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A Molecular Orbital Study of Ionization Potentials of Organic Compounds Utilizing the ω-Technique[1]

BY ANDREW STREITWIESER, JR.[2]

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The ω-technique in the simple l.c.a.o. theory is applied to a variety of organic compounds. A comparison of the method with Pople's s.c.f. method shows that the use of the ω-parameter provides for electron repulsion effects in an empirical manner. Such a procedure is required when dealing with cations; for example, in the simple l.c.a.o. theory the ionization potentials of methyl, allyl and benzyl radicals should be identical. The experimental values which vary over a 2 e.v. range are well reproduced by the ω-technique. The method is applied to several organic radicals of current interest, including cyclopentadienyl and tropylium. Agreement with experimental results, where available, is excellent. With aromatic hydrocarbons, however, including examples of the non-alternant hydrocarbon type, the simple l.c.a.o. procedure gives a good correlation of ionization potentials: the ω-technique provides no advantage with such systems alone. Heteroatoms can be treated given two additional parameters characteristic of the heteroatom. A methyl group is treated as a pseudo-heteroatom donating two electrons to the π-system with parameter values differing slightly from those previously employed. Good agreement between calculated and experimental ionization potentials was obtained for a large number of methyl substituted hydrocarbons and radicals. Experimental potentials were used for chlorine, nitrogen and oxygen compounds to determine empirically the appropriate parameter values for those elements. The derived values are compared with those used previously in other applications in the literature. The ω-technique is extended to calculations of acetylenic and allenic systems. A simple model of an alkane is presented which requires only one additional disposable parameter. The derived value of zero for this parameter is used with the ω-technique to give good agreement between calculated and experimental ionization potentials for a variety of alkanes.

1. The ω-Technique

Stevenson[3,4] has obtained the electron impact ionization potentials of several aromatic hydrocarbons and has demonstrated an excellent correlation[5] with the energy required to remove an electron from the highest occupied molecular orbital as calculated from the simple (Hückel) molecular orbital method. The correlation fails, however, when applied to olefins and to radicals; for example, methyl, allyl and benzyl are radicals of the odd alternant hydrocarbon (a.h.) type[6] in which the highest occupied orbital is a non-bonding molecular orbital (n.b.m.o.). According to the simple l.c.a.o. theory the three radicals should have identical ionization potentials. The experimental ionization potentials are 9.88, 8.22 and 7.76 e.v., respectively,[7] a range of almost 50 kcal.!

This defect of the simple theory undoubtedly arises from a neglect of electronic repulsion terms; however, we have shown previously[4] that a simple modification of the Hückel theory gives good results even with these systems. In this modification which is taken from earlier work of Wheland and Mann[8] and which we call the "ω-technique,"[9] the energy of the positive ion formed on ionization is obtained after altering the coulomb integrals of individual carbons in proportion to the net positive charge associated with each carbon. In equation

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[2] Alfred P. Sloan Fellow; National Science Foundation Science Faculty Fellow, 1959–1961.

[3] D. P. Stevenson, private communication; *cf.* ref. 4.

[4] A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **6**, 149 (1959).

[5] F. A. Matsen has reported a similar correlation, *J. Chem. Phys.*, **24**, 602 (1956).

[6] C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940); C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A192**, 16 (1947).

[7] F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954); J. B. Farmer, I. H. Henderson, C. A. McDowell and F. P. Lossing, *ibid.*, **22**, 1948 (1954).

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

[9] The ω-symbol has been used previously in the same manner but without neglect of overlap by (a) N. Muller, L. W. Pickett and R. S. Mulliken, THIS JOURNAL, **76**, 4770 (1954); (b) N. Muller and R. S. Mulliken, *ibid.*, **80**, 3489 (1958).

1, ω is the proportionality constant determined empirically to be 1.4,[4,9b] q_r is the π-electron density on atom r and n_r is the number of π-electrons contributed by atom r (either one or two).

$$\alpha_r = \alpha_0 + \omega(n_r - q_r)\beta_0 \qquad (1)$$

The regression line correlating the electron impact ionization potential, **I**, with the calculated difference in bonding energy, χ (in units of β) between the positive ion and the neutral molecule, is[4]

$$I = 9.878 \pm 0.073 - (2.110 \pm 0.050)\chi \qquad (2)$$

The success of this method in correlating the ionization potentials of a number of hydrocarbons prompted the present extension to a number of new systems including radicals, non-alternant hydrocarbons, methyl, chlorine, oxygen and nitrogen substituted compounds, acetylenes, allenes and saturated hydrocarbons. The results are summarized in Table I and are discussed in subsequent sections. The total π-energies in the simple l.c.a.o. method are given in the form of equation 3 in which n is the total number of π-electrons, α_0 and β_0 are the standard coulomb and bond integrals, respectively.

$$E_\pi = n\alpha_0 + M\beta_0 \qquad (3)$$

Values of β_{rs} were assigned to different carbon–carbon bonds as follows: all "aromatic bonds" were given the value β; all "single bonds"[10] (*e.g.*, bonds which are single in all Kekule structures, such as the 9,10 bond in azulene) were assigned 0.9 β and the double bonds in acenaphthylene and fulvene were assigned 1.07 β. α and β values for the heteroatoms (methyl, chlorine, oxygen, nitrogen) are discussed below. The π-energy for the cation is given for the first cycle of iteration.

In all cases we have compared the calculated ionization potentials with the electron impact experimental values where these are available on the basis that such values represent vertical transitions. This presumption may be incorrect[11] and experimental photoionization and ultraviolet values have been included in the tables for comparison. However, it should be noted that the correlation curve was based on electron impact values; comparison with such values may result in better internal self-consistency.

2. Comparison with Pople's S.c.f. Theory

Introduction of the ω-parameter effects a heightening of the coulombic attraction between a π-electron and the effectively more electronegative carbon center. Alternatively, use of this parameter amounts to a recognition of decreased electronic repulsion in the electron-deficient molecule. It is of interest to compare this method with the semi-empirical molecular orbital method of Pople[12] in which electron repulsion terms are explicitly considered in a single-configuration theory. In this theory, which is derived from the self-consistent field theory developed by Roothaan,[12f] the matrix elements between atoms r and s are reduced with suitable approximations to[12a,12b]

$$F_{rr} = U_{rr} + \frac{1}{2}P_{rr}\gamma_{rr} + \sum_{s(\neq r)}(P_{ss} - 1)\gamma_{rs} \qquad (4)$$

$$F_{rs} = \beta_{rs} - \frac{1}{2}P_{rs}\gamma_{rs} \qquad (5)$$

U_{rr} corresponds approximately to α_r of the simple Hückel theory and β_{rs} has its usual meaning. P_{rs} has the same definition as the bond order, p_{rs}, of the simple theory but is defined between all pairs of atoms. P_{rr} corresponds to the electron densities in the Hückel theory, q_r; γ_{rs} are the electron repulsion terms. When the γ_{rs} terms are neglected, this theory reduces to the simple Hückel theory.[12a]

Two approximations to the Pople method may be considered. In the first we neglect all γ_{rs} except for r = s. Then

$$F_{rr} = U_{rr} + \frac{1}{2}q_r\gamma_{rr} \qquad (6)$$

$$F_{rs} = \beta_{rs} \qquad (7)$$

If these elements are compared to the matrix elements in the ω-approximation

$$F_{rr} = (\alpha_r + \omega\beta) - q_r\omega\beta \qquad (8)$$

$$F_{rs} = \beta_{rs} \qquad (9)$$

we find that the elements are the same except that the term in the diagonal elements containing an empirical parameter, $-q_r\omega\beta$, replaces a term $^1/_2q_r\gamma_{rr}$, in the former approximation. However, the magnitude of $^1/_2\gamma_{rr}$, 5.3 e.v.,[12c] differs substantially from $-\omega\beta$, 2.9 e.v. The value used for the parameter ω apparently allows for an average effect of other electrons. Our value of β obtained from the correlation line, eq. 2, −2.11 e.v., agrees closely with the value used by Pople, −2.130 e.v.[12a]

In the second approximation to the Pople method, we neglect all γ_{rs} except for r = s and for atoms r and s bonded. Since the bond distances are relatively constant, γ_{rs} may be replaced by $c\gamma_{rr}$, in which c is about 0.7.[12c] We obtain

$$F_{rr} = U_{rr} + \frac{1}{2}q_r + c\sum_{s}(q_s - 1)\gamma_{rr} \qquad (10)$$

in which the summation is now taken over the atoms s bonded to r. Thus, an analogous ω-treatment would differentiate among primary, secondary and tertiary carbons and would consider the charge densities of the adjoining carbons. A possible treatment of this sort might be of the type

$$F_{rr} = \alpha_0 + (1 - q_r)\omega\beta + \sum_{s}(1 - q_s)\omega'\beta \qquad (11)$$

which involves a second parameter, ω'. Our treatment amounts to neglecting the variations in the last term and includes it as an average effect within α. The approximation is again partially compensated by the choice of an empirical value for the coefficient of the second term. Hence, the ω-approximation may be considered to be related to Pople's method with additional simplifying approximations coupled with an empirical parameter; electron repulsion with distant atoms is treated as an average effect and is not given explicit form. Nevertheless, the difference between the methods is substantial, and the present analysis, although

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[10] The single bond in biphenyl was assigned 0.87 β.

