

Bowman and McPherson-based spectrometers were 1.0 and 0.3 nm, respectively. First, the PL spectrum was obtained in air by using beam-expanded laser lines. Without disturbing the sample geometry, 5 M OH⁻/0.1 M S₂O₈²⁻ electrolyte was added and the EL spectrum was obtained at the potential of interest by the pulse sequence given above. The electrolyte was then changed to 5 M OH⁻ and the PL spectrum taken at the same potential used in the EL experiment, again without altering the sample geometry.

EL Efficiency. The integrated EL efficiency, $\bar{\phi}_{EL}$, was estimated by placing the probe head of the EG & G radiometer as close as possible (within ~ 1 cm) to the sole exposed CdSe crystal face. The electrode was pulsed to a given potential for 1 s as described above and the total emitted energy (in μ J) per pulse measured with the EG & G Model 550-3 accessory. Total coulombs passed during this pulse were measured with the digital coulometer. These measurements were repeated as a function of potential. The instantaneous, steady-state EL efficiency, ϕ_{EL} , was determined in the same geometry and has been described previously, differing only in the use of the EG & G radiometer.⁶ A measurement of ϕ_r and $\bar{\phi}_{EL}$ in the same geometry was made by first placing the EG & G radiometer about 3 cm from the electrode and angled so that it would not obstruct a laser beam incident "head on" on the electrode. The radiometer probe head was then covered with a Laser-Gard Ar ion laser goggle window (optical density of 11 at 514.5 nm) on top of a Corning 2-64 filter and $\bar{\phi}_{EL}$ measured. The electrolyte was then changed to 5 M OH⁻ and the CdSe electrode irradiated with 514.5-nm light at the potential used in the $\bar{\phi}_{EL}$ determination. Emitted light was detected with the radiometer and sample in the same geometry employed for the $\bar{\phi}_{EL}$ measurement; the incident light was detected with the Scientech power energy meter. This experiment was repeated at several potentials. The electrolyte was then made 0.1 M in S₂O₈²⁻ and $\bar{\phi}_{EL}$ measured at several potentials. Finally, $\bar{\phi}_{EL}$ was determined with the filters removed and the radiometer repositioned to minimize the distance to the electrode. The filter-covered radiometer was also placed in several other geometries to

determine to what extent ϕ_r and $\bar{\phi}_{EL}$ scaled together. It should be mentioned that for all of the efficiency measurements described in this section the flat-response window of the radiometer was removed, thereby minimizing the electrode-radiometer distance. Consequently, measured values were corrected by a factor determined at larger distances where the window could be added and removed without disturbing the relative electrode-radiometer geometry; the correction factor used for the CdSe sample was in good agreement with the manufacturer's value for the wavelength region involved. For the experiments in this section, electrolytes were stirred magnetically while being N₂ purged.

Effects of Surface Treatment on PL Properties. A cell suitable for PEC studies was assembled in the Aminco-Bowman spectrometer. PL spectra of CdSe were obtained sequentially in air, water, and 3 M NaOH by using a single geometry and a resolution of 1.0 nm. The beam-expanded 514.5-nm line of the Ar ion laser was masked to fill the CdSe surface and delivered ~ 2 mW of power in all experiments. The Corning 3-66 filter and neutral density filters were used while the emission band and reflected excitation spike, respectively, were scanned. Without disturbing the geometry, the electrode was brought into circuit in the 3 M NaOH electrolyte at 0.0 V vs. SCE and irradiated until ~ 7 mC of charge had been passed (PEC etching). At this point the electrode was taken out of circuit. A stable emission intensity was observed after several seconds at which time the emission spectrum was recorded under conditions identical with those previously used in this experiment. The PEC etch was repeated for various irradiation periods, and spectra were recorded after each treatment. Solutions were stirred by a N₂ purge.

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A Theory of Nuclear Substitution and the Hemistructural Relationship. The Origin of Bond Length and Bond Energy Additivity

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Abstract: A general problem that arises in the treatment of substituent effects on rates and equilibria of chemical reactions is evaluating the changes in energy and geometric structure that occur when a fragment is removed from a molecule and replaced by a new one. This question is approached from an ab initio viewpoint using analytical SCF Hartree-Fock theory. For different series of compounds, relative substituent effects on reaction rates, equilibria, or molecular properties are often very similar and can be described in terms of group contributions plus interactions between groups. The origin of this phenomenon is examined by considering a common geometry constraint, which has been generalized to define a hemistructural relationship. For diatomics (A-A, A-C, C-C), it is equivalent to bond-length additivity. An important consequence of the hemistructural relationship is that all of the information necessary for determining the properties of the hemistructural molecule (A-C) can be obtained from the two parent structures (A-A and C-C). *No new information is needed.* Ultimately, all empirical observations of transferable substituent effects and molecular properties can be traced to this fact. The hemistructural relationship serves as a fundamental basis for transferability within the Born-Oppenheimer, nonrelativistic limit. Some of the consequences of this transferability are examined, and it is shown that the response of the total energy (E), the kinetic energy (T), and the total potential energy (V) to multiple substituent effects is fundamentally simpler than the corresponding response of the orbital energy (E_o) and the individual potential energy components (V_{nn} , V_{ne} , V_{ee}). The Hellmann-Feynman theorem is used to show that when fragment transfer (A-A + C-C \rightarrow 2A-C) is described by first-order corrections to the wave function, an equilibrium A-C bond length will occur at the mean of corresponding A-A and C-C equilibrium bond lengths for arbitrary A,C fragments. An important result is that bond length and bond energy additivity can be observed even when large interactions (compared to deviations from additivity) occur between the A,C fragments. Additivity is observed because compensating changes in electronic structure take place in the two molecular fragments. Such a result is a fundamental departure from existing ideas on substituent effects and suggests that models of molecular structure based on interactions between transferable groups will require significant revision.





I. Introduction

It is well known that the energy of a molecule can often be expressed as the sum of the energies of its individual bonds and that these bond energies can frequently be "transferred" from one molecule to another.¹⁻³ The degree to which bond energies are

invariant from one molecule to another has been thought to depend on the extent to which each molecular fragment experiences similar attractions and repulsions in different environments.³ This concept of bond or fragment transferability has played a fundamental role in shaping our concepts of chemical bonding and structure.

A simple example illustrating these points is a comparison of

Table I. Experimental Heats of Atomization and Ionization Potentials of Benzene and Azabenzenes

	ΔH_A (kcal/mol) ^a		IP _V (eV) ^b			
 benzene	1318.2		9.24	9.24		
 pyridine	1194.3	9.59 (n)	9.73 (π_A)	10.50 (π_s)		
 pyrazine	1070.9	9.63 (n+)	10.18 (π_A)	11.35 (n-)	11.77 (π_s)	13.9 (π)
 pyrimidine	1070.8	9.73 (n-)	10.41 (π_s)	11.23 (n+)	11.39 (π_A)	13.9 (π)

^a Reference 6. ^b Reference 7.

ΔH_f^{298} for benzene, toluene, and *p*-xylene. The three experimental heats of formation are 19.82, 11.95, and 4.29 kcal/mol, respectively.⁵ The average heat of formation for benzene and *p*-xylene is 12.055 kcal/mol, which deviates by only 0.105 kcal from the experimental value for toluene. This close correspondence to additivity can be easily "explained" by two arguments: (1) the "electronic structures" of the methyl groups, the benzene rings, and the 1,4 hydrogens do not depend on the particular molecule of which they are a part; (2) interactions between the 1- and 4-substituents are neglected.⁴

However, there are cases of comparable additivity where the applicability of the "constant structure" argument could be questioned. For example, the heat of atomization (ΔH_A) for pyridine is only 0.25 kcal lower than the mean heats of atomization for benzene and pyrazine or pyrimidine (Table I).⁶ This degree of additivity is somewhat surprising, since the structural perturbations are taking place within a "delocalized" aromatic ring. It may seem a bit rash to assume that each of the two nitrogens in pyrazine or pyrimidine is simply the electronic equivalent of the nitrogen in pyridine. If the electronic energy of pyrazine or pyrimidine is analyzed in classical terms, we might expect to find a dipolar contribution arising from the interactions of the two nitrogens. Classically, this might be described as an internal dipole-dipole repulsion, and it should lead to a breakdown in the additivity of ΔH_A for pyrazine and pyrimidine, since the effect is not only different for pyrazine and pyrimidine, but is absent for pyridine and benzene.

If the ionization potentials⁷ of pyrimidine, pyridine and benzene (see Table I) are compared and interpreted within the framework of Koopmans' theorem, it is apparent that additive heats of atomization do not necessarily require additive orbital energies. The antisymmetric π orbital of pyridine (πB_2) is 0.585 eV (13.5

kcal) higher than the corresponding mean for pyrimidine and benzene, while the symmetric π orbital (πB_1) is 0.675 eV (15.6 kcal) lower than the mean. The combined deviation from the mean amounts to 2.1 kcal which is an order of magnitude larger than the deviation observed for the heats of atomization (0.20 kcal).

The ionization data (through Koopmans' theorem)^{8,9} show that the lone pair orbitals of pyrazine and pyrimidine are split by roughly 40 kcal. Significantly, the splitting is unsymmetrical relative to the lone pair orbital of pyridine, so that the lone pair orbital energy of pyridine is over 20 kcal higher than the mean lone pair orbital energy of pyrazine or pyrimidine. These observations do not provide a convincing argument that the additivity observed in the heats of atomization is due to a uniform electronic structure of the nitrogens in pyrazine, pyrimidine, and pyridine.

Additivity is also frequently observed for electronic energies calculated using SCF Hartree-Fock techniques.¹⁰ In one such example,^{10a,b} the electronic energy of pyridine has been calculated as -210.88630 au (Table II). The mean electronic energy of benzene and pyrazine (using the same basis set and experimental geometries) is -210.89019 au. The deviation amounts of 2.4 kcal. By contrast, the sum of the orbital energies for pyridine deviates from the mean by over 65 kcal (Table II). The core orbitals alone contribute 8 kcal to the total deviation. The core orbitals of the nitrogens in pyrazine are influenced by the other nitrogen since the orbital energy of each nitrogen 1s core is about 30 kcal lower than in pyridine. The lowering of the N-1s core energies in pyrazine relative to pyridine shows that the field experienced by an electron close to the nucleus of the 1-nitrogen is altered substantially by replacing a C-H group at the 4 position with another nitrogen. Even though both C-H and N carry the same nuclear charge and the same formal electronic charge, the effective field of each group at even "remote" centers in the molecule is different. The C-H and N at the 4 position are not behaving as either spherical charge distributions centered on nuclear point charges or as multipoles whose field falls off so rapidly that it is ineffective near the 1 position.

Constant electronic structure and lack of interaction between substituents are sufficient conditions for observing additivity relationships.^{2,3,11} It has also been thought that these conditions

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







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Table II. Calculated Energies of Benzene, Pyridine, and Pyrazine

	$E_T(\text{au})$	$\delta E_T^{\text{mean}, a}$ kcal	$E_O(\text{au})^g$	$\delta E_O^{\text{mean}, b}$ kcal	$E_O^{\text{core}}(\text{au})^g$	$\delta E_{O, \text{core}}^{\text{mean}, c}$ kcal	$\Delta \epsilon_{\text{N1S}}$ (kcal/mol)
	-197.354 137		-65.0277		-56.2757		
	-210.886 30	2.4	-69.516	65.8	-60.230	8.1	0
	-224.426 24		-74.214		-64.210		-35.8, -23.8
	-230.374 5		-78.750		-68.120		
	-246.326 53	-7.5	-83.70101	79.4	-72.60052	18.2	0
	-262.254 66		-88.9051		-77.13899		-28.7
	-230.476		-77.655		-67.523		
	-246.417	-1.88	-82.549	18.8	-71.997	9.4	0
	-262.352		-87.503		-76.501		-20.4

^a $\delta E_T^{\text{mean}} = E_T(\text{pyridine}) - 1/2[E_T(\text{benzene}) + E_T(\text{pyrazine})]$. ^b $\delta E_O^{\text{mean}} = E_O(\text{pyridine}) - 1/2[E_O(\text{benzene}) + E_O(\text{pyrazine})]$.
^c $\delta E_{O, \text{core}}^{\text{mean}} = E_{O, \text{core}}^{\text{pyridine}} - 1/2[E_{O, \text{core}}^{\text{benzene}} + E_{O, \text{core}}^{\text{pyrazine}}]$. ^d Reference 10a,b. ^e Reference 10c,d. ^f Reference 10e. ^g E_O and $E_{O, \text{core}}$ are the sum of the appropriate orbital energies (ref 10) and have not been multiplied by two.

are necessary.^{2,3} Support for this idea has come from first-order perturbation theory,⁹ which shows that additive changes in the Hamiltonian ($H_1 + H_2$) translate into additive changes in the first-order energy, $\delta E_m^{(1)}$:

$$\delta E_m^{(1)} = \langle \psi_m^0 | H_1 + H_2 | \psi_m^0 \rangle = \langle \psi_m^0 | H_1 | \psi_m^0 \rangle + \langle \psi_m^0 | H_2 | \psi_m^0 \rangle \quad (1)$$

where ψ_m^0 is the unperturbed wave function. Since the first-order energy correction is additive and does not involve changes in wave function, it may seem natural to associate energy additivity with constant electronic structure.

