two possibilities could be denoted by − and + superscripts, respectively, leading to four types of substituent, $-I^-$, $-I^+$, $+I^-$, and $+I^+$. The double classification based on these criteria is illustrated schematically in Figure 5.

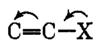
The substituents dealt with in this paper are of the −I type, with the further subdivision

$-I^+$ type: F, OR, NR_2

$-I^-$ type: CF_3, RC=O, C≡N, NO_2, COOR

In all these cases, the $-I^+$ substituents are those with the most electronegative atom directly attached to the hydrocarbon, while the $-I^-$ types have the electronegative atom one position removed. This is a consequence of the widespread charge alternation noted in Figures 1–4.

It may be noted that the ± superscript of this classification corresponds to the label used for a "mesomeric displacement" if the substituent is attached to an unsaturated system. Thus the usual charge displacement diagram



for a +M mesomeric substituent leads to a high electron density on the β carbon as shown for a $-I^+$ group in Figure 5. The CNDO calculations confirm this behavior, but also suggest that this feature of the $-I^+$ substituent and the consequent charge alternation apply even in saturated molecules. In both cases the alternation is associated with "back-donation" of lone-pair electrons in molecular orbitals of π-type relative to the C–X bond (that is, with a nodal plane through the C–X bond).

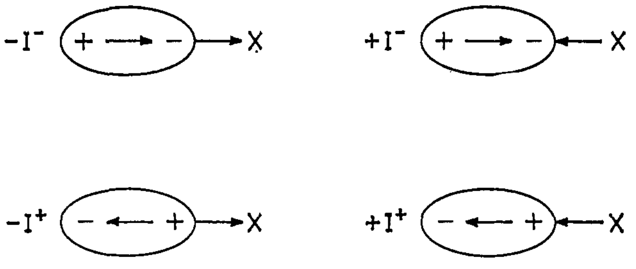


Figure 5. Schematic representation of types of inductive substituent.

More refined calculations to test the theory of electron distribution presented in this paper are clearly needed as well as studies of other related physical properties. In the meantime, the satisfactory reproduction of so many details of electric dipole data does constitute evidence in its favor.

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Interaction of a Methyl Group with a Triple Bond. Molecular Self-Consistent Field Calculation on Methylacetylene

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Abstract: An accurate molecular orbital calculation for a minimum basis set of Slater orbitals (H exponent, 1.2) has yielded an analysis of the methyl–triple bond interaction in methylacetylene. The calculated dipole moment of 0.70 D. (microwave value, 0.75 D.) is mostly due to a π-system polarization (0.88 D.) in the direction $HC^-(1)$-$C^+(2)C^-(3)H_3{}^+$, reduced by an opposite σ polarization of the molecule. The methyl group, which shows a negligible π-inductive effect on the acetylenic group, donates 0.056 and 0.026 electron respectively to the σ and π system of the acetylene residue. The suggestion by Dewar that the dipole moment may arise primarily from σ polarization is not in agreement with these results. Assumption of suitable localized MO's yields calculated π-electron delocalization energies of 3.26 kcal in C_2H_6 and 7.62 kcal in $HCCCH_3$. The existence of negligible π-electron overlap populations across the C–C single bonds in methylacetylene and ethane is discussed. The first (vertical) ionization potential is calculated (by Koopmans' theorem) at 10.24 ev (experimental value, 10.36 ev) in $HCCCH_3$. Results are also compared with those for $HCCCH_3$ obtained earlier by parameterization from acetylene and ethane.

The dipole moment (0.72–0.77 D.)[2] of the small hydrocarbon methylacetylene is a simple example of a large electronic interaction between an alkyl group and an unsaturated hydrocarbon to which it is bonded. In many approximate molecular orbital studies of such molecules, the methyl group is treated as a pseudo-π-electron system ($C\equiv H_3$), and it has been suggested[3a] that π-electron resonance accounts for the charge-transfer effects. On the other hand, an inductive model for the π-electron system has been proposed,[3b] in which the alkyl group polarizes the unsaturated system by changing the electronegativity of the unsaturated carbon atom to which it is bonded; in the extreme form of this theory, neither resonance nor charge transfer is invoked between the alkyl group and the unsaturated group.