[11] J. D. Morrison, *J. Chem. Phys.*, **21**, 1767 (1953); **29**, 1312 (1958).

[12] (a) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953); (b) A. Brickstock and J. A. Pople, *ibid.*, **50**, 901 (1954); (c) N. S. Hush and J. A. Pople, *ibid.*, **51**, 600 (1955); (d) J. A. Pople, *Proc. Royal Soc. (London)*, **A233**, 233 (1955); (e) J. A. Pople, *J. Phys. Chem.*, **61**, 6 (1957); (f) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 61 (1951).

TABLE I

IONIZATION POTENTIALS OF ORGANIC COMPOUNDS

Compound	Hydrocarbon radicals M,^{a} compound	M,^{a} cation	χ	I (e.v.) calcd., eq. 2	I (e.v.) electron impact	I (e.v.) ultraviolet and photoioniz.
Cyclopropenyl	3.000	4.933	1.933	5.80		
Cyclopentadienyl	5.854	6.356	0.502	8.82	8.69^{a}	
Tropylium	8.543	10.188	1.645	6.41	6.60^{a}	
1,2,3-Triphenylcyclopropenyl	28.683	30.341	1.658	6.38		
Perinaphthenyl	17.827	19.045	1.217	7.31		
Benzhydryl	17.301	18.465	1.164	7.42	7.32^{a}	
Triphenylmethyl	25.800	27.039	1.239	7.26		
Unsubstituted hydrocarbons						
Azulene	13.287	14.02	0.74	8.32^{b}		
Acenaphthylene	16.560	17.106	.546	8.73		
Fluoranthene	22.348	22.980	.632	8.54		
Fulvene	7.539	7.924	.385	9.07		
Biphenyl	16.293	16.810	.517	8.79		
Methyl compounds^{l}						
Propylene	8.262	8.224	−0.038	9.96	9.84^{i}	9.73^{m}
2-Butene	14.374	14.633	.259	9.33	9.28^{i} 9.27^{o}	9.24^{m}
Isobutene	14.386	14.594	.208	9.44	9.35^{i} 9.26^{o}	
Trimethylethylene	20.489	20.974	.485	8.86	8.85^{i} 8.89^{o}	8.8^{m}
Tetramethylethylene	26.596	27.296	.700	8.40	8.53^{o}	
1,3-Pentadiene	10.770	11.262	.492	8.84	8.68^{o}	
Isoprene	10.766	11.199	.433	8.96	9.08^{c}	8.86^{m}
1,4-Pentadiene	10.526	10.969	.442	8.94	9.58^{o}	
Hexatriene	7.189	7.786	.597	8.62		
Cyclopentadiene	11.013	11.470	.457	8.91	8.9^{d}	8.58^{m}
Cycloheptatriene^{n}	13.374	14.316	.942	7.89		
Toluene	14.115	14.527	.411	9.01	9.23^{c}	8.82^{m}
o-Xylene	20.228	20.758	.531	8.76	8.97^{e}	8.56^{m}
m-Xylene	20.231	20.758	.527	8.77	9.02^{e}	8.56^{m}
p-Xylene	20.229	20.723	.495	8.83	8.88^{e}	8.45^{m}
1,2,3-Trimethylbenzene	26.340	27.000	.659	8.49	8.75^{e}	
α-Methylnaphthalene	19.802	20.496	.695	8.41		7.96^{m}
β-Methylnaphthalene	19.799	20.464	.665	8.48		
Indene	16.792	17.383	.591	8.63		
Fluorene	22.593	23.217	.625	8.56		
Ethyl	6.155	6.730	.575	8.67	8.78^{f} 8.67^{g}	
i-Propyl	12.297	13.293	.996	7.78	7.90^{f} 7.43^{h}	
t-Butyl	18.429	19.760	1.332	7.07	7.42^{a} 6.90^{h}	
α-Methylallyl	8.966	9.973	1.007	7.75	7.71^{j}	
β-Methylallyl	8.940	9.812	0.872	8.04	8.03^{j}	
α,α-Dimethylallyl	15.103	16.306	1.203	7.34		
α,γ-Dimethylallyl	15.095	16.296	1.201	7.34		
m-Methylbenzyl	14.836	15.894	1.058	7.65	7.65^{k}	
p-Methylbenzyl	14.840	15.939	1.100	7.56	7.46^{k}	
Chlorine compounds						
Chloromethyl	5.648	5.866	0.218	9.42		
Dichloromethyl	11.295	11.700	.406	9.02		
Trichloromethyl	16.80	17.39	.59	8.64	8.78^{p}	
α-Chloroallyl	8.469	9.329	.860	8.06		
β-Chloroallyl	8.461	9.273	.812	8.16		
Vinyl chloride	7.776	7.533	− .243	10.39		10.00^{q}
1,1-Dichloroethylene	13.411	13.279	− .132	10.16		9.46^{r}
1,2-Dichloroethylene	13.410	13.287	− .123	10.14		9.62^{s} 9.96^{t}
Trichloroethylene	19.046	19.017	− .029	9.94	9.94^{u}	9.47^{m}
Tetrachloroethylene	24.679	24.761	.082	9.71		9.55^{v}
Chlorobenzene	13.634	13.986	.352	9.14	9.42^{u}	8.8^{w} 9.07^{m}
o-Dichlorobenzene	19.267	19.654	.387	9.06		9.06^{s}
p-Dichlorobenzene	19.267	19.651	.384	9.07		8.93^{s}
o-Chlorotoluene	19.748	20.201	.453	8.92		8.84^{s}

TABLE I (*continued*)

Compound	M,[a] compound	M,[a] cation	χ	I (e.v.) calcd., eq. 2	I (e.v.) electron impact	I (e.v.) ultraviolet and photoioniz.
	Hydrocarbon radicals					
m-Chlorotoluene	19.749	20.199	.450	8.93		8.83[s]
p-Chlorotoluene	19.748	20.189	.441	8.95		8.69[m]
Methyl chloride	11.60	10.91	− .69	11.33[x]	11.35[m]	11.28[m]
		Oxygen compounds				
Furan	10.356	10.807	0.451	8.93	9.03[u,y]	8.89[m,s]
α-Methylfuran	16.455	17.072	.617	8.58		8.39[s]
Phenol	13.490	13.894	.404	9.03	9.02[u,y]	8.50[m]
Anisole	19.492	19.902	.410	9.01	8.56[z]	8.20[m]
Methyl vinyl ether	13.637	13.595	− .042	9.97		8.93[s]
p-Hydroxybenzyl	14.215	15.302	1.087	7.58		
m-Methoxybenzyl	20.212	21.262	1.050	7.66		
p-Methoxybenzyl	20.215	21.304	1.089	7.58		
Benzofuran	16.121	16.692	0.571	8.67		
Dibenzofuran	21.298	22.538	.609	8.59		
Methyl alcohol	11.400	10.97	− .43	10.79	10.88[m]	10.85[m]
Dimethyl ether	17.400	17.24	− .16	10.22	10.5[m]	10.00[m]
		Nitrogen compounds				
Aniline	11.566	12.181	0.615	8.58	8.23[z]	7.70[m]
Pyrrole	8.574	9.177	.602	8.61	8.97[m,z]	8.20[s] 8.9[aa]
Pyrrocoline	13.743	14.980	1.237	7.27		
Methylamine	9.400	9.55	0.15	9.56	9.41[m,bb]	8.97[cc]
Dimethylamine	15.400	15.81	.41	9.01	9.55[m] 8.93[bb]	8.24[cc]
Trimethylamine	21.400	21.98	.58	8.66	9.3[m] 8.32[bb]	7.82[cc]
		Acetylenes				
Acetylene	2.800	2.100	−0.700	11.36	11.42[m]	
Methylacetylene	8.929	8.660	− .268	10.44	10.39[m] 10.54[dd]	
Dimethylacetylene	15.049	15.138	.089	9.69	9.85[m]	
Vinylacetylene	5.307	5.493	.185	9.49	9.90[m]	
Phenylacetylene	11.143	11.510	.368	9.10	9.15[m]	
Propargyl	3.464	4.193	.729	8.34	8.25[m]	
Diacetylene	5.974	6.021	.047	9.78		
Diphenylacetylene	19.509	20.137	.628	8.55		
Methylphenylacetylene	17.276	17.790	.514	8.79		
γ-Phenylpropargyl	11.915	12.954	1.038	7.69		
γ-Methylpropargyl	9.608	10.555	0.947	7.88		
		Allenes				
Allene	11.343	11.192	−0.151	10.19	10.16[ee]	
Methylallene	17.451	17.618	.167	9.53	9.57[ee]	
1,1-Dimethylallene	23.557	23.962	.405	9.02		
Butatriene-π_z,[ff]	5.332	5.617	.285	9.28		
Butatriene-π_y,[ff]	20.424	20.535	.111	9.64		
		Alkanes[gg]				
Methane			−1.600	13.25	13.12[m]	
Ethane			−0.900	11.78	11.65[m]	
Propane			− .550	11.04	11.21[m]	
Butane			− .393	10.71	10.80[m]	
Pentane			− .316	10.54	10.55[m]	
Hexane			− .276	10.46	10.43[m]	
Heptane			− .251	10.41	10.35[m]	
Octane			− .236	10.38	10.24[m]	
Nonane			− .227	10.36	10.21[m]	
Decane			− .214	10.33	10.19[m]	
Polymethylene			− .200	10.30	(10.15)[hh]	
Cyclopropane			− .666	11.29	10.23[ii]	
Cyclobutane			− .550	11.04		
Cyclopentane			− .480	10.89	11.1[jj]	
Cyclohexane			− .433	10.79	10.4−11.0[kk]	
Cycloheptane			− .400	10.72		
Cyclooctane			− .375	10.67		
Isobutane			− .434	10.79	10.79[o,ll]	
2-Methylbutane			− .297	10.50	10.60[o]	