The second-order energy correction is given by

$$\delta E_m^{(2)} = \sum_{k \neq m} \langle \psi_m^0 | H_1 + H_2 | \psi_k^0 \rangle / (E_m^0 - E_k^0) \quad (2)$$

The second-order energy correction is due to changes in wave function and is generally nonadditive because of the squared term in the numerator of eq 2. Consequently, it has been thought that energy additivity will hold to the extent that the wave function remains constant and second-order energy corrections are negligible. Energy additivity apparently depends on the degree to which electronic structure is constant and the degree to which net interactions between substituents are absent or constant. However, this conclusion is not in accord with experimental examples⁶ (e.g., pyridine and others⁵) which indicate that additivity can apparently be observed even when large interactions (compared to deviations from additivity) occur between substituents. This, in turn, implies that compensating changes in electronic structure take place in other portions of the molecule so that additivity is somehow preserved. Such a result is a fundamental departure from existing ideas on substituent effects and would not be anticipated from models based on classical or traditional concepts. This prompts us to find a more general description of the energy changes and structural perturbations which accompany replacement of one molecular fragment by another.

II. A Theory of Nuclear Substitution

A. Hemistructural Relationship: Definition. In considering the energetic consequences of replacing a subset of nuclei in a

molecule, it is useful to distinguish between electronic structure and geometric structure. Geometric structure pertains to the coordinates of the nuclei, while electronic structure includes the spatial distribution of electron density. It is well established that bond lengths and bond angles are often transferable between molecules and that bond lengths frequently can be predicted by assigning covalent radii to various atoms.¹ In such a case, an origin can be defined for each of three diatomic structures (e.g., A-A, A-B, B-B) so that the nuclear coordinates of "A" in A-B are the same as for the corresponding "A" in A-A. Likewise, the coordinates of "B" in A-B are the same as for the corresponding "B" in B-B.

This idea can be generalized in order to specify a *hemistructural* relationship. If an origin can be defined so that a subset of nuclei in molecule C have the same nuclear charges and coordinates as a subset of nuclei in molecule D and the remaining nuclei in C have the same nuclear charges and coordinates of a subset of nuclei in molecule E, then C is hemistructural to D and E. C can be referred to as a hemistructural molecule which is derived from the parent molecules, D and E. It would also be possible for C to share a hemistructural relationship with more than two other molecules, and further generalization can be introduced by allowing C to represent more than a single molecule.

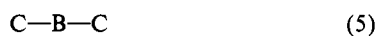
A simple example of a hemistructural relationship is illustrated by the geometry of toluene compared to the corresponding geometries of benzene and *p*-xylene. To a good approximation,¹² one-half of the toluene molecule can superimpose on a corresponding half of *p*-xylene, while the other half of toluene can superimpose on benzene. As a result, toluene is approximately hemistructural to benzene and *p*-xylene.

It is interesting that the hemistructural relation holds to a reasonable degree for the examples of energy additivity discussed in section I. The C-C and C-N bond lengths in benzene and the azabenzenes are essentially constant,¹³ as are the corresponding bond lengths and bond angles in benzene, toluene, and *p*-xylene.¹²

(12) "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London, 1958.

Other examples include methane, bromomethane, and dibromomethane where heats of formation are additive to within 0.5 kcal.^{5,14} In addition, it is noteworthy that the hemistructural relation also holds for cases of energy nonadditivity.¹ This suggests that the hemistructural relationship is a suitable point to begin a theoretical study of substituent effects and the initial breakdown from energy additivity that occurs for larger perturbations. We shall initially inquire as to what constraints the hemistructural relationship imposes upon the total energy and the nuclear forces of the hemistructural molecule. In Appendix II, it is shown that the hemistructural geometry may correspond to an equilibrium geometry as a consequence of these constraints.¹⁵

B. The Hemistructural Relationship: A Fundamental Basis of Transferability. The theoretical consequences of the hemistructural relationship (at the Hartree-Fock level) can be discovered by examining how the Fock matrix differs for the three molecules sharing the hemistructural relationship. For convenience the structures of the three hemistructural molecules can be symbolized as



where A, B, and C represent molecular fragments containing arbitrary nuclei. ABC is hemistructural to ABA and CBC, and it could be said that the three molecules form a hemistructural set.

The Fock matrix elements are dependent upon the kinetic energy integrals, electron repulsion integrals, nuclear-electron attraction integrals, and the molecular orbital coefficients of the occupied MO's. Since we are interested in comparing Fock matrix elements, it will be advantageous to evaluate the various integrals using a basis set which is mathematically complete¹⁶ and *not* necessarily associated with particular nuclei. As long as the basis set is complete,¹⁶ it is unnecessary to change basis functions when the nuclei are altered. The *i*th basis function can be represented as ϕ_i .

The kinetic energy integrals are of the form:

$$T_{ij} = -\frac{\hbar^2}{2m} \langle \phi_i | \nabla^2 | \phi_j \rangle \quad (6)$$

The kinetic energy operator, ∇^2 , contains coordinates of electron

α and is independent of the nuclear coordinates. Since ϕ_i and ϕ_j do not depend on nuclear coordinates, the same kinetic energy integrals can be used in setting up the Fock matrices for ABA, ABC, and CBC.

The electron repulsion integrals are of the form:

$$V_{ee}^{ijkl} = \left\langle \phi_i(\alpha) \phi_j(\alpha) \left| \frac{1}{r_{\alpha\beta}} \right| \phi_k(\beta) \phi_l(\beta) \right\rangle = \langle ijkl \rangle \quad (7)$$

The operator, $1/r_{\alpha\beta}$, depends on the distance between electron α and electron β and is independent of nuclear coordinates. The basis functions ϕ_i , ϕ_j , ϕ_k , ϕ_l are also independent of nuclear positions so that the same electron-repulsion integrals can be used for the Fock matrices corresponding to ABA, ABC, and CBC. The nuclear-electron attraction integrals are of the form:

$$V_{ne}^{ija} = -Z_a \left\langle \phi_i \left| \frac{1}{r_{na}} \right| \phi_j \right\rangle \quad (8)$$

The operator, $1/r_{na}$, depends on the coordinates of nucleus *a* and electron α , while the basis functions ϕ_i and ϕ_j are independent of nuclear position. As a result, each nuclear attraction integral, V_{ne}^{ija} , depends on the coordinates of only *one* nucleus. This coordinate for ABC can be obtained from one of the two parents, ABA or CBC, if nuclear geometry is additive (i.e., the hemistructural condition is applicable). Consequently, each of the nuclear-electron attraction integrals for ABC can be obtained from one or the other of the two structures (ABA and CBC) to which it is hemistructural.¹⁵

The fundamental significance of the hemistructural relationship is now apparent: the hemistructural relationship is special, since all integrals necessary for constructing the Fock matrix for hemistructural ABC (i.e., T_{ij} , V_{ee}^{ijkl} , V_{ne}^{ija}) can be obtained from the two parent structures (ABA or CBC). If ABA, ABC, and CBC are not members of the same hemistructural set,¹⁵ the V_{ne}^{ija} for ABC will not necessarily be transferable from ABA and CBC, and new information (i.e., new V_{ne}^{ija}) must be introduced to construct the Fock matrix for ABC. Consequently, the properties of ABC will no longer depend on the same parameters or information (i.e., T_{ij} , V_{ee}^{ijkl} , V_{ne}^{ija}) as ABA and CBC, and the relationship between the three structures will become more obscure. The hemistructural relationship is unique in the sense that *all* of the information (i.e., T_{ij} , V_{ee}^{ijkl} , V_{ne}^{ija}) necessary for constructing the Fock matrix and for determining the Hartree-Fock wave function and energy of the hemistructural molecule (ABC) can be transferred from the parent structures (ABA and CBC).¹⁷ This is also true for the exact nonrelativistic energy and wave function since correlation effects can be introduced through configuration interaction in terms of Slater determinants which are constructed from the Hartree-Fock orbitals.^{18,19} The fact that the hemistructural molecule contains only information which is common to the parents (i.e., geometric coordinates, T_{ij} , V_{ee}^{ijkl} , V_{ne}^{ija}) places an important constraint on the relationship of the hemistructural wave function and energy with the wave function and energy of each parent. In this sense, the hemistructural molecule contains no new information.

One expected consequence is that properties of the hemistructural molecule may often be related in a simple manner (e.g., additive or quadratic) to the properties of the two parents, but this, of course, will not be general. Nonetheless, once the Fock matrix for ABC is defined, the question of how properties of the hemistructural molecule depend on information transferred from the parent structure is solved in principle. In the next section, we will examine some generalizations which can be applied without detailed computation.

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(15) The examples cited above are not intended to lead the reader into believing that the hemistructural relationship is limited to equilibrium geometries. Note that each point on the A-B-C potential surface will correspond to a point on the A-B-A potential surface where the geometric coordinates of the A,B fragments are identical and to a point on the C-B-C potential surface where the geometric coordinates of the B,C fragments are identical. Each group of three corresponding points constitutes a hemistructural set, and there will be one hemistructural set for each point on the A-B-C potential surface (i.e., infinite). The examples noted above (e.g., benzene, toluene, and xylene) are special cases where energy *minima* on three potential energy surfaces are connected through a hemistructural relationship. See Appendix II for a further development of this idea.

(16) (a) Examples of complete basis sets include three-dimensional Cartesian polynomials and spherical Gaussians located at all possible points in space with all possible exponents (also see: S. F. Boys, *Proc. R. Soc. London, Ser. A*, **200**, 542 (1950)). (b) For more detailed discussion, see: B. Klahn and W. A. Bingel, *Int. J. Quantum Chem.*, **11**, 943 (1977). (c) Non-nuclear-centered basis sets are commonly used in numerical calculations dealing with solid-state phenomena. For example, see: (d) G. P. Kerker, S. G. Louie, and M. L. Cohen, *Phys. Rev. B*, **17**, 706 (1978); (e) K. H. Lau and W. Kohn, *Surf. Sci.*, **75**, 69 (1978); (f) N. H. March and M. P. Tosi, *Proc. R. Soc. London, Ser. A*, **330**, 373 (1972).

(17) The transferability noted at the integral level translates into transferability at the density matrix level. See eq I-1, eq I-10, and the discussion in Appendix I. Note that the density matrix elements are not simply additive, but can be constructed from transferable terms.

(18) E. A. Hylleraas, *Z. Phys.*, **48**, 469 (1928).

(19) F. L. Pilar, "Elementary Quantum Chemistry", McGraw-Hill, New York, 1968.

C. How Is the Energy of the Hemistructural Molecule Related to the Energies of the Parent Molecules? a. The Hemistructural Fock Matrix. Since the large majority of ab initio calculations on molecules are based on Hartree-Fock theory, it would be useful to answer this question at the Hartree-Fock level. Extending the result to include correlation effects is straightforward and will be presented later.