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[1] National Science Foundation Postdoctoral Fellow, 1966–1967.

[2] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, p 77.

[3] (a) See A. Lofthus, *J. Am. Chem. Soc.*, **79**, 24 (1957), and references quoted therein; (b) see, *e.g.*, A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).

Yet another approach[4] turns attention from the π system to the σ system as the primary, though not necessarily the only source of the large dipole moment. Dewar's suggestion[4] is that carbon–carbon bond dipole moments arising from differences in hybridization, or, equivalently, from electronegativity differences, may account for a major part of the observed dipole moments in alkyl-substituted unsaturated hydrocarbons.

In light of the confusion created by the different approaches outlined above and by the arbitrariness in the choice of parameters which they employ, it was felt desirable to carry out an accurate, *ab initio* molecular orbital calculation, including all electrons explicitly. Fortunately, computer programs are now available[5] which have made it possible to obtain an accurate wave function for methylacetylene, the smallest example of the type of molecule discussed above. We shall first present the molecular orbital coefficients, eigenvalues, total energies, dipole moment, and population analysis.[6] Then we shall evaluate the relative importance of σ- and π-electron contributions to the dipole moment, at the same time noting the importance of delocalization of the π electrons, both with regard to energy stabilization and charge transfer. In the process of obtaining these results, we shall evaluate the energy stabilization in ethane due to delocalization of the π-electron density, *i.e.*, the density contributed by the filled degenerate molecular orbitals. An explanation will be offered for the fact that the π-electron contribution to the overlap population between the singly bonded carbon atoms in ethane, methylacetylene, propylene, etc., is found to be of negligible magnitude. Finally, we shall compare the present accurate results with results from a previous method, in which the one-electron Hamiltonian matrix elements for methylacetylene were based on those of ethane and acetylene.[7]

Procedure

The molecular orbitals were expanded as linear combinations of a minimum basis set of Slater-type atomic orbitals.[8] Slater exponents[8] were used for the carbon atoms, and an exponent of 1.2 was used for the hydrogen atoms. The reason for this choice of exponents has been given in a previous study of hydrocarbon wave functions.[5a] All molecular integrals were calculated accurately with IBM 7094 computer programs which have been extensively discussed elsewhere.[5] Of crucial importance was a program recently written by Palke and Ellis for calculating four-center, two-electron integrals involving more than two Slater-type 2p functions.[5b,c] Most integrals were obtained with an accuracy of better than five decimal places, while a few integrals had errors as large as 2×10^{-5} au. We thus expect all quantities derived from the calculated wave function to be accurate to at least three decimal places.

The geometry for methylacetylene (Table I) was based on a recent analysis of microwave data:[9] $r_{H(1)C(1)} = 1.056$ A, $r_{C(1)C(2)} = 1.206$ A, $r_{C(2)C(3)} = 1.459$ A, and $r_{C(3)H(2,3,4)} = 1.102$ A. Tetrahedral angles were assumed for the methyl group.

Table I. Molecular Geometry[a,b]

Center	x	y	z
C_1	0.0	0.0	−5.03619
C_2	0.0	0.0	−2.75710
C_3	0.0	0.0	0.0
H_1	0.0	0.0	−7.03177
H_2	1.96164	0.0	0.69916
H_3	−0.98082	1.69883	0.69916
H_4	−0.98082	−1.69883	0.69916

[a] See ref 9 for experimental data. [b] Coordinates are in atomic units.

