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An ab Initio Study of Diazoethene, a Propadienone Isoelectronic with a Bent Structure[∥]

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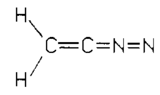
Abstract: Ab initio MP2/4-31G and MP2/6-31G* structural optimizations of diazoethene ($CH_2{=}C{=}N{=}N$) find this molecule to have a nonlinear C_s structure, in a manner analogous to the computational and experimental finding of other workers for the isoelectronic analogue propadienone ($CH_2{=}C{=}C{=}O$). Vibrational analysis at the MP2/4-31G level shows the bent structure to be a true minimum, with a diagnostically useful frequency at 2057 cm^{-1} due to the typical characteristic diazo N=N stretching mode. Matrix isolation techniques may be required to observe diazoethene, since the computed barrier to deazetation is only ~7 kcal/mol; however, a computed barrier of ~21 kcal/mol to inversion implies that the molecule should be bent under all conditions where it is observable.

Diazoethene (**1**, DE) is a highly cumulated molecule of much interest to theoretical and experimental chemists studying highly reactive molecules. Derivatives of DE have been invoked as reactive intermediates in solution-phase reactions,[1-3] although such species have only recently been trapped[4] and to date have not been directly observed. DE itself is a potential source of vinylidene (**2**), although this reaction has not been observed and may be difficult given the ease with which **2** rearranges to acetylene.[5] The elusiveness of DE and its derivatives encourages computational elucidation of its structure and chemistry, especially in light of the recent work on its isoelectronic analogue, propadienone (**3**, PD). A combination of experimental structural work[6-8] and ab initio calculations of increasing sophistication led to a reversal of the initial conclusion that PD was linear[9,10] and to an apparent consensus of theory and experiment that PD is in fact bent[11-13] in a fashion that was quite unusual for a cumulated molecule. Recent experimental work[14,15] led to conflicting computational predictions[15,16] concerning whether the next higher homologue, butatrienone (**4**), is experimentally nonlinear. The most recent computational results[15] indicate that **4** has so low a barrier to inversion (5.6 cm^{-1}, 16 cal/mol) that the molecule should be experimentally linear, as experimental data seem to indicate.[14,15] The work on compounds **3** and **4** exemplifies an increasing interaction between computational and experimental research that is leading to better, surer understanding of molecular structure.



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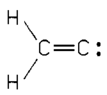

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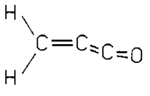

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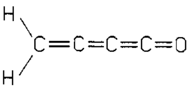

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DE and its derivatives were likely candidates for ab initio study, in light of the recent experimental interest in them.[4] A semiempirical study suggested that DE derivatives tend to be bent in a manner similar to PD.[17] We hoped to discover by ab initio treatment of DE itself whether indeed this molecule is computationally nonlinear as is PD and to find characteristic vibrational spectroscopic frequencies for possible future experimental identification of DE. Although the earlier study yielded such frequencies,[17] the low level of theory employed led to our desire to test these predictions at a more rigorous, trustworthy level of theory. Our ab initio results confirm the theoretical prediction of a bent structure for DE, and so suggest that DE derivatives may be in general bent cumulated molecules.

Computational Methods

All computations were carried out with the GAUSSIAN82 set of programs developed by Pople and co-workers.[18] Geometries at the various levels of approximation were optimized to <0.25 mhartrees/bohr and subjected to vibrational force constant analysis in order to confirm that geometries found were true minima. Harmonic vibrational analyses were performed with the GAUSSIAN82 analytical formulation for SCF wave functions and the numerical formulation for post-Hartree–Fock wave functions.

Results and Discussion

DE was first treated at the 4-31G[19] and 6-31G*[20] restricted Hartree–Fock self-consistent-field (HF–SCF) levels of theory. At the 4-31G level, a bent geometry was obtained as a stationary point, but a force constant analysis showed this structure to be a transition state—no diazoethene energy minimum structure was found at this level, but rather attempts at minimization led to cleavage of the C=N bond. Likewise at the 6-31G* level, despite

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[∥] Dedicated to Eino Ilmari Lahti.

