

Commentationes

Ground States of σ -Bonded Molecules*

III. Valence-Shell and π -Electron SCF MO Calculations for Conjugated Hydrocarbons**

N. COLIN BAIRD*** and MICHAEL J. S. DEWAR

Department of Chemistry, The University of Texas, Austin, Texas 78712, USA

Received July 31, 1967

Calculations of the bond orders, net charge densities and energy levels for the π -electrons in a number of conjugated hydrocarbons by the valence-electron SCF MO method and by the π -electron SCF MO method are compared. The distinctions between alternant and non-alternant hydrocarbons, and in bond orders among single, aromatic, and double bonds, established by π -electron methods is maintained to a high degree of approximation in the full valence-electron calculations. An excellent correlation exists between the π -electron energy levels calculated by the two methods. The valence-electron calculations indicate that the hyperconjugative release of electrons in neutral molecules such as propene and toluene is negligible, but that this release can be substantial in carbonium ions.

Ladungsdichten, Bindungsordnungen und Orbitalenergien von π -Elektronen in einer Reihe von konjugierten Kohlenwasserstoffen werden nach π -SCF MO-Methoden sowie nach einer Valenzelektronen-SCF MO-Methode berechnet. Der für die π -SCF MO-Methoden typische Unterschied von alternierenden und nichtalternierenden Kohlenwasserstoffen und die Möglichkeit der Klassifizierung der π -Bindungsordnungen nach einfachen, aromatischen oder Doppel-Bindungen bleiben bei der vollständigen Behandlung aller Valenzelektronen weitestgehend erhalten. Auch die Orbitalenergien der beiden Methoden korrelieren ausgezeichnet. Die Valenzelektronen-Rechnung zeigt, daß der Einfluß der Hyperkonjugation auf die Ladungsdichte in Molekülen wie Propen und Toluol vernachlässigbar ist, nicht dagegen bei Carboniumionen.

Comparaison des indices de liaison, des charges nettes et des niveaux d'énergie obtenus pour un certain nombre d'hydrocarbures conjugués par la méthode SCF MO à électrons de valence et la méthode SCF MO à électrons π . Les distinctions entre hydrocarbures alternants et non alternants, et, d'après les indices de liaison, entre des liaisons simples, aromatiques ou doubles, établies par les méthodes à électrons π , se maintiennent très bien dans les calculs à électrons de valence. Une excellente corrélation existe entre les niveaux d'énergie des électrons π calculés selon les deux méthodes. Les calculs d'électrons de valence montrent que le transfert d'électrons par hyperconjugaison dans des molécules neutres comme le propène ou le toluène est négligeable, alors qu'il peut s'avérer important dans ions carbonium.

Introduction

Until recently, almost all semiempirical MO calculations have been based on the Hückel σ , π approximation, the σ electrons being treated as "localized" and

* Part II: BAIRD, N. C., and M. J. S. DEWAR: J. Amer. chem. Soc. **89**, 3966 (1967).

** This research was supported by the Air Force Office of Scientific Research through Grant Number AF-AFOSR-1050-67.

*** ROBERT A. WELCH Postdoctoral Fellow.

the calculations being confined to the π -electrons. Although numerous attempts have been made to justify this approximation, none of them has been very convincing, and there has been little or no experimental evidence to show whether or not the effect of σ - π interactions in conjugated systems is really negligible.

We have recently introduced a semiempirical SCF MO method which explicitly considers all the valence electrons of organic molecules on an equal basis [1, 2, 3]. By applying this method to a series of conjugated hydrocarbons and comparing the results with those obtained from π -electron theories, the basic assumptions of the π theories can be tested quantitatively. It is also of interest to establish whether distinctions found from π theories, such as that between alternant and nonalternant hydrocarbons, and between classical and aromatic systems, are retained in the fuller treatment. As representative of SCF π calculation methods for the ground states of molecules, we have used the semiempirical LCAO-MO scheme developed recently in this laboratory [4, 5].

Valence-Shell Electron SCF MO Method [1, 3]

In this method, each valence-shell electron in the hydrocarbon molecule is explicitly considered. The molecular orbitals ψ_i are assumed to be a linear combination of the valence-shell atomic orbitals ϕ_u (1s for hydrogen; 2s and three 2p orbitals for carbon)

$$\psi_i = \sum_u C_{iu} \phi_u .$$

Our method (which has been termed the PNDDO approximation) is intermediate between the CNDO and NDDO approximations of POPLE et al. [6]. In it, enough three- and four-orbital integrals involving one-center overlap are included to make the calculations invariant to rotation, but one-center overlap between an *s*-AO and a *p*-AO is neglected. The remaining three- and four-orbital integrals can then be expressed in terms of standard two-orbital ones which are evaluated by semiempirical formulae.

One-Center Interactions

The one-center core-electron attraction and electron-electron repulsion integrals used in the calculations are taken from Klopman's atom energy analysis for neutral atoms [7]. The core-electron integral W_u^X for orbital ϕ_u of atom X:

$$W_u^X = \int \phi_{u(X)}(1) \left[-\frac{1}{2}\nabla^2 - V_X \right] \phi_{u(X)}(1) d\tau(1)$$

represents the kinetic energy of an electron in orbital ϕ_u and the attraction of this electron to the core of atom X. From the results of Klopman's analysis, $W_s^H = 13.595$ eV, $W_s^C = 49.884$ eV, and $W_p^C = 42.696$ eV.