Results and Discussion

The molecular orbital (MO) coefficients, eigenvalues, total energies, and dipole moments are presented in Table II. The population analysis[6] is given in Table III. This minimum basis set wave function gives about 70% of the observed atomization energy, calculated relative to minimum basis-set free atom energies.[10] The total energy differs from the total kinetic energy by less than 0.5%. Not surprisingly, the highest occupied MO's are those with π symmetry, although the highest occupied σ MO is almost degenerate with the lowest π MO. The eigenvalue of the highest occupied MO has a magnitude of 10.24 ev, within 0.2 ev of the experimental first ionization potential of methylacetylene (10.36 ev).[11]

One often finds dipole moments calculated from minimum basis-set wave functions to be in error by as much as a factor of 2.[12] We find, however, that the accurately calculated dipole moment of 0.70 D. for this methylacetylene wave function points in the expected direction ($^{-}HCCCH_3^{+}$) and is quite similar in magnitude to the experimental microwave value of 0.75 D.[2] In order to assess the contribution of the π-electron density to this calculated dipole moment, we have also computed a π-electron dipole moment, which is obtained as the difference between the centroid of the calculated π-electron density and that density obtained by placing one electron in each atomic basic orbital of π symmetry.[13] Appropriate orbitals of π symmetry are constructed from the three 1s orbitals of hydrogen in the usual manner:[3a] $(2H_2-H_3-H_4)/(6-6S)^{1/2}$ and $(H_3-H_4)/(2-2S)^{1/2}$, where H_2, H_3, H_4 are the methyl hydrogen 1s orbitals, and S is the overlap integral between any pair of them. These pseudo π orbitals mix, respectively, with the carbon $2p_x$ and $2p_y$ orbitals. To

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(4) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, pp 71–76.

(5) (a) For a detailed discussion of the programs used, see W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, 88, 2384 (1966), and references quoted therein. (b) See also, W. E. Palke and W. N. Lipscomb, *J. Chem. Phys.*, **45**, 3948 (1966). (c) The new, four-center molecular integral computer programs used in the present work were developed by W. E. Palke and D. E. Ellis and will be described by them in a forthcoming publication; see also W. E. Palke, Ph.D. Thesis, Harvard University, Sept 1966.

(6) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841 (1955).

(7) (a) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 88, 2353 (1966); (b) *ibid.*, 88, 2367 (1966).

(8) J. C. Slater, *Phys. Rev.*, 36, 57 (1930).

(9) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958). The methyl CH distance was taken as 1.102 A, the same value as was used for ethane by R. M. Pitzer and W. N. Lipscomb, *ibid.*, **39**, 1995 (1963). All other distances were Costain's r_s values.

(10) E. Clementi and D. L. Raimondi, *ibid.*, 38, 2686 (1963).

(11) K. Watanabe, F. Nakayama, and J. Motl, *J. Quant. Spectry. Radiative Transfer*, 2, 369 (1963).

(12) See, *e.g.*, B. J. Ransil, *Rev. Mod. Phys.*, 32, 245 (1960).

(13) Obviously, if more than a minimum basis set were being used, one would have to define atomic π orbitals in terms of this basis set, and then put the localized electrons into these orbitals. Our definition of the π dipole has been chosen to be independent of origin and also independent of nuclear charge.

Table II. Coefficients of Occupied Molecular Orbitals in the Methylacetylene Wave Function