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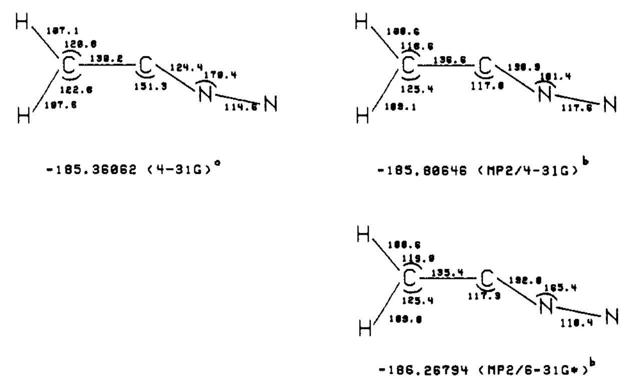


Figure 1. Computed structures for diazoethene. Footnote a: structure is a transition state. Footnote b: structure is an energetic minimum. All bond lengths are in picometers and all angles in degrees.

repeated efforts, C=N cleavage occurred computationally without our finding an energy minimum of DE structure. By constraining the DE structure to be of C_{2v} symmetry, a 6-31G* stationary point was found, which force constant analysis showed to be also a transition state leading (upon bending) to dissociation. These SCF-only findings (Figure 1) for DE are rather different than those for PD, which is found to be an energetically bound molecule with a linear structure at the 6-31G** SCF level.[10]

Therefore, we carried out post-Hartree–Fock (post-HF) level computations using second-order many-body perturbational (MP2)[21,22] expansion to obtain correlation energies. At both the MP2/4-31G and MP2/6-31G* levels, stationary points were found, with geometric parameters as shown in Figure 1. The two geometries are very similar, with the major significant difference being a shortening in the C–N bond length going from the MP2/4-31G level (136.9 pm) to the MP2/6-31G* level (132.9 pm). Such bond shortening is a well-known phenomenon in comparing results from these two basis sets.[23] Given the disparity of results for 6-31G* versus 4-31G levels at the SCF-only level, the geometric similarity at the MP2 level implies that the qualitative structural properties found in both MP2 calculations are mostly a result of using the electron-correlated post-HF level wave function. This is analogous to the findings for PD,[11-13] which is found to be bent only at the post-HF level of computational treatment. Radom found that omission of polarization functions did not greatly effect the computed geometry of PD *if electron correlation was included*.[10] The same is true of our DE results. Although use of unpolarized basis sets is known sometimes to give questionable molecular bond angles,[23] the likeness of unpolarized MP2/4-31G to polarized MP2/6-31G* basis set results indicates that correlation effects are of crucial importance in finding a qualitatively proper computational structure here, with basis set effects being of secondary importance.

Limited availability of resources prevented our computation of MP2/6-31G* vibrational frequencies for DE. We did obtain MP2/4-31G harmonic-estimate frequencies (Table II), which we corrected from values actually computed by a multiplicative factor of 0.981, for reasons described below. At this level, DE is indeed found to have all positive vibrational frequencies (vide infra), and hence it is an energetic minimum, not a transition state. Given the similarity of the MP2/6-31G* and MP2/4-31G optimized structures, and based on the arguments given above concerning the relative importance of basis set selection versus use of electron-correlated wave functions, it is not unreasonable to assume that a MP2/6-31G* or higher level calculation would also find a bent global minimum structure for DE.

The geometric properties of the MP2/6-31G* structure for DE are interesting by comparison to structural properties of related small molecules. The computed N–N bond length of 116.4 pm in DE is similar to the 113.1 pm MP2/6-31G* dinitrogen bond length[24a] (experimental value 109.8 pm[24b]) and to the 6-31G* N–N bond length of 113.6 pm in Moffat's 6-31G* structure for diazomethane, (**5**).[25] The DE C=N bond length is 132.9 pm, substantially longer than the C=N bond in Moffat's structure for **5** (127.9 pm) and the typical experimental C=N length of ~110 ppm.[24b] This implies a substantially decreased bond order in the DE C–N bond relative to diazomethane, attributable to poor overlap in the in-plane C=N π bond. Use of localized SCF orbitals with the MP2/4-31G geometry shows the presence of a lone-pair type in-plane orbital on C_2, exactly as expected for the bent structure where resonance form **1Z**—which lacks the in-plane π bond—is a substantial contributor.

