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Use of Hückel Methodology with ab Initio Molecular Orbitals: Polarizabilities and Prediction of Organic Reactions[1]

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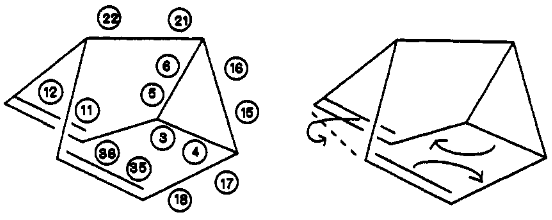
The strengths of Hückel theory are its simplicity, its equivalence to topology as formulated in graph theory, and its many useful applications, especially to π-systems in organic chemistry. Its weakness is its approximate nature. The converse has been true of ab initio and semiempirical molecular orbital theory—while quantitatively more exact, the many corresponding simple applications of Hückel theory have been inaccessible.

We now report that the exact translation of Hückel methodology[2] to ab initio and semiempirical MOs is possible. In this communication we focus attention on group–group (e.g., bond–bond) polarizability. Bond–bond polarizability has been an interesting index in π-bond Hückel theory, albeit of limited scope. We present illustrative examples demonstrating how Hückel π-electron concepts can be extended to three-dimensional systems including σ-bonds with their conjugative effects and with ab initio sophistication far beyond the original Hückel framework.

Bond–bond polarizability offers the ability to predict which bonds in any given molecule will weaken and which will strengthen when a reaction is initiated by bond scission or formation of some other bond. Atom–bond and atom–atom polarizabilities similarly deal with charge–bond and charge–charge effects.

What makes treatment of both σ- and π-systems possible in the more sophisticated approximations is the availability of molecular orbitals expressed in terms of natural hybrid orbitals (NHOs).[3] These basis orbitals are the components of the bonds of organic chemistry. Additionally, NHOs have the property of comprising an orthogonal basis set in parallel to the assumed orthogonality of the Hückel p-orbital basis. Hence, every application of Hückel theory relying on basis set orthogonality can be used with the more sophisticated MOs.

We have taken a variety of typical organic reactants and subjected these to ab initio calculation, followed by determination of the group–group (e.g., bond–bond) polarizabilities.[4–6] The consequence is almost precisely parallel to typical organic chemical "electron pushing" in predicting which bonds will affect which bonds and in what manner. The method, however, also provides a measure of the extent of each interaction.



BOND 1		BOND 2		Polarizability	
Orb r	Orb s	Orb t	Orb u	3-21G	6-31G*
3	4	12	36	-0.0921	-0.0921
3	4	11	12	0.0617	0.0616
3	4	3	11	-0.2614	-0.2614
12	36	11	12	-0.2802	-0.2614
12	36	3	11	0.3900	0.3900
5	6	11	12	0.0162	0.0162
21	22	11	12	0.0027	0.0027
11	12	15	16	0.0015	0.0015
3	4	15	16	0.0225	0.0225
12	36	15	16	-0.0060	-0.0060
21	22	3	4	0.0016	0.0016

Figure 1. Semibullvalene bond–bond polarizabilities.

Where bonds or atoms have a positive mutual polarizability, an increase in bond order or electron density at one site results in an increase at the other. The reverse is true for a negative polarizability, where an increase in bonding or density at one site results in a decrease at the second site, and conversely.

A first example of interest is semibullvalene, a molecule synthesized first in 1966 and shown[7] to undergo an exceptionally rapid degenerate Cope rearrangement. Figure 1 gives the NHO orbital numbers of greatest interest. Each hybrid orbital number is encircled. p-Orbitals 11, 12, 35, and 36 comprise two π-bonds. The remaining orbitals are hybrids in σ-bonds. We note, for example, that π–π-overlap between orbitals 12 and 36 leads to the σ-bond formation of the Cope rearrangement.

Figure 1 gives in tabular form the bond–bond polarizability between pairs (bond 1 and bond 2). Indeed, the bond–bond polarizabilities correctly correspond to the experimentally observed bonds breaking and formed in the proper relationship. Thus, the polarizability 3–4:12–36 is negative and large, indicating that as π–π-overlap occurs between orbitals 12 and 36 to form a σ-bond, the three–ring bond 3–4 is weakened, and conversely. As overlap 3–4 is weakened, we can see from the positive bond–bond polarizability that the π-bond 11–12 (and equivalently 35–36) is also weakened. However, losing bond 3–4 leads to increased bonding 3–11 (and 4–35), thus forming new π-bonds. Similar effects are seen resulting from bonding between π-orbitals 12 and 36. In addition, we have listed some bond pairs whose polarizabilities are lower and which are not involved experimentally in the facile degenerate Cope rearrangement.