TABLE I (*continued*)

2-Methylpentane	− .254	10.41	10.34[o]
3-Methylpentane	− .274	10.46	10.30[o]
2,3-Dimethylbutane	− .317	10.55	10.24[o]
Neopentane	− .375	10.67	10.29[mm]

[a] F. P. Lossing, private communication; F. P. Lossing J. B. DeSousa, THIS JOURNAL, **81,** 281 (1959); A. G. Harrison and F. P. Lossing *ibid.*, **82,** 1052 (1960). [b] The previous calculated **I**, 8.30 e.v.,[4] results from azulene with all β's equal. [c] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20,** 1021 (1952). [d] J. Hissel, *Bull. soc. roy. sci. Liege*, **21,** 457 (1952). Another value, 8.4 ± 0.1 e.v., is quoted without additional details by W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A179,** 201 (1941), but this value is lower than the spectroscopic value, 8.58 e.v. [e] F. H. Field and J. L. Franklin, *J. Chem. Phys.*, **22,** 1895 (1954). [f] J. B. Farmer and F. P. Lossing, *Canad. J. Chem.*, **33,** 861 (1955). [g] J. A. Hipple and D. P. Stevenson, *Phys. Rev.*, **63,** 121 (1943). [h] D. P. Stevenson, private communication; see *Discussions Faraday Soc.*, **10,** 35 (1951). [i] R. E. Honig, *J. Chem. Phys.*, **16,** 105 (1948). [j] C. A. McDowell, F. P. Lossing, I. H. S. Henderson and J. B. Farmer, *Canad. J. Chem.*, **34,** 345 (1956). [k] J. B. Farmer, F. P. Lossing, O. G. H. Marsden and C. A. McDowell, *J. Chem. Phys.*, **24,** 52 (1956). [l] Model H of ref. 4 was used with the parameter values: $h_x = 3.0$; $k_{cx} = 0.7$. [m] Summarized in F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, and K. Watanabe, *J. Chem. Phys.*, **26,** 542 (1957). [n] Calculated assuming no interaction between the 2 and 7 positions. [o] Recently reported by J. Collin and F. P. Lossing, THIS JOURNAL, **81,** 2064 (1959). [p] Ref. 26. [q] W. C. Price and W. T. Tuttle, *Proc. Roy. Soc.* (*London*), **A174,** 207 (1940). [r] J. P. Teegan and A. D. Walsh, *Trans. Faraday Soc.*, **47,** 1 (1951). [s] K. Watanabe and T. Nakayama, ASTIA report no. AD-152934. [t] *trans*-Compound: T. M. Sugden, A. D. Walsh and W. C. Price, *Nature*, **148,** 373 (1941). [u] Ref. 27. [v] A. D. Walsh, *Trans. Faraday Soc.*, **41,** 35 (1945). [w] W. C. Price, *Chem. Revs.*, **41,** 257 (1947). [x] See text. [y] Ref. 32 and 33. [z] Ref. 40. [aa] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A179,** 201 (1941). [bb] Ref. 43. [cc] K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26,** 1773 (1957). [dd] J. Collin and F. P. Lossing, THIS JOURNAL, **80,** 1568 (1958). [ee] J. Collin and F. P. Lossing, *ibid.*, **79,** 5848 (1957). [ff] π_z refers to the "butadiene-like" π-system; π_y refers to the orthogonal "2-butene-like" π-system. [gg] χ determined from equations 17 and 18. [hh] Obtained by extrapolation. [ii] F. H. Field, *J. Chem. Phys.*, **20,** 1734 (1952). [jj] J. Hissel, *Bull. soc. roy. sci. Liege*, **21,** 457 (1952). [kk] Reported experimental values: 11.0 e.v. (A. Hustrulid, P. Kusch and J. T. Tate, *Phys. Rev.*, **54,** 1037 (1938); 11.0 e.v. (J. Hissel, ref. *d*); 10.4 e.v. (ref. 58). [ll] Other values range from 9.8–11.1 e.v.; see ref. 19 and 64. [mm] Actually the appearance potential of $C_4H_9^+$; neopentane gives no parent ion; see ref. 19, p. 119.

illuminating, can in no way be regarded as a justification for either method. As with any other semiempirical method, the proof as in the eating of the proverbial pudding lies in the final numerical results.

3. Radicals

In our previous paper[4] we showed that the ω-technique correlates well the ionization potentials of several radicals of odd a.h.'s. We now apply the ω-technique to the calculation of some additional radicals of general interest. The results are summarized in Table I. Cyclopentadienyl cation is degenerate because of its symmetry and according to the Jahn–Teller rule should not exist as such. Nevertheless, as in the similar case of benzene cation treated earlier[4] the positive charge was assumed to be evenly distributed around the molecule for application of equation 1. The predicted pattern for the series, cyclopropenyl, cyclopentadienyl and tropylium, 5.80, 8.82 and 6.41 e.v., respectively, is still in accord with qualitative expectations based on the Hückel theory. It is interesting that the ionization potential of cyclopentadienyl is higher than that of any other hydrocarbon radical, calculated or measured, except for methyl radical itself. The calculated values for cyclopentadienyl and tropylium radicals are in excellent agreement with the experimental electron impact values of Lossing,[13] 8.69 and 6.60 e.v., respectively. The relatively low ionization potentials calculated for tropylium radical and 1,2,3-triphenylcyclopropenyl radical are also in qualitative agreement with the known stability of the corresponding cations which have been isolated as salts.[14]

These calculations were carried through one cycle of iteration. In our previous paper,[4] we reported that further iterations with some cations gave convergence to values not greatly different from those of the first iteration. With benzyl and related cations, however, subsequent iteration gave progressive divergence. This effect has been studied further and has been found to be a function of the assumed value of ω. Benzyl cation gave convergence on repeated iteration using ω = 1.0. The total π-energy of the convergent value in this case, $M = 9.446$, differs little from that of the first iterated value, $M = 9.402$; the convergent or self-consistent values of the charge densities at each carbon differed from the average of the Hückel and first iteration values by only ±0.008 unit (average deviation; maximum deviation, 0.18 unit). Similar results were obtained with the cinnamyl and 2-phenylallyl cations. Iterations of benzyl cation with ω = 1.2 converged although ω = 1.3 gave a slow divergence. For values of ω = 0, 1.0, 1.2, the convergent values of χ, 0, 0.725 and 0.885, respectively, yield a good straight line which passes through the estimated "self-consistent" values of χ, 0.958 and 1.029, for ω = 1.3 and 1.4, respectively. The last value is close to the first iterated value for benzyl cation with ω = 1.4[4]; the difference corresponds to a change in the ionization potential of only 0.06 e.v. Clearly, in some cases the value of ω of 1.4 gives satisfactory energies although it overcompensates the electron distribution, probably because of reasons of symmetry among others. The eigenvectors of the molecular orbitals are expected to be an order of magnitude less accurate than the eigenvalues. This study confirms the validity of accepting first iterated values of the energies as sufficiently accurate for most purposes. In cases in which divergence occurs, the self-consistent values can be defined in terms of extrapolations from quantities obtained with smaller values of ω.

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(13) F. P. Lossing, private communication.

(14) W. E. Doering and L. H. Knox, THIS JOURNAL, **76,** 3203 (1954); M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2021 (1956); H. J. Dauben, F. A. Gadecki, K. M. Harmon and D. L. Pearson, THIS JOURNAL, **79,** 4558 (1957); R. Breslow, *ibid.*, **79,** 5318 (1957).

4. Non-alternant Hydrocarbons

It is of interest to determine how well Stevenson's correlation of ionization potentials of aromatic hydrocarbons with simple Hückel energy levels (*vide supra*) would work with other systems, particularly non-alternant hydrocarbons. In the absence of direct experimental data, the comparison can be effected with ionization potentials from the ω-technique. These values are also compared to those obtained by Hedges and Matsen[15] who used an approximate a.s.m.o. ("ASMOH") method. The comparison is summarized in Table II.

It is apparent that for aromatic hydrocarbons the ω-technique gives results which are, on the whole, little better than the simple Hückel method. Even non-alternant "aromatic" hydrocarbons such as azulene, acenaphthylene and fluoranthene have essentially the same ionization potentials by both methods. Since the ω-technique has been shown to be rather reliable for a variety of types of compounds, the simple molecular orbital predictions of ionization potentials of aromatic hydrocarbons are likely to be valid. In the case of a compound such as fulvene which is more properly considered to be a polyene, the two methods give noticeably different ionization potentials; in such cases the ω-technique should be preferred.