Only two types of one-center electron repulsion integrals are distinguished, A_X^+ and A_X^- , representing the energy of repulsion between two valence electrons of same and of opposite spins, respectively:

$$A_X^- = \iint \phi_{u(X)}(1) \phi_{u(X)}(1) \frac{e^2}{r_{12}} \phi_{v(X)}(2) \phi_{v(X)}(2) d\tau(1) d\tau(2)$$

$$A_X^+ = A_X^- - \iint \phi_{u(X)}(1) \phi_{v(X)}(1) \frac{e^2}{r_{12}} \phi_{u(X)}(2) \phi_{v(X)}(2) d\tau(1) d\tau(2) .$$

For hydrogen and carbon, KLOPMAN gives the values $A_H^- = -12.845$ eV, $A_C^- = -11.144$ eV, and $A_C^+ = -10.44$ eV [7].

Two-Center Interactions

The two-center integrals required in the calculations include the one-electron resonance integrals, the two-electron repulsion integrals and the two-center core-electron attraction integrals. For each atom pair in the molecule, these interactions are first evaluated in terms of a local coordinate system in which the Y and Z axes of the two atoms are parallel and the X axes coincide. These basic integrals are then transformed into the appropriate interactions for the actual coordinate system of the molecule.

a) Two-Center Electron Repulsion Integrals

The two-orbital, two-electron Coulomb repulsion integrals γ_{uv}

$$\gamma_{uv} = \iint \phi_{u(X)}(1) \phi_{u(X)}(1) \left(\frac{e^2}{r_{12}} \right) \phi_{v(Y)}(2) \phi_{v(Y)}(2) d\tau(1) d\tau(2), X \neq Y$$

required are evaluated from a semiempirical formula similar to that suggested previously by KLOPMAN [8] and by OHNO [9]:

$$\gamma_{uv} = -e^2/[R_{XY}^2 + (\rho_u + \rho_v)^2]^{1/2}.$$

Here R_{XY} is the distance in Å between the centers X and Y , and the parameters ρ_u and ρ_v are defined in terms of the one-center electron repulsion integrals A^- :

$$\rho_u = \rho_X \quad (\text{if } \phi_u \text{ is an } s \text{ or } p_n \text{ atomic orbital})$$

$$\rho_u = \rho_X \exp[-R_{XY}/2(\rho_X + \rho_Y)] \quad (\text{if } \phi_u \text{ is a } p_\sigma \text{ atomic orbital})$$

$$\rho_X = \frac{-e^2}{2A_X^-}.$$

The theoretical justification for these formulae has been discussed previously [1].

In the local coordinate system, the majority of the three- and four-orbital, two-center electron repulsion integrals are required to be zero by reason of symmetry. The approximation is made in our method that *all* such interactions are zero in the local system. The two-center, two-, three- and four-orbital electron repulsion integrals in the coordinate system of the molecule are then simply linear combinations of the two-orbital integrals γ_{uv} calculated for the local coordinate systems.

b) Two-Center Core-Electron Interactions

The attractive interaction V_{uY} between an electron in orbital ϕ_u of atom X with the core of a different atom Y

$$V_{uY} = \int \phi_{u(X)}(1) [-V_Y] \phi_{u(X)}(1) d\tau(1)$$

is approximated as the core charge Z_Y^* of Y times the negative of the average electron-electron repulsion between orbital ϕ_u and all the valence shell orbitals of Y :

$$V_{uY} = -Z_Y^*/N_Y \cdot \sum_v^Y \gamma_{uv}$$

where N_Y is the number of valence orbitals of Y . To be consistent with the treatment of electron repulsion integrals, all two-center core-electron interactions which depend on the overlap of two different orbitals of the same atom are neglected.

c) One-Electron Resonance Integrals

The resonance integral β_{uv}

$$\beta_{uv} = \int \phi_u(\mathbf{x})(1) \left[-\frac{1}{2} \nabla^2 - \sum_{\mathbf{W}} V_{\mathbf{W}} \right] \phi_v(\mathbf{x})(1) d\tau(1)$$

is approximated by the formula

$$\beta_{uv} = \frac{\beta_{\mathbf{XY}}^0 S_{uv} (I_u + I_v)}{[R_{\mathbf{XY}}^2 + (\rho_{\mathbf{X}} + \rho_{\mathbf{Y}})^2]^{1/2}}$$

in which S_{uv} is the overlap integral between the Slater orbitals ϕ_u and ϕ_v . Slater best atom effective nuclear charges (1.0 for H, 3.25 for C) are employed. The valence-state ionization potentials I_u and I_v for neutral atoms are evaluated from Klopman's atom energy scheme, whence the values $I_s = 13.595$ eV for hydrogen, and $I_s = 17.952$ eV, $I_p = 10.764$ eV for carbon.