MO		$1a_1$	$2a_1$	$3a_1$	$4a_1$	$5a_1$	$6a_1$	$7a_1$	$1e_x$	$1e_y$	$2e_x$	$2e_y$
Orbital energies[d] (au)		−11.3290	−11.2900	−11.2697	−1.0369	−0.9385	−0.7015	−0.5974	−0.5898	−0.5898	−0.3763	−0.3763
Basis function												
C_1	1s	−0.0009	0.0562	0.9943	−0.1057	0.1526	0.0883	0.0259	0.0	0.0	0.0	0.0
	2s	0.0007	−0.0065	0.0242	0.2967	−0.3973	−0.3168	−0.0082	0.0	0.0	0.0	0.0
	$2p_z$	0.0005	−0.0037	0.0035	0.1340	−0.1030	0.4505	−0.3075	0.0	0.0	0.0	0.0
	$2p_x$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0983	0.0	0.6168	0.0
	$2p_y$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0983	0.0	0.6168
C_2	1s	−0.0011	0.9942	−0.0566	−0.1575	0.0754	−0.1051	−0.0418	0.0	0.0	0.0	0.0
	2s	0.0051	0.0234	−0.0094	0.4081	−0.2213	0.2966	0.2201	0.0	0.0	0.0	0.0
	$2p_z$	0.0048	−0.0025	0.0040	−0.0127	0.3075	0.0405	0.4732	0.0	0.0	0.0	0.0
	$2p_x$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1859	0.0	0.5792	0.0
	$2p_y$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1859	0.0	0.5792
C3	1s	−0.9952	−0.0006	−0.0010	−0.1418	−0.1378	0.0314	0.0121	0.0	0.0	0.0	0.0
	2s	−0.0281	−0.0039	0.0004	0.4611	0.4393	−0.1235	−0.0873	0.0	0.0	0.0	0.0
	$2p_z$	0.0012	0.0029	−0.0004	−0.0749	0.0451	−0.2104	−0.4836	0.0	0.0	0.0	0.0
	$2p_x$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5791	0.0	−0.1744	0.0
	$2p_y$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5791	0.0	−0.1744
H_1		0.0001	−0.0001	−0.0044	0.0622	−0.1177	−0.3965	0.1918	0.0	0.0	0.0	0.0
H_2		0.0056	−0.0003	0.0000	0.0818	0.1149	−0.0855	−0.1501	0.4141	0.0	−0.1937	0.0
H_3		0.0056	−0.0003	0.0000	0.0818	0.1149	−0.0855	−0.1501	−0.2071	0.3586	0.0969	−0.1678
H_4		0.0056	−0.0003	0.0000	0.0818	0.1149	−0.0855	−0.1501	−0.2071	−0.3586	0.0969	0.1678

Electronic energy	174.2491 au
Nuclear repulsion	58.6661 au
Total energy	115.5830 au
Kinetic energy	115.0646 au
Atomization energy	
Calculated[a]	0.7158 au
Experimental[b]	1.0666 au

Total dipole moment 0.698 (0.781)[c] D.
π-Electron dipole moment 0.884 (0.941)[c] D.

[a] An optimized minimum basis set[10] was used for the free-atom energies. [b] The experimental heat of atomization at 0°K was obtained from the heats of atomization of elements given by T. L. Cottrell in "The Strength of Chemical Bonds," 2nd ed, Butterworth and Co., Ltd., London, 1958, and the $\Delta H_f°$ value for methylacetylene given by F. Rossini, K. S. Pitzer, R. M. Braun and G. C. Pimentel in "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. [c] The quantities in parentheses are the dipole moments calculated from the gross atomic charges (total and π only) listed in Table III. [d] Unoccupied MO's have the following positive eigenvalues: 0.3155, 0.3155, 0.4931, 0.6294, 0.6415, 0.6415, 0.6767, and 1.3618.

Table III. Population Analysis

		Gross orbital charges	Gross atomic charges Total	π electron[a]
C_1	1s	1.997	−0.220	−0.054
	2s	1.094		
	$2p_z$	1.075		
	$2p_x$	1.027		
	$2p_y$	1.027		
C_2	1s	1.997	−0.040	+0.028
	2s	1.051		
	$2p_z$	1.020		
	$2p_x$	0.986		
	$2p_y$	0.986		
C_3	1s	1.995	−0.407	−0.214
	2s	1.245		
	$2p_z$	0.953		
	$2p_x$	1.107		
	$2p_y$	1.107		
H_1	1s	0.822	+0.178	...
H_2	1s	0.837	+0.163	+0.080

	Overlap populations Total	π electron
C_1-C_2	1.875	1.005
C_2-C_3	0.789	0.012
C_1-H_1	0.823	...
C_3-H_2	0.777	...