Table I. MP2/4-31G Computed Vibrational Frequencies of Diazoethene

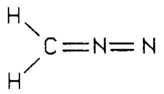
freq[a]/ cm^{-1}	symmetry	description	intensity (kM/mol)
3188	A′	asym C—H stretch	7.1
3080	A′	sym C—H stretch	20.3
2057	A′	N=N stretch	326.3
1584	A′	sym CH_2 in-plane bend + C=C stretch[b]	33.7
1426	A′	sym CH_2 in-plane bend + C=C stretch[b]	55.6
1111	A′	asym CH_2 in-plane bend	28.7
1007	A″	CH_2 out-of-plane bend	34.1
833	A′	C=N stretch	28.1
786	A″	out-of-plane mode[c]	0.01
559	A′	in-plane bending mode	7.1
304	A″	out-of-plane mode[c]	3.5
286	A′	in-plane bending mode	2.4

[a] Scaled by a factor of 0.981 from actual computed frequencies. Description based on dominant atomic motions in normal mode analysis. [b] Strongly coupled modes. Lower frequency mode contains greater component of C=C stretch. [c] Out-of-plane motions.

Table II. MP2/4-31G Computed Vibrational Frequencies of Diazoethene in the Linear Transition State

freq[a] (cm^{-1})	symmetry	description	intensity (kM/mol)
3150	B_2	asym C—H stretch	26.5
3084	A_1	sym C—H stretch	52.0
2255	A_1	C=C=N=N sym stretch	995.9
1826	A_1	C=C=N=N asym stretch	1.2
1568	A_1	sym CH_2 in-plane bend	15.8
1113	B_2	asym CH_2 in-plane bend	2.9
1026	B_1	CH_2 out-of-plane bend	23.9
909	A_1	C=N stretch	0.6
536	B_1	N=N out-of-plane bend	7.7
385	B_2	N=N in-plane wag	5.1
196	B_1	out-of-plane mode	0.06
−500	B_2	C=C=N in-plane bend/stretch	40.9

[a] As computed (no scaling correction).



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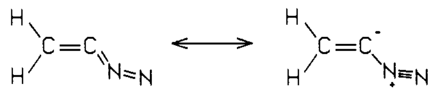

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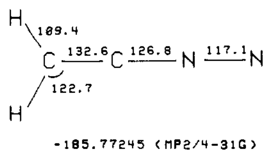
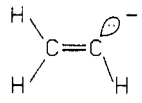
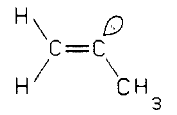


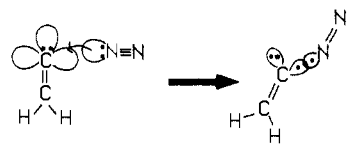
Figure 2. MP2/4-31G linear transition state to C–C–N angle inversion of diazoethene. All bond lengths are in picometers and all angles in degrees.

One may reasonably formulate DE as a dinitrogen molecule chelated to a vinylidene fragment. Computed structures of vinylidene itself are comparable to the vinylidene fragment of DE, with a C=C bond length of 134.2 pm at the double-ζ plus polarization level[26] and 130.7 pm at the MP2/6-31G* level.[26] One may also compare DE to the 3-21G+ structure of vinyl and 2-propenyl anions,[27] which haveC=C bond lengths of 135.8 and 135.0 pm, respectively. Although the anionic C=C bond lengths are somewhat longer than the C=C in DE, the anionic calculations were done at the SCF-only level, hence one would expect some shortening of these bonds with inclusions of MP2 effects analogous to those in our DE calculation. However, chemically it makes sense to consider DE as vinylidene plus dinitrogen. Since





the most likely pathway for decomposition of DE would be deazetation to give neutral dinitrogen plus vinylidene, the reverse process—nucleophilic addition of dinitrogen to vinylidene—should well represent DE.



