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Overlap Partitioning as a Tool for Predicting Molecular Rearrangements

R. L. FLURRY, JR., DONNA BREEN, and DONNA L. HOWLAND
Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

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A partitioned total diatomic overlap is suggested as a tool for predicting the course of rearrangements in carbonium ions and other reactive intermediates by use of CNDO molecular orbital calculations.

Ein Aufteilungsmodus für die zweiatomige Gesamt-Überlappung wird vorgeschlagen. Damit läßt sich der Verlauf von Carbonium-Umlagerungen, bzw. anderer reaktiver Zwischenstufen, mittels CNDO-Rechnungen voraussagen.

Proposition d'un procédé de partition du recouvrement diatomique total pour la prédiction du cours des réarrangements dans les ions carbonium et autres intermédiaires réactifs par l'emploi de calculs d'orbitales moléculaires CNDO.

Within the various π-electron theories, a number of indices have been proposed for predicting the chemical reactivity of a system [1]. Such indices have not yet become popular within the semi-empirical all-valence-electron theories. Most calculations of reactivities which utilize these theories have thus far been based upon the direct calculation of reaction surfaces [2]. However, due to the approximate nature of such calculations, the validity of such energy surfaces is doubtful. Furthermore, the calculation of such surfaces by even relatively simple approximate theoretical schemes is very time consuming since calculations for many geometric arrangements are required. It thus seems desirable to develop reaction indices which will yield qualitative information about the course of a chemical reaction and which will not require repeated calculations involving only slightly different geometries. We propose here such an index to be used within the CNDO approximation for predicting the course of molecular rearrangements of reactive intermediates.

We define the partitioned total diatomic overlap as

$$T_{\mathrm{AB}} = 2 \sum_{\mu \in \mathrm{A}} \sum_{\nu \in \mathrm{B}} P_{\mu\nu} S_{\mu\nu}, \tag{1}$$

where the $P_{\mu\nu}$ are the elements of the first order density matrix (one-half the Coulson bond order) and the $S_{\mu\nu}$ the elements of the overlap matrix, both matrices being constructed from the starting basis set. The summations are over all basis functions on atom A (indexed μ) and on atom B (indexed ν). This quantity is identical in form to the total overlap population of a bond when overlap is explicitely included in the calculations [3]. However, we are using an approximation which totally neglects all overlap. The partitioned overlap thus cannot be taken to physically represent a charge distribution. It is more closely related in concept to the Coulson bond order [4] as applied to the π-electron theories. The effect of including the overlap with the total bond order is twofold. It yields the correct sign for the index, as, for example, when a net bonding occurs between two orbitals oriented such that both the overlap and the bond order are negative. Since bonding between dissimilar atoms is roughly proportional to overlap, the index involving both order and overlap also places values involving different atoms on approximately the same scale.

A justification for the use of an overlap partitioning comes from the recent energy partitioning analysis of Fischer and Kollmar [5]. They partition the energy of a molecule into one-center and two-center terms. These terms are further broken down into nuclear-electronic potential energy, electronic repulsion and exchange, nuclear repulsion, and resonance energy terms. The resonance energy predominates in the two-center terms. This resonance energy is defined as

$$E^R_{AB} = 2 \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} \beta_{\mu\nu} S_{\mu\nu}, \tag{2}$$

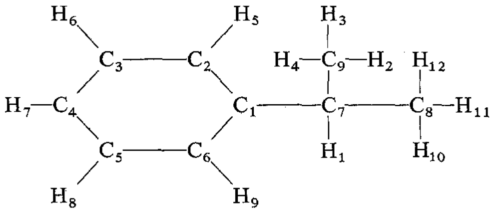
where the $\beta_{\mu\nu}$ is an energy factor. Except for the energy factor, Eq. (2) is identical to Eq. (1).

In applying the partitioned diatomic overlap to molecular rearrangements a calculation is performed on the reactive intermediate and on the parent hydrocarbon. A significant increase in the index between two atoms in the reactive intermediate indicates that there is a tendency for these atoms to be bonded in the rearranged product. The kinetically preferred product will be the one arising from the migration involving the greatest increase in the index. The T_{AB} value for the bond being broken in the rearrangement shows the largest decrease.