[a] The π-electron contributions to the gross atomic charges on the carbon atoms are obtained by adding the negative π-electron orbital charges to atomic core charges of +2. The π-electron contribution to the methyl hydrogen gross charges is most easily obtained by the condition of electroneutrality. The σ-electron contributions are the difference between total and π-electron charges.

whatever extent our definition of the π-electron (and similarly, σ-electron) dipole moment is meaningful, we may say that the charge transfer in methylacetylene is predominantly a π-electron effect (see Table II). In fact, the σ-electron dipole moment, which is equivalent to the difference between the total and π-electron dipole moments, points in the opposite direction, thus indicating a back polarization of σ electrons to offset the large polarization occurring in the π-electron density.

Further insight into the charge distribution may be obtained from the population analysis. To give some indication of the reliability of gross atomic point charges (as given by a Mulliken population analysis[6]) as a measure of the molecular charge distribution, we have compared the dipole moments calculated in terms of them with the accurately computed values from the detailed wave function (Table II). The point-charge dipole moments are reasonably close to the correct values: ~10% too large for the total dipole moment, and ~6% too large for the π-electron dipole moment.[14] Let us then first consider the contribution to the gross atomic charges made by the σ-electron density (see footnote *a*, Table III). We find that of the over-all transfer of 0.082 electron from the methyl group to the acetylene group, 0.056 electron is donated by the σ-electron density. We emphasize that this result is not in conflict with the fact that the σ-electron dipole moment (calculated both with the actual σ-electron

[14] The π-electron dipole moment in terms of point charges is defined analogously to the accurate π-electron dipole moment defined previously, with point charges being assigned to atomic centers instead of electrons being assigned to atomic orbitals as before.

density and with the point charge approximation to it) implies the opposite direction of charge transfer. An over-all dipole moment depends not only on charge transfer between various groups, but also on the internal polarization of these groups. A similar situation was previously discussed for the case of toluene, in which the total calculated dipole moment had the expected direction in spite of a small gross negative charge on the methyl group.[7b] The π-electron contribution to the gross atomic charges of methylacetylene also indicates some electron donation by the methyl group (0.026 electron), and the polarity of the π-electron atomic charges, alternately positive and negative, clearly corresponds to the calculated direction of the π-electron dipole moment. Our final conclusion about the source of the dipole moment of methylacetylene and the validity of the hypotheses mentioned in the introductory section will be discussed in the next section, where the importance of π-electron delocalization is first considered.

We next examine the overlap populations, *i.e.*, the amounts of electron charge which the Mulliken population analysis assigns to each pair of atoms, and which are expected to be related to the strength of covalent bonding between each pair of atoms.[6] The C≡C overlap population (1.875) is negligibly different from that (1.875) which one obtains from acetylene itself,[5a] using the same C≡C distance (to within 0.001 A) and basis set. There is no experimental indication that replacing an acetylenic hydrogen with a methyl group has any appreciable effect on the triple-bond distance.[15] The C–C single-bond overlap population (0.789) is noticeably larger than the corresponding value for ethane (0.710),[5a] in accord with the marked shortening of the C–C bond length observed in methylacetylene.[15] The methyl C–H overlap population (0.777) is essentially the same as the values for ethane (0.785)[5a] and methane (0.780).[5a] Experimental bond lengths[16] suggest a slight weakening of the methyl C–H bond as one goes from methane to ethane to methylacetylene. Experimental stretching frequencies[17,18] and force constants[18] offer no clear-cut trend.

We wish finally to emphasize that the overlap population corresponding to π bonding across the C–C single bond of methylacetylene is negligible (+0.012). This result is in conflict with previous findings[2] on less accurate wave functions and will be discussed in the next section.

π-Electron Delocalization

The foregoing analysis of the methylacetylene wave function has clearly suggested that the observed dipole moment of methylacetylene is due primarily to a polarization of the π-electron density, in contrast to Dewar's proposal, which puts primary emphasis on the σ electrons. Postponing until the last section our evidence that the methyl group exerts no appreciable inductive effect on the acetylenic π orbitals, we now proceed to evaluate the contribution of delocalization to the π-electron polarization. Of course, the present discussion of π-electron density implies an arbitrary partitioning of the total molecular electron density. However, it is necessary to adopt this procedure so that our results may be compared with previous results in which the unique importance of π electrons and π-electron delocalization is assumed.

