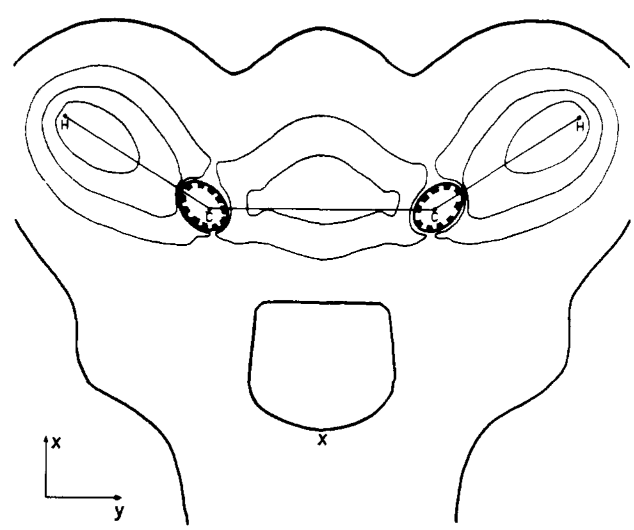

Figure 4. Section of the deformation density of complex II in the plane containing the acetylene ligand and the midpoint of the Ni–Ni line. Contour interval: 0.03 $e(au)^{-3}$. Negative deformation densities beyond -0.09 $e(au)^{-3}$ are not represented. Bold line is for zero deformation density.

map similarly computed for II. In order to obtain more possibilities of comparison with experimental work, calculations were started on other binuclear complexes, including $Cr_2(O_2CH)_4$.

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(1) The electronic deformation density distribution, $\Delta\rho(r)$, is defined as the difference between a molecular electronic density distribution and the superposition of spherically averaged atomic distributions.[2]
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(9) 1 $e(au)^{-3}$ = 6.74876 e $Å^{-3}$.
(10) The Fe–Fe overlap population is -0.05. This value has to be compared for instance to a similarly computed overlap population of $+0.16$ between the nonbridged iron atoms in $Fe_3(CO)_{12}$.[11]
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(19) A quantitative comparison should allow for thermal motion and limited resolution which reduce the sharpest features in the experimental map.[17] As a matter of fact, both electron accumulation and deficiencies are found larger by the calculation than by the experiment, as already noticed by Johansen for other metal complexes.[3]
(20) The Mulliken population analysis of the molecular wave function attributes a population of 1.77 to 1.94 e to each d orbital, except d_{z^2}. As expected from the presence of a σ bond, the population of d_{z^2} is significantly lower, 1.48 e, that is, less than the atomic averaged orbital population.
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M. Bénard
Laboratoire de Chimie Quantique
Institut Le Bel, Université Louis Pasteur
4 rue B. Pascal, 67000 Strasbourg, France
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On the Hartree–Fock Theory of Local Regions in Molecules

Sir:

The direct determination of localized orbitals for large molecules has received increasing attention in the past years.[1] This concept is useful in particular if different local basis sets are used for the expansion of localized orbitals belonging to different localization centres (subsystems). Several authors have discussed the use of such local or fluctuating basis sets. Matsuoka[2] and the present authors[3] have modified the Adams–Gilbert equations[1] for this case; Mehler[4] has derived a variational method for nonorthogonal group functions based on local energy functionals; Payne[5] has given equations for the determination of the Hartree–Fock determinant with the lowest energy under the variational restriction imposed by the local basis sets. It is the last paper by Payne on which we want to comment.

We start from a set of (occupied) localized orbitals $\{\varphi_{i\alpha}\}$ and a corresponding set of local basis functions $\{\chi_{ip}\}$; i denotes the subsystem, α refers to different orbitals, and p refers to different basis functions belonging to the same subsystem. We expand each orbital in terms of basis functions of the same subsystem

$$|\varphi_{i\alpha}\rangle = \sum_p C_{ip,i\alpha}|\chi_{ip}\rangle \quad (1)$$

where all $C_{ip,j\alpha}$ values with $i \neq j$ are constrained to be zero. The reciprocal orbitals are defined by

$$|\tilde{\varphi}_{i\alpha}\rangle = \sum_{j\beta} |\varphi_{j\beta}\rangle\, S^{-1}{}_{j\beta,i\alpha} \quad (2)$$

with $S_{j\beta,i\alpha} = \langle\varphi_{j\beta}|\varphi_{i\alpha}\rangle$.