5. Heteroatoms

a. Introduction.—Heteroatoms, X, atoms other than carbon, may be incorporated into a π-lattice in the simple l.c.a.o. method by the use of appropriate values for the associated parameters, α_x and β_{cx}. These values are conveniently given in terms of the standard β_0 by the use of dimensionless parameters, h_r and k_{rs}[16]

$$\alpha_r = \alpha_0 + h_r\beta_0 \qquad (13)$$

$$\beta_{rs} = k_{rs}\beta_0 \qquad (14)$$

An ideal procedure to evaluate these parameters would start with a correlation between some experimental property and a calculated quantity established for hydrocarbon systems and apply this correlation to a number of compounds containing one or more of the heteroatoms under test with systematic variation of h_x and k_{cx}. Such a procedure would not only determine the best values of these parameters to use with the given correlation but would also reveal whether unique values would apply generally to a variety of compounds containing the heteroatom. Unfortunately, this ideal procedure has never been followed *in toto* and has only rarely been used in part. With the additional variations of the neglect or non-neglect of overlap, the use of an empirical auxiliary inductive parameter,[17] etc., the result has been a profusion of suggested parameter values in the literature. Such values vary from inspired guesses partly based on theory to choices derived from systematic variations which best correlate calculated quantities with some application (usually assumed and not proved) of simple l.c.a.o. theory. Nevertheless, the extensive work reported makes it clear that no one set of precise parameter values will serve the same heteroatom in all compounds and in all applications. However, by the consideration of several subclasses, a remarkable self-consistency appears to be developing.

We must distinguish, for example, the nitrogen in pyridine from that in pyrrole. In one case the heteroatom contributes one electron to the π-system; in the other it contributes two. In one case the heteroatom contributes a nuclear charge of + 1 to the core potential, in the other the contributed nuclear charge is +2. Clearly, α for a heteroatom which contributes two electrons should be considerably more negative than α for the same heteroatom in a π-system to which it contributes one electron; *i.e.*, $h_{\ddot{\mathrm{x}}} > h_{\dot{\mathrm{x}}}$. It will be convenient to treat these two types as two different atoms with independent values of $h_{\ddot{\mathrm{x}}}$ and $h_{\dot{\mathrm{x}}}$, respectively.

We also expect a variation in k_{cx} but such variation is expected in any event because the bond distances for $\mathrm{C{-}\ddot{X}}$ and $\mathrm{C{=}X}$ are normally rather different. However, because of the relative constancy of bond distances of a given type, we may conveniently refer to $k_{\mathrm{C-X}}$, k_{CX} and $k_{\mathrm{C=X}}$, for a single bond (as in a pyrrole), aromatic bond (as in pyridine) and double bond (as in methyleneimine), respectively.

A number of electron impact ionization potentials are available for π-systems which contain heteroatoms. The successful application of the ω-technique to ionization potentials of unsaturated hydrocarbons suggests its use to obtain completely empirical and independent parameter values for heteroatoms. These values may then be compared with those commonly used in the literature to determine how generally useful a single set of values may be.

Matsen[18] has suggested that h_x be derived from the ionization potentials of the corresponding hydrides since β_{cx} is not involved in these cases. We have adopted this suggestion modified for application of the ω-technique. We assume that the value $\omega = 1.4$ found to apply to carbon compounds applies as well to the heteroatoms. Justification for this assumption will be found below. With this method, the π-energy of the hydride, $\mathrm{H}_n\ddot{\mathrm{X}}$, is $2\alpha_0 + 2h_{\ddot{\mathrm{x}}}\beta_0$; the energy with one electron removed is $\alpha_0 + (h_{\ddot{\mathrm{x}}} + \omega)\beta_0$. Hence

$$\chi = \omega - h_{\ddot{\mathrm{x}}} \qquad (15)$$

From the ionization potentials and eq. 2, we determine χ, hence $h_{\ddot{\mathrm{x}}}$. These $h_{\ddot{\mathrm{x}}}$ values are then used for $\ddot{\mathrm{X}}$ in other π-systems in which k_{cx} is varied to give best agreement between calculated and experimental ionization potentials. Note the implicit assumption that ionization of $\mathrm{H}_n\ddot{\mathrm{X}}$ involves removal of an electron from the same p-like orbital in $\ddot{\mathrm{X}}$ that is involved in π-bonding to a π-system. The additional s-hybridization that is usually involved in an unshared electron pair in $\mathrm{H}_n\ddot{\mathrm{X}}$ is ignored. Note also the assumption that the electron removed in ionization of the π-system actually is

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(15) R. M. Hedges and F. A. Matsen, *J. Chem. Phys.*, **28**, 950 (1958). The α parameter was chosen to agree with the photoionization value for naphthalene. For comparison with electron impact results and with our calculations we have increased their values by 0.56 e.v.

(16) C. A. Coulson, *Trans. Faraday Soc.*, **42**, 106 (1946).

(17) R. D. Brown, *Quart. Rev.*, **6**, 63 (1952).

(18) F. A. Matsen, THIS JOURNAL, **72**, 5243 (1950).

TABLE II

COMPARISON OF IONIZATION POTENTIALS BY THE SIMPLE M.O. METHOD WITH THE ω-TECHNIQUE

Compound	I^a (e.v.) expl. (e.i.)	I (e.v.) photoionization	$m_j{}^b$	Simple M.o. I^c (e.v.) calcd. eq. 12	ω-Technique I (e.v.) calcd. eq. 2	ASMOH I (e.v.) calcd. (ref. 15)
Benzene	9.52	9.24[d]	1.000	9.55	9.53	9.93
Naphthalene	8.68	8.12[e]	0.618	8.60	8.63	8.68
Phenanthrene	8.62		.605	8.57	8.50	8.50
Anthracene	8.20		.414	8.09	8.11	7.81
Tetracene	7.71		.295	7.80	7.81	7.48
3,4-Benzphenanthrene	8.40		.568	8.48	8.36	8.44
Pyrene			.445	8.17	8.13	7.62
Azulene			.491	8.29	8.32	
Acenaphthylene			.715	8.85	8.73	
Fluoranthene			.618	8.60	8.54	
Fulvene			.711	8.84	9.07	
Biphenyl			.738	8.90	8.79	9.09
Toluene	9.23	8.82[d]	.923	9.36	9.01	
o-Xylene	8.97	8.58[d]	.879	9.25	8.76	
m-Xylene	9.02	8.58[d]	.891	9.28	8.77	
p-Xylene	8.88	8.48[d]	.852	9.18	8.83	
1,2,3-Trimethylbenzene	8.75		.874	9.23	8.49	
α-Methylnaphthalene		7.96[e]	.581	8.51	8.41	
β-Methylnaphthalene			.603	8.56	8.48	
Indene			.702	8.81	8.63	
Fluorene			.727	8.87	8.56	

[a] For references see ref. 4 and Table I. [b] The energy of the highest occupied orbital given as: $\epsilon_j = \alpha + m_j\beta$. [c] The least squares regression line derived from the first six compounds is given as $I = (2.48 \pm 0.17)m_j + 7.07 \pm 0.09$ (eq. 12). [d] From F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, New York. 1957. [e] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

a π-electron. This requirement is not met for many ionization potentials and is discussed for individual cases below.

$h^{\cdot\cdot}_{\mathrm{x}}$ values derived by this method are summarized in Table III.

TABLE III

$h^{\cdot\cdot}_{\mathrm{x}}$ VALUES FROM IONIZATION POTENTIALS OF HYDRIDES

X	Hydride	Ionization potential, e.v.[a]	$h^{\cdot\cdot}_{\mathrm{x}}$	$h^{\cdot\cdot}_{\mathrm{x}}$, rounded value adopted
CH_3	CH_4	13.12	2.94	3.0
O	H_2O	12.67	2.72	2.7
N	NH_3	10.52	1.72	1.7
F	HF	16.38	4.48	4.5
Cl	HCl	12.78	2.77	2.8
Br	HBr	11.69	2.25	2.2

[a] "Best value" average cited in appendix of ref. 19.

b. Methyl Compounds.—In an earlier study[4] of molecular orbital models for a methyl group, best results were obtained with a so-called heteroatom model, in which the methyl group is treated as a single heteroatom which contributes a pair of π-electrons to the system and is characterized in the usual way by $h^{\cdot\cdot}_{\mathrm{x}}$ and k_{cx}. We assume, in effect, that the electrons in the C–H bonds behave as though they were a single electron pair located on a single heteroatom. By any *a priori* theoretical standard this assumption is clearly rather drastic and perhaps unrealistic. Nevertheless, it is convenient to apply and actually gives good results. We should emphasize, therefore, the purely empirical justification for this model involving pseudo-π orbitals compared to the more "real" π-orbitals of "true" heteroatoms.

In conjunction with $h_{\mathrm{x}} = 3.0$ derived from methane, we find satisfactory results for methyl-substituted unsaturated systems with $k_{\mathrm{cx}} = 0.7$. These parameter values differ somewhat from those previously used[4] but give better over-all agreement. The new h_{x} value also provides a successful application to saturated hydrocarbons (*vide infra*).

Calculations for a variety of compounds are summarized in Table I. Methylene groups as in fluorene and cyclopentadiene, etc., were treated as divalent methyl groups.