Table 1. *Partitioned diatomic overlap*

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}
H_1	1.0142	−0.0026	−0.0028	0.0026	0.0000	0.0000	0.0000	0.0000	0.0007	0.0027
H_2	−0.0026	1.0044	−0.0056	−0.0051	0.0001	0.0000	0.0000	0.0000	0.0000	−0.0001
H_3	−0.0028	−0.0056	1.0026	−0.0049	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001
H_4	0.0026	−0.0051	−0.0049	0.9945	0.0048	0.0000	0.0000	0.0000	0.0000	0.0002
H_5	0.0000	0.0001	0.0001	0.0048	1.0041	−0.0051	−0.0001	0.0000	−0.0001	0.0002
H_6	0.0000	0.0000	0.0000	0.0000	−0.0051	1.0078	−0.0052	−0.0001	0.0000	0.0000
H_7	0.0000	0.0000	0.0000	0.0000	−0.0001	−0.0052	1.0061	−0.0052	−0.0001	0.0000
H_8	0.0000	0.0000	0.0000	0.0000	0.0000	−0.0001	−0.0052	1.0078	−0.0051	0.0000
H_9	0.0007	0.0000	0.0000	0.0000	−0.0001	0.0000	−0.0001	−0.0051	1.0063	0.0000
H_{10}	0.0027	−0.0001	0.0001	0.0002	0.0002	0.0000	0.0000	0.0000	0.0000	0.9961
H_{11}	−0.0028	0.0001	−0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0002	−0.0049
H_{12}	−0.0028	0.0005	0.0001	−0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	−0.0049
C_1	−0.0001	0.0021	−0.0024	−0.0025	−0.0055	0.0022	0.0002	0.0022	−0.0054	−0.0018
C_2	0.0017	0.0002	0.0002	−0.0002	0.6804	−0.0047	0.0022	0.0002	0.0021	0.0001
C_3	0.0000	0.0000	0.0000	0.0001	−0.0053	0.6793	−0.0047	0.0022	0.0002	0.0000
C_4	0.0000	0.0000	0.0000	0.0000	0.0021	−0.0046	0.6798	−0.0046	0.0021	0.0000
C_5	0.0001	0.0000	0.0000	0.0000	0.0002	0.0022	−0.0047	0.6793	−0.0052	0.0000
C_6	−0.0041	0.0000	0.0001	0.0001	0.0021	0.0002	0.0022	−0.0047	0.6810	0.0000
C_7	0.6567	0.0005	0.0006	0.0018	−0.0043	0.0000	0.0000	0.0000	−0.0041	0.0014
C_8	0.0016	−0.0020	0.0019	−0.0020	0.0000	0.0000	0.0000	0.0000	0.0000	0.6727
C_9	−0.0003	0.6706	0.6717	0.6728	0.0014	0.0000	0.0000	0.0000	0.0000	−0.0020

Typically the T_{AB} values for directly bonded atoms involving single bonds are slightly less than unity and isolated double bonds are slightly greater than unity. For non-bonded interactions in neutral molecules, the T_{AB} values between two hydrogens or between a hydrogen and a heavier atom are typically less than 0.005, while those between two heavier atoms are typically less than 0.02. Table 1 shows the full $\boldsymbol{T}$ matrix for a typical neutral molecule, isopropyl benzene, with the atom numbering as in I.



I

The standard CNDO/2 approximations and parameterization were used [6], and all calculations were performed on a PDP–10 digital computer. Standard bond lengths and angles were also used. The hydrogens on C_8 and C_9 were staggered with respect to the bonds on C_7 and the phenyl ring was perpendicular to the C_1—C_7—C_8 plane.

Table 2 shows selected elements of the $\boldsymbol{T}$ matrix for a typical reactive intermediate, the α-phenyl-*n*-propyl carbonium ion I_a. The numbering is the same as in Table 1 except that H_{12} has been removed. In conformation *A* the carbonium