In light of the apparently poor stabilization given by C=N "double" bond, we attempted to estimate the stability of DE to inversion about the C=C=N angle and to deazetation. High-level energetic mapping of the in-plane bending and C=N stretching reaction coordinates was beyond our resources. However, we computed the MP2/4-31G geometry (Figure 2) and vibrational harmonic-estimate frequencies (Table II) for DE constrained to a linear C_{2v} geometry. The vibrational frequency analysis clearly shows this structure to be a transition state, with one computed imaginary mode. Interestingly, the computed transition state has quite short C=C and C=N bonds by comparison to the ground-state bent structure, as might be expected by the better orbital overlap in the linear structure. The linear transition structure MP2/4-31G energy is −185.77245 hartrees, compared to the analogous ground-state energy of −185.80646 hartrees, corresponding to a C=C=N angle inversion barrier of 21.3 kcal/mol for DE at this level of theory (ignoring the effects of zero-point-energy corrections). Although use of higher level basis sets and greater levels of configuration interaction might alter this somewhat, so high a barrier seems to imply that DE will exhibit the spectroscopic properties of a bent molecule, and will not be a time-average linear molecule with a low inversion barrier.

Figure 3 summarizes a series of MP2/4-31G calcuations upon DE where the C=N bond length was gradually stretched from the ground-state value of 136.9 pm to 300.0 pm, with optimization of other internal coordinates. After localizing the approximate

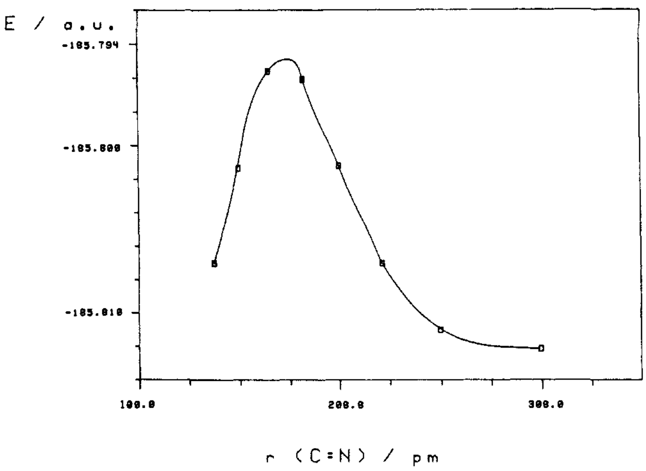


Figure 3. MP2/4-31G reaction coordinate for deazetation of diazoethene.

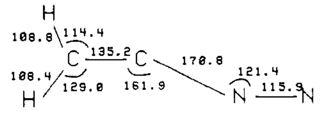


Figure 4. MP2/4-31G deazetation transition state structure. All bond lengths are in picometers and all angles in degrees.

deazetation transition-state geometry in this manner, we obtained computationally the energetic maximum for this reaction coordinate at the MP2/4-31G level, the geometry of which is shown in Figure 4. With a MP2/4-31G energy of −185.7954 hartrees, this transition state lies 6.9 kcal/mol above the ground state (again without accounting for zero-point corrections in ground- and transition-state energies). As noted above, changes in the computational basis set or electron correlation level could cause this value to change somewhat, but probably not greatly. Experimentally, diazomethane (**5**) undergoes unimolecular decomposition with an activation energy of 32–36 kcal/mol and an Arrhenius pre-exponential term estimated at a variety of values ranging[29] from 10^{11}–10^{12} to $10^{13.8}$. Assuming 6.9 kcal/mol as a reasonable estimate for the DE deazetation activation energy, and using the most pessimistic estiate for the Arrhenius preexponential *A*-factor based on diazomethane decomposition work ($10^{13.8}$), we find the half-life of DE at 27 and −90 °C to be 1.2 ns and 0.3 ms, respectively. One has to reach the temperature range of matrix isolation experiments to find reasonable half-lives for DE by this crude analysis—at 77 K a half-life of 117 h is predicted. Naturally, this is a very low level estimate of the kinetic stability of DE that could easily be in error by a factor of 10 in either direction. Still, our computations *qualitatively* indicate that experimental observation of DE is most likely to be successful if carried out under matrix isolation conditions, rather than in gas or solution phase. In conjunction with the barrier to angle inversion (vide supra), DE is computationally predicted to be observably bent under any conditions where it is likely to be stable to deazetation.