In general, the agreement with the available experimental results is excellent. As in our earlier results, the ionization potentials for benzene derivatives tend to be somewhat lower than the experimental values. The average deviation for 21 compounds is ±0.1 e.v., about the same as the experimental error. The most serious deviation occurs in the case of 1,4-pentadiene, for which the calculated ionization potential is 0.6 e.v. lower than the reported value (Table I). The error is undoubtedly due to the overestimation of the hyperconjugation energy in the hydrocarbon cation by this technique or perhaps in part because the molecule is not planar as assumed in the calculations.

The results in Table I are given as the first iteration values. Since the methyl derivatives are not even-alternant systems, the hydrocarbons will have uneven charge distributions; in principle, the energies should be corrected for the charge distribution using the ω-technique. These corrections were calculated for a number of cases. For methyl substituted allyl radicals, benzyl radicals, ethylenes

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(19) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

and benzenes the corrected energies were 0.03–0.04 β per methyl higher than the original energies.[20] The changes, consequently, are both small and rather uniform and may be neglected. The corrections for the simple alkyl radicals (ethyl, isopropyl, *t*-butyl) were somewhat larger, 0.04–0.06 β per methyl group, but are at least partially compensated by the similar changes in the same direction produced by further iterations of the corresponding cations. Hence, within the reliability of the method, the simple first iteration results are adequate.

Although the parameters in our procedure were chosen to correlate with electron impact ionization potentials, it is of interest to compare the results with ultraviolet and photoionization values. These quantities are listed in the last column of Table I and are generally lower than the electron impact results. The difference is greater but relatively uniform for the aromatic compounds.[21]

Calculations of ionization potentials have gained added significance because of the demonstrated correlations between ionization potentials and the spectra and equilibrium constants of charge transfer complexes.[22,23] The excellent correlation of Merrifield and Phillips[23] between ionization potentials of aromatic hydrocarbons and the formation constants of the tetracyanoethylene complexes has been replotted using electron impact ionization potentials. An excellent straight line is again obtained. These authors have pointed out that the equilibrium constants for the xylenes follow the same pattern as the ionization potentials, although the total change in the latter is hardly greater than the experimental error. This pattern is not followed by the calculated ionization potentials. The present technique clearly cannot be relied upon to reproduce such small variations within a family although somewhat larger changes as in the dimethylethylenes and in the methylallyl radicals are reproduced satisfactorily.

The formation constants of tetracyanoethylene complexes have been reported[23] for several hydrocarbons for which electron impact ionization potentials are not available. The corresponding ionization potentials determined from the correlation curve for some of these hydrocarbons are summarized in Table IV. The agreement between these values and those calculated by the ω-technique is excellent for pyrene and fluorene. The rather poor agreement for biphenyl undoubtedly reflects steric hindrance to complex formation by this non-planar system. The ionization potentials derived by Briegleb and Czekalla[22c] from the spectra of other charge transfer complexes relate to photoionization and ultraviolet ionization potentials.

TABLE IV

IONIZATION POTENTIALS FROM TETRACYANOETHYLENE COMPLEXES

Hydrocarbon	K^a	TCNE, I, e.v.	I, e.v. ω-technique
Pyrene	29.5	8.24	8.13
Fluorene	18.0	8.48	8.56
Biphenyl	4.09	9.18	8.79

[a] Equilibrium constant for formation of complex with tetracyanoethylene (ref. 23).

The values for the hyperconjugation energy per methyl group of neutral molecules and radicals given by the present method model, 0.11–0.15 β (5–7 kcal./mole where β = 2.1 e.v.), are somewhat smaller than those given by the previous model but are still somewhat larger than the probable true values, undoubtedly because of neglect of electron correlation effects. The earlier conclusion is reaffirmed, however, that the conjugation effect of a methyl group in stabilizing a positive charge is substantial and important. An important defect of the simple molecular orbital theory is the overly large conjugation and hyperconjugation energies calculated for many compounds. The probable relative unimportance of hyperconjugation energies in normal neutral systems has been emphasized at the recent Conference on Hyperconjugation.[24] Professor M. J. S. Dewar has suggested[25] that E_π for a methylated hydrocarbon in the present method be taken as the parent unsaturated hydrocarbon but that $E_{\pi}{}^{+}$ be calculated as before with the methyl groups included; *i.e.*, that hyperconjugation be neglected in the neutral molecule but used to stabilize the cation. Because of the relative constancy of the hyperconjugation energy per methyl in the neutral systems as calculated in this paper, Dewar's suggestion will undoubtedly work—probably as well as our method. However, somewhat different parameter values may be necessary for the best correlation. Nevertheless, the present method is more convenient for our computer calculation, is empirically effective, and should not be misleading if the calculated quantities are used with circumspection.

c. **Chlorine.**—The experimental ionization potential of trichloromethyl radical, 8.78 e.v.,[26] is reproduced using h_{Cl} = 2.8 and k_{C-Cl} = 0.38. Similarly, the electron impact potential of trichloroethylene, 9.94 e.v.,[27] requires k_{C-Cl} = 0.37.[28] An average value, k_{C-Cl} = 0.37, was used with h_{Cl} = 2.8 for calculations of a number of chlorine compounds. The results are summarized in Table I. On the whole, the agreement is good. The calculated value for chlorobenzene is low as in the case of methyl substituted benzenes. The calculated values are generally higher than the ultraviolet and photoionization values, as expected. The application of the present method to methyl chloride is amusing and successful. The heteroatom model of a methyl group was used with h_{CH_3} = 3 as before, k_{CH_3-Cl} was estimated as the product of k_{C-CH_3} and k_{C-Cl}, (0.7)(0.37) = 0.26.

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[20] These corrections were actually obtained for h_X = 3.5, k_{CX} = 0.8. They are not expected to change significantly in the new model.

[21] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[22] (a) H. McConnell, J. S. Ham and J. R. Platt, *ibid.*, **21**, 66 (1953); (b) R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958); (c) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).

[23] R. E. Merrifield and W. D. Phillips, THIS JOURNAL, **80**, 2778 (1958).

[24] *Cf.*, papers published in *Tetrahedron*, **5**, 105–274 (1959).

[25] Personal communication.

[26] J. B. Farmer, I. H. S. Henderson, F. P. Lossing and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

[27] J. D. Morrison and A. J. C. Nicholson, *ibid.*, **20**, 1021 (1952).

[28] $k_{C=C}$ for the carbon–carbon double bond was taken as 1.07 as before.

In the above treatment it is assumed that only one chlorine orbital contributing two electrons is effective in participating in a π-bond lattice. The further assumption in most of the cases that the experimental ionization potentials refer to π-electron ionization seems justified since ionization from an unshared pair on chlorine requires relatively high energy.

In other recent work, parameter values used for chlorine have covered the range, $h_{\mathrm{Cl}} = 0.5\text{–}2.5$ and $k_{\mathrm{C-Cl}} = 0.33\text{–}1$.[18,29] The low value for h_{Cl} is derived from the assumption that h-values are proportional to electronegativity differences[30] and ignores the difference in core potentials for the contribution of one or two electrons to the π-system (*vide supra*). The high value for $k_{\mathrm{C-Cl}}$ was simply assumed for simplicity with no justification. Hence, our parameter values are reasonably consistent with the reasonable values used by others.

Preliminary calculations with fluorine substituents were not successful in the present approximation which involved but one cycle of iteration. In this approximation no trihalomethyl radical could have an ionization potential larger than that of methyl radical itself; *i.e.*, for $h_{\mathrm{x}} = \infty$, the system reduces to that of a methyl radical whereas for $h_{\mathrm{x}} < \infty$, electron density will be distributed to the central carbonium ion causing stabilization. The experimental ionization potential of trifluoromethyl radical, 10.10 e.v.,[26] is slightly higher than methyl radical, 9.95 e.v.[31] Fluorine is so electronegative (Table III) that iterations of the radical itself to self-consistency apparently are required or, alternatively, an inductive parameter is necessary. Because of this complication no further treatment of fluorine compounds was undertaken at this time. Bromine and iodine derivatives were not treated because of a scarcity of appropriate electron impact data for evaluation, although for bromine, values of $h_{\mathrm{Br}} = 2.2$ and $k_{\mathrm{C-Br}} = 0.2\text{–}0.3$ seem reasonable.

d. Oxygen.—Electron impact ionization potentials are available for furan, 9.00 e.v.,[32,33] 9.05 e.v.,[27] and phenol, 9.01 e.v.,[33] 9.03 e.v.[27] Using $h_{\mathrm{O}} = 2.7$, $k_{\mathrm{C-O}}$ was varied and ionization potentials were calculated for these compounds. Interpolation from plots of **I** *vs.* $k_{\mathrm{C-O}}$ yielded the values, $k_{\mathrm{C-O}} = 0.53$ and 0.61, respectively. The rounded average, $k_{\mathrm{C-O}} = 0.6$, was adopted for subsequent calculations. The parameters, $h_{\mathrm{O}} = 2.7$ and $k_{\mathrm{C-O}} = 0.6$, give calculated ionization potentials of 8.9 and 9.03 e.v. for furan and phenol, respectively, in good agreement with the experimental values. A few additional checks are available. From the photoionization potentials of furan and α-methylfuran, 8.89 and 8.39 e.v., respectively,[34] the E.I. potential of α-methylfuran may be estimated as 8.53 e.v., in excellent agreement with the calculated value, 8.58 e.v.