The empirical parameters $\beta_{\mathbf{XY}}^0$ are determined by a fitting process for the calculated heats of formation for a few small molecules. In our original method [1], we used the relation

$$\beta_{\mathbf{XY}}^0 = (\beta_{\mathbf{XY}}^0 \beta_{\mathbf{XY}}^0)^{1/2}.$$

However it has been found [3] that in order to increase the accuracy of the method in predicting heats of formation, and to enable the method to be extended to elements other than hydrogen and carbon, this relationship must be discarded and heteronuclear β^0 values evaluated empirically. For hydrocarbons, the following values for β^0 are used in this paper:

$$\begin{aligned} \beta_{\text{HH}}^0 &= 27.884 \text{ pm} , \\ \beta_{\text{CH}}^0 &= 40.718 \text{ pm} , \\ \beta_{\text{CC}}^0 &= 51.427 \text{ pm} . \end{aligned}$$

π -Electron SCF MO Method

Our π -electron SCF MO method is a variant of the Pople procedure for conjugated molecules [10], and has been discussed in full elsewhere [4, 5]. The "fixed R " version of this theory was used so that the molecular geometry could be kept identical with that used in the valence-shell SCF MO calculations.

Molecular Geometries

As in previous calculations with the valence-shell SCF MO method [1, 2, 3], a "standard" set of bond angles and distances is used. The bond angles around the unsaturated carbon atoms were taken as 120° , except in strained systems where the angles can be calculated from symmetry or are known. The standard bond distances used are

C-C ("double")	1.337 Å
C-C ("single")	1.483 Å
C-C ("aromatic")	1.397 Å
C-H ("double")	1.083 Å
C-H ("aromatic")	1.084 Å

Single and double bond lengths were used for butadiene, fulvene, methylenecyclopropene, dimethylenecyclobutene, cyclobutadiene, ethylene, the radicalenes, for the exocyclic bonds in styrene. Aromatic bond lengths were used in all other cases.

Results and Discussion

Before launching into a comparison of the calculations, it is interesting to compare the treatment of π -electrons by the valence-shell and by the π -electron

SCF MO methods, by a comparison of the semiempirical treatments of the various integrals used in the calculations.

Term for π -AO's	π -Electron Method [4, 5]	Valence-Shell Electron Method [1, 3]
One-center interactions	From atomic spectra	From atomic spectra
Polarization of σ core	Assumed zero	Explicitly calculated
Nearest-neighbor resonance integrals β_{uv}	From thermocycle and tractrix equation ^a	$\beta_{uv} = \frac{\beta_{XY}^0 S_{uv} (I_u + I_v)}{[R_{XY}^2 + (\rho_X + \rho_Y)^2]^{1/2}}$
Non-nearest-neighbor resonance integrals β_{uv}	Assumed to be zero	As above
Two-center electron repulsion integrals γ_{uv}	$\gamma_{uv} = e^2/[R_{XY}^2 + (\rho_X + \rho_Y)^2]^{1/2}$	$\gamma_{uv} = e^2/[R_{XY}^2 + (\rho_X + \rho_Y)^2]^{1/2}$
Two-center core-electron attraction integrals V_{uX}	$-\gamma_{uv} Z_X$	Negative of average valence-electron repulsions
Two-center overlap	Neglected	Neglected

^a There is a good proportionality between the π method β_{uv} and S_{uv} for each type of interaction.

Since there are significant differences between the methods, particularly in the treatment of core polarization and non-nearest neighbor resonance integrals, there is no a priori reason to expect the calculations for a given conjugated network to be very similar.

π -Bond Orders


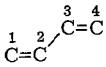







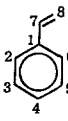
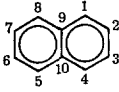
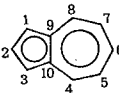

The mobile bond order

$$P_{uv} = 2 \sum_i^{\text{occ.}} C_{iu} C_{iv}$$

defines the strength of the π -bond between a pair of neighboring p_π orbitals ϕ_u and ϕ_v . A clear differentiation in bond orders between classically single, double and aromatic π -bonds was found in our π -electron calculations. On the basis of the distinction and constancy of the single and double bond orders, it was concluded that hydrocarbons for which only one unexcited resonance structure can be written are "localized" to the extent that the bonding energy of the molecule can be written accurately as a sum of single and double bond energies. It is therefore important to establish the effect of explicitly including resonance integrals for nonneighbors and polarization of the cores in the π -MO calculations.

The π -bond orders calculated for the unsaturated molecules by the two SCF methods, and by the Hückel method, are given in Tab. 1, along with the π overlap charges from the Extended Hückel Method [11]. In all cases, the agreement between the SCF bond orders is very good. Exactly the same order of π -bond