Another illustrative example is the fascinating Grob fragmentation reported quite some years ago by Marshall,[8] in which a departing sulfonate and a boride moiety are equatorial on a trans-decalin framework and 1,4 to one another. The reaction led[8] to a *trans,trans*-cyclodecadiene. For simplicity in our calculations, we have used chloride rather than mesylate and trimethyl boride in place of the hydroxyboride intermediate moiety. The reactant and the polarizabilities are given in Figure 2. The table entries of Figure 2 are bond–bond values except for the last three. The last entry is an atom–atom polarizability between the chloride and boron atoms, while the remaining two

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(1) (a) For the previous Zimmerman paper, note: Zimmerman, H. E.; Sulzbach, H. M.; Tollefson, M. B. *J. Am. Chem. Soc.* **1993,** *115,* 6548–6556.

(2) For authoritative coverage, see: Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.

(3) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980,** *102,* 7211–7218. (b) Reed, A.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988,** *88,* 899–926.

(4) (a) NBO outpout in an NHO basis is now available in Gaussian92.[5] Polarizabilities were computed with SELPOLAR.[6] This program extracts the NHO eigenvectors from Gaussian92[5] output in an NHO basis[3] as well as the eigenvalues. The polarizabilities are obtained from the expression

$$P(r,s,t,u) = \epsilon_{rs}\epsilon_{tu}\sum_{k}^{\text{occ}}\sum_{l}^{\text{vir}}\frac{(C_{rk}C_{sl} + C_{rl}C_{sk})(C_{tk}C_{ul} + C_{tl}C_{uk})}{(E_l - E_k)}$$

Here the ϵ_{rs} and ϵ_{tu} elements are +1 or −1 depending on the basis set overlap and were obtained from the Fock matrix signs. (b) The results are semiquantitatively independent of the basis set employed.

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(6) Zimmerman, H. E. University of Wisconsin, 1993. Executables are available from the author in VAX VMS format.

(7) (a) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966,** *88,* 183–184. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. S. *J. Am. Chem. Soc.* **1967,** *89,* 3932–3933.

(8) Marshall, J. A.; Bundy, G. *J. Am. Chem. Soc.* **1966,** *88,* 4291–4292.

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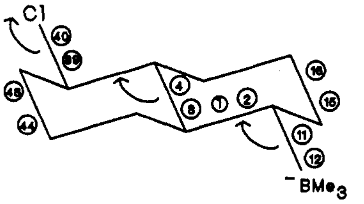


MOIETY A		MOIETY B		Polarizability	
Orb r	Orb s	Orb t	Orb u	STO-3G	6-31G*
11	12	39	40	0.0013	0.0014
11	12	3	4	0.0078	0.0059
11	12	11	3	-0.0822	-0.0712
11	12	15	16	0.0069	0.0056
11	12	11	15	-0.0737	-0.0651
11	12	43	44	-0.0000	-0.0000
39	40	3	4	0.0158	0.0161
39	40	43	44	0.0113	0.0129
39	40	39	4	-0.1309	-0.1288
11	12	4	39	-0.0040	-0.0039
12	12	3	4	0.0065	0.0035
40	40	3	4	-0.0122	-0.0164
12	12	40	40	-0.0022	-0.0019

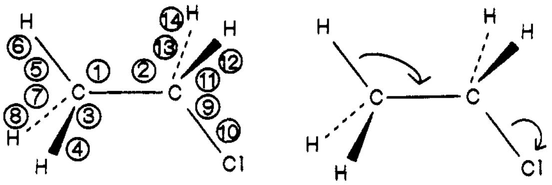
Figure 2. Grob fragmentation of a *trans*-decalin and some corresponding polarizabilities. All moieties are bonds except the last three entries in the table, which are atom–bond, atom–bond, and atom–atom interactions, respectively.

are atom–bond values indicating interaction between the chlorideand the boron with the central σ-bond orbital 3–4.