In order to analyze π-electron delocalization in the MO framework, we must define localized MO's.[19] For the MO's corresponding to the localized acetylenic π bond, we have simply taken the π MO's of the acetylene wave function, employing the same C≡C distance and basis set as was used for methylacetylene. The localized π MO's for the methyl group will clearly be linear combinations of the methyl carbon 2p orbitals and the pseudo π orbitals constructed from the hydrogen 1s orbitals. Assuming that these linear combinations may be obtained as the eigenvectors of an effective one-electron Hamiltonian,[3a] we must decide on the most appropriate choice for the matrix elements of this Hamiltonian, *i.e.*, the diagonal elements for the hydrogenic and methyl carbon π orbitals, and the off-diagonal element between them. Although the choice must necessarily be somewhat arbitrary, one would expect that either ethane or methane would be a reasonable reference molecule. *A priori* one might prefer methane, since Mulliken has suggested that appreciable π-electron delocalization may exist in the ethane molecule.[3a] However, since the corresponding matrix elements of the minimum basis-set one-electron Hamiltonians of methane[5a] and ethane,[5a] involving carbon 2p and hydrogen 1s orbitals, differ by less than 0.01 au, this choice between ethane and methane is not critical. In fact, if the matrix elements were taken from methylacetylene itself, essentially the same result would be obtained. In the work discussed below, we have simply taken the necessary matrix elements from the one-electron Hamiltonian of the methane wave function, calculated with the same basis set and CH distance as was employed in the methylacetylene calculation. The coefficients obtained for the localized methyl group π MO's are respectively 0.5957 and 0.5156 for the normalized carbon and hydrogenic π orbitals.

Before proceeding further we must emphasize that the localized MO's of the methyl and acetylenic fragments of methylacetylene are by no means orthogonal to each other, having an overlap integral of 0.124. An important physical consequence of this nonorthogonality is that in the normalized antisymmetrized wave function constructed with the localized π MO's, appreciable antibonding exists between the π orbitals of the adjacent methyl and acetylenic carbon atoms: the π-electron overlap population between these two atoms is −0.081. For comparison, the π bond of acetylene has an overlap population of +1.001.[5a] The correspondence of this antibonding to nonbonded repulsions in the valence bond method has already been discussed by Mulliken and Parr[20] for the case of

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(15) L. E. Sutton, Ed., "Interatomic Distances Supplement," Special Publication No. 18, The Chemical Society, London, 1965, pp M74S, M96S.

(16) Reference 9 and L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.*, **42**, 851 (1965), and references quoted therein.

(17) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp 306, 337, 344.

(18) Distinct values of the CH stretching force constant in methane and ethane have been given by G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952).

(19) Our localization of the π-electron MO's *changes* the total wave function and is not to be confused with the procedures of C. Edmiston and K. Ruedenberg (*Rev. Mod. Phys.*, **35**, 457 (1963)) and D. Peters (*J. Chem. Soc.*, 2901 (1964)), which do not affect the total wave function.

(20) R. S. Mulliken and R. G. Parr, *J. Chem. Phys.*, **19**, 1271 (1951).

benzene and butadiene. However, in benzene or butadiene, subsequent π-electron delocalization more than offsets this antibonding. Here, on the other hand, we are discussing cases of higher order conjugation (methylacetylene, ethane, etc.) in which the antibonding, expressed here in terms of overlap population, may just barely be overcome (or a bit of antibonding may remain) after π-electron delocalization is allowed to take place. Thus, the negligible π-electron overlap population between C_2 and C_3 in the methylacetylene wave function does not imply that π-electron delocalization has had no effect on π bonding across the single bond, but rather indicates that the antibonding in the hypothetical localized wave function is just cancelled by the process of delocalization. Similarly, in the case of ethane, a C–C π-electron overlap population of -0.074, computed when the degenerate MO's are constrained to be localized methyl π orbitals, is reduced to -0.022 in the completely delocalized wave function.[5a,21a]