Our ab initio findings of a bent DE strengthen the conclusion of an earlier semiempirical paper by one of us,[17] which concluded that diazoethenes in general tend to be bent, based on MNDO and MINDO/3 calculations. Although the semiempirical C–C–N bond angle was substantially larger (137°) than the ab initio result, the qualitative finding of a bent, zwitterionic structure for DE at the semiempirical level is indeed in agreement with the higher level results. In addition, the computed MNDO vibrational frequencies were in reasonable agreement with our ab initio values, at least for a priori experimental prediction. Overall, MNDO gave

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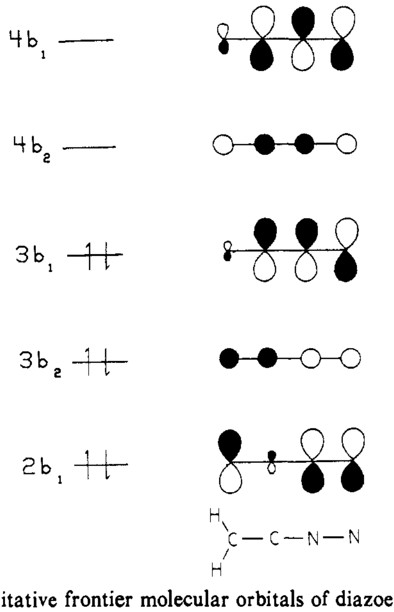
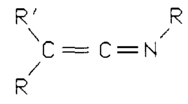


Figure 5. Qualitative frontier molecular orbitals of diazoethene. Molecular orbital energies and their atomic orbital coefficients are not represented according to scale.

a more strongly bound, less bent C=C=N moeity in DE[17] than the ab initio work. Given the lack of explicit inclusion of correlation effects in MNDO, it is perhaps surprising that the semiempirical method worked as well as it did.

The bent nature of DE, PD, and similar molecules may be interpreted in various ways. Brown and Dittman noted that the bent structure of PD can be attributed to a strong contribution to the ground-state wave function by the configuration corresponding to double-electron excitation from highest occupied σ-type molecular orbital (MO) to the lowest unoccupied MO of like symmetry, based upon CAS-SCF post-HF computations.[12] Such electronic configurational mixing could easily turn a shallow, linear single-minimum potential-well molecule into a bent double-minimum system like PD, as pointed out by Radom.[11] Since DE is isoelectronic with PD, it is not unexpected that it, too, should share a tendency toward easy geometric perturbation by admixture of low-lying excited state character into the ground state. Figure 5 shows a qualitative Walsh diagram of the frontier molecular orbitals of linear DE, omitting the lowest ten of the fourteen doubly occupied MOs in the major ground-state configuration (C_{2v} symmetry for the orbitals is used in the figure). The admixture of excited state configuration $(9a_1)^2(2b_1)^2(3b_2)^2(3b_1)^0(4b_1)^2$ is symmetry-allowed. Bending of the C–C–N angle will stabilize such excited configurations by decreasing the antibonding character of C–N interaction in the $4b_1$ MO. A significant admixture of this excited state configuration with the ground state would be favored by in-plane bending, yielding the substantial lone-pair-type localization noted earlier. In fact, a generalized valence bond computation utilizing perfect pairing of orbitals $3b_1$ and $4b_1$ finds coefficients of 0.96 and −0.29 for the two-configuration wave function, using a 4-31G basis set and the MP2/6-31G* geometry. (This calculation was carried out with the program GAMESS.[32,33]) This indicates the strong admixture of the excited configuration in the ground state, as qualitatively suggested. The extreme degree of bending in DE (118° versus 145° in propadienone) may be rationalized as being due to the relative stability of zwitterionic resonance form **1Z** relative to **1**. The diazo moiety is much better able to accommodate zwitterionic resonance of the sort that is conducive to bending DE than is the ketene moiety C=C=O, hence one might qualitatively expect DE to be more bent than propadienone, once one perceives the likelihood that either might be bent.

