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A SIMPLE MOLECULAR ORBITAL TREATMENT OF HYPERCONJUGATION*

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Abstract—A modification of the simple molecular orbital theory has been successfully applied to the treatment of ionization potentials of unsaturated molecules. Of the several models examined for the hyperconjugative effect of a methyl group, best results were obtained for a model in which the methyl group is treated as a single "heteroatom" which donates two electrons to the π system.

As part of a program to investigate the quantitative and semi-quantitative application of the simple molecular orbital theory with neglect of overlap to organic chemistry, we have examined the treatment of ionization potentials. The resulting correlation has been used in an examination of several models for a methyl group.

Ionization potentials in the simple theory

In the simple molecular orbital (Hückel) theory all of the Coulomb integrals, α_r, are taken to be the same; all of the exchange integrals, β_{rs}, for bonded atoms are taken as equal. β for non-neighboring atoms are taken as zero and all overlap integrals of the type, $S_{rs}(r \neq s)$, are taken as zero. The energy, ϵ_j, of each molecular orbital, ψ_j, is obtained in the form of equation (1):

$$\epsilon_j = \alpha + m_j\beta \tag{1}$$

The ionization potential, I, should be given by the energy of the highest occupied molecular orbital.[1] Stevenson[2] has obtained the ionization potentials of a number of polycyclic aromatic hydrocarbons by electron impact and has demonstrated for this related family of compounds an excellent correlation between the experimental ionization potentials and the corresponding energies of the highest occupied molecular orbitals. His results are summarized in Table 1 and are plotted in Fig. 1. An attempt to extend this simple treatment to other compounds fails. Although styrene fits quite well, the points for ethylene and butadiene fall far from Stevenson's correlation line. To some extent the discrepancy is due to the use of a common value for β.

The bond distances in ethylene and butadiene differ substantially from those in the aromatic hydrocarbons. Making the usual assumption that β is proportional to the overlap integral, β_{rs} for a double bond becomes 1·07 β, in which β is now the exchange integral for the C–C bond in benzene. Similarly, β_{rs} for the single bond in butadiene becomes 0·91 β. The effect of the use of these values for β_{rs} in ethylene, butadiene and styrene are shown by the crosses in Fig. 1. In the first two cases the change is too small to produce any substantial improvement in the correlation.

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* This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF49(638)-105. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[1] S. A. Matsen, *J. Chem. Phys.* **24**, 602 (1956).

[2] D. P. Stevenson, personal communication.

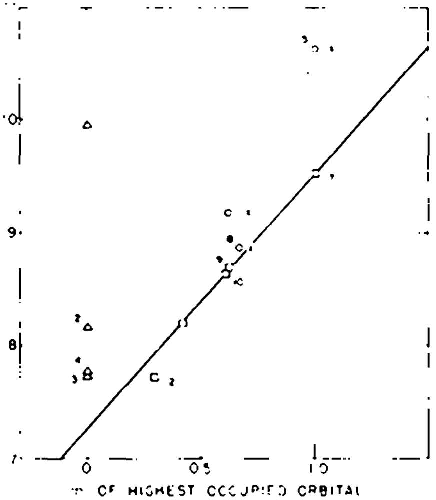

Fig. 1. Ionization potentials in the simple molecular orbital theory. Numbers correspond to compounds in Table 1.

Table 1. Ionization potentials of simple π systems

No.	Compound	$I_{\text{calcd.}}$ (eV)	Simple MO m_j	χ (ω 1·4)	$I_{\text{calcd.}}$ (eV) eq. (4)	Δ ($I_{\text{calcd.}}$ $I_{\text{exp.}}$)
1	Methyl	9·95[4]	0	0	9·88	0·07
2	Allyl	8·16[4]	0	0·785	8·22	0·06
3	Pentadienyl	7·73[5]	0	1·018	7·74	0·01
4	Benzyl	7·76[4, 6]	0	1·001	7·76	0·00
5	Ethylene	10·62[7]	1·000 (1·070)[*]	−0·370	10·66	0·04
6	Butadiene	9·18[8]	0·618 (0·708)[*]	0·310	9·22	0·04
7	Benzene	9·52[9, 10]	1·000	0·167	9·53	0·01
8	Styrene	8·86[9]	0·662 (0·718)[*]	0·445	8·94	0·08
9	Naphthalene	8·68[9]	0·618	0·592	8·63	−0·05
10	Phenanthrene	8·62[6]	0·605	0·653	8·50	0·12
11	Anthracene	8·20[6]	0·414	0·839	8·11	0·09
12	Naphthacene	7·71[6]	0·295	0·982	7·81	0·10

[*] Values of m_j for unequal β.

A further important discrepancy is found in an attempted extension of the simple treatment to radicals of the alternant hydrocarbon type.[3] In these radicals, as exem-

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[3] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* A **192**, 16 (1947).
[4] F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.* **22**, 621 (1954).
[5] D. P. Stevenson, personal communication.
[6] J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, *J. Chem. Phys.* **22**, 1948 (1954).
[7] R. E. Honig, *J. Chem. Phys.* **16**, 105 (1948).
[8] J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.* **79**, 5848 (1957).
[9] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.* **20**, 1021 (1952).
[10] F. H. Field and J. L. Franklin, *J. Chem. Phys.* **22**, 1895 (1954).

plified by methyl, allyl, benzyl and pentadienyl radicals, the highest occupied molecular orbital is a singly occupied non-bonding orbital. Hence, these radicals should all have the same ionization potential according to the simple theory. Experimentally, the ionization potentials of these radicals vary over a range of more than 2 eV. The discrepancy is demonstrated in Table I and in Fig. 1. These results demonstrate that without modification the simple molecular orbital treatment is of limited usefulness in the correlation of ionization potentials.