The Fock matrix element, F_{ij} , for a closed-shell system is given by

$$F_{ij} = H_{ij}^c + \sum_k \sum_l P_{kl} [\langle ijkl \rangle - \frac{1}{2} \langle ikjl \rangle] \quad (9)$$

where H_{ij}^c is the core matrix element which is constructed from the sum of the corresponding kinetic energy matrix element

$$T_{ij} = T_{ij} = -\frac{\hbar^2}{2m} \langle \phi_i | \nabla_\alpha^2 | \phi_j \rangle \quad (10)$$

and the nuclear-electron attraction matrix element,⁹

$$V_{ne}^{ij} = -\sum_a \frac{Z_a}{r_{a\alpha}} \left\langle \phi_i \left| \frac{1}{r_{a\alpha}} \right| \phi_j \right\rangle \quad (11)$$

P_{kl} is an element of the density matrix and is given by

$$P_{kl} = 2 \sum_\nu^{\text{occ}} a_{\nu k} a_{\nu l} \quad (12)$$

where $a_{\nu k}$ represents the coefficient of the k th basis function in the ν th MO. In eq 9, the term involving the double summation over k and l introduces the average effects of electron repulsion so that

$$V_{ee}^{ij} = \sum_k \sum_l P_{kl} [\langle ijkl \rangle - \frac{1}{2} \langle ikjl \rangle] \quad (13)$$

The kinetic energy matrix, T , for the hemistructural molecule is identical with those for the corresponding parents (eq 6 and 10), while each nuclear-electron attraction matrix element (V_{ne}^{ij}) consists of a contribution from each parent molecule (eq 8 and 11). The coulomb integrals, $\langle ijkl \rangle$, and the exchange integrals, $\langle ikjl \rangle$, are common to the hemistructural molecule and its parents, but the electron repulsion matrix, V_{ee} , will change since the wave functions (and therefore P_{kl}) for the hemistructural molecule and its parents are different. It is important to recognize that a perturbation (e.g., a change in nuclear charge) produces a change in F only through V_{ne} and P_{kl} .

b. The Hemistructural Wave Function. It is useful to note that the perturbed molecular orbitals, ψ_ν (e.g., for ABC or CBC), can be expanded in terms of the same basis functions as the unperturbed molecular orbitals, ψ_ν^0 (for ABA).

$$\psi_\nu^0 = \sum_m a_{\nu m}^0 \phi_m \quad (14)$$

$$\psi_\nu = \sum_m (a_{\nu m}^0 + a'_{\nu m}) \phi_m \quad (15)$$

In Appendix I it is shown that the MO coefficients for CBC ($a_{\nu m}^0 + a'_{\nu m}$) can be expressed in terms of the corresponding coefficients for ABA and ABC in the small perturbation limit. If $a'_{\nu m}$ represents the change in $a_{\nu m}^0$ for the perturbation A-B-A to A-B-C and if $a''_{\nu m}$ represents the corresponding change for the perturbation A-B-A to C-B-A, then the changes in the coefficients for the double perturbation, A-B-A to C-B-C, are given by

$$a'_{\nu m} = a''_{\nu m} + a'_{\nu m} \quad (16)$$

It should be emphasized that the additivity observed in the coefficients depends not only on the magnitude of the perturbation, but also on the unique constraints imposed upon the Fock matrix and upon V_{ne} by the hemistructural relationship. The restriction imposed by the magnitude of the perturbation may be necessary for $a'_{\nu m} = a''_{\nu m} + a'_{\nu m}$, but it is not sufficient.

c. Behavior of the Total Energy and the Energy Components. The change in coefficients, $a'_{\nu m}$ (eq I-5, 16), can be used to express

the new kinetic and potential (V_{ne} , V_{ee}) energies:

$$T = 2 \sum_\nu^{\text{occ}} \sum_i \sum_j (a_{\nu j}^0 + a'_{\nu j}) T_{ij} (a_{\nu i}^0 + a'_{\nu i}) \quad (17)$$

$$V_{ne} = 2 \sum_\nu^{\text{occ}} \sum_i \sum_j (a_{\nu j}^0 + a'_{\nu j}) (V_{ne}^{ij} + \delta V_{ne}^{ij}) (a_{\nu i}^0 + a'_{\nu i}) \quad (18)$$

$$V_{ee} = \sum_\nu^{\text{occ}} \sum_i \sum_j (a_{\nu j}^0 + a'_{\nu j}) (V_{ee}^{ij} + \delta V_{ee}^{ij}) (a_{\nu i}^0 + a'_{\nu i}) \quad (19)$$

The kinetic energy matrix elements, T_{ij} , are not affected by the perturbation so that the change in kinetic energy depends only on the change in coefficients, $a'_{\nu j}$. The potential energies are a function of the corresponding matrix elements as well as the coefficients, $a_{\nu j}$. The result is that the kinetic energy is governed by a fundamentally simpler relationship than V_{ne} or V_{ee} . One consequence of this simpler relationship is that when changes in $a'_{\nu j}$ are additive (i.e., $a'_{\nu j} = a''_{\nu j} + a'_{\nu j}$), the kinetic energy may be additive (to first order in $a'_{\nu m}$) without V_{ne} or V_{ee} being additive. This disparity in behavior between T and V_{ne} is particularly interesting since both are one-electron properties.

The behavior of the kinetic energy is an important result since the total energy, including the nuclear repulsion energy (V_{nn}), is related to the kinetic energy through the virial theorem¹⁹

$$E = -T = (V_{ee} + V_{ne} + V_{nn})/2 = V/2 \quad (20)$$

Important situations where the virial theorem is applicable include atoms and ions in bound electronic states, molecules at equilibrium geometries, and Born-Oppenheimer transition states. In Appendix II, it is shown that the virial theorem, in the simple form of eq 20, also applies to the hemistructural molecule under certain conditions.

We have now derived a set of sufficient conditions for observing energy additivity. While these conditions are less restrictive and more general than constancy of electronic structure, they are not necessarily the final answer to the question of additivity.

(i) Hemistructural Relationship. This relationship allows construction of the Fock matrix for the hemistructural molecule from information obtainable from the parent molecules. *No new information is necessary to describe the properties of the hemistructural molecule.*¹⁷

(ii) Perturbation Theory. For first-order corrections to the molecular orbitals the changes in coefficients, $a'_{\nu m}$ (eq I-10), are related to δV_{ne}^{ij} by a set of simultaneous linear equations (eq I-9). When the hemistructural relationship is applicable, δV_{ne}^{ij} is given by the sum of *independent* contributions from each nucleus, so that the $a'_{\nu j}$ are determined by *independent* contributions from each nucleus.

(iii) Additivity of Kinetic Energy. Conditions i and ii are sufficient for the $a'_{\nu j}$ to be expressed as $a'_{\nu j} = a''_{\nu j} + a'_{\nu j}$, and from eq 16 and 17 it can be seen that this leads to additivity for the linear terms (e.g., $a_{\nu j}^0 T_{ij} a'_{\nu i}$) contributing to the kinetic energy.²⁰ A significant point is that kinetic energy additivity does not require any special assumptions concerning the maintenance of constant electron density over localized regions of space. Consequently, equivalent groups are *not a necessary* prerequisite for energy additivity. It is particularly significant that this applies even in the limiting case of first-order corrections to the MO coefficients.

(iv) The Virial Theorem. If $E = -T$, additive kinetic energies are equivalent to additive total energies. When the virial theorem is not applicable (e.g., ions derived by vertical ionization), the kinetic energy may still be additive, but the total energy will no longer equal $-T$.

III. Discussion

A. Contrasting Behavior of the Total Energy and Energy

(20) The *bilinear* terms (e.g., $a'_{\nu j} T_{ij} a'_{\nu i}$) contribute to *nonadditivity* in the kinetic energy. Note that V_{ne} and V_{ee} will have a nonadditive contribution even from the linear terms in $a'_{\nu j}$, since the operators as well as the coefficients change with the perturbation (see eq 17-19).

Components. The kinetic energy has been shown to follow a fundamentally simpler relationship than the potential energy components, V_{nn} , V_{ne} , V_{ee} . However, the virial theorem places a constraint on the total potential energy, V ($V = V_{nn} + V_{ne} + V_{ee}$), so that $E = -T = V/2$.²¹ Consequently, the "complications" present in the individual components cancel away in the sum (V), and E follows the same simple relationship as the kinetic energy (or V). It is important to realize that E can be additive or non-additive, even though the deviations from additivity in V_{nn} , V_{ne} , and V_{ee} can be one or more orders of magnitude higher than in the total energy.

We can gain some appreciation of this by examining the nuclear repulsion energies appropriate for the benzene, toluene, and *p*-xylene examples encountered earlier. The nuclear repulsion energies between the 1,4 substituents in the three molecules are 67, 538, and 4391 kcal, respectively. The mean value of V_{nn} for benzene and *p*-xylene is 2229 kcal which deviates by 1691 kcal from the actual value for toluene! The heats of formation are additive to within 0.11 kcal, and if this value is substituted into eq 20 for E , we can note three important facts: (1) the kinetic energy must be additive to within 0.11 kcal; (2) the total potential energy ($V_{ee} + V_{ne} + V_{nn}$) must be additive to within 0.22 kcal; (3) the sum of V_{ee} and V_{ne} for toluene will be far from additive and will deviate from the mean by 1690.78 kcal and in the opposite direction from V_{nn} . The significant point is that E , T , and V can be additive to within a kilocalorie, even though the individual components of V (V_{ee} , V_{ne} , V_{nn}) may deviate from additivity by hundreds of kilocalories.

B. Contrasting Behavior of the Total Energy and Orbital Energy.

Since the virial theorem does not apply to the orbital energy, E_o , and since V_{ee} and V_{nn} will generally be nonequal and nonadditive, the orbital energy will generally be less additive than the total energy. The total orbital energy is twice the sum of the individual orbital energies (for closed-shell systems) and is given by¹⁹

$$E_o = T + V_{ne} + 2V_{ee} \quad (21)$$

For comparison, the total energy is given by

$$E = T + V_{ne} + V_{ee} + V_{nn} \quad (22)$$

The difference between E and E_o is that V_{nn} is replaced by an extra V_{ee} term. We have seen from the previous example and eq 18 and 19 that V_{ne} and V_{ee} can deviate substantially from additivity. The virial constraint forces the total potential energy to show the same additivity as the total energy (to within a factor of 2). If V_{nn} is replaced by V_{ee} , the deviations from additivity in the individual potential energy components will not necessarily cancel away in E_o . Consequently, it is possible for the total energy to be additive without the orbital energies or E_o showing a comparable degree of additivity. An example of this effect occurs in the case of benzene, pyridine, and pyrazine (Table II) where the total energy is additive to within 2.4 kcal, but the total orbital energy is only additive to 65 kcal.

This fact has important consequences with regard to many of the past MO treatments of substituent effects. These approaches are based on the behavior of the orbital energy which will respond to multiple substitution in a different and fundamentally more complicated fashion than the total energy. As a result, treatments based on HOMO/LUMO interactions, PMO, or frontier orbital theory will require modification to meet this problem.^{22,23}

If a perturbation is small enough, it is possible for orbital energies or the potential energy components, V_{nn} , V_{ne} , and V_{ee} ,

to be individually additive. Under such conditions, the total energy would also be additive. However, it is unlikely that this situation accounts for a significant number of cases where additivity is observed. It certainly does not apply to the benzene, pyridine, pyrazine example in Table II or even to the "trivial" case of benzene, toluene, or *p*-xylene. The large nonlinearity in V_{nn} (1691 kcal) ensures comparable nonlinearity in V_{ee} and V_{ne} . The present results show that the peculiar geometric arrangement implied by the hemistructural relationship will permit additive total energies even though orbital energies or V_{nn} , V_{ne} , and V_{ee} are essentially nonadditive.

C. Energy Additivity and Bond Length Additivity Do Not Depend on Group Transferability. Earlier accounts of additive substituent effects have emphasized the necessity of constant electronic structure for the substituents and the molecular fragment to which the substituents are attached.²³ However, there is nothing inherent in eq 16 and 17 which would require constant electron density in a particular region of space or over a specific molecular orbital as a prerequisite for additivity. It is clear that constant electronic structure is a sufficient criterion for additivity, but the present results show that it is not necessary.