The energy E of the Slater determinant built up from the nonorthogonal orbitals of eq 1 depends on the nonzero orbital coefficients $C_{ip,i\alpha}$. The determinant with the lowest E is, of course, characterized by vanishing partial derivatives of E with respect to the $C_{ip,i\alpha}$:

Table I. Comparison of Results for CH_4 Using (a) Payne's Equations (eq 4) and (b) a Steepest-Descent Method[a]

Definition of Subsystems

subsystem	orbital	basis functions
1	1s (C)	C: s_1
2 . . . 5	σ (CH)	C: sp_1, sp_2
		H: s_1, s_2

Orbital Coefficients (σ_{CH})
(a) 0.41410, 0.46094, 0.21333, 0.07166

(b) 0.38516, 0.58661, 0.19381, −0.02778

Total Energy
(a) −39.8242
(b) −39.8354

[a] A modified 4-31G basis set[6] is used, where the 2s and 2p groups are replaced by Gaussian lobes with distance $0.437/\sqrt{\eta}$ from the C nucleus in the bond directions. All values are given in atomic units.

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$$\frac{\partial E}{\partial C_{ip,i\alpha}} = \langle \chi_{ip}|F - \rho F|\tilde{\varphi}_{i\alpha}\rangle = 0 \qquad (3)$$

here F denotes the Fock matrix and ρ the one-particle density matrix.

Payne's equations[5] read

$$\langle \chi_{ip}|(1 - \rho + \rho_i)F(1 - \rho + \rho_i)|\varphi_{i\alpha}\rangle = \epsilon_{i\alpha}\langle \chi_{ip}|\varphi_{i\alpha}\rangle \qquad (4)$$

with

$$\rho_i = \sum_{\alpha} |\varphi_{i\alpha}\rangle\langle\varphi_{i\alpha}|$$

They are equivalent to

$$\langle \chi_{ip}|F - \rho F|\varphi_{i\alpha}\rangle = 0 \qquad (5)$$

The conditions of eq 3 and eq 5 lead to the same result only in two cases: (a) if orbitals from different subsystems are mutually orthogonal, or (b) if a common basis set is used for all subsystems. For nonorthogonal orbitals, expanded in different local basis sets, neither a nor b holds, so that Payne's equations[5] do not yield the determinant with the lowest energy, contrary to his assertion. The reason for this discrepancy is as follows. In the derivation of eq 4, Payne uses a Schmidt orthogonalization

$$|\varphi'_{j\beta}\rangle = \sum_{k\gamma} |\varphi_{k\gamma}\rangle W_{k\gamma,j\beta} \qquad (6)$$

which leaves $|\varphi_{i\alpha}\rangle$ invariant.

The $i\alpha th$ column of W therefore has the structure $W_{j\beta,i\alpha} = \delta_{j\beta,i\alpha}$; clearly, this is also the case for the $i\alpha$th column of the inverse transformation W^{-1} and for the $i\alpha$th row of $(W^{-1})^T$. This structure is, in general, not the correct one, however, for the $i\alpha$th column of $(W^{-1})^T$, contrary to Payne's statement. Payne's statement holds for orthogonal transformations, where $(W^{-1})^T = W$, but the transformation in eq 6 from nonorthogonal to orthogonal orbitals is, of course, not orthogonal. The transformation eq 6 does not change the Slater determinant, nor the orbital $|\varphi_{i\alpha}\rangle$, but it does change the partial derivatives $\partial E/\partial C_{ip,i\alpha}$.