Effect of α as a function of charge

The defect in the treatment of ionization potentials demonstrated above undoubtedly arises from the neglect of electron-repulsion terms in the simple theory. This problem can be handled by the use of more elaborate molecular orbital techniques; several calculations of ionization potentials by using such techniques have been reported,[11] the most extensive of which are the recent semi-empirical self-consistent molecular orbital calculations of Hush and Pople.[12] In the simple theory for families of related neutral systems the effects of electron-repulsion terms are apparently relatively constant and are absorbed in the empirical values used for the parameters, α and β. The change of a neutral system to a cation is accompanied by a decrease in electron repulsion which is not effectively constant for different systems. The net effect of a decrease in electron repulsion can be approximated by a corresponding increase in Coulomb attraction; i.e., by an increase in the effective electronegativity of appropriate atoms in the system. In the simple theory this would involve an increase in the absolute values of appropriate α's. Wheland and Mann[13] introduced the assumption that the increase in α of a carbon atom in an unsaturated cation is proportional to the positive charge on the atom. We have followed this assumption with the use of equation (2), but have treated the proportionality constant, ω, as a disposable parameter:

$$\alpha_r = \alpha_0 + \omega(1 - q_r)\beta \tag{2}$$

For each compound, the usual simple molecular orbital energy equations were set up and solved with neglect of overlap. An electron was removed from the highest occupied molecular orbital, and the resulting charge distribution was determined. Equation (2) then gave the change in the α of each carbon for each of several assumed values of ω. These α values were used to set up a new energy matrix, from which the energy of the cation was determined in the usual way. The ionization potential is then given by equation (3):

$$I = E(\text{cation}) - E(\text{hydrocarbon}) = \alpha + \chi\beta \tag{3}$$

The use of the same values of β for the neutral hydrocarbon or radical and the cation implies that there is no change in molecular geometry during the ionization process. Hence, the calculated energy changes relate to the vertical ionization potentials such as are given by electron-impact methods. For each of several values of ω, the χ values were plotted against the corresponding experimental ionization potentials.

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[11] Examples are: O. Chalvet and R. Daudel, *C.R. Acad. Sci., Paris* **235**, 960 (1952); I. Tanaka and C. Komatsu, *J. Chem. Phys.* **23**, 976 (1955); H. C. Lefkovits, J. Fain and F. A. Matsen, *Ibid.* 1690.

[12] N. S. Hush and J. A. Pople *Trans. Faraday Soc.* **51**, 600 (1955).

[13] G. W. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 264 (1949).

Best agreement was obtained for ω 1·4. The data for this case are plotted in Fig. 2. An excellent linear correlation is obtained; the least-squares correlation line is given in equation (4), in which the uncertainties are given as the standard deviations:

$$I\,(\mathrm{eV}) = (-2{\cdot}110 \pm 0{\cdot}050)\chi + 9{\cdot}878 \pm 0{\cdot}073 \qquad (4)$$

By using equation (4), the χ values were converted to calculated ionization potentials. These values are compared with the experimental values in Table 1. The maximum deviation is only 0·1 eV. The average deviation, 0·05 eV, is about the same magnitude as the usual experimental error. Considering the wide variety of structural

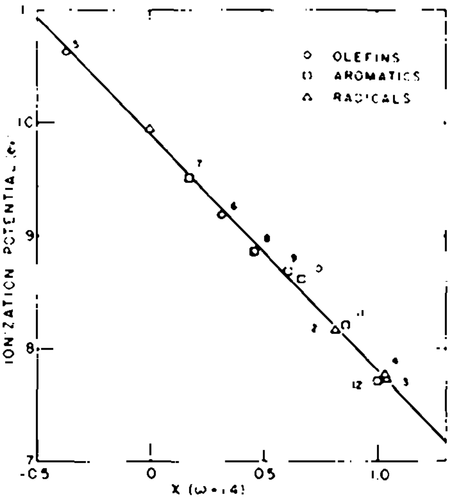

Fig. 2. Correlation of ionization potentials of simple π systems with calculated energy differences. The linear correlation is taken as the standard. Numbers correspond to compounds in Table 1

Table 2. Successive iterations for butadiene cation

No. of iterations	q_1	q_2	χ
0	0·652	0·848	
1	0·729	0·771	0·310
2	0·669	0·831	0·332
3	0·716	0·784	0·312
4	0·679	0·821	0·326
5	0·708	0·792	0·314
6	0·685	0·815	0·323
7	0·703	0·797	0·316
8	0·689	0·811	0·321
9	0·700	0·800	0·317
10	0·691	0·809	0·320
11	0·698	0·802	0·318
∞	0·695*	0·805*	0·319*

* Estimated.

types involved—radicals, olefins and aromatic hydrocarbons—and the range of almost 3 eV covered, the agreement is indeed remarkable for such a crude theory.

3,4-Benzphenanthrene was not included in the standard correlation because of the possibility that the strain in this hydrocarbon might introduce anomalous effects. However, the χ value for 3,4-benzphenanthrene, 0·721, corresponds to 8·36 eV in excellent agreement with the experimental ionization potential, 8·40 eV.[5] For graphite, the value of χ equals ω, hence I (calcd.) is 6·93 eV, in poor agreement with the experimental value, 4·39 eV, quoted by Mulliken[14] for the work function of graphite.