For compounds containing a CH_3–O bond, $k_{\mathrm{CH_3-O}}$ was estimated as follows: k for a methyl group attached to an oxygen contributing 2p electrons may be estimated as $(k_{\mathrm{CH_3-O}})(k_{\mathrm{C-O}}) = (0.7)(0.6) = 0.4$; however, since the unshared pairs on such an oxygen usually involve some s hybridization, the actual value is probably somewhat lower. A rough guess might be $k_{\mathrm{CH_3-O}} = 0.3$. Use of this value with methyl alcohol gives a calculated ionization potential of 10.79 e.v. in reasonable agreement with the experimental value of 10.88 e.v.[19] For dimethyl ether the calculated value, 10.22 e.v., is a little lower than the single reported experimental value, 10.5 e.v.[19,35] Calculations were made for a number of oxygen compounds with results summarized in Table I.

Unfortunately, the extensive ionization potential data available for aldehydes and ketones are not suitable for the present purpose. The first ionization potential of these compounds usually involves an oxygen lone-pair electron which is not part of the π-system.[36–38] In the "ether-oxygen" compounds treated above, the oxygen has a lone-pair in addition to the electron pair contributed to the π-system; we assumed that the former has the higher ionization potential.

A π-system ionization potential calculation for most carbonyl compounds thus should yield a potential higher than that observed. However, even such a calculation is not straightforward from our present parameter values. The bond integral for a carbonyl group could be obtained by our usual assumption of proportionality to overlap integrals: $k_{\mathrm{C=O}} = k_{\mathrm{C-O}}(S_{\mathrm{C=O}}/S_{\mathrm{C-O}}) = (0.6)(0.214/0.160) = 0.8$. The core of an ether-oxygen in a π-lattice has two positive charges; hence, a high α value is realistic and necessary. A carbonyl oxygen, however, contributes but a single positive charge to the core of a π-system and a lower α value is appropriate. We might expect the difference, $h_{\ddot{\mathrm{O}}} - h_{\dot{\mathrm{O}}}$, to have the approximate magnitude of ω; thus $h_{\dot{\mathrm{O}}}$- would be $\sim$1.3. The values, $k_{\mathrm{C=O}} = 0.8$ and $h_{\dot{\mathrm{O}}} = 1.3$, applied to formaldehyde yield a calculated π-ionization potential of 12.38 e.v., substantially higher than the experimental value, 10.8 e.v.[19] The bond integral value used here may be a poor one; the assumption of proportionality to overlap integrals may be seriously questioned in this connection and a higher value for $k_{\mathrm{C=O}}$ may actually be more valid. However, the use of a higher $k_{\mathrm{C=O}}$ value would raise the calculated ionization potential still more.

Parameter values derived previously vary over a wide range, $h_{\ddot{\mathrm{O}}} = 0.5 - 4$, $k_{\mathrm{C-O}} = 0.7 - 1.4$.[16,29a,39]

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(29) (a) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952); (b) R. Bersohn, *ibid.*, **22**, 2078 (1954); (c) T. Anno and A. Sado, *Bull. Chem. Soc. Japan*, **28**, 350 (1955).

(30) C. A. Coulson, "Valence," Oxford University Press, London, 1952, p. 242.

(31) F. P. Lossing, K. U. Ingold and I. H. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

(32) I. Omura, K. Higasi and H. Baba, *Bull. Chem. Soc. Japan*, **29**, 501 (1956).

(33) H. Baba, I. Omura and K. Higasi, *ibid.*, **29**, 521 (1956).

(34) K. Watanabe and T. Nakayama, ASTIA Report No. AD 152934.

(35) T. M. Sugden, A. D. Walsh and W. C. Price, *Nature*, **148**, 373 (1941).

(36) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 158 (1947).

(37) K. Higasi, I. Omura and H. Baba, *Bull. Chem. Soc. Japan*, **28**, 504 (1955); *Nature*, **178**, 652 (1956).

(38) K. Higasi, T. Nozoe and I. Omura, *Bull. Chem. Soc. Japan*, **30**, 408 (1957).

(39) (a) G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935); (b) M. G. Evans, J. Gergely and J. De Heer, *Trans. Faraday Soc.*, **45**, 312 (1949); (c) V. Gold, *ibid.*, **46**, 109 (1950); (d) J. G. M. Bremner and W. C. G. Bremner, *J. Chem. Soc.*, 2335 (1950); (e) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951); (f) K. Nishimoto and R. Fujishiro, *Bull. Chem.*

e. Nitrogen.—Using $h_N = 1.7$ from the ionization potential of ammonia (Table III), calculations of pyrrole and aniline were carried out with various values of k_{C-N}. The results are less satisfactory than those of the comparable oxygen cases. Reproduction of the electron impact ionization potential of aniline, 8.23 e.v.,[33] requires $k_{C-N} = 0.9$; that for pyrrole, 8.97 e.v.[33,40,41] requires $k_{C-N} = 0.43$. The average value, $k_{C-N} = 0.7$, yields the calculated ionization potentials: aniline, 8.50 e.v.; pyrrole, 8.58 e.v. Part of the discrepancy may be due to the difficulty in determining mass spectral potentials of amines.[42] No further tests of the derived parameters are available except for the methylamines. The calculation of k_{Me-N} in the same way as in the oxygen case yields 0.4; using this value we calculate for methylamine, dimethylamine and trimethylamine, 9.56, 9.01 and 8.66 e.v., respectively, in reasonably satisfactory agreement with the experimental values, 9.41, 8.93 and 8.32 e.v.,[42,43] respectively.

The mass spectral data for pyridines are not suitable for our purpose. As with the carbonyl compounds, ionization of these heterocycles undoubtedly involves the non-bonding nitrogen electrons.[33,44,45] The same line of reasoning used with a carbonyl oxygen (*vide supra*) gives for a pyridine-type of nitrogen: $h = 0.3$, $k = 0.8$; however, these values are rather crude.

The calculations are summarized in Table I. At this stage extensive additional calculations are not warranted.

Nitrogen compounds form the most extensive set of heteroatom π-systems reported in the literature. A summary of derived parameter values is instructive. Orgel's[39e] treatment of dipole moments yields $h = 2$ for an amino-type nitrogen assuming $k = 1.2$; from the color of dyes and dipole moments, Dewar[46] derives $k = 1$ assuming $h = 2$ from calculations on pyrrole. Our value for h for an amino-nitrogen compares reasonably well with these assignments; however, other treatments based on dipole moments and resonance energies yield values of h of 0–0.8 and k of 0.3–1.[47] Jaffe's[29a] procedure yields $h = -0.70$ and $k = 0.06$, values which do not seem reasonable for other applications.

Amino- and pyridine-type nitrogens have frequently been assigned the same Coulomb integral values[48]—an unjustifiable procedure (*vide supra*). The various derivations of h and k for a pyridine-type nitrogen in the literature show reasonable consistency and agreement with our values. Considerations of dipole moments have led to $h = 0.5$–1 and $k = 0.8$–1.2.[39e,46,49] The partial rate factors for radical substitution on pyridine yield $h = 0.5$, $k = 1$.[50] Comparison of simple l.c.a.o. and s.c.f. calculations yield $h = 0.1$–0.25 and $k = 0.9$–1.[51] A recent study of the azo group has yielded $h = 0.5$, $k_{CN} = 0.7$.[52] Hence, it seems clear that $h = 0.5$ and $k = 1$ are appropriate assignments for pyridine-type nitrogens, in reasonable agreement with our findings.

f. Discussion.—The parameter values for heteroatoms derived from the present work are summarized in Table V. Since the proportionality of bond integrals frequently has been assumed for various carbon–carbon bonds, we examine this assumption for heteropolar bonds. In Table VI we compare k_{CX} as derived in this work to the ratio of the overlap integral, S_{CX}, with that of the "standard" benzene bond. For first row elements, the correspondence is actually rather good. We can estimate that k for a carbon–fluorine bond should be about 0.5–0.6. The correspondence does not work for C–Cl, the overlap integral being too high in comparison to the bond integral. The correspondence probably breaks down because of the difference in principal quantum numbers of the orbitals comprising the π-orbital.

TABLE V

SUMMARY OF PARAMETER VALUES

	h_X	k_{CX}
C	2.8	0.37
$-\ddot{O}-$	2.7	.6
$O=$	~1.3	~ .8
$>\ddot{N}-$	1.7	.7
$-N=$	~0.3	~ .8

TABLE VI

COMPARISON OF BOND INTEGRALS AND OVERLAP INTEGRALS

Bond	Representative compound	Length, Å.[a]	S_{CX}/S_0[b]	k[c]
C–C	Benzene	1.397	1.00	1.0
C–N	Pyrrole	1.42	0.75	0.7
C–O	Phenol	1.36	.66	.6
C–F	Fluorobenzene	1.30	.59	
C–Cl	Chlorobenzene	1.70	.65	.37

[a] "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publications No. 11, The Chemical Society, London (1958). [b] Slator overlap integrals calculated from R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949). [c] Present work.