Table 1. π -Electron Bond Orders

Molecule	Bond	Bond Order From Valence- Shell Method	Bond Order From SCF π Method	Hückel Bond Order	Extended Hückel Method Overlap Charge (π) [11]
Ethylene	 1—2	1.000	1.000	1.000	0.425
<i>Trans</i> - Butadiene	 1—2 2—3	0.977 0.215	0.969 0.246	0.894 0.447	0.394 0.073
Methylene- cyclopropene	 1—2 2—3 1—4	0.265 0.939 0.916	0.242 0.943 0.940	0.453 0.818 0.758	
Trimethylene- cyclopropane	 1—2 1—4	0.206 0.954	0.232 0.944	0.385 0.832	
Cyclobutadiene	 1—2 1—4	1.000 0.000	1.000 0.000	1.000 0.000	
Tetramethylene- cyclobutane	 1—5 1—2	0.956 0.203	0.945 0.228		
Dimethylene- cyclobutene	 1—5 2—3 1—2 1—4	0.962 0.951 0.198 0.179	0.955 0.939 0.220 0.200	0.871 0.785 0.388 0.301	
Fulvene	 1—6 2—3 3—4 1—2	0.950 0.945 0.250 0.219	0.934 0.923 0.304 0.251	0.759 0.778 0.520 0.449	0.301 0.311 0.148 0.127
Benzene	 1—2	0.667	0.667	0.667	0.240
Styrene	 7—8 2—3 3—4 1—2 1—7	0.976 0.670 ^a 0.665 ^a 0.650 ^a 0.218	0.968 0.671 ^a 0.664 ^a 0.646 ^a 0.248	0.911 0.679 0.659 0.610 0.406	
Naphthalene	 1—2 9—10 2—3 1—9	0.773 0.590 0.548 0.510	0.762 0.572 0.564 0.521	0.725 0.518 0.603 0.555	0.269 0.172 0.206 0.189
Azulene	 1—2 4—5 5—6 1—9 4—10 9—10	0.666 0.663 0.641 0.608 0.582 0.329	0.664 0.656 0.645 0.610 0.604 0.290	0.656 0.644 0.639 0.596 0.586 0.401	0.232 0.234 0.226 0.216 0.210 0.107
Benzene Wheland Intermediate	 1—2 2—3	0.802 0.546	0.812 0.548	0.789 0.577	

^a Average of bonds *cis* and *trans* to exocyclic double bond.

strengths is found in each of the molecules by the two sets of calculations, even for the nonalternant hydrocarbons. In contrast, a number of inversions in bond order arise when the SCF results are compared with those of the Hückel and Extended Hückel methods.

The quantitative correlation between bond order given by the two SCF methods is illustrated in Fig. 1. The only significant deviations from the excellent linear correlation occur for the 3 – 4 bond in fulvene, and 9 – 10 bond in azulene, both essential single bonds. These deviations arise primarily from changes in the π -orbital charge densities due to the inclusion of core polarization in the valence-shell calculations. The electron densities of the 3 and 4 positions in fulvene are overemphasized by the π method calculations, resulting in too large a bond order between these orbitals, and conversely for the 9 and 10 positions in azulene.

It is particularly satisfying that the bond orders between π orbitals in hydrocarbons should be virtually unchanged from the π calculations in our valence-shell method, since the total π bonding energy of a molecule (and hence its predicted heat of formation) is very sensitive to these quantities, as are the predicted bond lengths. The quantitative correlation between the bond orders of the two SCF methods is then a major factor in explaining the superiority of our π method in predicting the energies of molecules as compared to the Hückel method. Evidently the explicit inclusions of electron repulsions and the variation in the magnitude of resonance integrals with distance are of much greater importance

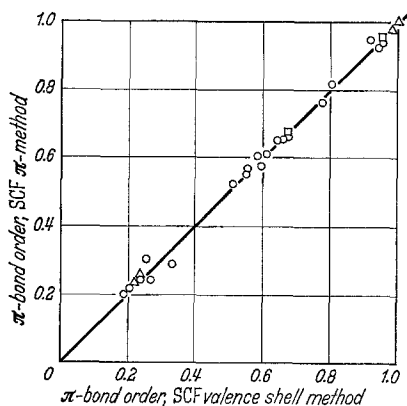


Fig. 1. π -Bond orders in hydrocarbons. \circ = single point; \triangle = two almost coincident points; \square = four almost coincident points

than the inclusion of core polarization and nonneighbor resonance integrals in π -electron calculations.

It is also satisfying that the differentiation in mobile bond orders between classically single, aromatic and double bonds between unsaturated carbon atoms remains unaffected in the valence-shell calculations, as the following ranges indicate:


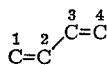




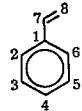
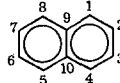
Bond Type	Range of π -Bond Orders
Double	0.96 ± 0.04
Aromatic	0.64 ± 0.07
Single	0.25 ± 0.08

Charge Density Distributions

In both the SCF and Hückel π -electron theories, there is a quantitative distinction between alternant and non-alternant neutral hydrocarbons. In the former, no charge transfer occurs between the π -orbitals, whereas substantial polarities are generally predicted for the latter. This distinction only occurs in these calculations, however, if the cores of the molecules are assumed to be unpolarized. There is no a priori reason for this distinction to be retained in the valence-shell calculations where core polarization is allowed for explicitly.