The calculations described amount to the first iteration of a self-consistent field treatment. The resulting charge densities may be expected in general to differ from the starting Hückel charge densities. The effect of the use of ω is to spread the charge density more evenly throughout the molecule. In several cases, the effect of successive iterations was examined. The charge densities obtained from the first iteration described above were used to derive new α's, by using equation (2). The energy matrix was changed accordingly and was rediagonalized to yield new values of χ and the charge densities. This procedure could be repeated until self-consistency was obtained if the series was convergent. The results of such successive iterations applied to butadiene are given in Table 2 in which q_r is the charge density. In this case the self-consistent charge densities differ only slightly from the simple Hückel charge densities. The final value of χ differs from the value given by the first iteration by an amount which corresponds to about 0·02 eV. In the large aromatic hydrocarbons the charge is

TABLE 3. EFFECT OF ω ON CHARGE DENSITIES OF SOME AROMATIC HYDROCARBON CATIONS

Position	q_r (Hückel)	q_r (first iteration)
Naphthalene		
1	0·819	0·869
2	0·931	0·907
9	1·000	0·949
Anthracene		
1	0·903	0·920
2	0·952	0·934
9	0·807	0·889
11	0·992	0·952
Phenanthrene		
1	0·884	0·930
2	0·998	0·946
3	0·901	0·922
4	0·946	0·926
9	0·828	0·880
11	0·973	0·936
12	0·970	0·960

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[14] R. S. Mulliken, *Phys. Rev.* 74, 736 (1948).

spread throughout most of the molecule, and the simple Hückel charge densities would not be expected to differ greatly from self-consistent charge densities. In Table 3 are listed the Hückel charge densities and the charge densities obtained from the first iteration for several aromatic hydrocarbons. The self-consistent charge densities will fall between the individual values. The changes involved are only a few hundredths of a unit at each position. Consequently we would not expect the value for χ which corresponds to the use of self-consistent charges to differ significantly from the values obtained in the first iteration in these cases.

The situation with cations of odd alternant hydrocarbons such as allyl and benzyl is rather different, however. In these cases the so called "starring process" can be carried out such that the number of starred positions is one more than the number of unstarred positions and no two starred positions are adjacent. In the Hückel approximation the positive charge density in these cations resides only on starred positions; these charge densities may be expected to differ substantially from the self-consistent charges. Table 4 lists the results for successive iterations of the allyl cation.

Table 4. Successive iterations for allyl cation

No. of iterations	q_1	q_2	χ
0	0·500	1·000	
1	0·621	0·757	0·785
2	0·534	0·934	0·877
3	0·597	0·806	0·802
4	0·552	0·896	0·851
5	0·584	0·830	0·813
6	0·560	0·880	0·844
7	0·579	0·842	0·818
8	0·565	0·870	0·835
9	0·575	0·850	0·823
10	0·568	0·864	0·827
∞	0·571	0·858	0·825
equation (6)	0·624	0·753	0·787

The self-consistent charges fall about midway between the Hückel values and those given by the first iteration. The final value of χ differs from the value from the first iteration by an amount which corresponds to only 0·08 eV. The series of successive iterations for the benzyl cation, however, was not convergent. As shown in Table 5, the charge densities at different positions show increasing oscillation with progressive iteration. Starting with charge densities derived from a perturbation treatment (*vide infra*) which should be closer to self-consistent charges, successive iterations give oscillating charges with consequent variations in χ. This situation is probably associated with the form of molecular orbitals in aromatic rings. For comparison with related systems, our procedure was to start with Hückel charges and to use χ resulting from the first cycle of iteration.

Because of its symmetry, the case of benzene is unique. The degeneracy of the highest orbitals leads to different cations, which probably cannot be made self-consistent by our procedure. Without further justification, we assumed an even distribution of positive charge on all six carbons and obtained χ from one cycle of iteration.

An alternative procedure for calculating the variation of the cation energy with ω involves the use of an approximation method. Coulson and Longuet-Higgins[15] have expanded the change in energy in a Taylor's series, the first two terms of which, equivalent to a second-order perturbation, are given in equation (5):

$$\delta E = \sum_r q_r \delta\alpha_r + \tfrac{1}{2} \sum_r \sum_s \pi_{r,s} \delta\alpha_r \delta\alpha_s + \dots \qquad (5)$$

They obtained simple expressions for the second derivatives, $\partial^2 E/\partial\alpha_r \partial\alpha_s$, identical to the atom-atom polarizabilities, $\pi_{r,s}$, in terms of the energies and coefficients of the Hückel orbitals.

TABLE 5. SUCCESSIVE ITERATIONS FOR BENZYL CATION

No. of iterations	q_1	q_2	q_3	q_4	q_7	χ
Starting with Hückel charges						
0	1·000	0·857	1·000	0·857	0·429	
1	0·811	0·873	0·906	0·800	0·830	1·001
2	1·014	0·858	0·967	0·904	0·430	1·178
3	0·805	0·863	0·931	0·760	0·847	1·012
4	1·015	0·874	0·942	0·940	0·412	1·187
5	0·798	0·844	0·955	0·726	0·879	1·024
…	—	—				—
10	1·022	0·950	0·853	1·049	0·323	1·298
11	0·756	0·762	1·043	0·623	1·011	1·112
—	—	—		—		
19	0·724	0·646	1·173	0·527	1·113	1·329
20	0·996	1·090	0·695	1·204	0·230	1·583
Starting with perturbation charges						
0	0·857	0·882	0·912	0·848	0·706	
1	0·970	0·848	0·974	0·855	0·532	1·101
2	0·863	0·879	0·921	0·826	0·710	1·017
—	—	—	—	—	—	—
7	0·972	0·874	0·940	0·907	0·495	1·109
8	0·851	0·848	0·957	0·773	0·765	1·022

Equations (2) and (5) may be combined to yield equation (6):

$$\delta E = \chi \simeq \omega \sum_r q_r(1 - q_r) + \frac{\omega^2}{2} \sum_r \sum_s \pi_{rs}(1 - q_r)(1 - q_s) \qquad (6)$$

This equation has been applied to a number of cations of odd alternant hydrocarbons.

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[15] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* A **191**, 39 (1947).