This is interesting, but by itself gives little insight into the nature of possible deviations from the equivalent group concept. The analysis of forces in Appendix II indicates that the equivalent group is sacrificed, at least in part, to satisfy the constraints on the wave function imposed by the requirement of maintaining an equilibrium geometry when fragments are transferred from one molecule to another. Preserving an equilibrium geometry depends on whether or not changes in the force field due to new nuclear charges and positions can be exactly offset by redistribution of electron density. The analysis in Appendix II shows that such cancellation is possible at the hemistructural geometry, but there is no requirement that electronic reorganization must be limited to the spatial region associated with any particular fragment. Since at least part of this electronic reorganization is a response to offset the changes in the nuclear component of the force at each nucleus, it would not be a surprise to find that cancellation of the nuclear and electronic forces actually requires changes in electron density near each of the nuclei, particularly those nuclei closest to the site of perturbation. It is important to note that electron redistribution associated with first-order MO corrections does not perturb the additivity of the first-order kinetic energy terms (eq 16 and 17), which through the virial theorem (eq 20) become equivalent to additive contributions to the total energy. Consequently, we have the remarkable paradox that a molecule can be divided into transferable fragments, on the basis of nuclear positions, and that these fragments apparently make transferable contributions to the total energy without the necessity of maintaining constant electronic structure.

The idea of the equivalent group has been an important organizing feature of structural chemistry ever since 1807 when Dalton proposed that molecules consist of atoms bound together in definite proportions.²⁴ Today, the equivalent group appears in many empirical treatments of molecular structure^{1-3,25} and chemical reactivity.²⁶ The present work demonstrates that expressing the total energy in terms of group contributions does not require constant electronic structure for the component fragments of a molecule. Restructuring the equivalent group models into

(21) (a) A number of authors have realized that the simple form of the virial theorem allows E to be related solely to $-T$ (ref 2) or to $(V_{ne} + V_{ee} + V_{nn})/2$ (ref 21b,c). An important contribution of the present paper is the derivation of the result which describes the effect of nuclear substitution on T . Allen and Shull effectively set up a model which assumes T is additive. (b) A. Liberles, A. Greenberg, and J. E. Eilers, *J. Chem. Educ.*, **50**, 676 (1973). (c) E. Scarzafava and L. C. Allen, *J. Am. Chem. Soc.*, **93**, 311 (1971).

(22) Examples include: (a) Ian Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley, New York, 1976; (b) Giese, *Angew. Chem., Int. Ed. Engl.*, **16**, 125 (1977).

(23) Several authors have noted that the orbital energy and total energy do not always correlate with respect to changes in some molecular property. For examples dealing with Walsh's rules, see: (a) L. Z. Stenkamp and E. R. Davidson, *Theor. Chim. Acta*, **30**, 283 (1973); (b) R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974).

(24) J. R. Partington, "A Short History of Chemistry", 3rd ed., Harper & Row, New York, 1960, p 173.

(25) Examples include CPK molecular models: (a) J. M. Timko, S. S. Moore, D. M. Walba, P. C. Hiberty, and D. J. Cram, *J. Am. Chem. Soc.*, **99**, 4207 (1977); empirical force-field calculations: (b) R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany, and D. McNally, *J. Phys. Chem.*, **75**, 1264 (1971); (c) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 4628 (1972); (d) N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972). Various empirical models of molecular geometry have also been reviewed: (e) L. S. Bartell, *J. Chem. Educ.*, **45**, 755 (1968).

conformance with this picture and, in particular, obtaining parameters which reproduce correct energies as well as other properties (e.g., dipole moments, vibrational frequencies, NMR chemical shifts, polarizabilities) should prove to be an interesting challenge.

D. Principle of Transferability and Group Contributions to Molecular Properties. The concept of transferability²⁷ is central to the development of the hemistructural relationship and has been used in several contexts in developing previous approaches for treating multiple substituent effects.²⁶ Methods such as atoms in molecules,²⁸ diatomics in molecules,²⁹ molecules in molecules,³⁰ fragment molecular orbital theories,³¹ and simulated ab initio MO theory³² (SAMO) use an *assumed* transferability at the matrix element level as a convenient approximation. Marcus' development of conformal sets³³ comes remarkably close to the hemistructural relationship in a number of aspects, but the definition of conformal sets is closely intertwined with the formalism of Hückel π -MO theory³⁴ and the *assumed* transferability of Hückel matrix elements. Localized orbital^{2,35} approaches carry the *assumed* transferability to the level of specific regions of electron density and their associated energy. Finally, group additivity schemes¹⁸ assume that molecular properties can be expressed as a sum of transferable contributions from individual fragments. The present contribution does not assume transferability, but demonstrates it as a consequence of a simple geometric relationship. The transferability of integrals used in the Fock matrix is not readily apparent when the integrals are expressed in terms of conventional nuclear-centered and nuclear-dependent basis functions. In fact, the transferability is not even applicable in such a basis set, but the fundamental simplicity of the hemistructural relationship is unmasked by the choice of nuclear independent basis functions (eq 6-8): at the Hartree-Fock and nonrelativistic limits, the energy and molecular orbitals are independent of basis set and must behave as if the hemistructural integrals transfer from the parent structures.

Transferable fragments and localized orbitals^{2,35} are two ways of accounting for the fact that molecular properties can often be expressed in terms of group contributions plus interactions between groups. The present development shows that neither condition is necessary. The fact that bond energies in equivalent bonding situations may appear additive without the maintenance of constant electronic structure in the bonding regions (or elsewhere) is an interesting paradox and will be explored in more detail.³⁶

E. Molecular Forces and Bond Length Additivity. In Appendix II, it is shown that coefficient additivity (e.g., eq 16) leads to the prediction that the hemistructural geometry (e.g., A-C) will be a zero force structure (i.e., energy minimum or maximum) if the parent structures (A-A and C-C) are zero force structures.^{15,37,38} In the case where one group is common to both parents (e.g., the "B" fragment in ABA and CBC), coefficient additivity is not sufficient to guarantee that the hemistructural ABC will be a zero force structure. In particular, the geometry of the B fragment should be more susceptible to residual forces than the A and C fragments and the relevance of this finding to various problems (e.g., transition-state structure, hydrogen-bond potentials) is currently under investigation.

F. Relationship between Energy Additivity and Bond Length Additivity. Bond length additivity for the molecules A-A, A-C, and C-C holds for the first-order force terms as well as for the second-order force terms outlined in eq II-6 of Appendix II, whereas bond energy additivity holds only for the first-order kinetic energy terms (see eq 16 and 17). Consequently, bond length additivity and the concept of "covalent radii" do not necessarily require bond energy additivity. It is interesting to note that some time ago Pauling made an equivalent generalization based upon his empirical examination of bond lengths and bond energies.^{1a}

G. Future Developments. 1. Solutions, Solid-State Materials, Surfaces, and Energy Transfer. The theoretical approach presented here has the advantage of leading to both pictorial and quantitative descriptions for properties of molecules which do not have to be defined in definite structural terms. Consequently, it should be particularly applicable to problems concerned with interactions on surfaces, in the solid state, in solvation phenomena, and in energy transfer.

(37) Bond length additivity can be described in terms of a specific radius assigned to each fragment¹ or in terms of total bond length conservation for the process, $A-A + C-C \rightarrow A-C + A-C$. A sufficient requirement for assigning a radius to each fragment is that electronic reorganization on fragment transfer is limited to first-order corrections (Appendix II). If this condition applies to an entire set of molecules generated from pairwise combination of n fragments (e.g., A-A, A-B, A-C, A-D, ..., B-B, B-C, B-D, ..., C-C, C-D, ..., D-D, ...), then a unique radius can be assigned to each fragment, all bond lengths will be the sum of the corresponding fragment radii, and reactions such as $A-B + C-D \rightarrow A-C + B-D$ will be accompanied by conservation of total bond length. Note that if the first-order condition applies to molecules within separate subsets and fails to apply to molecules in different subsets, then a given fragment may have a different radius in each subset. This point will be pursued in future papers.

(38) A referee has raised an instructive point with regard to applying this result to a case where one parent (e.g., R-R) has no zero force geometry except at the dissociated limit. The other two structures (S-R and S-S) have their respective energy minimum at a finite value for the internuclear distance (e.g., r_{sr} and $r_{ss} = r_s + r_r$, respectively). It is convenient to pick an origin at the midpoint of the two symmetrical structures, so that the zero force geometry for R-R occurs with the left R at $-\infty$ and the right R at $+\infty$. The coordinates for the zero force structure of S-S correspond to $-r_s$ for the left S fragment and to $+r_s$ for the right fragment. The analysis given in Appendix II predicts a zero force structure for R-S at the hemistructural geometry with respect to the zero force structures of the two parents, R-R and S-S. This prediction would place the S in S-R at $-r_s$ and the R in S-R at $+\infty$, which corresponds to dissociated S-R and to a zero force structure. The prediction is correct, but incomplete since the nonhemistructural zero force geometry for S-R, corresponding to an internuclear distance of r_{sr} , is missed.

The analysis presented in Appendix II shows that when fragment transfer between various structures can be described in terms of first-order MO corrections (i.e., coefficient additivity, eq 16), the bond distances separating the fragments at a zero force geometry can be described in terms of a sum of covalent radii. One obvious possibility with regard to nonhemistructural energy minima is the significance of second or higher order corrections to the MO coefficients, and there are a few examples reported by Pauling where bond length additivity breaks down for the experimental bond lengths.¹ Pauling cites bond length data for compounds involving elements in the first four rows of groups 4 through 7, and there are four substantial breakdowns of bond length additivity: these involve using the bond lengths of H-H, F-F, HO-OH, and H₂N-NH₂ to derive single-bond covalent radii for hydrogen, fluorine, oxygen, and nitrogen.¹ The deviations are particularly intriguing, since satisfactory covalent radii can be derived for H, F, O, and N from other compounds (e.g., CH₃-H, CH₃-F, CH₃-OH, CH₃-NH₂) containing these four elements. This suggests something unusual about H-H, F-F, HO-OH, and H₂N-NH₂ compared to CH₃-H, CH₃-F, CH₃-OH, CH₃-NH₂, and similar molecules. These deviations and the relationship between higher order MO corrections and the existence of nonhemistructural zero force geometries are currently undergoing examination.

(26) (a) J. N. Brønsted and K. J. Pedersen, *Z. Phys. Chem. (Leipzig)*, **108**, 185 (1924); (b) R. P. Bell, "Acid-Base Catalysis", Oxford University Press, London, 1941; (c) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1340 (1936); (d) L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, 1940; (e) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); (f) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963; (g) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962); (h) E. R. Thornton, *ibid.*, **89**, 2915 (1967); (i) D. A. Forsyth, *ibid.*, **95**, 3594 (1973); (j) C. D. Johnson, *Chem. Rev.*, **75**, 755 (1975).

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(29) (a) F. O. Ellison, *J. Am. Chem. Soc.*, **85**, 3540 (1963); (b) J. C. Tully, *J. Chem. Phys.*, **64**, 3182 (1976).

(30) W. von Niessen, *J. Chem. Phys.*, **55**, 1948 (1971).

(31) For example: (a) M. K. Orloff and D. D. Fitts, *J. Am. Chem. Soc.*, **85**, 3721 (1963); (b) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2353 (1966); (c) L. J. Weimann and R. E. Christoffersen, *ibid.*, **95**, 2074 (1973); (d) M. H. Whangbo, H. B. Schlegel, and S. Wolfe, *ibid.*, **99**, 1296 (1977); (e) W. H. Fink, *J. Chem. Phys.*, **66**, 1968 (1977); (f) M. Klessinger, *Theor. Chim. Acta*, **49**, 77 (1978).

(32) J. E. Eilers and D. R. Whitman, *J. Am. Chem. Soc.*, **95**, 2067 (1973).

(33) R. A. Marcus, *J. Chem. Phys.*, **43**, 2643 (1965).

(34) E. Hückel, *Z. Phys.*, **70**, 204 (1931).

(35) For example: (a) S. Rothenberg, *J. Am. Chem. Soc.*, **93**, 68 (1971); (b) D. A. Kleier, T. A. Halgren, J. H. Hall, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **61**, 3905 (1974); (c) W. England, M. S. Gordon, and K. Ruedenberg, *Theor. Chim. Acta*, **37**, 177 (1975). (d) Somewhat related to the localized orbital is the transferable atomic potential; see: G. Nicolas and Ph. Durand, *J. Chem. Phys.*, **70**, 2020 (1979).

(36) J. R. Murdoch and D. E. Magnoli, *J. Am. Chem. Soc.*, in press.

