orbital interactions, together with the concept of σ aromaticity,[33d] to cyclic transition states involving σ orbitals led Verhoeven to the idea of σ assistance, namely that cyclic transition states containing $(4q + 2)$ σ electrons are preferred. This concept of σ assistance accounts for the preferred formation of odd-membered rings in (di)radical cyclization and of

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(48) (a) Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 143. (b) Verhoeven, J. W. *Ibid.* **1980**, *99*, 369.

even-membered transition states in intramolecular hydrogen or hydride migration.[48b]

Concluding Remarks

Hoffmann's dissection of orbital interactions into the through-space and through-bond varieties has made a profound contribution to our understanding of the physical and chemical properties of molecules. It has been the prime objective of this Account to discuss the results of recent experiments which are being carried out to test the predictions of through-bond effects and to asseess the chemical and physical significance of these interactions. There seems to be no doubt that through-bond interactions can be significant even when the interacting orbitals are separated by six σ bonds. Through-bond effects are chemically imprtant as well, and the Birch reduction seems to be a useful chemical probe for exploring these interactions. Many other electron-transfer reactions may also be influenced by through-bond effects. Indeed the possibility of either an electron or a "positive hole" being "transmitted" through bonds, over large distances within a molecule, is intriguing and is being actively investigated by ourselves and, I hope, others!

Note Added in Proof. The model may be improved by allowing the π basis MO to mix with lower lying σ MO's as indicated in footnote 19 of ref 20. Indeed Professor K. D. Jordan has informed the author that good agreement between experimental data and the model is obtained through consideration of the mixing of the π basis MO with only the HO-σ-MO and the SHO-σ-MO.