The values of χ derived in this way for allyl, benzyl and pentadienyl cations, 0·787, 0·972 and 1·020, respectively, are close to the values obtained by the rediagonalization process. The first and dominant term in equation (6) may be written in the form of equation (7), which shows its relationship to the "solvation energy parameter", Σq_r^2 recently derived by Mason[16] by a Born charging process:

$$\delta E \simeq \omega(1 - \Sigma q_r^2) \tag{7}$$

The application of the Born charging concept to individual carbon atoms within a molecule is subject to a variety of criticisms. However, the resulting function was shown to correlate excellently with a number of carbonium ion reactivities in solution. The relationship of the resulting function to equation (7) demonstrates that Mason's results are equivalent to a first-order perturbation correction of the cation energy; the explicit value of ω in his treatment is absorbed in the slopes of the linear correlations. Inasmuch as the correction applies as well to cations in the gas phase in which solvation energies are obviously not involved, our interpretation of the Σq_r^2 function would appear to be more satisfactory than its interpretation as a "solvation energy parameter".

Muller and Mulliken[17] have applied a more elaborate molecular orbital theory with inclusion of overlap to the stabilization energies of several cations. Using the same type of variation of α with charge, they obtained best agreement with $\omega = 1·4$ in precise agreement with our findings.

The slope of the correlation line, equation (4), corresponds to the value of β. This value, $-2·11$ eV or $-48·6$ kcal, is much larger than the value of about -20 kcal usually used for this parameter. The latter value is usually derived from empirical resonance energies of aromatic hydrocarbons and at most is suitable for use only for calculating similar resonance energies. Estimates of the vertical resonance energy of benzene of 65 to 80 kcal[18] correspond to values of β of $-1·4$ to $-1·7$ eV. Some other estimates of β are $-2·2$ eV from the polarographic reduction of conjugated hydrocarbons,[19] $-2·7$ eV from ultraviolet spectra,[19] and $-2·3$ eV from phosphorescence spectra.[20] The value which we obtained fits in well with these determinations.

Models for hyperconjugation

Having established a standard correlation for unsaturated molecules, we examined several models for the hyperconjugation effect of a methyl group, using the relatively abundant data on electron-impact ionization potentials available for unsaturated hydrocarbons and radicals containing methyl groups. The first extensive theoretical treatment of hyperconjugation was that of Mulliken *et al.*,[21] who used a molecular orbital theory with inclusion of overlap. The hyperconjugative effect of the methyl group in this work was considered to operate through a *p* orbital on the methyl

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[16] S. F. Mason, *J. Chem. Soc.* 808 (1958).

[17] N. Muller and R. S. Mulliken, *J. Amer. Chem. Soc.* **80**, 3489 (1958).

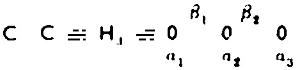
[18] D. F. Hornig, *J. Amer. Chem. Soc.* **72**, 5772 (1950); R. S. Mulliken and R. G. Parr, *J. Chem. Phys.* **19**, 1271 (1951); C. A. Coulson and S. C. Altmann, *Trans. Faraday Soc.* **48**, 293 (1952); G. Glockler, *Disc. Faraday Soc.* **10**, 26 (1951).

[19] G. J. Hoijtink and J. van Schooten, *Rec. Trav. Chim. Pays-Bas* **71**, 1089 (1952); *Ibid.* **72**, 691, 903 (1953).

[20] G. G. Hall, *Proc. Roy. Soc.* **A213**, 113 (1952).

[21] R. S. Mulliken, C. A. Rieckc and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941).

carbon and a virtual p orbital formed by the three hydrogens operating as a pseudo-atom. In effect, the methyl group is treated in the simple theory as a vinyl group with modified α and β parameters (see Fig. 3).



$$\mathrm{C} \quad \mathrm{C} \equiv \mathrm{H}_3 \equiv \underset{\alpha_1}{0} \overset{\beta_1}{} \underset{\alpha_2}{0} \overset{\beta_2}{} \underset{\alpha_3}{0}$$

FIG. 3. The methyl group as a modified vinyl group in the simple theory

The several subsequent treatments have differed mainly in the values assigned to these parameters and in the inclusion or neglect of overlap. The different parameters used are commonly given in terms of the standard α and β by use of equations such as (8) and (9). Values assigned by various authors to the different parameters associated with equations (8) and (9) and with Fig. 3 have been in the following ranges: h_1, 0 to $-0{\cdot}1$; h_2, 0 to $-0{\cdot}1$; h_3, 0 to $-0{\cdot}5$; k_1, $0{\cdot}5$ to $0{\cdot}8$; k_2, $2{\cdot}0$ to $4{\cdot}8$.[22]

$$\alpha_r = \alpha + h_r\beta \tag{8}$$

$$\beta_r = k_r\beta \tag{9}$$

Conjugation model (model C)

After reviewing the various values for the parameters used in the literature, we adopted the values $h_1 = 0$, $h_2 = -0{\cdot}1$, $h_3 = -0{\cdot}3$, $k_1 = 0{\cdot}8$ and $k_2 = 2{\cdot}8$. In setting up the energy matrices, methyl groups were treated as vinyl groups with these parameter values. The energies of each hydrocarbon or radical and the corresponding cation were carried through one cycle of iteration as described above. The χ values for

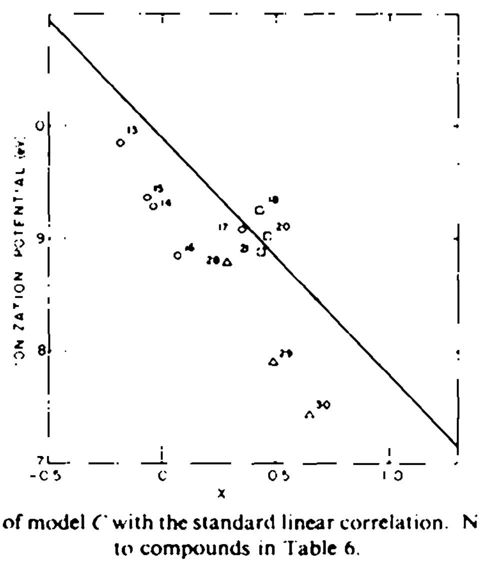


FIG. 4. Comparison of model C with the standard linear correlation. Numbers correspond to compounds in Table 6.