Note that our results were obtained without the use of an auxiliary inductive parameter. It may be that the ω-technique compensates for this parameter which apparently is necessary in simple l.c.a.o. studies of heteroatom systems.[39g] It would appear

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Soc. Japan, **31**, 1036 (1958); (g) R. D. Brown and B. A. W. Collier, *Austral. J. Chem.*, **12**, 152 (1959).

(40) I. Omura, H. Baba and K. Higasi, *J. Phys. Soc. Japan*, **10**, 317 (1955).

(41) J. Hissel, *Bull. Soc. Roy. Sci. Liege*, **21**, 457 (1952), reports I = 9.2 ± 0.2.

(42) J. Collin, *Canad. J. Chem.*, **37**, 1053 (1959).

(43) I. Omura, K. Higasi and H. Baba, *Bull. Chem. Soc. Japan*, **29**, 504 (1956), give 9.41, 9.21 and 9.02 e.v., respectively.

(44) I. Omura, H. Baba, K. Higasi and Y. Kanaoka, *ibid.*, **30**, 633 (1957).

(45) K. Higasi, I. Omura and H. Baba, *J. Chem. Phys.*, **24**, 623 (1956).

(46) M. J. S. Dewar, *J. Chem. Soc.*, 2329 (1950).

(47) (a) M. J. S. Dewar, *Trans. Faraday Soc.*, **42**, 764 (1946); (b) S. S. Perez, M. A. Herraez and F. J. Igea, *Anales real soc. españ. fis. y quim.* (*Madrid*), **50B**, 243 (1954); (c) J. G. Burr, *J. Chem. Phys.*, **26**, 431 (1957).

(48) Examples: H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1949); E. Gyoerffy, *Compt. rend.*, **232**, 515 (1951); R. D. Brown, *J. Chem. Soc.*, 2670 (1951); I. M. Bassett and R. D. Brown, *ibid.*, 2701 (1954); R. D. Brown, *Australian J. Chem.*, **8**, 100 (1955); and ref. 17.

(49) P. Löwdin, *J. Chem. Phys.*, **19**, 1323 (1951).

(50) R. D. Brown, *J. Chem. Soc.*, 272 (1956).

(51) R. D. Brown and A. Penfold, *J. Chem. Phys.*, **24**, 1259 (1956); R. D. Brown and M. L. Heffernan, *Austral. J. Chem.*, **10**, 211 (1957); R. McWeeny and T. E. Peacock, *Proc. Phys. Soc.*, **70A**, 41 (1957).

(52) F. Gerson and E. Heilbronner, *Helv. Chim. Acta*, **41**, 2332 (1958).

that our parameter values, derived empirically and with the ω-technique, would give satisfactory results in some other applications of the simple l.c.a.o. method itself, especially if combined with a reasonable auxiliary inductive parameter. However, for the treatment of carbonium ions without the ω-technique the $h_{\ddot{x}}$ values derived here seem to be too high; in particular, the present parameter values do not give a good account of electrophilic aromatic substitution without the ω-technique. Other calculations suggest that for simple l.c.a.o. calculations without the ω-technique, our $h_{\ddot{x}}$ values should be decreased by 0.7–1 unit.

Although we did not examine oxonium and ammonium π-systems, we would expect h for the positive nitrogen of a pyridium salt, for example, to be about ω larger than that for the neutral nitrogen and, hence, to be about equal to $h_{\ddot{\mathrm{N}}}$. This expectation is shared by Brown and Collier.[39g] Recently derived values for h_{N^+} are 1.4–2.4,[53] in rough agreement with these thoughts.

6. Acetylenes

In the attempted application of the ω-technique to the ionization potentials of acetylenic compounds, several difficulties arise in principle. The ω-technique introduces an empirical parameter which approximately corrects for electron repulsion effects. The π-system is considered separately from a sigma-framework; the effects of the latter are contained in the empirical parameter, ω, which, however, is treated as a constant for all π-systems. The difference in the sigma-framework of acetylenic and allenic systems from that in olefins and in aromatic hydrocarbons might be reflected in a substantial change in ω. Nevertheless, the satisfactory results obtained with heteroatoms and with saturated hydrocarbons (section 8) suggest that such changes may be unimportant.

We encounter a further problem in the detailed handling of the two orthogonal π-systems of an acetylene. We obtained satisfactory results with the simplest model in which only one of the π-systems is considered to be involved in the ionization process, the other being ignored. In the cases in which the two π-systems differed, the more extensive was considered to be involved in the ionization process.

The assumption of β_{rs} proportional to S_{rs} yields for the triple bond distance of 1.20 Å.[54] the value 1.38 β_0. The other required quantity is the Coulomb integral, α, for an acetylenic carbon. The relative acidity of acetylenes suggests that this carbon be considered somewhat electronegative relative to a "standard" benzene carbon. Preliminary calculations showed, however, that the use of the same α for olefinic, aromatic and acetylenic carbons gives satisfactory results *for the calculation of ionization potentials*. This assumption may not work with other molecular orbital applications.

For acetylene treated as a two-atom π-system with β taken as a variable, the ω-technique molecular orbital equations are solved easily; equation 2 and the experimental electron impact ionization potential of acetylene, 11.42 e.v.,[19] gives directly a value of $k_{\mathrm{C}\equiv\mathrm{C}}$ of 1.43 which is reasonably close to that obtained by the assumption of proportionality to overlap integrals. In subsequent calculations the rounded value, $k_{\mathrm{C}\equiv\mathrm{C}} = 1.40$, was adopted. This value yields 11.36 e.v. for the ionization potential of acetylene which is sufficiently close for our purposes.

Calculations have been performed for a number of acetylenic compounds. From the known or presumed bond distances of other types of bonds the overlap integral values were used to determine k_{rs}. The resulting values are summarized in Table VII. The value for the "single" bond in propargyl radical was estimated as 1.02 on the basis that this bond length should be somewhat shorter than the bond in allyl radical ($k = 1.00$) but longer than that between two triple bonds ($k = 1.04$). The value for a methyl group bonded to an acetylenic carbon was obtained from the value of 0.7 for an aromatic methyl substituent (section 5b) corrected for the bond shortening by assumed proportionality to carbon 2p overlap integrals.

TABLE VII

k_{rs} VALUES FOR CARBON–CARBON BONDS

Bond type	Length, Å.[a]	k_{rs}
$-\mathrm{C}\equiv\mathrm{C}-$	1.20	1.40
$>\mathrm{C}=\mathrm{C}<$	1.34	1.07
$=\mathrm{C}-\mathrm{C}=$	1.46	0.90
$=\mathrm{C}-\mathrm{C}\equiv$	1.42[b]	0.97
$\equiv\mathrm{C}-\mathrm{C}\equiv$	1.38	1.04
$\equiv\mathrm{C}-\mathrm{C}$		1.02[c]
$\mathrm{H_3C}-\mathrm{C}\equiv$	1.46	0.75[d,e]
$\mathrm{H_3C}-\mathrm{C}=$	1.50	0.7[e]
$>\mathrm{C}=\mathrm{C}=$	1.30[f]	1.18
$=\mathrm{C}=\mathrm{C}=$	1.27	1.24

[a] Ref. 54. [b] Assumed as the average of $=\mathrm{C}-\mathrm{C}=$ and $\equiv\mathrm{C}-\mathrm{C}\equiv$. [c] Assumed. [d] Obtained from $(0.7)(S_{1.46}/S_{1.50})$. [e] Methyl group as heteroatom model; *cf.* section 5b. [f] Ref. 56.

The results of the calculations for a variety of acetylenic compounds are summarized in Table I. On the whole, the method seems to be reasonably successful, the average deviation being about 0.1 e.v. Franklin and Field[55] have estimated the electron impact ionization potential of diacetylene to be about 10.9 e.v., in serious disagreement with the calculated value of 9.78 e.v. Our calculated value of 9.49 e.v. for vinylacetylene is also considerably lower than the reported value of 9.9 e.v. The discrepancies are related since the diacetylene value was derived from mass spectral data on vinylacetylene. With the remaining cases, on the other hand, the agreement is excellent. Calculated values are included in Table I for some acetylene compounds for which experimental data are not available.

7. Allenes

In the extension of the method used for acetylenes to allenes, we regard the latter for the purposes of calculation as an "olefin" conjugated with a

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[53] R. D. Brown and A. Pennfold, *Trans. Faraday Soc.*, **53**, 397 (1957); S. Mataga and N. Mataga, *Z. Phys. Chem. N. F.*, **19**, 231 (1959).

[54] L. E. Sutton, *Tetrahedron*, **5**, 118 (1959).

[55] J. F. Franklin and F. H. Field, THIS JOURNAL, **76**, 1994 (1954).

methylene group. From the C=C bond distance of 1.30 Å. in allene[56] the assumption of k_{rs} proportional to S_{rs} yields 1.18 for the resonance integral of this bond. For the $CH_2=C$ bond, k_{rs} is estimated from the value of 0.7 for a CH_3–C bond by assuming a proportionality to carbon 2p overlap integrals as in the methylacetylene case; $k_{CH_2=C} = (0.7)(S_{1.30\,Å.}/S_{1.50\,Å.}) = 0.98$—we adopt the rounded value of 1. Because of the greater s character of the sp^2 bonds to hydrogen in the allenic methylene group compared to the sp^3 bonds of a methyl group, the electrons in the former are expected to be more firmly held. The equivalent pseudoheteroatom donating two electrons to the π-system would thus have a greater electronegativity; *i.e.*, the value of h_X should be greater than the value, 3.0, used for an aromatic substituent methyl group. Best results were obtained for $h_X = 4.4$. The calculations for allene and methylallene are compared with the experimental values in Table I. Because an additional disposable parameter, $\alpha_{CH_2=}$, is involved in these calculations the results, with only two cases, are not too meaningful; however, the reasonable value of the parameter and the excellent agreement in both cases is encouraging. The method was applied to a couple of additional cases for which experimental data are not available; the results are summarized in Table I. In the case of butatriene the two orthogonal π-systems are of equal extent. Ionization could involve loss of an electron from the butadiene-like π-system (π_z) or the 2-butene-like π-system (π_y). Calculations of both systems were made; the former has the lower calculated ionization potential.