2. Geometry Nonadditivity and HOMO/LUMO Separations.

The extension of the theory to examples where deviations from geometry and coefficient additivity occur appears to be straightforward. One factor, related to the energy separation of occupied and vacant orbitals,³⁹ is the contribution of higher order perturbation terms.⁹ This will affect the behavior of the MO coefficients with respect to δV_{ne} (eq I-9) as well as the relationship between the two-electron repulsion terms in eq I-6. The virial theorem (eq 20 and II-1) and the Hellmann-Feynman theorem (eq II-2) also place important constraints on the dependence of the MO coefficients as a function of δV_{ne} (eq 17-19) and its derivatives (eq II-7-9, II-19-22). Treating deviations from geometry additivity would have important applications in the prediction of transition-state structure, structures of analogous stable intermediates, geometries of metal complexes, and geometry changes due to acquisition or loss of an electron. Prediction of force constants and isotope effects are other potential areas of investigation.

IV. Summary and Conclusions

Some examples of bond energy additivity appear to be explicable in terms of equivalent groups, but there are a number of cases where bond energy additivity persists even after the equivalent group concept has broken down (e.g., benzene, pyridine, and pyrazine). The failure of existing concepts to account for this relatively simple phenomenon prompted the present approach for treating nuclear substitution.

The finding that all integrals for hemistructural ABC can be obtained from ABA and CBC places a fundamental constraint on the relationship between the properties of the three structures. In the present paper, some of the consequences of this integral transferability are examined within the limiting case of first-order corrections to Hartree-Fock wave functions.

An important result is that the kinetic energy responds to perturbations in a simpler fashion than the potential energy components (V_{nn} , V_{ne} , V_{ee}), and one ultimate consequence is that changes in the total energy tend to be much more additive than the corresponding changes in the orbital energy. This fact is expected to have considerable impact on future applications of perturbational treatments of structure and reactivity (e.g., frontier MO theory) which are formulated in terms of orbital energy instead of total energy.

A significant point is that even though the response of the *individual* potential energy components to perturbations is more complex than the corresponding response of the kinetic energy, the virial theorem requires that the *total* potential energy ($V = V_{nn} + V_{ne} + V_{ee}$) and the total energy behave in the same fashion as the kinetic energy. Consequently, the behavior of the kinetic energy is of prime importance in analyzing the effects of nuclear substitution.

Bond length additivity has been demonstrated as a limiting case when fragment transfer ($A-A + C-C \rightarrow 2A-C$) is described by first-order corrections to the MO coefficients. Within this first-order framework, energy changes due to fragment transfer may be additive or nonadditive, and consequently bond length additivity does not necessarily require bond energy additivity. The

fact that bond length additivity may fail for A-B and B-C distances in A-B-A, A-B-C, and C-B-C before it fails for the A-C distance is an important result which will be developed in future work.

It is also shown that the additivity of the kinetic energy²⁰ is equivalent to additivity of the total energy, but this additivity does *not* require constant electronic structure in any particular region of space. Even in the limit of a small perturbation, equivalent groups are not a prerequisite for additivity relationships.

This first-order treatment of nuclear substitution has altered long-held views on the relationship between molecular structure and empirical dissections of molecular properties into group contributions. The present work has also provided a firm theoretical foundation for several concepts which have been established empirically for years. Nonetheless, it would be unrealistic³⁸ to expect that all aspects of chemical bonding can be described as first-order effects. The extension of the present work to higher order corrections and the elucidation of more general effects on molecular properties, structure and dynamics is now underway.

Appendix I

The Hemistructural Wave Function: First-Order Corrections. From eq 12, it can be seen that the perturbed density matrix element P_{kl} is given by⁴⁰

$$P_{kl} = 2 \sum_{\nu}^{\text{occ}} (a_{\nu k}^0 + a'_{\nu k}) (a_{\nu l}^0 + a'_{\nu l}) \quad (\text{I-1})$$

$$P_{kl} = P_{kl}^0 + 2 \sum_{\nu}^{\text{occ}} a'_{\nu k} a_{\nu l}^0 + 2 \sum_{\nu}^{\text{occ}} a_{\nu k}^0 a'_{\nu l} + 2 \sum_{\nu}^{\text{occ}} a'_{\nu k} a'_{\nu l}$$

Substituting eq (I-1) into eq 13,

$$\delta V_{ee}^{ij} = 4 \sum_k \sum_l \sum_{\nu}^{\text{occ}} a'_{\nu k} a_{\nu l}^0 \Theta_{ijkl} + 2 \sum_k \sum_l \sum_{\nu}^{\text{occ}} a'_{\nu k} a'_{\nu l} \Theta_{ijkl} \quad (\text{I-2})$$

where $\Theta_{ijkl} = \langle ijkl \rangle - 1/2 \langle ikjl \rangle$. The new molecular orbitals, ψ_{ν} , depend on the change in the Fock matrix which is given by

$$\delta F = \delta V_{ee} + \delta V_{ne} \quad (\text{I-3})$$

where δV_{ne} is the change in V_{ne} due to the perturbation. ψ_{ν} can be expanded in terms of ψ_{μ}^0 so that

$$\psi_{\nu} = \psi_{\nu}^0 + \sum_{\mu} b_{\nu\mu} \psi_{\mu}^0 \quad (\text{I-4})$$

From eq I-4 and eq 15,

$$a'_{\nu m} = \sum_{\mu} b_{\nu\mu} a_{\mu m}^0 \quad (\text{I-5})$$

and substituting eq I-5 into eq I-2, δV_{ee}^{ij} becomes

$$\delta V_{ee}^{ij} = 4 \sum_{\nu}^{\text{occ}} \sum_{\mu} b_{\nu\mu} \sum_k \sum_l a_{\mu k}^0 a_{\nu l}^0 \Theta_{ijkl} + 2 \sum_{\nu}^{\text{occ}} \sum_{\mu} \sum_{\xi} b_{\nu\mu} b_{\nu\xi} \sum_k \sum_l a_{\mu k}^0 a_{\xi l}^0 \Theta_{ijkl} \quad (\text{I-6})$$

For the special case of a small perturbation, perturbation theory⁹ (second order in energy; first order in wave function) can be used to relate ψ_{ν} (eq I-4) to δF . The coefficients (eq I-4), $b_{\alpha\beta}$, are given by⁴¹

$$b_{\alpha\beta} = \frac{\langle \psi_{\alpha}^0 | \delta F | \psi_{\beta}^0 \rangle}{E_{\alpha}^0 - E_{\beta}^0} = \frac{\sum_j \sum_l a_{\beta j}^0 [\delta V_{ne}^{ij} + \delta V_{ee}^{ij}] a_{\alpha j}^0}{E_{\alpha}^0 - E_{\beta}^0} \quad (\text{I-7})$$

For small perturbations, only the first term of eq I-6 makes a significant contribution to δV_{ee}^{ij} ^{39b} and on substitution into eq I-7

(39) (a) Substituting eq I-7 into eq I-6, it can be shown (see ref 9) that δV_{ee}^{ij} is approximated by $\delta V_{ee}^{ij} \approx 4 \sum_{\nu}^{\text{occ}} \sum_{\mu}^{\text{unocc}} b_{\nu\mu} \sum_k \sum_l a_{\mu k}^0 a_{\nu l}^0 \Theta_{ijkl} + 2 \sum_{\nu}^{\text{occ}} \sum_{\mu}^{\text{unocc}} b_{\nu\mu} b_{\nu\xi} \sum_k \sum_l a_{\mu k}^0 a_{\xi l}^0 \Theta_{ijkl}$. (b) Equation I-7 gives a good description of the changes to the MO coefficients when the $b_{\nu\mu}$ terms are small (i.e., $b_{\nu\mu} < 1.0$). In such a case, one could anticipate that the second term of eq I-6, which contains the product, $b_{\nu\mu} b_{\nu\xi}$, may be smaller than the first term, which contains only one $b_{\nu\mu}$ coefficient. It is recognized that the size of $b_{\nu\mu}$ may not be the only factor involved in regulating the relative magnitude of the first and second terms of eq I-6, but for one specific example of a perturbation (a series of mononuclear atoms and ions where the nuclear charge represents the perturbation) it can be shown analytically that the second term of eq I-6 vanishes (within the first-order framework), even though individual terms in the summations are nonzero. This has been verified by higher order numerical calculations (D. E. Magnoli, Thesis, UCLA, 1980), which also show that the first term of eq I-6 dominates the second term until some of the $b_{\nu\mu}$ approach and exceed one. The generality of this result and the effect of including higher order corrections to the MO coefficients are under examination.

(40) When the relative order of perturbed and unperturbed orbitals is unchanged, application of eq I-1 is straightforward. In other cases, proper numbering of the orbitals will ensure a correspondence between $a_{\nu k}^0$ and $a'_{\nu k}$. All perturbations relevant to the present paper can be treated within an isoelectronic and isonuclear framework (see ref 44 and 45).

gives⁴²

$$b_{\alpha\beta} = \frac{1}{E_{\alpha}^0 - E_{\beta}^0} \left[\sum_i \sum_j a_{\beta i}^0 \left\{ 4 \sum_{\nu} \sum_{\mu} b_{\nu\mu} \sum_k \sum_l a_{\mu k}^0 a_{\nu l}^0 \Theta_{ijkl} + \delta V_{ne}^{ij} \right\} a_{\alpha j}^0 \right] \quad (\text{I-8})$$

which on rearrangement is equivalent to

$$b_{\alpha\beta} = \frac{1}{E_{\alpha}^0 - E_{\beta}^0} \left[4 \sum_{\nu} \sum_{\mu} b_{\nu\mu} \sum_i \sum_j \sum_k \sum_l a_{\beta i}^0 a_{\alpha j}^0 a_{\mu k}^0 a_{\nu l}^0 \Theta_{ijkl} + \sum_i \sum_j a_{\beta i}^0 a_{\alpha j}^0 \delta V_{ne}^{ij} \right] \quad (\text{I-9})$$

The unknowns in eq (I-9) are $b_{\nu\mu}$ on the right-hand side and $b_{\alpha\beta}$ on the left-hand side. The energies E_{α}^0 and E_{β}^0 as well as the coefficients $a_{\alpha j}^0$, $a_{\beta i}^0$, $a_{\mu k}^0$, and $a_{\nu l}^0$ and the integrals Θ_{ijkl} are fixed and do not vary with the perturbation. The only variables are the nuclear-electron attraction matrix elements, δV_{ne}^{ij} . Equation I-9 permits a self-consistent solution for $b_{\nu\mu}$ within the perturbation framework imposed by eq I-7. The self-consistent aspect of eq I-9 permits the recovery of a portion of the higher order terms omitted by the more common expression, eq I-7. A full treatment will be presented elsewhere.⁴¹ Alternative forms of self-consistent perturbation theory have been presented.⁴³

Equation I-9 can be applied to three hemistructural molecules (e.g., structures 3-5) by treating A-B-A as the unperturbed reference. The two perturbations are represented by the change in structure from A-B-A to A-B-C (C-B-A) and from A-B-A to C-B-C. Since C and A are generally not isonuclear or isoelectronic, the associated energy changes could easily amount to thousands of kilocalories or more, and the applicability of perturbation theory is not immediately obvious. This apparent problem can be overcome by adding extra molecules or fragments to each structure in order to achieve an isonuclear and isoelectronic condition. As an example, the unperturbed reference becomes (A-B-A + 2C), the first perturbed structure becomes (A-B-C + C + A), and the second perturbed structure is represented by (C-B-C + 2A). The energy differences are now reduced to the range of zero to tens of kilocalories and represent a small fraction of the total molecular energies.⁴⁴ Total energy differences, as well as relative energy differences, are substantially reduced, and the addition of extra structures results in no loss of chemical significance.⁴⁵ These extra structures will not be written out again and will be implicitly assumed hereafter. In a subsequent paper, an example is presented in which a 495 000-kcal difference between ABA and CBC (which represents 75% of the total energy for CBC) is reduced to 44 kcal by maintaining the perturbation within an isoelectronic and isonuclear framework. The 44 kcal represents less than ~0.006% of the total energy of ABA + 2C or CBC + 2A. The absolute and relative energy reductions reflect the fact that changes in individual orbital energies, Mulliken populations, electron densities, and density matrix elements are relatively small in going from A-B-A + 2C to A-B-C + C + A to C-B-C + 2A for at least one actual example. A more quantitative analysis concerning the applicability of this form of perturbation theory is in progress.³⁶

The change in V_{ne} on going from A-B-A to C-B-C is given by the sum of the separate changes in V_{ne} on perturbing A-B-A to A-B-C and to C-B-A. The fact that eq I-9 represents a set of simultaneous linear equations and that changes in V_{ne} are additive and assignable to changes in individual nuclei is significant since changes in the coefficients (i.e., $b_{\nu\mu}$) must also be additive and assignable to changes in individual nuclei.⁴⁶ From eq I-5 it can be seen that if the changes in $b_{\nu\mu}$ are additive, then changes in $a'_{\nu m}$ will also be additive. If $a'_{\nu m}$ is associated with the perturbation ABA to CBC, then $a'_{\nu m}$ can be divided into two parts. One term ($a'_{\nu m}$) is associated with changing nuclear positions and charges in the right-hand fragment and corresponds to the perturbation ABA to ABC.