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[22] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.* **45**, 339 (1949); C. A. Coulson and V. A. Crawford, *J. Chem. Soc.* 2052 (1953); D. Peters, *Ibid.* 646 (1957); A. Loftus *J. Amer. Chem. Soc.* **79**, 24 (1957); N. Muller, L. W. Pickett and R. S. Mulliken, *Ibid.* **76**, 4770 (1954); Y. I'Haya *J. Chem. Phys.* **23**, 1165, 1171 (1955); Y. I'Haya, *Bull. Chem. Soc., Japan* **28**, 369, 376 (1955); H. H. Jaffe, *J. Chem. Phys.* **20**, 778 (1952); B. Pullman, M. Mayot and G. Berthier. *Ibid.* **18**, 257 (1950); A. Pullman and J. Metzger, *Bull. Soc. Chim. Fr.* **15**, 1021 (1948); G. Berthier and B. Pullman, *Trans. Faraday Soc.* **45**, 484 (1949); E. Heilbrenner and M. Simonetta, *Helv. Chim. Acta* **35**, 1049 (1952).

a number of methyl-substituted olefins, polyenes, aromatic hydrocarbons and radicals and the corresponding ionization potentials calculated from equation (4) are listed in Table 6, together with the experimental ionization potentials. The results are also plotted in Fig. 4. Comparison of the experimental points in Fig. 4 with the standard correlation line shows extremely poor agreement. Clearly the conjugation model, at least with the parameters assumed, is a poor one for the hyperconjugative effect of a methyl group. In general the model gives much less stabilization of a carbonium ion than does a methyl group.

Inductive model (model I)

Mackor *et al.*[23] have recently used an inductive model successfully for the effect of a methyl group on the basicities of aromatic hydrocarbons. In this model, any conjugation effect to a methyl group is ignored. Instead the methyl group by its inductive effect is considered to make the attached carbon somewhat more electropositive by the assignment of a small negative $\Delta\alpha$. Wheland and Pauling[24] have used a similar model in their original treatment of the orientation effect in aromatic substitution. Preliminary calculations suggested the use of $\delta\alpha = 0{\cdot}5\ \beta$. By using Lossing's values for the ionization potentials of *iso*propyl and *tert.*-butyl radicals (see Table 6), a damping effect of further methyl substitution on the same carbon is indicated. Hence, in the calculations, the results of which are listed in Table 6, the following values of $\delta\alpha$ were used for different extents of methyl substitution: $-0{\cdot}5\beta$ (one methyl group), $-0{\cdot}9\beta$ (two methyl groups), $-1{\cdot}1\beta$ (three methyl groups). If Stevenson's values for *iso*propyl and *tert.*-butyl radicals (see Table 6) are used, the damping factor disappears. These calculations were carried out before ω was established as 1·4. The $\delta\alpha$ values used were

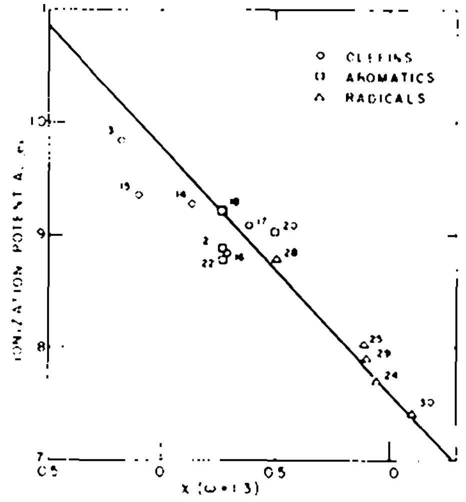

FIG. 5. Comparison of model *I* with correlation line for $\omega = 1{\cdot}3$. Numbers refer to compounds in Table 6.

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[23] E. L. Mackor, G. Dallinga, J. H. Kruizinga and A. Hofstra, *Rec. Trav. Chim. Pays-Bas* **75**, 836 (1956); E. L. Mackor, A. Hofstra and J. H. Van der Waals, *Trans. Faraday Soc.* **54**, 186 (1958).

[24] G. W. Wheland and L. Pauling, *J. Amer. Chem. Soc.* **57**, 2086 (1935).

Table 6. Comparison of calculated and experimental ionization potentials of various models of a methyl group

No.	Compound	$I_{\text{expt.}}$ (eV)	Model C x	Model C $I_{\text{calcd.}}$ (eV)	Model I x (ω 1·3)	Model I $I_{\text{calcd.}}$ (eV) (ω 1·3)	Model I-C x	Model I-C $I_{\text{calcd.}}$ (eV)
13	Propylene	9·84^{25}	0·18	10·26	0·23	10·28	0·065	10·02
14	2-Butene (*trans*)	9·28^{25}	0·04	9·96	0·08	9·61	0·214	9·43
15	*iso*Butene	9·35^{25}	0·06	10·01	0·15	10·11	0·103	9·66
16	Trimethyl-ethylene	8·85^{25}	0·06	9·75	0·24	9·27	0·389	9·07
17	Isoprene	9·08^{26}	0·35	9·14	0·32	9·09	0·397	9·04
18	Toluene	9·23^{26}	0·43	8·97	0·26	9·21	0·302	9·24
20	*m*-Xylene	9·02^{27}	0·46	8·91	0·42	8·88	0·392	9·05
21	*p*-Xylene	8·88^{27}	0·44	8·95	0·21	9·33	0·321	9·20
22	Mesitylene	8·79^{27}	–	—	0·18	9·39		—
24	α-Methylallyl	7·71^{28}	–		0·85	7·95	0·871	8·04
25	β-Methylallyl	8·03^{28}	—	–	0·83	7·99	0·870	8·04
26	*m*-Methyl-benzyl	7·65^{29}	—	–		–	0·990	7·79
27	*p*-Methyl-benzyl	7·46^{29}	—	–		–	1·033	7·74
28	Ethyl	8·78^{30} 8·67^{31}	0·28	9·29	0·50	8·71	0·572	8·67
29	*iso*Propyl	7·90^{30} 7·43^{32}	0·49	8·85	0·90	7·84	0·959	7·86
30	*tert.*-Butyl	7·42^{33} 6·90^{32}	0·64	8·53	1·10	7·40	1·253	7·24