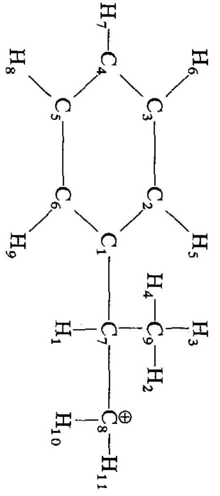
matrix for isopropyl benzene

H_{11}	H_{12}	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
−0.0028	−0.0028	−0.0001	0.0017	0.0000	0.0000	0.0001	−0.0041	0.6567	0.0016	−0.0003
0.0001	0.0005	0.0021	0.0002	0.0000	0.0000	0.0000	0.0000	0.0005	−0.0020	0.6706
−0.0001	0.0001	−0.0024	0.0002	0.0000	0.0000	0.0000	0.0001	0.0006	0.0019	0.6717
0.0001	−0.0001	−0.0025	−0.0002	0.0001	0.0000	0.0000	0.0001	0.0018	−0.0020	0.6728
0.0000	0.0000	−0.0055	0.6804	−0.0053	0.0021	0.0002	0.0021	−0.0043	0.0000	0.0014
0.0000	0.0000	0.0022	−0.0047	0.6793	−0.0046	0.0022	0.0002	0.0000	0.0000	0.0000
0.0000	0.0000	0.0002	0.0022	−0.0047	0.6798	−0.0047	0.0022	0.0000	0.0000	0.0000
0.0000	0.0000	0.0022	0.0002	0.0022	−0.0046	0.6793	−0.0047	0.0000	0.0000	0.0000
0.0002	0.0000	−0.0054	0.0021	0.0002	0.0021	−0.0052	0.6810	−0.0041	0.0000	0.0000
−0.0049	−0.0049	−0.0018	0.0001	0.0000	0.0000	0.0000	0.0000	0.0014	0.6727	−0.0020
1.0017	−0.0055	−0.0019	0.0000	0.0000	0.0000	0.0000	0.0003	0.0004	0.6713	0.0020
−0.0055	1.0012	0.0020	0.0000	0.0000	0.0000	0.0000	0.0000	0.0007	0.6713	−0.0021
−0.0019	0.0020	3.9524	0.9420	0.0073	−0.0120	0.0074	0.9418	0.7218	0.0129	0.0085
0.0000	0.0000	0.9420	4.0181	0.9547	0.0082	−0.0117	0.0083	0.0003	−0.0010	−0.0025
0.0000	0.0000	0.0073	0.9547	3.9891	0.9530	0.0089	−0.0117	0.0015	0.0000	0.0001
0.0000	0.0000	−0.0120	0.0082	0.9530	4.0119	0.9532	0.0082	0.0001	0.0000	0.0000
0.0000	0.0000	0.0074	−0.0117	0.0089	0.9532	3.9889	0.9546	0.0015	0.0000	0.0000
0.0003	0.0000	0.9418	0.0083	−0.0117	0.0082	0.9546	4.0163	0.0007	−0.0011	0.0011
0.0004	0.0007	0.7218	0.0003	0.0015	0.0001	0.0015	0.0007	3.9606	0.7013	0.7042
0.6713	0.6713	0.0129	−0.0010	0.0000	0.0000	0.0000	−0.0011	0.7013	4.0053	0.0099
0.0020	−0.0021	0.0085	−0.0025	0.0001	0.0000	0.0000	0.0011	0.7042	0.0099	4.0106

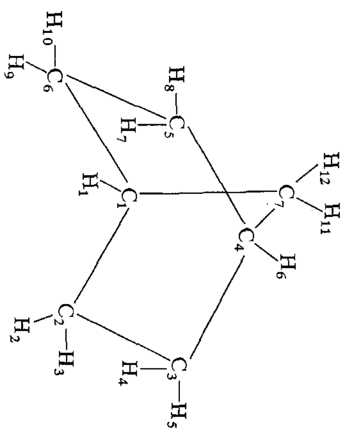
Table 2. *Relevant elements of the partioned overlap matrix for the α-phenyl-n-propyl carbonium ion in several conformations*[a]

	Bond											
	C_1—C_8	Δ	C_1—C_7	Δ	C_9—C_8	Δ	C_9—C_7	Δ	H_1—C_8	Δ	H_1—C_7	Δ
Isopropylbenzene	0.0129	–	0.7218	–	0.0099	–	0.7042	–	0.0016	–	0.6567	–
Cation A	0.0380	0.0251	0.6639	−0.0579	0.0108	0.0009	0.6930	−0.0112	0.0032	0.0016	0.6535	−0.0032
Cation B	0.0269	0.0140	0.6776	−0.0442	0.0108	0.0009	0.6913	−0.0129	0.0030	0.0014	0.6505	−0.0062
Cation C	0.0148	0.0019	0.7001	−0.0217	0.0302	0.0203	0.6630	−0.0412	0.0049	0.0033	0.6500	−0.0067
Cation D	0.0176	0.0047	0.6988	−0.0230	0.0148	0.0049	0.6869	−0.0146	0.0173	0.0157	0.6275	−0.0292