To complement this discussion of delocalization in terms of relief of antibonding, we have calculated the energy gain which accompanies the delocalization of the π-electron density in methylacetylene. Using the localized MO's defined above, we find the vertical delocalization energy of methylacetylene to be 7.62 kcal. Mulliken and Parr have obtained a formula[3a,20] which reproduces accurately the heats of formation of saturated acyclic hydrocarbons and ethylene and acetylene, molecules in which no ordinary conjugation occurs. Thus deviations of predicted and observed heats of formation, when this formula is applied to conjugated unsaturated molecules, are equated to π-electron delocalization energies. For methylacetylene, this formula leads to an "observed" resonance energy of 3.09 kcal,[3a] which is based on standard single and multiple bond lengths. We now add to this value the compression energy, 1.1 kcal,[3a] required to shorten the C–C single bond to its actual length in methylacetylene. This "observed" vertical resonance energy of 4.2 kcal must now be corrected further because the empirical formula of Mulliken and Parr does not include what Mulliken has called second-order hyperconjugation:[3a,20] even for the saturated hydrocarbons, which are predicted to have no delocalization energy by the formula, it is claimed that some delocalization occurs across C–C single bonds.[3a] Since this type of conjugation energy is included in theoretical calculations, it must be added to the "observed" values, before the latter may be compared with the theoretical values. Although different types of single bonds might be expected to have different amounts of second-order hyperconjugation energy, following Mulliken and others,[3a] we assume that the π-electron delocalization energy in ethane is a reasonable approximation for all C–C single-bond, second-order hyperconjugation energies. Using an accurate ethane wave function[5a] and the localized methyl π orbital defined above, we have calculated the vertical delocalization energy of ethane to be 3.26 kcal.[21b] Hence a quantity of approximately this magnitude should be added to the value of 4.2 kcal quoted above. Since the C–C single-bond distance in methylacetylene is somewhat shorter than in ethane, the correction should presumably be slightly larger than 3.26 kcal. Thus a lower limit to the "observed" vertical resonance energy of methylacetylene is 7.5 kcal, in strikingly close agreement with the theoretical value of 7.62 kcal. However, as Mulliken has pointed out, agreement of this type may be fortuitous.[21c]

Our main interest in π-electron delocalization is its importance as a contributing factor to the dipole moment of methylacetylene. Although the localized methyl π MO's are already polarized in the same direction as the dipole moment of the delocalized wave function, we find that π-electron delocalization considerably strengthens the polarity of the π-electron density: the localized wave function has a π-electron dipole moment of 0.394 D., compared to the value of 0.884 D. for the delocalized wave function. We are therefore finally able to conclude, in agreement with previous MO studies, that a satisfactory account of the methylacetylene dipole moment can be given in terms of π-electron delocalization, although we find that (1) the π-electron effect is somewhat offset by reverse polarization of the σ electrons, and (2) part of the π-electron polarization is inherent in the methyl group. Furthermore, in the next section we shall see that there is no indication from the present calculation that the methyl group exerts an inductive effect on the acetylene π orbitals. Dewar's emphasis on the σ-electron density is consistent with our observation that most of the electronic charge donated by the methyl group (in terms of population analysis) does indeed come from the σ-electron density. However, Dewar's hypothesis about the source of the dipole moment is not borne out by the present calculation.

In the absence of a more accurate wave function for a molecule of this complexity, we can only hope that we have emphasized those molecular properties which will not be qualitatively different when it becomes feasible to obtain still better wave functions. We now turn to a comparison of some of these molecular properties with those derived earlier from more approximate wave functions.