In order to illustrate these points we have done a calculation for CH_4 using a modified 4-31G basis set.[6] In Table I results from Payne's equations (eq 4) are compared with values from a steepest-descent method[7] which is based on eq 3. The total energy from Payne's method is, by ~7 kcal, higher than the lowest which can be obtained with the given local basis sets. It is open to question if the deviations from the lowest variational energies are the reason for the ill-behaved rotational barrier heights in Payne's paper.[5]

We want to conclude with a remark concerning the computational effort. With Payne's method no computational simplification is achieved with respect to the conventional HF-LCAO method. Actually, the diagonalization time is smaller, because the modified Fock matrix in eq 4 is block diagonal, but this is compensated for by an additional effort in constructing the modified matrix. The direct calculation of localized nonorthogonal orbitals in connection with the use of local basis sets leads to a considerable computational simplification, however, if approximations for interactions between different subsystems are introduced into the method[3,7]

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H. Stoll,* G. Wagenblast, H. Preuss

Institut für Theoretische Chemie der Universität Stuttgart D-7000 Stuttgart, West Germany

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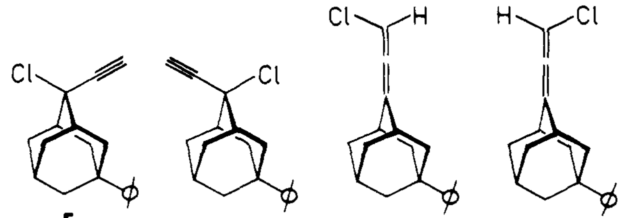
Shape and Inversion of an Allenic Anion[1]

Sir:

We recently reported[2] the synthesis and configurational assignment of several epimeric pairs of 1,4- (or 2,5-) disubstituted adamantanes, among them the acetylenes I and the allenes II. It was noted that the availability of these pairs would



E I Z E II Z

make possible a number of stereochemical studies, and we report here the first of these investigations, which is concerned with the shape of allenic anions. According to one published report,[3] α-haloallenic anions should be linear, but doubt was expressed in another.[4] Information on this point may become important since allenic anions have begun to play a role in synthesis.[5] The conclusion of the present work is that the anions of II are bent, and that the inversion barrier between them must be at least 22 kcal/mol.

Treatment of 0.3 M solutions of (Z)-I with catalytic amounts of t-BuOK in t-BuOD at 30 °C leads to complete exchange within seconds, as shown by ^{1}H NMR; under the same conditions, (E)-II exchanges its allenic proton with a half-life of 4 min. Similar data apply to the "norphenyl" parent compounds. Again under the same conditions, (E)- and (Z)-II do not interconvert significantly; thus, the (E)-II solution contains only 2% of the epimer after 4 h. Clearly, the anions of II must be bent, with a rate constant of epimerization ~2000 times slower than that of exchange, which fixes the free-energy barrier ~5 kcal/mol above that of the proton abstraction; the latter equals 21.5 kcal/mol. The very low degree of epimerization is not due to a lopsided equilibrium ratio as may be seen by the following experiment.

The slow epimerization is accompanied by base-promoted solvolysis (presumably by way of the corresponding carbene) which is several times faster. At 100 °C, if solutions 0.003 M in both substrate and base are allowed 30 min for reaction, the 35% (E)-II which remains unsolvolyzed has epimerized to the extent of 20%, and, similarly, the 45% (Z)-II that has not yet decomposed contains 13% (E)-II. From the approach to equilibrium, one can calculate[6] that K equals 1.08 in favor of the Z isomer. The time dependence of the epimerization processes, corrected for solvolysis, gives $\Delta G^{\ddagger} = 27$ kcal/mol.

The barriers calculated above are those in the energy profiles beginning from the substrates. In order to determine the epimerization barrier of the anion itself, the pK_a must be estimated; this can be done as follows. For acetylene, pK_a values ranging from 19 to 25 have been reported;[7] if the chlorine inductive effect (compare acetic acid, pK_a of 4.8, and chloroacetic acid, 2.8) is taken into account, this range for I would

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