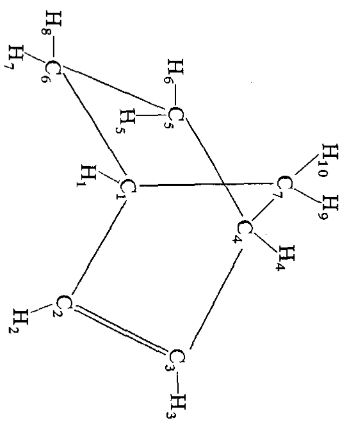
[a] Conformation A, as described in text. Conformation B, same as A except that the phenyl ring has been rotated 90° about C_1–C_7. Conformation C, same as A except C_8 has been rotated so that the plane C_9–C_7–C_8 is perpendicular to H_{10}–C_8–H_{11}. Conformation D, H_1–C_7–C_8 perpendicular to H_{10}–C_8–H_{11}.



Ia



II

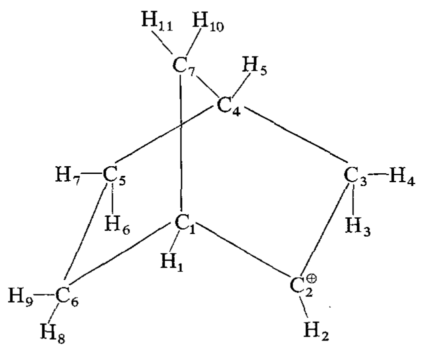


III

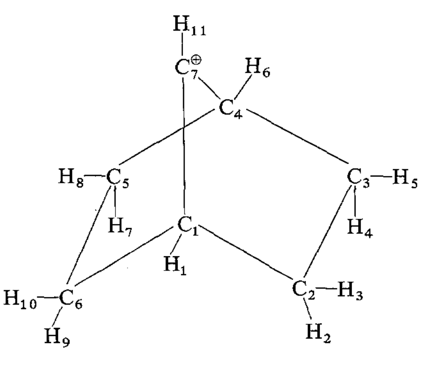
ion center is planar and oriented such that its vacant π-orbital is coplanar with the C_1—C_7 bond. All other atomic positions are unchanged. Note that $T_{C_1C_8}$ has a value of 0.0380 in contrast to a corresponding value for the same two atoms of 0.0129 in the neutral molecule. This change of 0.0251 in the value of the index indicates a probable migration. In fact, these two atoms are those which would be involved in a phenyl migration.

Table 2 also shows the pertinent ***T*** matrix elements for geometries in which phenyl, methyl and hydrogen migration would be favored in the α-phenyl-*n*-propyl carbonium ion. Note from the changes in the ***T*** matrix elements that the correct order of migratory aptitude, phenyl > methyl > hydrogen [7], is predicted. Also the phenyl migration is favored when the face of the ring is toward the center to which it is migrating. In fact, side-on phenyl migration is predicted to be less favorable than hydrogen migration. (Note, however, that for this particular carbonium ion, the migratory aptitude would not necessarily determine the observed product. If the product was to arise from the rearranged carbonium ion, its stability would determine the product.)

A study of the partitioned diatomic overlap in the cations of norbornane II and norbornene III is interesting. Pertinent values of T_{AB} are shown in Table 3. The 2 cation II_a very clearly shows the course of the known rearrangements of this system. There is a significant increase in $T_{C_2C_6}$ and a decrease in $T_{C_1C_2}$ and $T_{C_1C_6}$. This is consistent with the known carbon skeleton rearrangement. It does not, of course, pretend to answer the classical, non-classical carbonium ion question. It merely says that the interactions between carbons 2 and 6 increase in the carbonium ion while the interactions of these atoms with carbon atom 1 decrease. Also evident are the known hydride migrations, H_4—C_2 and H_9—C_2, although the order of the interactions are not the same as the order of the observed rates of these migrations [8]. This is undoubtedly due to the fact that the geometry of the ion is significantly different from that of the neutral molecule, which was used in our calculations. The 7 cation II_b shows increased 2–7 interaction and decreased 1 – 2 interaction, although the effect is not as great as in the 2 cation. This is consistent with the fact that the 7 cation rearranges to some extent to produce the bicyclo-[3, 2, 0]-heptane ring system [9].