The net charges calculated for the π -AO's, the σ -electron core, and the entire atom are listed in Tab. 2 for the alternant hydrocarbons considered. There is a sharp differentiation in the charges between the alternants having significant angle strain in their σ -bonds and those without. In the unstrained alternants, the net charges for the π orbitals are exceedingly small (-0.006 to $+0.007$ e) and conse-

Table 2. *Net Charges in Alternant Hydrocarbons*

Molecule	Position	π Orbital Net Charge	σ Core Net Charge	Atomic Net Charge
Ethylene	 1	0.000	+0.055	+0.055
<i>Trans</i> -Butadiene	 1	+0.001	+0.068	+0.070
	2	-0.001	+0.006	+0.005
Cyclobutadiene	 1	0.000	+0.007	+0.007
Tetramethylene- cyclobutane	 1	+0.027	-0.048	-0.020
	5	-0.027	+0.097	+0.070
Dimethylene- cyclobutene	 1	+0.036	-0.059	-0.023
	2	+0.020	0.000	+0.020
	5	-0.056	+0.115	+0.059
Benzene	 1	0.000	+0.018	+0.018
Styrene	 1	+0.007	-0.036	-0.029
	3	+0.004 ^a	+0.015 ^a	+0.019 ^a
	7	+0.001	+0.017	+0.018
	8	-0.001	+0.063	+0.062
	4	-0.002	+0.022	+0.020
	2	-0.006 ^a	+0.030 ^a	+0.024
Naphthalene	 2	+0.003	+0.017	+0.020
	9	0.000	-0.016	-0.017
	1	-0.003	+0.027	+0.024

^a Average for atoms cis and trans to the exocyclic double bond.

quently the approximation of zero π charge transfer holds very well. In these systems, the net charge of the σ -electron cores, and of the whole carbon atoms, are seen to be mainly dependent upon the type of carbon atom involved:

Type of Carbon Atom	Range of σ -Charges	Range of Total Charge
CH ₂	+0.062 \pm 0.008	+0.062 \pm 0.008
CH	+0.018 \pm 0.012	+0.015 \pm 0.010
C	-0.026 \pm 0.010	-0.023 \pm 0.006

Hence the greater the number of hydrogen atoms bonded to a given carbon atom, the less is the electron density of its σ core, and of the atom as a whole. One could therefore empirically allow for the effects of core polarization in π calculations for such systems by decreasing the Coulomb integral of carbon as the number of bonded H atoms is decreased. This effect has been established in recent π calculations by ROOS and SKANCKE [12].

The approximation of zero π -charge transfer in alternant hydrocarbons is less applicable when strained systems are considered. The results for tetramethylenecyclobutane and dimethylenecyclobutene indicate that the π -charges for such systems are an order of magnitude greater (-0.056 to $+0.036$ e) than those for the unstrained alternants. The σ -core charges here display the same type of dependence upon carbon atom type as do those for the unstrained alternants, although the effects are larger.

The net charges in several nonalternant hydrocarbons are given in Tab. 3. Here the σ -, π -, and total charges are generally several orders of magnitude greater than those in the nonalternants. The distinction between alternants and nonalternants is consequently maintained on a semi-quantitative basis in the valence-shell method. Note also that the core and total charges maintain qualitatively the same type of dependence on carbon type as that found for the alternants.

The π -charges for the nonalternants predicted by the SCF and Hückel methods are also listed in Tab. 3. Unfortunately, the correlation between the π -charges predicted by the two SCF methods is not very good (Fig. 2). The agreement in the ordering of π -density within individual molecules between the π methods is fairly

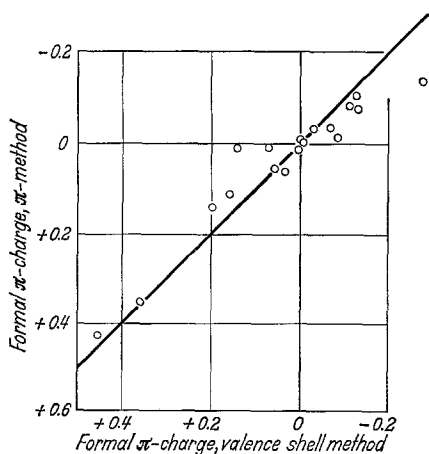


Fig. 2

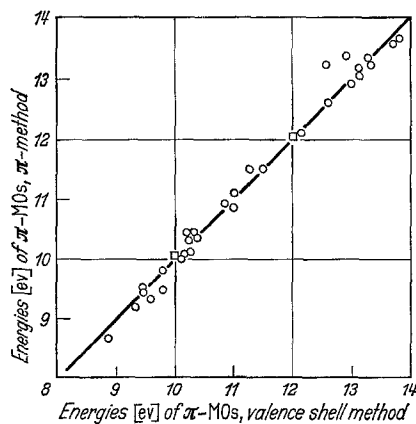
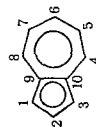
Fig. 2. Formal π -charges in hydrocarbons

Fig. 3

Fig. 3. Energies of π -MO's in hydrocarbons

Table 3. Net Charges in Nonalternant Hydrocarbons

Molecule	Position	π Orbital Net Charge	σ Core Net Charge	Atomic Net Charge	SCF π Theory π Charge	Hückel π Theory π Charge
Methylene- cyclopropene	1	+0.148	-0.131	+0.017	+0.018	+0.062
	2	+0.061	-0.066	-0.005	+0.058	-0.062
	4	-0.270	+0.240	-0.030	-0.133	
Trimethylene- cyclopropane	1	+0.078	-0.105	-0.027	+0.009	+0.062
	4	-0.078	+0.146	+0.068	-0.009	-0.062
Fulvene	6	+0.038	+0.070	+0.107	+0.065	+0.378
	3	+0.004	+0.013	+0.017	-0.005	-0.073
	1	0.000	-0.057	-0.057	+0.001	-0.047
	2	-0.023	+0.032	+0.009	+0.028	-0.092
Azulene	4	+0.200	-0.064	+0.136	+0.146	+0.145
	6	+0.166	-0.032	+0.133	+0.117	+0.130
	2	+0.040	+0.026	+0.036	+0.018	-0.047
	9	-0.061	+0.007	-0.053	-0.033	-0.027
	5	-0.107	+0.041	-0.066	-0.081	+0.014
1	-0.119	+0.093	-0.026	-0.099	-0.172	
Benzene Wheland Intermediate	3	+0.456	-0.206	+0.249	+0.429	+0.333
	1	+0.360	-0.221	+0.139	+0.357	+0.333
	2	-0.125	+0.046	-0.079	-0.072	0.000