determined as the best values for ω = 1·3. The calculated ionization potentials in Table 6 and the correlation line in Fig. 5 are those derived from a linear correlation with the standard points, with ω = 1·3. The δx values would probably require slight alterations for use with ω = 1·4. From the results listed in Table 6 and plotted in Fig. 5, it is apparent that the correlation is fair. Because of the simplicity of the model, this type of treatment would probably be satisfactory for many purposes. For the present purposes, however, we sought a model which would not only reproduce experimental ionization potentials to within a few tenths of an electron volt but would also reproduce trends within related families of molecules. Model I shows serious deficiencies in reproducing patterns with related compounds; for example, the difference between

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[25] R. E. Honig, *J. Chem. Phys.* **16**, 105 (1948).

[26] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.* **20**, 1021 (1952).

[27] F. H. Field and J. C. Franklin, *J. Chem. Phys.* **22**, 1895 (1954).

[28] C. A. McDowell, F. P. Lossing, I. H. S. Henderson and J. B. Farmer, *Canad. J. Chem.* **34**, 345 (1956).

[29] J. B. Farmer, F. P. Lossing, O. G. H. Marsden and C. A. McDowell, *J. Chem. Phys.* **24**, 52 (1956).

[30] J. B. Farmer and F. P. Lossing, *Canad. J. Chem.* **33**, 861 (1955).

[31] J. A. Hipple and D. P. Stevenson, *Phys. Rev.* **63**, 121 (1943).

[32] D. P. Stevenson, personal communication; see *Disc. Faraday Soc.* **10**, 35 (1951).

[33] F. P. Lossing, personal communication.

2-butene and *iso*butene is exaggerated; there is almost no calculated difference between α- and β-methylallyl radicals (*vide infra*). This situation would not be expected to change significantly for appropriate calculations with ω = 1·4. Nevertheless, model *I* showed much better over-all agreement than did model *C*.

Inductive–conjugation model (model I-C)

The encouraging results with the inductive model suggested its combination with the conjugation model. The methyl group is again treated as a modified vinyl group but the attached carbon is made effectively electropositive by the assignment of a negative $\delta\alpha$. Based on some preliminary calculations, we adopted the following values of h and k relating to the α and β quantities in Fig. 3: h_1, 0·3; h_2, 0·3; h_3, 0·6; k_1, 0·8; k_2, 2·8. The values of α assigned to the carbon and hydrogen of the methyl group are such as to make these atoms at least as electropositive as the attached carbon. For compounds containing two or three methyl groups on a single carbon, corresponding values used for h_1 are -0·6 and 0·9, respectively; i.e., no damping factor was used. The results of the calculations carried through one iteration are listed in Table 6 and are plotted in Fig. 6. In Fig. 6, the Lossing values for *iso*propyl and *tert.*-butyl radicals were used. On the whole, this model is fairly successful. The average deviation between experimental and calculated ionization potentials is less than 0·2 eV. On closer examination, however, we find important limitations in tracing the patterns within families of compounds. For example, α-methylallyl radical and β-methylallyl radical calculate to have the same ionization potential. We would expect a conjugated methyl group to stabilize allyl cation more than a cross-conjugated methyl group; experimentally, these radicals differ in ionization potential by 0·3 eV. Similarly, the methyl group in *p*-methylbenzyl radical calculates to provide substantially less stabilization of the cation than is experimentally observed. Consequently,

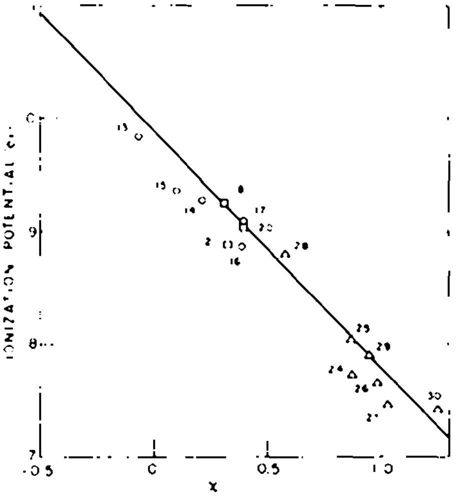

Fig. 6. Comparison of model *I-C* with experimental ionization potentials, with ω = 1·4. Numbers correspond to compounds in Table 6.

TABLE 7. CALCULATIONS FOR MODEL H

No.	Compound	$I_{\text{expt.}}$ (eV)	M hydro-carbon	M cation	x	$I_{\text{calcd.}}$ (eV)	Hyperconjugation per methyl: Hydro-carbon	Hyperconjugation per methyl: Cation
13	Propylene	9·84[24]	8·889	8·870	0·019	9·92	0·149β	0·500β
14	2-Butene (*trans*)	9·28[24]	15·624	15·930	0·306	9·23	0·142	0·480
15	*iso*Butene	9·35[24]	15·644	15·890	0·246	9·36	0·152	0·460
16	Trimethyl-ethylene	8·85[24]	22·363	22·914	0·551	8·72	0·141	0·448
17	Isoprene	9·08[25]	11·392	11·839	0·447	8·94	0·141	0·279
18	Toluene	9·23[26]	14·741	15·157	0·416	9·00	0·141	0·390
19	*o*-Xylene	8·97[27]	21·480	22·033	0·553	8·71	0·140	0·333
20	*m*-Xylene	9·02[26]	21·484	22·031	0·547	8·73	0·142	0·332
21	*p*-Xylene	8·88[26]	21·480	21·987	0·507	8·81	0·140	0·310
23	1, 2, 3-Tri-methyl-benzene	8·75[27]	28·217	28·909	0·692	8·42	0·139	0·314
24	α-Methylallyl	7·71[27]	9·595	10·627	1·032	7·70	0·167	0·414
25	β-Methylallyl	8·03[27]	9·566	10·453	0·887	8·01	0·138	0·240
26	*m*-Methyl-benzyl	7·65[28]	15·462	16·529	1·067	7·64	0·167	0·414
27	*p*-Methyl-benzyl	7·46[28]	15·467	16·579	1·112	7·53	0·138	0·240
28	Ethyl	8·78[29]	6·784	7·410	0·626	8·56	0·184	0·810
		8·67[30]	—	—	—	—	—	—
29	*iso*Propyl	7·90[29]	13·552	14·634	1·082	7·60	0·176	0·717
		7·43[31]	—	—	—	—	—	—
30	*tert.*-Butyl	7·42[32]	20·307	21·750	1·443	6·83	0·169	0·650
		6·90[31]	—	—	—	—	—	—