II_a



II_b

Table 3. *Relevant elements of the partioned overlap*

	Bond							
	Norbornane:[a]							
	C_6–C_2	Δ	C_7–C_2	Δ	C_1–C_2	Δ	C_7–C_1	Δ
Norbornane	0.0140	—	0.0098	—	0.6864	—	0.6805	—
7 Cation	0.0206	0.0066	0.0228	0.0130	0.6717	−0.0147	0.7089	0.0284
2 Cation	0.0355	0.0215	0.0141	0.0043	0.6537	−0.0327	0.6680	−0.0125

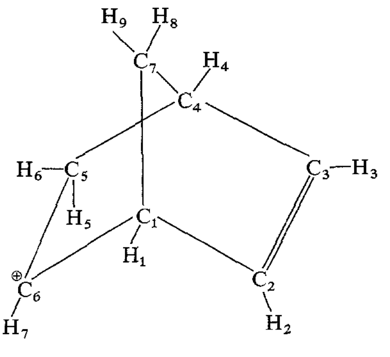
	Bond							
	Norbornene:[b]							
	C_2–C_7	Δ	C_6–C_7	Δ	C_2–C_6	Δ	C_1–C_7	Δ
Norbornene	0.0142	—	0.0079	—	0.0173	—	0.7125	—
7 Cation	0.0447	0.0305	0.0115	0.0036	0.0212	0.0039	0.7389	0.0264
6 Cation	0.0194	0.0052	0.0103	0.0024	0.0363	0.0190	0.7025	−0.0100

[a] Standard bond lengths and bond angles were used.

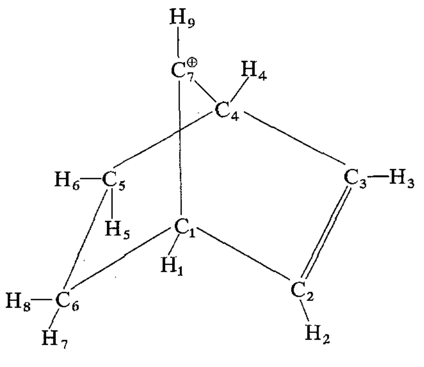
[b] Structure from crystallographic data; Macdonald, A. C., Trotter, J.: Acta crystallogr. **19**, 456 (1965).

In the case of the norbonenyl cations III_a and III_b, the most predominant feature is the interaction of carbon atom 7 with the carbons of the double bond in the 7 cation III_b. The change in the partitioned overlap is the largest we have thus far found for any two atoms which are not directly bonded in the classical structure. This is again consistent with the chemistry of the system.

The partitioned diatomic overlap yields no direct information about the energy of a system; consequently, it cannot predict the product of a thermodynamically controlled reaction. It does yield information about the directions of probable migrations. As such, it should be useful in predicting rearrangements in which the product formation is kinetically controlled, and it should show the most probable directions for distortions when direct energy surface calculations are required.



III_a



III_b

matrix for the cations of norbornane and norbornene

H_5–C_2	Δ	H_5–C_3	Δ	H_4–C_2	Δ	H_4–C_3	Δ	H_{10}–C_2	Δ	H_{10}–C_6	Δ
0.0008	—	0.6672	—	−0.0001	—	0.6681	—	−0.0039	—	0.6672	—
0.0008	0	0.6696	−0.0014	0.0010	0.0011	0.6703	0.0022	−0.0041	−0.0002	0.6696	0.0024

H_4–C_2	Δ	H_4–C_3	Δ	H_3–C_2	Δ	H_3–C_3	Δ	H_9–C_2	Δ	H_9–C_6	Δ
0.0137	0.0129	0.6517	−0.0155	0.0096	0.0097	0.6545	−0.0136	0.0021	0.0060	0.6683	0.0005

C_1–C_6	Δ	C_1–C_2	Δ	H_6–C_6	Δ	H_6–C_5	Δ	H_5–C_6	Δ	H_5–C_5	Δ
0.6453	—	0.7103	—	0.0004	—	0.6711	—	−0.0002	—	0.6708	—
0.6369	−0.0084	0.6932	−0.0171	0.0005	0.0001	0.6731	0.0020	0.0004	0.0006	0.6726	0.0018
0.6864	0.0495	0.6777	−0.0326	0.0119	0.0115	0.6565	−0.0146	0.0089	0.0091	0.6601	−0.0101

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Note Added in Proof: It has recently been shown that the quantity we have called the partitioned diatomic overlap is very similar in magnitude to the overlap population as computed for single systems by non-empirical methods. Kaufman, J. J.: Int. J. quant. Chemistry **IV S**, in press (1970).

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Professor R. L. Flurry
Department of Chemistry
Louisiana State University
New Orleans, Louisiana 70122, USA