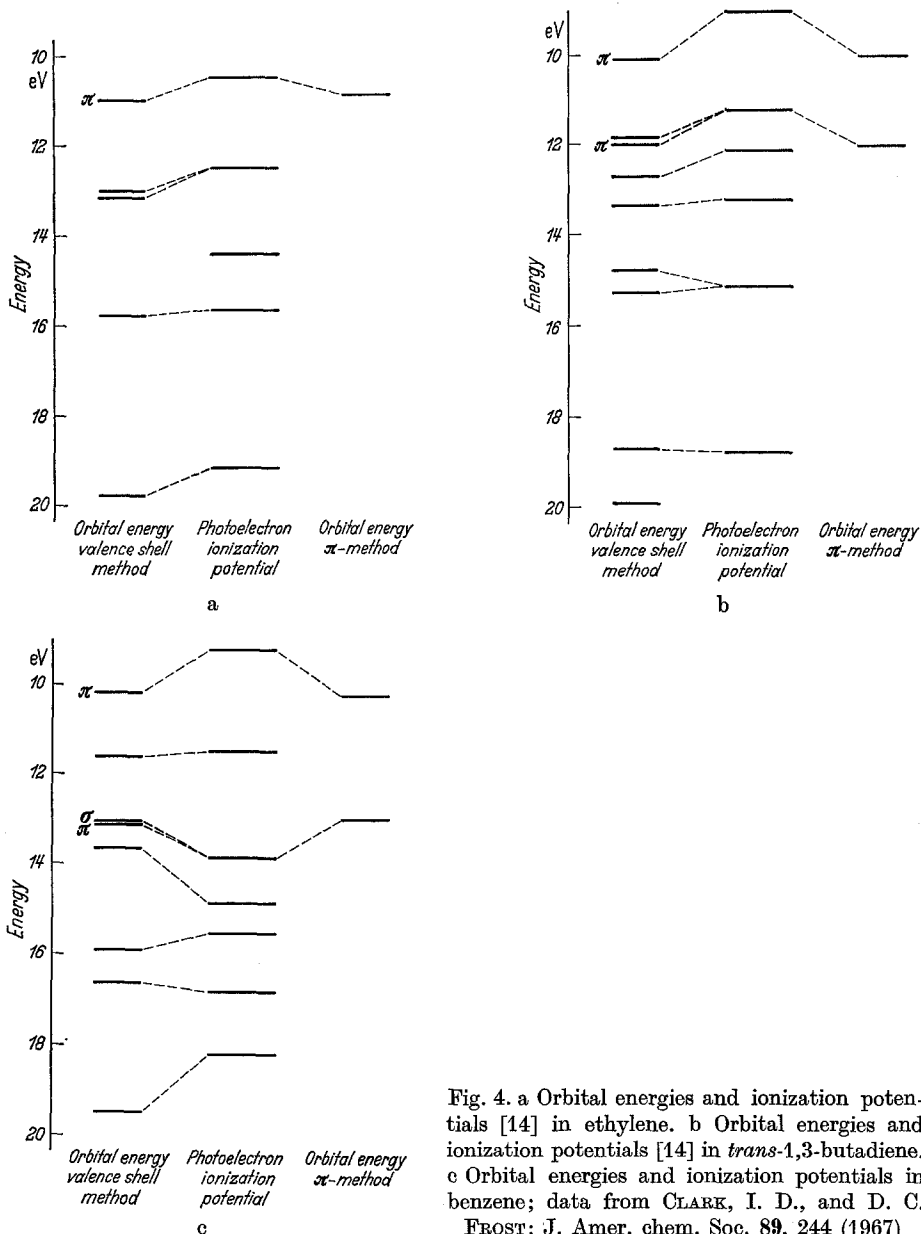


Fig. 4. a Orbital energies and ionization potentials [14] in ethylene. b Orbital energies and ionization potentials [14] in *trans*-1,3-butadiene. c Orbital energies and ionization potentials in benzene; data from CLARK, I. D., and D. C. FROST: J. Amer. chem. Soc. 89, 244 (1967)

satisfactory, however, with complete agreement found for azulene and trimethylenecyclopropane, and with only a minor inversion occurring in fulvene. The agreements with the valence-shell calculations are less satisfactory for the Hückel results.