this model is of limited usefulness. This situation is not improved by any reasonable changes in the values used for the parameters. At least in the simple theory with neglect of overlap, the vinyl model is a poor representation of a methyl group.

Heteroatom model (model H)

Matsen[34] and Stevenson[35] have used a model in which the methyl group is treated as a single heteroatom, X, which contributes a pair of electrons to the π system. In applying this model we used $\beta_{C-X} = 0{\cdot}8\beta$ and tried various values of α_X. Best results were obtained with $h_X = 3{\cdot}3$. The α of the attached carbon was not altered. The results of the calculations with this model, carried through one cycle of iteration, are listed in Table 7 and are plotted in Fig. 7. Table 7 also records the total bonding energies in the form of M values for each hydrocarbon or radical and the corresponding

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[34] F. A. Matsen, *J. Amer. Chem. Soc.* **72**, 5243 (1950).

[35] D. P. Stevenson, personal communication; also see F. H. Field and J. L. Franklin, *Electron Impact Phenomena* p. 124. Academic Press, New York (1957).

cation. Each total energy is of the form of equation (10) in which n is the number of π electrons and $M\beta$ is the total π-bonding energy:

$$E = n\alpha + M\beta \tag{10}$$

The agreement, on the whole, is quite good. The aliphatic olefins fit well. The trend in the aromatic hydrocarbons is reproduced except for *p*-xylene. It is interesting that all four models used give a higher calculated ionization potential for *p*-xylene than for *m*-xylene and suggest that the experimental values may be slightly in error. The aromatic hydrocarbons in absolute value, however, are significantly displaced from the correlation line (*vide infra*). The effect of a methyl group attached to allyl radical or to benzyl radical is excellently accounted for in this model. The average deviation between experimental and calculated ionization potentials for these three sets of compounds is only 0·11 eV. The situation with the simple alkyl radicals is difficult to evaluate. The calculated result for ethyl radical agrees fairly well with both Stevenson's and Lossing's experimental values. The values given by these authors differ by 0·5 eV for *iso*propyl radicals and for *tert*.-butyl radicals (see Table 7). The points for the three alkyl radicals are shown by pairs of crosses in Fig. 7. All we can say at this time is that the calculated results are apparently reasonably close to the actual values. The calculated ionization potentials for these simple radicals are very dependent on the parameter values used. The observed trends suggest that $\beta_{C\text{-}X} = 0{\cdot}7\beta$ may be a better assumption. For this value of $\beta_{C\text{-}X}$, preliminary results indicate that the associated α_X has a h_X value of about 3.0.

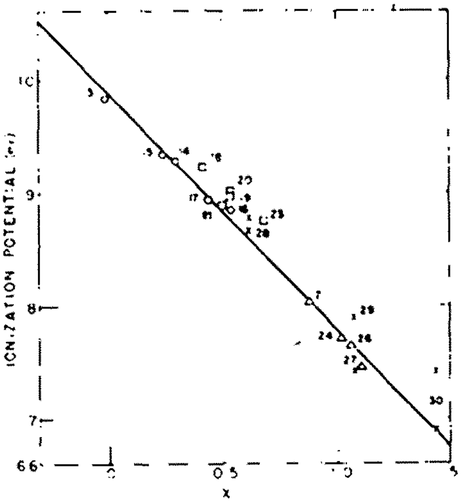

Fig. 7. Comparison of model *H* with experiment. Numbers correspond to compounds in Table 7.

It should be noted that in the model used the methyl group heteroatom was considered to have no inductive effect on the attached carbon; α for the attached carbon was not changed and no "auxiliary inductive parameter"[34] was used. When attempts were made to include such an inductive effect by assigning a small negative h to the

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[34] R. D. Brown, *Quart. Rev.* 6, 63 (1952).

TABLE 8. SUCCESSIVE ITERATIONS OF PROPYLENE CATION (MODEL H)

No. of iterations	q_1	q_2	q_3	χ
0	1·918	0·536	0·547	—
1	1·884	0·561	0·555	0·019
2	1·890	0·551	0·559	0·044
3	1·889	0·557	0·554	0·033
4	1·889	0·553	0·558	0·035
5	1·889	0·556	0·556	0·035
6	1·889	0·554	0·557	0·035
∞	1·889	0·554	0·556	0·035

TABLE 9. SUCCESSIVE ITERATIONS OF ETHYL CATION (MODEL H, $h_x = 3·5$)

No. of iterations	q_1	q_2	χ
0	1·909	0·091	—
1	1·827	0·173	0·572
2	1·850	0·150	0·765
3	1·844	0·156	0·710
4	1·846	0·154	0·725
5	1·845	0·155	0·721
6	1·845	0·155	0·722
7	1·845	0·155	0·722

attached carbon, it was found impossible to get reasonable agreement with the correlation curve.