Whatever the reasons for the computed geometry and stability of DE, experimental confirmation of the existence of DE is still necessary to support the computations. Use of the computed MP2/4-31G vibrational frequencies that proved DE to be an energetic minimum (Table II) should be experimentally very useful. To estimate an experimental vibrational spectrum, we assumed that the C–H stretching frequencies of DE should be very similar to those of diazomethane and found that multiplication of the computed DE C–H frequency estimates by a corrective factor of 0.981 gives a good fit to the appropriate experimental diazomethane C–H frequencies of 3188 and 3077 cm^{-1}. The same correction may not be appropriate to all of the computed DE frequencies, but in the absence of experimental data, a single corrective factor seems sufficient. The most diaganostic estimated frequency for experimental detection should be the strong N=N stretching mode at 2057 cm^{-1}, which is similar both to the frequency in diazomethane[29] (2102 cm^{-1}) and that in model compound **6** (2045 cm^{-1}).[30] Thus, the infrared spectral signature of DE should be that of a typical diazo compound in the region of energy higher than 2000 cm^{-1}. In agreement with the calculated weak, long C=N bond, the C=N stretching mode—with frequency 833 cm^{-1}—is of substantially lower energy than either typical hydrazone frequencies at 1615–1700 cm^{-1},[31] or the (mostly) C=N stretch in diazomethane at 1170 cm^{-1}.[30] It is somewhat difficult to identify clearly the lower energy frequencies with simple modes in DE, since a mixture of heavy-atom and hydrogen motions occurs to a substantial extent at the bent geometry. Qualitatively, DE appears to be a fairly flexible molecule, with vibrational modes that are consistent with those expected of a perturbed diazo compound. These should prove useful in experimental detection of DE, especially the strong mode at 2057 cm^{-1}, a relatively uncluttered infrared spectral region.



(R = n-butyl, R' = ethyl)

6

Conclusion

Our work indicates that the trend toward nonlinearity found by other workers in post-HF computed structures of cumulenones is also followed in the isoelectronic analogue, diazoethene. We find diazoethene to be a computationally bound species that should in principle be experimentally accessible, and identifiable by comparison to the computed vibrational frequencies. Consistent with the formulation of DE as a weakly bonded complex of dinitrogen and vinylidene, a low barrier of 7 kcal/mol to deazetation is predicted; however, matrix isolation techniques should give reasonable kinetic stability. A relatively high barrier to C=C=N inversion is predicted, indicating that the molecule is indeed a bent species under conditions where it is stable.

Nonlinearity in highly cumulated hetero-substituted cumulenes may be a general phenomenon that will be found in other compounds, now that the possibility is recognized, although, of course, extremely low barriers to inversion of such molecules would hinder or prevent identification of their nonlinearity. Future computational and experimental work is needed before this is clarified, but the work on propadienone and diazoethene shows that computational methods to explore this interesting possibility are available.

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dertake this independent project while still a doctoral student. A generous grant of computer time was made available by Fairfield University on its VAX 8600 facility. Finally, we acknowledge use of computation time provided by the University of Massachusetts Materials Research Laboratory at the Cornell University Production Supercomputer Facility, which is supported in part by the National Science Foundation, the state of New York, and International Business Machines Corp.

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Transferability of Natural Bond Orbitals

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Abstract: We have examined the transferability of C–H bonds (σ_{CH}) and amine lone pairs (n_N) in the framework of the natural bond orbital (NBO) method applied to a series of small organic molecules at the ab initio RHF/6-31G* level. We determined root-mean-square deviations for σ_{CH}, n_N NBOs in all pairs of molecules and compared these with corresponding values for localized molecular orbitals (LMOs), which have been employed in many previous discussions of bond transferability. Although the degree of bond transferability is found to be similar for NBOs and LMOs when chemical substitution occurs directly at an atom of the transferred unit, the transferability of NBOs is found to be significantly superior (by factors of 2–4 over corresponding LMOs) when the perturbation of the bond environment is more remote. Thus, an NBO *better* corresponds to the classical concept of a transferable localized bond than does an LMO. The interactions between a localized bond and its chemical environment which limit the concept of bond transferability are discussed in terms of an approximate decomposition into orthogonality (steric), rehybridization (Bent's rule), and chemical delocalization (hyperconjugative) effects.

I. Introduction

The concept of the transferable chemical bond is one of the central empirical tenets of chemistry.[1] As is well-known, the bond concept allows one to rationalize many molecular properties (bond enthalpies,[2a] interatomic distances,[2b] IR stretching frequencies,[2c] dipole moments,[2d] and others[2e,f]) in terms of intrinsic bond contributions, approximately transferable from one molecular environment to another.