8. Saturated Hydrocarbons

A quantum mechanical treatment of ionization potentials of alkanes was first developed by Hall[57] who used an equivalent orbital representation. Even after appropriate simplifying assumptions, however, as many as four disposable parameters were required, the values of which were determined by the experimental data. The values assigned did give an excellent reproduction of the experimental ionization potentials. A similar method involving group parameters was used by Franklin[58] and was applied not only to alkanes but to numerous functional derivatives. A simplified model which was applied by Hall[59] to olefins served as the basis for a treatment of alkanes by Stevenson.[60] In this modified model, it is assumed that there is associated with each carbon of an alkane a pseudo-π-orbital that carries two "mobile" electrons. The required group parameters correspond to the coulomb and bond integral parameters of the corresponding simple molecular orbital model. The treatment reproduced the experimental results well, and it is interesting to note that the parameter required for the bond integral, β, between saturated carbons was $^1/_3$ the value of β for unsaturated carbons.[60,61] This value seems rather large.

In this paper the model of an alkane used by Stevenson is combined with the ω-technique in a calculation of ionization potentials. The coulomb integral for a saturated carbon is assumed to be the same as that used previously for the methyl group, $h_x = 3$ (section 5b). If the same value of ω is assumed to apply to a saturated carbon, only one additional parameter is required, the bond integral, β_{C-C}, between saturated carbons. This parameter is expected to be small; indeed, a value insignificantly different from zero appears to work rather well.

In this treatment the pseudo-π energy of methane is $2(\alpha + 3\beta)$. The energy of methane cation is $\alpha + 3\beta + \omega = \alpha + 4.4\beta$. The energy difference which corresponds to the ionization potential is $-\alpha - 1.6\beta$, hence, $\chi = -1.6$. From the correlation equation previously established, this value of χ corresponds to I = 13.25 e.v.; the experimental value is 13.12 e.v. For ethane and the higher alkanes, the corresponding secular matrices are already diagonalized since the bonding terms are taken as effectively zero and since the overlap integral terms as usual are neglected. The eigenvalues for each hydrocarbon are simply the coulomb energies. Since each orbital is doubly occupied the total pseudo-π energy of an alkane of n carbons is $2n\alpha + 6n\beta$. This result is satisfactory because the pseudo-π electrons are actually used for C–H and C–C bonding; it means that the delocalization energy of saturated hydrocarbons is negligible, consistent with the observed constancy of bond energies and with results expected from electron correlation effects. Although bonding interaction terms are negligible, the molecular orbitals must still be considered to encompass the entire molecule and to serve as group representations of the model. If these bonding terms are taken as finite (although small) and equal for all bonded saturated carbons, the form of the molecular orbitals is identical with that of the corresponding polyene in the usual simple molecular orbital approximation. For these compounds the molecular orbitals have been given as a general equation,[62] which may be represented as equation 16, in which c_{rj} is the coefficient of the rth atom in the jth molecular orbital; n is the total number of carbons.

$$c_{rj} = \sqrt{\frac{2}{n+1}}\,\sin\frac{rj\pi}{n+1} \qquad (16)$$

In the present case each molecular orbital is doubly occupied and the ionization process involves loss of an electron from the highest molecular orbital; thus, the positive charge density on each carbon is given by c_{rn}^2. Application of the ω-technique to the first iteration changes the totally degenerate set of n-orbitals of energy, $\alpha + 3\beta$, to a set of molecular orbitals of energies $\alpha + (3 + \omega c_{rn}^2)\beta$, from which the total pseudo-π energy of the alkane cation is derived. The absolute values of the coefficients of the end carbons are the smallest in the nth molecu-

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(56) J. Overend and H. W. Thompson, *J. Opt. Soc. Amer.*, **43**, 1065 (1953).

(57) G. G. Hall, *Proc. Roy. Soc.* (*London*), **A205**, 541 (1951).

(58) J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954).

(59) G. G. Hall, *Trans. Faraday Soc.*, **49**, 113 (1953).

(60) D. P. Stevenson, Symposium on Mechanisms of Homogeneous and Heterogeneous Hydrocarbon Reactions at American Chemical Society Meeting, Kansas City, March, 1954, No. 29, p. 19.

(61) D. P. Stevenson, private communication.

(62) (a) E. Hückel, *Z. Physik*, **76**, 628 (1932); (b) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A193**, 447 (1948); (c) F. G. Fumi, *Nuovo cimento*, **8**, 1 (1951).

lar orbital, ψ_n; hence, the two end carbons of an n-alkane chain are the least electronegative in the alkane cations and the electron lost must come from an orbital having an energy of $\alpha + (3 + c_{1n}{}^2\omega)\beta$. It follows for n-alkanes and $\omega = 1.4$ that χ is given simply by

$$\chi = -\left(0.2 + \frac{2.8}{n+1}\sin^2\frac{n\pi}{n+1}\right) \qquad (17)$$

Values of χ, the corresponding calculated ionization potentials and the experimental values for n-alkanes are summarized in Table I. In general, the agreement is good; the average deviation for the ten compounds of only 0.1 e.v. is especially satisfactory since in this method the only adjustable parameter used which was not determined by other data was the bond integral which was taken as zero.[63]

The present treatment can be applied similarly in a straightforward manner to branched chain alkanes and cycloalkanes. Equation 17 can be rewritten as equation 18 in which ρ is the amount of positive charge on the atom bearing the least amount of positive charge in the alkane cation obtained by removing an electron from the highest (most antibonding) Hückel orbital.

$$\chi = -(0.20 + \omega\rho) \qquad (18)$$

In cycloalkane cations the charge is distributed uniformly around the ring; hence $\rho = 1/n$. Some results are summarized in Table I. Unfortunately, the experimental data for most of these systems are poor and it is difficult to evaluate the significance of the discrepancies. The deviation for cyclopropane is not unexpected; one would not expect the same parameter values to hold for small ring compounds which have pseudo-unsaturation character. The calculated value for cyclopentane is in approximate agreement with the single reported value. The values reported for cyclohexane vary widely. The calculated value, 10.79 e.v., agrees well with the unweighted average of the experimental values, 10.8 ± 0.3 e.v.

Electron impact ionization potentials for several branched alkanes recently have been published by Collin and Lossing.[64] The agreement with the calculated values (Table I) is satisfactory—the average deviation is about 0.1 e.v. However, the observed slight decrease in ionization potential, which is less than the experimental error, for the structural change, 2-methylpentane–3-methylpentane, is calculated instead as a slight increase. The calculated value for 2,3-dimethylbutane is 0.3 e.v. higher than the reported value. This discrepancy and the possible deviation with neopentane points out the limitations of this simple calculation; nevertheless, the over-all agreement obtained with the saturated hydrocarbons is promising and demonstrates again the versatility of application of the ω-technique.

It may be emphasized that for most purposes, alkanes may be treated satisfactorily from a localized bond viewpoint. The effect of structure on ionization potential demonstrates convincingly, however, that the positive charge in an alkane cation is distributed over the entire molecule. In the usual approximations, a molecular orbital concept is required to adequately interpret alkane cations and energy changes involving such cations. Nevertheless, we must also emphasize that in the present treatment the use of $\beta = 0$ between saturated carbons is an artificial empirical device which will work only when no other types of bonds are present. Hence, the present treatment cannot be applied to the calculation of alkyl substituted radicals, olefins and aromatics.

Calculations.—The calculations were mostly performed on an I.B.M. 701 high speed digital computer using slight modifications of the programs used previously.[4,65]

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[63] According to this treatment a plot of χ_{expl} *vs.* $(2 - \frac{1}{n+1}\sin^2 n\pi/n + 1)$ should give a straight line of slope ω and intercept h_X. In such a plot the points actually show a tendency to curve. The best straight line through the points, however, gives $\omega = 1.34$ and $h_X = 2.87$. The use of these values reproduces the experimental ionization potentials with an average deviation of ±0.08 e.v., which is inappreciably better than the results obtained with the parameter values used above ($\omega = 1.4$, $h_X = 3$).

[64] J. Collin and F. P. Lossing, THIS JOURNAL, **81**, 2064 (1959).

[65] The eigenvalues and eigenvectors of the occupied orbitals, the electron densities and bond orders as given by the simple molecular orbital procedure for many of the compounds in this paper have been prepared as Appendices and deposited as Document Number 6222 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $6.25 for photoprints, or $2.50 for 35 mm. microfilm, payable to Chief, Photoduplication Service, Library of Congress.