In several systems we examined the effect of further iteration to determine whether this model would converge generally to a self-consistent energy and pattern of charge densities and to see if the self-consistent value differed importantly from the first iterated values. Propylene cation (Table 8) and ethyl cation (Table 9) converged rapidly. The self-consistent value of χ for propylene differs from first iterated value by an amount which corresponds to 0·1 eV and agrees better with the experimental value. The calculations in the ethyl case were made using a value of h for the methyl group heteroatom, X, of 3·5. The final χ value differed from the first iterated value by an amount which corresponds to a reduction in the ionization potential of 0·3 eV. A similar result would be expected for $h = 3·3$. This result further suggests the use of a smaller β_{C-X}. Toluene (Table 10) was found to be unstable to successive iterations. The charge densities as in the benzyl case oscillated and gave progressive divergence. The charge densities of the first and second iterations were averaged and were used to initiate a new series of iterations. The use of these charges (SCF charges) gave a first iteration χ corresponding to a calculated ionization potential of 9·17 eV, in good agreement with experiment. However, the system was still unstable and showed the same type of progressive divergence noted above, probably for the same reasons as the instability of benzyl.

Hyperconjugation energies tabulated in Table 7 were derived for each of the hydrocarbons or radicals and the corresponding cations by subtracting from the total energy the energy of the parent unsubstituted compound and the energies of the attached methyl groups. The hyperconjugation energies per methyl group for the hydrocarbons and radicals are relatively constant at 0·14–0·18β (7–9 kcal/mole). These relatively large energy values will become substantially reduced when the effects of bond contraction and electron correlation are considered. The hyperconjugation energies for the cations are much larger and more variable. The results agree with the common organic chemical view that a methyl group stabilizes a carbonium ion much more than a neutral hydrocarbon or radical. The observed variations also agree with qualitative organic thought; the methyl group in ethyl cation does much better at stabilizing a positive charge than does the methyl group in crotyl cation which in turn is better than the methyl group in *p*-methylbenzyl cation.

TABLE 10. SUCCESSIVE ITERATIONS OF TOLUENE CATION (MODEL *H*)

No. of iterations	q_7	q_1	q_2	q_3	q_4	χ
Starting with Hückel charges						
0	1·935	0·654	0·920	0·933	0·705	–
1	1·969	1·073	0·726	0·700	1·107	0·416
2	1·934	0·564	0·964	1·002	0·569	0·552
3	1·970	1·120	0·704	0·653	1·197	0·555
4	1·936	0·548	0·965	1·030	0·526	0·636
5	1·970	1·123	0·706	0·634	1·228	0·597
.	.	.	.	.	.	.
10	1·936	0·556	0·942	1·062	0·500	0·675
11	1·969	1·105	0·723	0·612	1·256	0·620
Starting with SCF charges						
0	1·952	0·819	0·845	0·851	0·838	
1	1·928	0·667	0·920	0·929	0·708	0·334
2	1·696	1·067	0·727	0·702	1·105	0·420
3	1·934	0·567	0·963	1·001	0·570	0·547
4	1·970	1·118	0·704	0·654	1·196	0·553
5	1·936	0·549	0·965	1·030	0·526	0·635

Because of the simplicity of the simple molecular orbital theory and its many theoretical deficiencies the success or failure of a model in the simple theory cannot strictly be used as evidence for or against specific effects embodied in the model. The success of model *H*, however, does *suggest* that appropriately oriented sigma electrons in an alkyl group are available for π conjugation; i.e., that substantial stabilization of carbonium ions by hyperconjugation does occur. There is no reason in principle why other alkyl groups could not also be treated by the same model, albeit, perhaps with slightly altered values of β_{C-X} and α_X. There are not enough ionization potential data, however, for meaningful comparisons using the present technique.

Other systems

The techniques described in this paper were applied to the calculation of the ionization potentials of several compounds which have not been experimentally determined. These values are listed in Table 11. It is interesting that the β-phenylallyl radical calculates to have an ionization potential similar to that of the allyl radical itself; cinnamyl radical, in which the phenyl group is now directly conjugated, calculates to have a lower ionization potential. This effect of conjugation versus non-conjugation is also seen to a lesser extent in 1- and 2-phenylbutadiene.

TABLE 11. IONIZATION POTENTIALS OF SOME UNMEASURED COMPOUNDS

Compound	x	I (eV)
1-Methylbutadiene	0·510	8·80
Cinnamyl radical	1·094	7·57
β-Phenylallyl radical	0·798	8·20
Stilbene	0·687	8·43
1-Phenylbutadiene	0·648	8·52
2-Phenylbutadiene	0·545	8·73
Azulene	0·748	8·30
Pyrene	0·826	8·13

Calculations

Most of the calculations were performed with an IBM 701 digital computer. The secular matrix was input as the half-matrix. The off-diagonal elements, which are non-zero only when a bond exists between the corresponding atoms, were used to set up a list of the bonds which was later printed as a "bond-key" and served as a check that the input matrix actually corresponded to the desired compound. The matrix diagonalization program which utilized the Jacobi method was written by Mr. John Newhaus. The eigenvectors and eigenvalues were used to compute the required charge densities, bond orders and atom–atom polarizabilities by the usual equations.[15] Different programs were written for the calculations using equation (6), the repeated successive iterations of various compounds and calculations with various values of ω. The last program gave single iteration results with the ω values of 0·5, 0·75, 1·0 and 1·5. Unfortunately, because of an error in the program, the calculations for each value of ω after the first were made not on the Hückel charge densities but on the charge densities resulting from the previous ω. Hence the interpolated values for $\omega = 1{\cdot}4$ for a number of cases in model I and model I-C correspond in effect to more than one cycle of iteration. The results for these compounds differ from the true first iterated values by an amount which corresponds to only a few hundredths of an electron volt in the ionization potential. In the programs used with the heteroatom model the appropriate changes were incorporated to account for the contribution of two electrons by each "heteroatom".

Acknowledgement—We thank Dr. D. P. Stevenson for several valuable discussions and for information in advance of publication.