It is fortunate that the calculated π -bonding energies of the hydrocarbons are not very sensitive to errors in the π -charges of the observed order of magnitude. The effect of such errors, due to neglect of core polarization in the π calculations,

Table 4. *Energy Levels in Hydrocarbons (eV)*


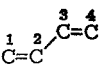





Molecule	Level Type	Energy Level From Valence-Shell Theory	Energy Level From SCF π Theory	Difference
Ethylene	 π	10.965	10.855	+0.110
	σ	13.000		
	Total			+0.110
<i>Trans</i> -Butadiene	 π	10.139	10.070	+0.069
	σ	11.850		
	π	11.994	12.060	-0.066
	σ	12.723		
	Total			+0.003
Methylene-cyclopropane	 π	9.582	9.350	+0.232
	σ	10.749		
	σ	11.739		
	π	12.554	13.202	-0.648
	σ	14.379		
Total			-0.416	
Trimethylene-cyclopropane	 π	10.250 ^a	10.094 ^a	+0.156
	σ	10.680 ^a		
	π	12.883	13.357	-0.474
	σ	13.400		
	Total			-0.162
Dimethylene-cyclobutene	 π	10.005	10.053	-0.048
	π	10.377	10.366	+0.011
	σ	11.222		
	σ	11.341		
	σ	12.144		
	π	13.096	13.148	-0.052
	σ	14.413		
Total			-0.089	
Tetramethylene-cyclobutane	 π	9.783	9.492	+0.291
	π	10.840 ^a	10.942 ^a	-0.102
	σ	11.124 ^a		
	σ	11.290		
	π	13.274	13.322	-0.048
	σ	13.947		
Total			+0.039	
Fulvene	 π	10.076	10.008	+0.068
	π	10.321	10.428	-0.107
	σ	11.543		
	σ	11.893		
	σ	12.061		
	π	12.968	12.899	+0.069
	σ	13.029		
Total			+0.020	

Table 4 (continued)


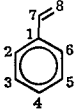
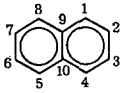
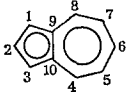


Molecule		Level Type	Energy Level From Valence-Shell Theory	Energy Level From SCF π Theory	Difference
Benzene		π	10.184 ^a	10.287 ^a	-0.103
		σ	11.634 ^a		
		σ	13.060		
		π	13.100	13.037	+0.063
		σ	13.659		
		Total			
Styrene		π	9.788	9.804	-0.016
		π	10.217	10.293	-0.076
		σ	11.234		
		π	11.428	11.506	-0.078
		σ	11.555		
		σ	12.707		
		σ	12.732		
		π	13.300	13.215	+0.085
		σ	13.503		
		Total			
Naphthalene		π	9.309	9.274	+0.035
		π	9.965	10.068	-0.103
		σ	11.008		
		π	11.011	11.110	-0.099
		σ	11.336		
		π	12.022	12.042	-0.020
		σ	12.151		
		σ	12.715		
		σ	13.000		
		σ	13.317		
		σ	13.552		
		π	13.788	13.627	+0.161
		σ	15.019		
		Total			
Azulene		π	8.851	8.666	+0.185
		π	9.476	9.432	+0.044
		π	11.256	11.489	-0.233
		σ	11.385		
		σ	11.404		
		σ	11.929		
		σ	12.078		
		π	12.137	12.107	+0.030
		σ	12.589		
		σ	13.009		
		π	13.688	13.577	+0.111
		σ	14.407		
		Total			

Table 4. (continued)

Molecule		Level Type	Energy Level From Valence-Shell Theory	Energy Level From SCF π Theory	Difference
Cyclobutadiene		π	9.428	9.525	-0.097
		σ	11.251		
		σ	12.191		
		σ	12.566		
		π	12.574	12.612	-0.038
		σ	16.042		
		Total			
Benzene Wheland Intermediate ^b		π^*	15.691	16.922	-1.231
		σ^*	17.046		
		π^*	17.228	18.657	-1.429
		σ^*	17.377		
		Total			

^a Indicates a degenerate level.

^b π^* and σ^* indicate quasi- π and quasi- σ energy levels.

will of course be much more important in the estimation of properties such as dipole moments. It is interesting that the valence-shell method predicts quite well the dipole moment of azulene (predicted 1.57 D, experimental 1.0 ± 0.05 D [13]) although too small a moment is calculated for fulvene (predicted 0.22 D, experimental estimation 1.2 D [13]).

One further aspect of the charges given by the valence-shell method is worthy of note. It is interesting that in about three-quarters of the positions for which charges are reported in Tabs. 2 and 3, the net π - and σ -charges are of opposite sign. This is particularly evident in compounds with three- and four-membered rings where the π -charge tends to escape from the ring, thus making it approach an "aromatic" structure with two π -electrons. In these cases, the escape of π -density is more favorable in the valence-shell method calculations since the net atom charge can be kept low by σ -electron transfer in the opposite direction.

Energy Levels

Self-consistent field one-electron energy levels are obtained for the conjugated hydrocarbons in both the π and valence-shell SCF MO calculations. Calculated values for both are listed in Tab. 4, in each case as far down as the σ level beneath the lowest π level. In order to make a fair comparison, the valence-state ionization potential for a p_π orbital in the π calculations is taken to be that (10.764 eV) calculated from the energy scheme for atoms used in the valence-shell method.

In all the unsaturated molecules considered, the highest occupied molecular orbital is predicted by the valence-shell method to be of the π type. In all cases which have more than two π -electrons, however, there are σ electron levels between the highest and lowest energy occupied π orbitals.