The second term ($a'_{\nu m}$) describes the change in coefficients for the perturbation ABA to CBA. The change in coefficient, $a'_{\nu m}$, is given by

$$a'_{\nu m} = a'_{\nu m} + a'_{\nu m} \quad (\text{I-10})$$

The total change in MO coefficients, $a'_{\nu m}$, for the perturbation ABA to CBC is equal to the sum of the changes in MO coefficients for the perturbation ABA to ABC and ABA to CBA.

Appendix II

Forces in the Hemistructural Molecule. In the Born-Oppenheimer approximation, the nuclear motions of a molecule can be viewed as occurring in a potential field provided by the electrons and nuclei. Consequently, the forces acting on a particular nucleus

(41) Although a full discussion of this application of perturbation theory will appear elsewhere, the highlights of some important points are covered below.

I. Materialization of Atoms into Empty Space. Since the basis set is nonnuclear centered and independent of nuclear charges and positions, it is worthwhile to address the question of whether or not the first-order treatment (i.e., eq I-7) is applicable to a problem where a nucleus moves from one point in space to a region which originally did not contain any nuclei. At first glance, it may seem that when an atom materializes at a point which had low electron density in the unperturbed system, all of the Fock matrix elements involving basis functions in the nearby volume will change dramatically, and, as a result, first-order treatments may break down. However, the situation is not so simple. It is instructive to consider a complete basis set consisting of spherical Gaussians with a continuous range of exponents located in each volume element of space (see ref 16). The unperturbed case can be taken to be an arbitrary molecule located at the origin in a defined, but arbitrary, orientation. In principle, a Fock matrix can be constructed and used to generate a set of orbital energies and molecular orbitals. The perturbation is a translation which moves the molecule an arbitrary distance from the origin (e.g., 50 Å). A new Fock matrix can be constructed and used to produce a perturbed set of molecular orbitals and orbital energies. Since the molecule has only been translated, it is clear that the orbital energies are unchanged. However, the MO's have undergone a subtle modification: for example, suppose a particular core orbital (e.g., MO 1) of the unperturbed molecule is largely represented by some combination of basis functions, including ϕ_1 . When the molecule is moved away by 50 Å, it is clear that ϕ_1 will no longer make a significant contribution to MO 1, which will now be represented by some new combination of basis functions, which made negligible contributions to the MO's of the unperturbed molecule. This may appear to be a case of a large change in coefficients, but if we look further, it will be seen that it is not the numerical values of the coefficients which have changed, but only the basis functions assigned to the coefficients. If the numerical values of the unperturbed coefficients are compared to the numerical values of the perturbed coefficients, a one-to-one correspondence will be found between the two sets of coefficients. The basis functions associated with each value of coefficient will differ. Similarly, the Fock matrix for the perturbed problem will contain numbers identical with those of the original Fock matrix but in different positions. In fact, the perturbed Fock matrix differs from the unperturbed Fock matrix by interchanges of appropriate rows and columns. The row and column interchanges have no effect on the values of the orbital energies or on the set of numerical values appearing as coefficients for each eigenvector. The coefficients will be associated with different basis functions, but will have identical values. When the appropriate row and column interchanges are carried out, the perturbed Fock matrix corresponds, element by element, to the unperturbed Fock matrix, and application of eq I-7 is straightforward and trivial.

Let us consider a second case where the unperturbed molecule is moved into a region close to a positive charge. When the row and column interchanges are performed on the perturbed Fock matrix and the elements are compared with the corresponding elements of the original Fock matrix, it will be seen that the values are no longer equal. If the effect of the positive charge on the electronic structure of the molecule is small, then application of eq I-7 is again straightforward. The point of these two examples is that simple translation of a molecule to a new region of space has no effect on the applicability of eq I-7, as long as the appropriate row and column interchanges are carried out and the translation does not result in a large electronic reorganization. The important point is not that a large change in coefficient of a particular basis function takes place on translation, but the extent to which the electronic structure of the fragment is perturbed by the translation.

The row and column interchanges are equivalent to "moving" the unperturbed MO's to the new position of the fragment or the molecule. The interchanges avoid the difficulty of trying to represent the new MO's in terms of orbitals centered some distance away. Note that after the appropriate row and column interchanges (or after any linear transformation of the matrix elements) are completed, the V_{ne} matrix elements of the transformed Fock matrix will still be a sum of contributions from individual nuclei, the V_{ee} matrix elements will be given by an equation of the form of eq I-2, and the kinetic energy matrix elements will still be transferable. Consequently, the application of linear transformations to the unperturbed and perturbed Fock matrices before application of first order perturbation theory will not alter the form of eq I-10 or the basic conclusions concerning "coefficient" additivity.

For our present purposes, these row and column interchanges need not be specified, but if the reader wishes to apply eq I-7 to actual numerical examples, the appropriate interchanges are necessary before attempting to calculate the

can be expressed as gradients of the potential field which is generated by the electrons and the other nuclei. Nuclear forces are of interest since the simple form of the virial theorem ($E = -T = V/2$, eq 20) can be applied when forces on the nuclei are zero. This allows us to express the total molecular energy, including nuclear repulsion, in terms of the electronic kinetic energy given by eq 17. When the forces acting on the nuclei are not zero, the virial theorem assumes a slightly different form¹⁹

$$E = -T - \sum_{m=1}^{3N} X_m \frac{\partial E}{\partial X_m} \quad (\text{II-1})$$

where N is the number of nuclei and the X_m represent the nuclear coordinates. Equation II-1 permits us to express the total energy, E , in terms of the kinetic energy and the forces acting on the nuclei (e.g., $\partial E/\partial X_m$). Equation II-1 is a useful expression since the geometry aspects of the hemistructural relationship apply at both equilibrium and nonequilibrium geometries. Each point on the potential surface for A-B-C will be hemistructural with respect to corresponding points on the potential surfaces for A-B-A and C-B-C. Since the geometry imposed by the hemistructural relationship results in certain constraints on the wave function (and

perturbed Fock matrix. Furthermore, while this analysis applies to a basis set consisting of Gaussian s orbitals distributed in space, it may not apply to every complete nuclear independent basis set, but this has no bearing on the results of the present paper. One example of a numerical calculation based on eq I-6 and I-7 has been carried out (D. E. Magnoli, Thesis, UCLA, 1980) and will appear in due course.

II. Isolectronic/Isonuclear Perturbations. If eq I-7 is applied to a perturbation which changes the number of nuclei or electrons, a number of awkward difficulties arise. An example is the series of perturbations A-A, A-C, C-C, where the A and C fragments are *not* isolectronic or isonuclear. This problem can be avoided in a number of ways, but one of the simplest is to consider the energy change for the "exchange reaction", A-A + C-C \rightarrow 2A-C. ΔE for this reaction is equivalent to twice the deviation of the A-C energy from the mean of the A-A and C-C energies. Note that A-A plus C-C are isolectronic and isonuclear with respect to 2A-C. See footnotes 44 and 45 for further discussion.

III. Criteria for Applying First-Order Perturbation Theory. This is discussed in the second paragraph after eq I-9 and again in ref 36, where numerical calculations have been carried out.

IV. Consistency of Perturbational Order. Equation I-7 is a standard formula (ref 9) for calculating first-order corrections to the molecular orbitals, while eq 17-19 are exact expressions if $a_{\mu n}$ is taken to be the difference in coefficient between the perturbed structure and the unperturbed structure. In the present application, eq 17-19 are approximate only because $a_{\mu n}$ is estimated from the first-order equation (I-7). In most applications of perturbation theory, the n th order estimates, $a_{\mu n}$ are substituted into a truncated power series expansion to give the $(n+1)$ th energy, whereas in the present case the n th order corrections ($n=1$) are substituted directly into the exact expressions (i.e., eq 17-19). The latter procedure results in the retention of all $(n+1)$ th order energy contributions and in a portion of the contributions out to the $(2n)$ th order. Thus, the present method apparently incorporates more information into the energy for a given order correction to the MO coefficients, but since some of the higher order contributions (i.e., those $>n+1$) are omitted and some are retained, the method is inconsistent with respect to the order of the calculated energy (i.e., the order with respect to energy is somewhere between $(n+1)$ th and $(2n)$ th order). In the present case where $n=1$, the two methods are equivalent in the sense that all terms of the same order are retained, provided that the same perturbation is used in both cases. However, the calculated numerical values may be different, and these points are being pursued.

One additional point should also be brought out concerning the order of the perturbation. The omitted term in eq I-6 will formally lead to a second-order energy and force contribution which is not explicitly accounted for in the present paper. For at least one specific perturbation, it can be shown analytically that the second term in eq I-6 is rigorously zero within the first-order framework (D. E. Magnoli, Thesis, UCLA, 1980). The generality of this result and the consequences of omitting the second term of eq I-6 are undergoing examination. In the meantime the reader is reminded that when the term "second order" is applied to energy or nuclear forces, none of the second-order contributions associated with the second term of eq I-6 are included. However, it should be emphasized that the major conclusions of the current paper (see section IV) will not be altered, even if the energy and force contributions associated with the second term of eq I-6 prove to be significant. Another reason for the use of eq 17-19 in conjunction with eq I-7 is because the usual perturbational equations (e.g., 1 and 2) are poorly adapted for calculating the kinetic energy, since the kinetic energy portion of the Fock matrix in the current basis set is invariant to the perturbation. Furthermore, the total energy calculated from eq 2 cannot be broken down into energy components because of the presence of cross terms, which arise from the squared term of eq 2.

electron densities), it would also be expected to produce certain constraints on nuclear forces.

If these constraints act to produce zero net force on each nucleus, the hemistructural geometry will satisfy the simple form of the virial theorem ($E = -T$) and may correspond to an equilibrium geometry.⁴⁷ While there are many experimental examples of this situation,¹ it is also known¹ that net nuclear forces may exist at the hemistructural geometry, so that the equilibrium geometry of A-B-C is distorted away from the hemistructural geometry defined by the equilibrium structures of A-B-A and C-B-C. Consequently, forces on the nuclei at the hemistructural geometry assume fundamental importance, since they can be related to the total molecular energy through the generalized virial theorem (eq II-1) and to geometry deviations from the hemistructural relationship imposed by the equilibrium geometries of A-B-A and C-B-C.

The force on a nucleus in the direction of nuclear coordinate X_m is given by the generalized Hellmann-Feynman theorem⁴⁸ as

$$\frac{dE}{dX_m} = \left\langle \Psi \left| \frac{\partial H}{\partial X_m} \right| \Psi \right\rangle \quad (\text{II-2})$$

where Ψ is the total wave function (nuclear and electronic) and H is the Hamiltonian operator. In the Hartree-Fock formalism this becomes¹⁹

$$\frac{\partial E}{\partial X_m} = \frac{\partial V_{nn}}{\partial X_m} + \frac{\partial V_{ne}}{\partial X_m} \quad (\text{II-3})$$

$$\frac{dE}{dX_m} = -Z_a \left[\sum_{b \neq a} \frac{Z_b}{R_{ab}^2} \frac{\partial R_{ab}}{\partial X_m} \right] + 2 \sum_{\mu}^{\text{occ}} \left(\psi_{\mu}^0 \frac{\partial V_{ne}}{\partial X_m} \psi_{\mu}^0 \right) \quad (\text{II-4})$$

where R_{ab} is the internuclear distance between nucleus a and nucleus b , and Z_a , Z_b are the respective nuclear charges.

Equation II-4 can be applied to three hemistructural molecules (A-A, C-A, C-C) in the following manner. For the special case where A-A and C-C are equilibrium structures (or Born-Oppenheimer transition states), no net forces exist on any of the nuclei. Using the hemistructural relationship, we can then inquire as to what forces exist on the nuclei in the A,C fragments of the hemistructural molecule C-A. The results are different in the examples of ABA, CBA, and CBC, so the simpler case will be examined first.