It is seen from the table in Figure 2 that as the boron–carbon bond 11–12 is weakened, C–Cl bond 39–40 is also predicted to weaken (i.e., a positive value of 0.0014). In contrast, the C–C bond 43–44 is also 1,4 with respect to B–C bond 11–12 but is scarcely affected by C–B (i.e., 11–12:43–44) scission. Both the C–Cl (39–40) and the C–B (11–12) bonds also show positive polarizabilities with the central C–C (3–4), which fragments in the reaction. Hence we see conjugation of the σ-bonds, with the closer bonds interacting more strongly. Further, the C–Cl bond interacts more strongly than the C–B bond in breaking the central C–C σ-bond, indicating more of an "electron pull" than an "electron push". Formation of the two new π-bonds in the reaction is predicted by the negative polarizability values between the C–Cl bond (39–40) and the developing π-bond due to overlap between orbitals 4 and 39. There is a similar effect (i.e., a negative polarizability) between the C–B bond 11–12 and the developing π-bond 11–3. Note that the polarizabilities are characteristically larger for hybrid pairs not originally bonded (i.e., "virtual bonds", such as 3–11) relative to those of the initial bonds. Also, significant differences between stronger π-type (viz., 11–12 with 11–3) and weaker σ-type (viz., 11–12 with 3–4) bonds are apparent in the calculated magnitudes. Thus, in predicting relative bond scission or formation tendencies, effects of the same type should be compared with one another; thus π- and σ-effects should be separately compared.

The atom–bond polarizability between the chlorine (40) and the central C–C bond 3–4 is negative (next to last entry), signifying that as bond 3–4 is broken, the electron density and charge on chlorine increase. The reverse effect is seen on the electron density on boron (i.e., the third from the last entry). With a positive sign for 12–12:3–4, we see a positive correlation between loss of electron density on the boron and loss of the σ-bond 3–4. Finally, the negative sign for 40–40:12–12 (the last entry of Figure 2) signifies development of electron density on the departing chloride but loss of electron density from the boron as the boron is released.

Thus, in this example, the mutual polarizability through a series of conjugating σ-bonds reflects "through bond electron delocalization" discussed so long ago by Hoffmann[9] for ground states and by Zimmerman[10] for triplet and singlet excitation transfer in "rodlike" molecules.



MOIETY A		MOIETY B		Polarizability	
Orb r	Orb s	Orb t	Orb u	3-21G	6-31G*
9	10	5	6	0.0185	0.0179
9	10	7	8	0.0016	0.0014
9	10	9	5	-0.1416	-0.1377
7	8	11	12	0.0054	0.0068
3	4	11	12	0.0008	0.0009
9	10	11	12	0.0007	0.0010
6	5	5	9	-0.1349	-0.1318
7	8	3	4	0.0009	0.0005
11	12	13	14	0.0011	0.0006
9	10	9	3	-0.0404	-0.0366
6	6	10	10	-0.0495	-0.0479
4	4	10	10	-0.0064	-0.0057

Figure 3. Ethyl chloride elimination.

More generally, we have found group–group polarizability as described to be a powerful tool. (a) Ethyl chloride trans elimination (Figure 3). (b) The exo vs endo reactivity of the 2-norbornyl chlorides is predicted by the larger (C2–Cl:Cl–C6) bond–bond polarizability between the *exo*-chloride compared with the endo isomer. The endo isomer shows an enhanced interaction between the C–Cl bond and the C7–C1 bond, in accord with known reactivity of some endo derivatives. (c) Interestingly, in the case of the 5,6-dehydronorbornyl derivatives, the enhanced *exo*-chloride reactivity correlates with high polarizabilities of the C–Cl bond with *both* the π-bond and the C1–C6 σ-bond; this provides support for more than just π-bond participation and accords with formation of nor-tricyclyl solvolysis products. (d) Analyses of the reverse Diels–Alder reactions of 2-cyanobicyclo[2.2.1]hept-5-ene and -[2.2.2]octene derivatives show that as the endo cyclic π-bond is dissipated, the σ-bonds weakened most are those whose loss leads to cyanoethylene, and the analysis predicts generation of the cyclopentadiene and cyclohexadiene, respectively. The bonding proximal to cyano is found to be affected more than the distal σ-bond. (e) The ring opening of cyclopropanols is still another example, where dissipation of the electron density on oxygen is accompanied by adjacent three-ring C–C bond weakening. (f) Interestingly, in decane the bond–bond polarizability becomes insignificant between C–C bonds only at the point where both of these have become terminal. More examples promise to be forthcoming.

Concluding, it is seen that mutual polarizability predicts complex organic reactivity and "electron pushing".[11] Clearly, this is merely a first application of the concept, and further utilizations of the mutual polarizability approach will follow as well as other applications relying on NHO orbital orthogonality.

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Supplementary Material Available: Four additional examples of group mutual polarizability (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) (a) Zimmerman, H. E.; McKelvey, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 3638–3645. (b) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933–3951.

(11) It is remarkable how readily organic chemical intuition, deriving heavily from over a century of known chemistry, is able, using electron pushing as a vehicle, to predict reaction mechanisms. Bond–bond polarizability can be construed as an independent and parallel mode of assessment of reactivity.