Although differences of as great as 0.65 eV do occur between the π -levels predicted from the π and valence-shell methods, the overall correlation between the predicted levels (Fig. 3) is excellent. The mean root square deviation is 0.17 eV

in a spread of some 5.0 eV. In addition, the deviations in each system tend to cancel each other out as indicated by the sum given in the last row for each molecule; the average value of the absolute deviation per molecule is only about 0.1 eV (2 kcal/mole). The only total deviation which exceeds 0.17 eV is that for the highly-strained nonalternant methylenecyclopropene. The inclusion of non-neighbor resonance integrals and σ -core polarization therefore leads only to very small changes in the total π energy, in agreement with the conclusions reached in the previous two sections.

It is of interest to compare the one-electron energy levels calculated by the two SCF MO methods with photoelectron ionization potentials. Such a comparison is given in Fig. 4 for ethylene, *trans*-butadiene and benzene by using the ionization potentials compiled by AL-JOUBOURY and TURNER [14]. The correspondence between the calculated and experimental levels here is very good, as were previous correlations of this type using both SCF MO methods [1, 15].

Hyperconjugation

It has been our thesis in past publications [16] that the phenomenon of hyperconjugation is unimportant in the ground state of neutral, unsaturated molecules but that it may be important in charged species. In order to test this conviction, we have carried out valence-shell calculations for the neutral molecules propene and toluene and for several carbonium ions (all carbon atoms are assumed to be coplanar; standard bond lengths used throughout). If hyperconjugation is an important factor in these molecules, the calculations for propene, toluene and the carbonium ions should display the following effects:

- a) The total electron density of the π system proper should increase or decrease due to hyperconjugation, and
- b) The bond order between the π orbital of the hyperconjugated carbon and the carbon atom to which it is bonded should be appreciable.

The calculated effects are:

Molecule	Change in Density of π System	Hyperconjugation Bond Order
Propene	-0.004	0.133
Toluene	-0.004	0.130
$(\text{CH}_3)_2\text{CH}^+$	-0.119	0.239
Wheland Intermediate of Benzene	-0.074	0.189

The hyperconjugative release of electron density from the methyl groups in the neutral molecules is almost negligible (0.004 e) whereas in the positive ions it amounts to about 0.1 electron. The π -bond orders of sp^2 - sp^2 bonds in the neutral molecules are approximately one-half of that of a classically single bond between unsaturated carbon atoms, and are only slightly larger than the π -bond order calculated for ethane of 0.09. In contrast there are two relatively large π -bond orders (0.19 and 0.24) in bonds of this type in positive ions.

Hence our valence-shell SCF MO calculations support the contention that the effects of hyperconjugation are minimal in ground states of neutral hydrocarbons but can be appreciable in carbonium ions.

Acknowledgements. The authors would like to thank Dr. C. G. VENTER, Mr. C. DELLANO and Mr. J. A. HASHMALL for assistance with the π -electron calculations.

References

1. DEWAR, M. J. S., and G. KLOPMAN: *J. Amer. chem. Soc.* **89**, 3089 (1967).
2. BAIRD, N. C., and M. J. S. DEWAR: *J. Amer. chem. Soc.* **89**, 3966 (1967).
3. — — To be published.
4. CHUNG, A. L.-H., and M. J. S. DEWAR: *J. chem. Physics* **42**, 756 (1965).
DEWAR, M. J. S., and G. J. GLEICHER: *J. Amer. chem. Soc.* **87**, 685, 692, 3255 (1965);
J. chem. Physics **44**, 759 (1966); *Tetrahedron* **21**, 1817, 3423 (1965); *Tetrahedron Letters* **1965**, 4503.
—, and C. C. THOMPSON JR.: *J. Amer. chem. Soc.* **87**, 4414 (1965).
—, G. J. GLEICHER, and C. C. THOMPSON JR.: *J. Amer. chem. Soc.* **88**, 1349 (1966).
5. —, and C. DELLANO: To be published.
6. POPLE, J. A., D. P. SANTRY, and G. A. SEGAL: *J. chem. Physics* **43**, S 129 (1965).
7. KLOPMAN, G.: *J. Amer. chem. Soc.* **86**, 1463 (1964).
8. — *J. Amer. chem. Soc.* **86**, 4550 (1964).
9. OHNO, K.: *Theoret. chim. Acta* **2**, 219 (1964).
10. POPLE, J. A.: *Trans. Faraday Soc.* **49**, 1375 (1953).
11. HOFFMANN, R.: *J. chem. Physics* **39**, 1397 (1963).
12. ROOS, R., and P. N. SKANCKE: *Acta chem. Scand.* **21**, 233 (1967).
13. WHELAND, G. W., and D. E. MANN: *J. chem. Physics* **17**, 264 (1949).
14. AL-JOBOURY, M. I., and D. W. TURNER: *J. chem. Soc.* **1964**, 4434.
15. DEWAR, M. J. S., and J. KELEMEN: *Tetrahedron Letters* **1967**, 2341.
16. — *Hyperconjugation*. New York: The Ronald Press Co. 1962.

Prof. Dr. M. J. S. DEWAR
Department of Chemistry
The University of Texas
Austin, Texas 78712, USA