Despite the empirical evidence supporting the concept of transferable chemical bonds, it has proven surprisingly difficult to provide a rigorous formal and numerical basis for this concept. In the formative years of quantum theory, the theoretical basis of the bond concept was extended by Pauling,[3a] Slater,[3b] and others,[3c] but this work was based on semiempirical wave functions that were directly constructed to incorporate the concept of transferable valence bonds, and could therefore provide only qualitative (and somewhat circular) support for the bond concept. As emphasis shifted toward ab initio SCF–MO and other more general forms of wave functions, it became less clear what constituted a chemical bond, or how the degree of bond transferability could be quantatively assessed.

Questions of bond transferability are intimately bound up with the definition of the bond itself. It is generally recognized that one cannot give a unique, mathematically precise quantum mechanical definition of a bond in terms of a definite Hermitian operator. The bond-like units are generally of lower symmetry than the Born–Oppenheimer molecular electronic Hamiltonian operator and cannot form a basis for an irreducible representation of the molecular point group of the Hamiltonian. These units therefore do not provide "good" quantum numbers for the description of the exact wave function. In a perturbative framework, however, such bond units may have approximate validity in the sense of providing a sufficiently accurate zeroth-order description of the system, e.g., as a suitably antisymmetrized separable product of bond functions. The bond description can thereby be justified if an optimized zeroth-order wave function corresponding to this description is of sufficient quantitative accuracy.

Given the specific form of a bond function for two different molecules, the transferability of the function can be assessed in general quantum mechanical terms. For example, if $\sigma_{CH}^{(A)}$, $\sigma_{CH}^{(B)}$ denote C–H bond functions from two molecules A, B, we can measure C–H bond transferability in terms of the "overlap error" δ_{AB},

$$\delta_{AB} = (1 - \langle \sigma_{CH}^{(A)} | \sigma_{CH}^{(B)} \rangle^2)^{1/2} \qquad (1a)$$

which, to leading order, is equivalent to a root-mean-square deviation integral,

$$\delta_{AB} \simeq \left[\int |\sigma_{CH}^{(A)} - \sigma_{CH}^{(B)}|^2 \, d\tau \right]^{1/2} \qquad (1b)$$

and whose value vanishes if and only if the overlap integral between these functions is unity.[4]

Lennard-Jones[5] first pointed out that the notion of C–H bonds in methane could be partially justified by transforming the delocalized SCF–MOs to "equivalent orbital" form, localized on individual C–H bond units. This observation was subsequently generalized to molecules of lower symmetry by Edmiston and Ruedenberg,[6a] Boys,[6b] and others,[6c] giving rise to the method of

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(1) See: Sidgwick, N. V. *Some Physical Properties of the Covalent Link in Chemistry*; Cornell University Press: Ithaca, NY, 1933 for an early discussion of bond additivity to various molecular properties.

(2) (a) Cottrell, T. L. *The Strengths of Chemical Bonds*; Butterworths Scientific Publications: London, 1958; Chapter 6 and Section 11.5, p 268. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7. (c) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill Book Company, Inc.; New York, 1955; pp 174–182. (d) Exner, O. *Dipole Moments in Organic Chemistry*; George Thieme: Stuttgart, 1975; pp 27–54. (e) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-Resolution Nuclear Magnetic Resonance*; McGraw-Hill Book Company, Inc.; New York, 1959; Chapters 7 and 11 (NMR chemical shifts). (f) Kauzman, W. J.; Walter, J. E.; Eyring, H. *Chem. Rev.* **1940**, *26*, 339–407. Kirkwood, J. G. *J. Chem. Phys.* **1937**, *5*, 479–491 (bond polarizabilities).

(3) (a) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367–1400. (b) Slater, J. C. *Phys. Rev.* **1931**, *37*, 481–489. (c) For example: Coulson, C. A. *Valence*, 2nd ed.; Oxford University Press: London, 1952.

(4) Qualitative error-bound considerations (see: Weinhold, F. *Adv. Quantum Chem.* **1972**, *6*, 299–331) suggest that δ_{AB} is of the order of fractional differences in properties calculated with the two functions $\sigma_{CH}^{(A)}$, $\sigma_{CH}^{(B)}$, so that, for example, the value $\delta_{AB} = 0.05$ would correspond to ~5% nontransferability in bond properties.

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