The combined electronic and nuclear component of force on a specific nucleus in the left-hand "A" fragment in A-A is given by

$$Z_{A_l}(N_{A_l} + N_{A_r}) + 2 \sum_{\mu}^{\text{occ}} a_{\mu}^0 V_{ne}^A a_{\mu}^0 = 0 \quad (\text{II-5})$$

where Z_{A_l} is the nuclear charge of the specific nucleus and N_{A_l} equals minus the term in brackets in eq II-4 where the summation extends over all nuclei in the left-hand "A" fragment except the specific nucleus associated with Z_{A_l} . The summation for N_{A_r} extends over all nuclei in the right-hand "A" fragment. V_{ne}^A equals the derivative matrix, $\partial V_{ne}/\partial X_m$, while a_{μ}^0 represents the vector of coefficients, $a_{\mu i}^0$, for ψ_{μ}^0 . Note that the hemistructural constraint allows V_{ne}^A for A-C to be taken directly from A-A. In general, eq II-5 will be repeated for each nuclear coordinate in the left and right fragments of A-A.

The force expression for a specific nucleus in the left-hand "C" fragment of C-C is given by

$$2 \sum_{\mu}^{\text{occ}} [a_{\mu}^0 V_{ne}^C a_{\mu}^0 + 2a_{\mu}^l V_{ne}^C a_{\mu}^0 + 2a_{\mu}^r V_{ne}^C a_{\mu}^0 + a_{\mu}^l V_{ne}^C a_{\mu}^l + 2a_{\mu}^r V_{ne}^C a_{\mu}^r + a_{\mu}^r V_{ne}^C a_{\mu}^r] + Z_{C_l}(N_{C_l} + N_{A_r} + \delta N_{C_r}) = 0 \quad (\text{II-6})$$

where a_{μ}^l (a_{μ}^r) represents the changes in coefficients due to replacement of the left- (right-) hand nuclei in A-A with the left- (right-) hand nuclei in C-C. δN_{C_r} is defined by $N_{C_r} - N_{A_r}$.

The form of this equation is particularly instructive since both the nuclear and electronic contributions divide cleanly into two

types: those that are functions of left-hand nuclei only (i.e., functions of Z and position) and those that are functions of both left- and right-hand nuclei. The general form of this equation can be expressed as

$$F_0(l) + F_1(l,r) = 0 \quad (\text{II-7})$$

where $F_0(l)$ equals

$$F_0(l) = 2 \sum_{\mu}^{\text{occ}} [a_{\mu}^0 V_{nc}^C a_{\mu}^0 + 2a_{\mu}^l V_{nc}^C a_{\mu}^0 + a_{\mu}^l V_{nc}^C a_{\mu}^l] + Z_{Cl}(N_{Cl} + N_{Ar}) \quad (\text{II-8})$$

and where $F_1(l,r)$ equals

$$F_1(l,r) = 2 \sum_{\mu}^{\text{occ}} [2a_{\mu}^l V_{nc}^C a_{\mu}^0 + 2a_{\mu}^l V_{nc}^C a_{\mu}^r + a_{\mu}^r V_{nc}^C a_{\mu}^l] + Z_{Cl}(\delta N_{Cr}) \quad (\text{II-9})$$

A necessary condition for satisfying eq II-7 is that $F_0(l) = -F_1(l,r)$. Consequently, the value of $F_1(l,r)$ at an equilibrium geometry depends only on the structure of the left-hand fragment and is entirely independent of the nuclear charges and coordinates of the right-hand fragment. For a broad class of structures, it can be shown that $F_0(l)$ and $F_1(l,r)$ vanish separately⁴⁹ at each zero force geometry, so that eq II-7 becomes

$$F_0(l) = F_1(l,r) = 0 \quad (\text{II-10})$$

The force on a nucleus in the "C" fragment of C-A is given by $F_0(l)$ if the hemistructural condition holds. Consequently, all the forces on the "C" nuclei will vanish in C-A, and it is possible to demonstrate a similar result for the "A" nuclei in C-A by

(42) Note that $b_{\alpha\beta} = -b_{\beta\alpha}$ and $b_{\alpha\alpha} = 0$ (ref 9).

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(44) Small changes in the relative energy are necessary for application of perturbation theory, but are not sufficient. It is convenient to limit eq I-6 through I-9 to perturbations within an isoelectronic, isonuclear framework, and this can be done without loss of generality in several ways. For example, ΔE for the reaction, A-B-A + C-B-C \rightarrow 2A-B-C, equals twice the deviation of the A-B-C energy from the mean of the A-B-A and C-B-C energies. This approach is particularly convenient for analyzing bond energies and bond distances (see ref 1c). An alternative, which is well suited for treating group-transfer reactions (see ref 45) as well as bond energies, involves adding "balancing" structures to achieve an isonuclear, isoelectronic condition.

(45) Considerable flexibility is possible when choosing these "balancing" structures. In the benzene, toluene, or *p*-xylene example, one choice might be benzene + 2CH₃, toluene + CH₃ + H, *p*-xylene + 2H. The equations given are for closed-shell systems, but adaptation to an open-shell formalism is straightforward. The numbers of doubly and singly occupied MO's for these three systems are identical, and all three structures of this example are isoelectronic. The character of the singly occupied MO's is appreciably different (two methyl radicals, one methyl radical plus one hydrogen atom, two hydrogen atoms), but this will not necessarily invalidate the application of perturbation theory. More serious problems are the changes in fragment geometry on transfer. These conceptual difficulties can be alleviated by another choice of structures, such as benzene + 2CH₃CH₃, toluene + CH₃CH₃ + CH₃-H, *p*-xylene + 2CH₃-H; the open-shell problem is eliminated, changes in nuclear positions and electron densities are minimal, and a closer correspondence between orbitals is likely, particularly if localized MO's are compared (viz., note that the number of C-C and C-H bonds is independent of the perturbation). In fact, the choice of "balancing" structures (e.g., 2CH₃CH₃, CH₃CH₃ + CH₃-H, 2CH₃-H) is arbitrary when the energy of toluene is expressed as the average of benzene and *p*-xylene plus a deviation. The average energy of the benzene balancing structures (2CH₃CH₃) and the *p*-xylene balancing structures (2CH₃-H) is always equal to the energy of the toluene balancing structures (CH₃CH₃ + CH₃-H). The deviation from additivity is independent of the choice of balancing structures.

It is also worth pointing out that the applicability of perturbation theory does not require that replacement of one group by another result in a small change in wave function in the spatial region occupied by the original substituent. The important factor is not that a fragment has moved to a new region of space (as in benzene + 2CH₃CH₃ \rightarrow toluene + CH₃CH₃ + CH₃-H \rightarrow *p*-xylene + 2CH₃-H), but the extent to which the structure of the fragment is perturbed by that movement. See footnote 41 for further discussion.

considering C-C as the unperturbed reference state and A-A as the double perturbation. As a result, the nuclear forces⁴⁹ in C-A will vanish if: (a) C-A is hemistructural to A-A and C-C; (b) nuclear forces in A-A and C-C vanish; (c) the changes in MO coefficients are due to *independent* contributions from independent changes in nuclei; (d) the separate vanishing condition applies to A-A and C-C.⁴⁹ $F_1(l,r)$ represents the extra force on one of the left-hand nuclei in C-C due to a change in the right-hand fragment from A to C. Since $F_1(l,r)$ equals zero, the left-hand nucleus does not experience any new force due to the change on the right in going from A to C. The change in force due to new nuclear charges and positions is precisely cancelled by the change in force due to the new distribution of electron density. Consequently, the left-hand nucleus in C is responding to the same forces in C-A as in C-C, as long as conditions a-d are in effect. This result provides further insight into the breakdown of the equivalent group concept: maintaining an equilibrium geometry when fragments are replaced in a molecule depends on whether or not redistribution of electron density can exactly offset changes in the force field due to new nuclear charges and positions; given conditions a-d, such cancellation is possible at the hemistructural geometry, but there is no requirement that the electronic reorganization is necessarily limited to the spatial region associated with any particular fragment. As a result, a fragment may exhibit an effectively constant "covalent radius"¹ in spite of possible changes in electron density.

Forces in the molecules ABA, CBA, and CBC can be examined in a similar manner. The force on a specific nucleus in the left-hand "A" fragment of ABA is given by

$$Z_{Al}(N_{Al} + N_B + N_{Ar}) + 2 \sum_{\mu}^{\text{occ}} a_{\mu}^0 V_{ne}^A a_{\mu}^0 = 0 \quad (\text{II-11})$$

(46) Equation I-9 can be put in the form $A \cdot b = V$ where V is a vector with components $\sum_i \sum_j a_{ij}^0 \delta V_{ij}^l$, b is a vector of the new coefficients, $b_{\alpha\beta}$, and A is a matrix whose elements contain the terms $\sum_i \sum_j \sum_k a_{ij}^0 a_{ik}^0 a_{jk}^0 \theta_{ijk}$. A is independent of the perturbation. The dimension of V is equal to $m(n-1)$ where n is the number of basis functions and m is the number of occupied orbitals. For the perturbation from A-B-A to A-B-C, V can be defined as V_{right} , while for the perturbation A-B-A to C-B-A, V can be defined as V_{left} . Solving $A \cdot b = V_{\text{right}}$ gives $b = b_{\text{right}}$ as a solution. For $V = V_{\text{left}}$, $b = b_{\text{left}}$. When A-B-C is hemistructural to A-B-A and C-B-C, V is given by $V = V_{\text{right}} + V_{\text{left}}$ for the perturbation A-B-A to C-B-C. Solving $A \cdot b = V_{\text{right}} + V_{\text{left}}$ gives $b = b_{\text{right}} + b_{\text{left}}$.

(47) Zero force on each nucleus may correspond to an energy *maximum*. There may also be *other* nuclear configurations in which the net force on each nucleus is zero.

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(49) First, consider a zero force homonuclear diatomic, D-D, and the diatomic, D-E°, where D is placed at the hemistructural position defined from D-D and the position of E° is optimized to produce a zero force structure. The force on E° is given by

$$F_0^{E^\circ}(r) = 0 \quad (\text{II-10a})$$

The force on F° in diatomic, F°-D, where D is placed at the hemistructural position and the position of F° is optimized to give a zero force structure, is given by

$$F_0^{F^\circ}(l) = 0 \quad (\text{II-10b})$$

The force on E° in the diatomic F-E° (E° located at the hemistructural position defined from D-E°) is given by

$$F_0^{E^\circ}(r) + F_1^{FE^\circ}(r,l) = F_r \quad (\text{II-10c})$$

and from eq II-10a, a zero force condition with respect to E° requires

$$F_1^{FE^\circ}(r,l) = 0 = F_r \quad (\text{II-10d})$$

This result is valid for any mononuclear fragment, F, which can pair with E° to produce a zero force structure. Note that eq II-10a,c,d are still valid if F-E° is shifted to a new position so that E° no longer occupies the hemistructural position defined from D-E°. Consequently, the separate vanishing of the two force terms is required for any zero force structure containing E°:

$$F_0^{E^\circ}(r) = F_1^{FE^\circ}(r,l) = F_r = 0 \quad (\text{II-10e})$$

The force on F° in the diatomic F°-E (F° located at the hemistructural position defined from F°-D) is given by

$$F_0^{F^\circ}(l) + F_1^{FE}(l,r) = F_l \quad (\text{II-10f})$$

A similar expression for a given nucleus in the left-hand "C" fragment of CBC is given by

$$2 \sum_{\mu}^{\text{occ}} [\mathbf{a}_{\mu}^0 \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^0 + 2 \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^0 + 2 \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^0 + \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^l + 2 \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^r + \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^r] + Z_{\text{C}}(N_{\text{C}} + N_{\text{B}} + N_{\text{A}} + \delta N_{\text{C}}) = 0 \quad (\text{II-12})$$

$\mathbf{V}_{\text{nc}}^{\text{C}}$ is a function only of the coordinates of one specific nucleus in the left "C" fragment of CBC, while \mathbf{a}_{μ}^0 , \mathbf{a}_{μ}^l , and \mathbf{a}_{μ}^r include a functional dependence on the nuclear charges and positions of the "B" nuclei. Consequently, eq II-12 can be separated into the analog of eq II-7

$$F_{0\text{B}}(l) + F_{1\text{B}}(l,r) = 0 \quad (\text{II-13})$$

where $F_{0\text{B}}(l)$ equals

$$F_{0\text{B}}(l) = 2 \sum_{\mu}^{\text{occ}} [\mathbf{a}_{\mu}^0 \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^0 + 2 \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^0 + \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^r] + Z_{\text{C}}(N_{\text{C}} + N_{\text{B}} + N_{\text{A}}) \quad (\text{II-14})$$

and $F_{1\text{B}}(l,r)$ equals

$$F_{1\text{B}}(l,r) = 2 \sum_{\mu}^{\text{occ}} [2 \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^0 + 2 \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^l + \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{C}} \mathbf{a}_{\mu}^r] + Z_{\text{C}}(\delta N_{\text{C}}) \quad (\text{II-15})$$

Using the property^{49,50} that $F_{0\text{B}}(l)$ and $F_{1\text{B}}(l,r)$ vanish separately, it is apparent that forces on the "C" nuclei are zero in CBA. Likewise, it can also be shown that the forces on "A" in CBA are zero by using CBC as the unperturbed reference and ABA as the double perturbation. In order for CBA to be an equilibrium (or zero force) structure, it must also be shown that the forces on the "B" nuclei vanish.⁵⁰

and from II-10b, a zero force condition with respect to F° requires

$$F_{1}^{\circ\text{E}}(l,r) = 0 = F_l \quad (\text{II-10g})$$

Again, this result is valid for any mononuclear fragment, E, which can pair with F° to produce a zero force structure. Consequently, the separate vanishing of the two force terms is required for any zero force structure containing F° :

$$F_{0}^{\circ}(l) = F_{1}^{\circ\text{E}}(l,r) = F_l = 0 \quad (\text{II-10h})$$

A zero force structure for F° -E^o requires satisfaction of both II-10e and II-10h which are equivalent to the separate vanishing condition

$$F_{0}^{\circ}(l) = F_{1}^{\circ\text{E}}(l,r) = F_{0}^{\circ}(r) = F_{1}^{\circ\text{E}}(r,l) = 0 \quad (\text{II-10i})$$

This result establishes that the two force terms in eq II-10c and II-10f vanish separately at any zero force geometry for arbitrary F° -E^o.

The force equations shown above involve displacements of the atomic fragments in any of the three Cartesian directions. The force can also be expressed in terms of the energy gradient with respect to any suitable coordinate, and for polynuclear fragments it is useful to consider coordinates which include movement of the fragment as a whole in the X, Y, or Z directions as well as coordinates describing internal changes in bond lengths and bond angles. The treatment of the internal coordinates involves a number of subtle points and will require full development elsewhere, but displacements of the individual fragments as intact units can be handled like displacements of individual atoms. Equations II-10a through II-10i are still applicable for forces associated with displacement of polynuclear E^o, E, F^o, and F fragments.

It is useful to note that the separate vanishing condition is reference dependent and requires at least one zero force geometry for D-E^o and F^o-D. For the present application (A-A, C-A, C-C), this is equivalent to the requirement that D-C and A-D have at least one zero force geometry. If this condition is met, then zero force geometries for A-A, A-C, and C-C require the separate vanishing of the F_0 and F_1 force terms. Note that if F_0 and F_1 vanish separately for C-C and A-A using D-D as reference, then F_0 and F_1 also vanish separately for C-C (A-A) using A-A (C-C) as reference.

(50) Equations II-10a through II-10i can be used to show that, using the zero force structure D-D as reference, the two force terms associated with D_1 or D_2 in the zero force structure D_1 - D_2 vanish separately. A similar result holds for the two force terms associated with E_1 or E_2 in the zero force structure, E_1 - E_2 . These results can be applied to the zero force structures A-B-A \equiv (A-B)-A \equiv E_1 - E_2 and C-B-C \equiv (C-B)-C \equiv D_1 - D_2 . Note that it has been implicitly assumed that the nuclear coordinates of the "B" fragment are the same in ABA and CBC.

The force on a "B" nucleus in ABA is given by

$$2 \sum_{\mu}^{\text{occ}} [\mathbf{a}_{\mu}^0 \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^0] + Z_{\text{B}}(N_{\text{A}} + N_{\text{A}} + N_{\text{B}}) = 0 \quad (\text{II-16})$$

and eq II-17 gives the force $(dE/dX_{\text{m}})_{\text{B}}$ on a "B" nucleus in CBC

$$2 \sum_{\mu}^{\text{occ}} [\mathbf{a}_{\mu}^0 \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^0 + 2 \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^0 + 2 \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^0 + \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^l + 2 \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^r + \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^r] + Z_{\text{B}}(N_{\text{A}} + \delta N_{\text{C}} + N_{\text{A}} + \delta N_{\text{C}} + N_{\text{B}}) = (dE/dX_{\text{m}})_{\text{B}} \quad (\text{II-17})$$

Separating eq II-17 into terms based on l, r, and B dependence,

$$(dE/dX_{\text{m}})_{\text{B}} = F_0(\text{B}) + F_1(l,\text{B}) + F_2(r,\text{B}) + F_3(l,r,\text{B}) \quad (\text{II-18})$$

where

$$F_0(\text{B}) = 2 \sum_{\mu}^{\text{occ}} [\mathbf{a}_{\mu}^0 \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^0] + Z_{\text{B}}(N_{\text{A}} + N_{\text{A}} + N_{\text{B}}) = 0 \quad (\text{II-19})$$

$$F_1(l,\text{B}) = 2 \sum_{\mu}^{\text{occ}} [2 \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^0 + \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^l] + Z_{\text{B}}(\delta N_{\text{C}}) \quad (\text{II-20})$$

$$F_2(r,\text{B}) = 2 \sum_{\mu}^{\text{occ}} [2 \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^0 + \mathbf{a}_{\mu}^r \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^r] + Z_{\text{B}}(\delta N_{\text{C}}) \quad (\text{II-21})$$

$$F_3(l,r,\text{B}) = 4 \sum_{\mu}^{\text{occ}} \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^r \quad (\text{II-22})$$

At this point it would be useful to reflect on the significance of this force analysis. First, it has been shown that within the limitation of first-order coefficient corrections, the force on a particular nucleus in C-C can be divided into two or more terms (e.g., eq II-7 through eq II-9). If a zero force structure for C-C exists, then each separate force term⁴⁹ must vanish. One of these terms is also the force on the corresponding nucleus in C-A at the hemistructural geometry, and from this it follows that if C-C and A-A are zero force structures, then C-A will also be a zero force structure at the hemistructural geometry. The separate vanishing of each force term represents a constraint on the behavior of the coefficients \mathbf{a}_{μ}^l and \mathbf{a}_{μ}^r , and if the constraint cannot be met, no zero force structure is possible within the first-order perturbation framework. Achieving a zero force structure may require more complicated electronic reorganization than allowed by first-order changes in the wave function. Higher level perturbations may eventually lead to a breakdown of coefficient additivity (eq 16), and the simple transferability of the force terms between the hemistructural molecule and the parent structures (eq II-7-10) will not apply. As a result, the hemistructural geometry may no longer correspond to a zero force structure.¹⁵ Similar remarks apply to the A-B-A, C-B-A, and C-B-C cases, and the circumstances which permit simultaneous realization of conditions b and c (vide supra) will require further examination.

The possibility that first-order perturbations may not allow separate vanishing of $F_1(l,\text{B})$, $F_2(r,\text{B})$, and $F_3(l,r,\text{B})$ is worth considering. In the case of $F_1(l,\text{B})$ and $F_2(r,\text{B})$, balance between electronic and nuclear terms can be achieved by variations in the coefficients as well as internuclear distances. However, $F_3(l,r,\text{B})$ contains only nuclear-electron attraction terms and lacks nuclear repulsion terms to cancel them out. Separate vanishing of $F_1(l,\text{B})$, $F_2(r,\text{B})$, and $F_3(l,r,\text{B})$ can occur only to the extent that the second-order electronic terms, $4 \sum_{\mu}^{\text{occ}} \mathbf{a}_{\mu}^l \mathbf{V}_{\text{nc}}^{\text{B}} \mathbf{a}_{\mu}^r$ (eq II-22) are zero. Consequently, we have the interesting result that the nuclear forces on the "A" and "C" fragments of CBA can be zero through the full second-order terms, while the forces on the "B" nuclei can be zero only through first-order and part of the second-order terms.

The fact that the hemistructural relationship may break down for the "B" nuclei before it does for the "A" and "C" nuclei could have important consequences for group transfer reactions such as C-B + A \equiv C + B-A where ABA, CBA, and CBC are transition states. If the C-A distance is hemistructural, while B

is shifted off of the hemistructural position toward C, for example,⁵² the C-B bond in CBA would be shorter (and stronger) than the C-B bond in CBC. This decrease in length for C-B would come at the expense of the B-A bond in CBA which would be longer (and weaker) than in ABA. The total bond length, C-B plus B-A, would be constant. The situation is somewhat analogous to Johnston's⁵¹ proposal concerning the conservation of bond order in transition states of atom-transfer reactions, where the bond order of one bond may be greater than $1/2$, while the bond order of the other is less than $1/2$. The total bond order is always conserved at unity. The speculation that Johnston's empirical principle of bond-order conservation may have its origins in a partial break-

down of the hemistructural relationship is currently under examination.

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(52) Lateral displacements along the A-C bond axis, as well as perpendicular displacements, may be possible.

Proton-Transfer Reactions between 9-Alkylfluorene and (9-Alkylfluorenyl)lithium in Ether

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Abstract: The rates of proton-transfer reactions between 9-substituted fluorenes and 9-substituted fluorenyllithium have been examined in ether at 25 and 71 °C. A high primary isotope effect ($k^H/k^D = 9.5$) and substantial secondary kinetic (1.11 ± 0.04) and equilibrium (1.19 ± 0.04) isotope effects are observed for fluorene. Surprisingly, intermolecular steric effects seem to play only a minor role in spite of the fact that the alkyl groups are located directly at the carbon involved in the proton transfer. The barriers for the endergonic cross reactions (i.e., those involving different alkyl groups in the anion and hydrocarbon) are half of the sum of the barriers for the two corresponding identity reactions (i.e., those involving the same alkyl groups in the anion and hydrocarbon). This leads to Brønsted slopes which vary from 0.7 for reactions of fluorenyl anion to 1.8 for reactions of 9-(*tert*-butyl)fluorenyl anion. The rates of the identity and cross reactions give approximate linear correlations with each other and with ΔpK and are dominated by an effect which correlates with σ^* . The substituent effect correlated by σ^* is inconsistent with a classical field or repulsive steric effect and may originate from solvation effects. The thermodynamic and kinetic relationships between the identity and cross reactions show that the transition states for the cross reactions are only responding to half of the substituent effect on the identity reactions and that the substituent effect on the equilibria appears absent from the cross-reaction transition states. The results can be consistent with Marcus' theory only if the substituent effect on the equilibria appears in steps separate from proton transfer. The results suggest that changes in solvation and proton transfer occur as discrete kinetic steps.

Introduction

Interaction of Alkyl Groups with Charged Centers. The question of how alkyl groups interact with anionic and cationic centers is one which has occupied organic chemists for decades.²⁻¹⁰ While

many anomalous phenomena in organic chemistry can be treated in terms of two competing effects, the description of alkyl substituent effects has "required" at least half a dozen. These include polarizability, hybridization, the field effect, the inductive effect, hyperconjugation, and steric hindrance. As a further complication, the relative substituent effects of alkyl groups often show inversions in going from one solvent to another^{6,7} and to the gas phase,³⁻⁵ and reversals of kinetic and thermodynamic effects have been reported.⁸ The results of the present investigation are of interest since it has proved possible to measure the alkyl substituent effect on the rates of identity reactions (where no thermodynamic contribution occurs since $\Delta pK = 0$) and to obtain a kinetic substituent effect free of any thermodynamic component due to a change in ΔG° of the reaction.

The Question of Aggregation of Fluorenyllithium Derivatives in Ether. Since the kinetic and equilibrium measurements have been carried out at relatively high concentration (0.2-0.4 M) in a relatively nonpolar solvent (ether), it is important to determine whether aggregation is exerting a significant influence on the rates and pK 's. Concentration effects are known to be important for

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