Comparison with Previous Results

In many previous molecular orbital studies it has been assumed that a simple relationship exists between diagonal matrix elements of the one-electron Hamiltonian (referred to below as α's) and intramolecular charge transfer.[3a] Recently, however, a new method for choosing one-electron Hamiltonian matrix elements was proposed, which was based not upon any assumptions about relationships between charge transfer and α's, but rather on the assumption that, as a first approximation, α's for large molecules can be transferred directly from smaller, related molecules.[22] In the case of methylacetylene, the α's were taken from ethane and acetylene. This choice of parameters, according to

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(21) (a) Some recent semiempirical calculations involving neglect of overlap (J. A. Pople and D. P. Santry, *Mol. Phys.*, **9**, 301 (1965); and J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965)) have indicated appreciable π bonding across the C–C bond of ethane. If the ethane wave function of ref 5a is expanded in terms of orthogonalized atomic orbitals (OAO's) (P.-O. Lowdin, *ibid.*, **18**, 365 (1950)), a C–C π-electron bond order of 0.219 is obtained, similar in magnitude to the results of Pople, *et al.* However, we emphasize that the OAO's are delocalized to an extent which makes their usefulness as "atomic orbitals" questionable. Furthermore, the semiempirical calculations are not necessarily to be considered as using OAO's. (b) Previous semiempirical values of the second-order hyperconjugation energy of ethane have ranged from 1.3 to 5.0 kcal; see ref 3a. (c) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959).

(22) See ref 7. A similar proposal was made by M. K. Orloff and D. D. Fitts, *J. Am. Chem. Soc.*, **85**, 3721 (1963).

previous rationales, would have implied that the methyl group was strongly π-electron attracting, since the α's for the methyl π orbitals were much more negative than the acetylene π α's. Surprisingly, however, this choice yielded a wave function whose dipole moment pointed in the expected direction, and which, in fact, exaggerated the polarization in this direction.[7b] This result is not so disturbing when one considers that the previous rationales ignored the importance of off-diagonal Hamiltonian matrix elements as a factor governing intramolecular charge transfer.

Values of α for methylacetylene are listed in Table IV. The values in column A were taken directly from the appropriate atoms of ethane[23] or acetylene.[23] Accurate values of α from the present calculation are given in column B. Comparison of the two columns shows that the previous proposal for obtaining α's is quite reasonable; it correctly takes account of the significant difference between orbitals on tetrahedral and digonal carbon atoms, and between σ and π 2p orbitals on unsaturated carbon atoms. However, Table IV also reveals that changes in values of α, of the order of 1 ev (0.0367 au), do occur, as the molecular environments of the atoms change in going from ethane and acetylene to methylacetylene. We emphasize that the carbon 1s α's are as sensitive as the α's of valence orbitals.

Table IV. Diagonal One-Electron Hamiltonian Matrix Elements for Methylacetylene (au)

Center	Orbital	A[a]	B[b]
C_1	1s	−11.294	−11.266
	2s	−1.460	−1.444
	$2p_z$	−0.749	−0.733
	$2p_x$	−0.169	−0.157
	$2p_y$	−0.169	−0.157
C_2	1s	−11.294	−11.289
	2s	−1.460	−1.490
	$2p_z$	−0.749	−0.824
	$2p_x$	−0.169	−0.180
	$2p_y$	−0.169	−0.180
C_3	1s	−11.277	−11.327
	2s	−1.449	−1.503
	$2p_z$	−0.386	−0.461
	$2p_x$	−0.354	−0.400
	$2p_y$	−0.354	−0.400
H_1	1s	−0.564	−0.553
H_2	1s	−0.501	−0.523

[a] Values in column A are taken directly from the one-electron Hamiltonian matrices for ethane and acetylene given in ref 5a. [b] Present work.

The approximate methylacetylene calculation[7b] referred to above depended upon the use of a calibrated Mulliken approximation for the off-diagonal matrix elements of the potential energy part of the one-electron Hamiltonian.[24] This approximation leads to errors, based on the present accurate results, for the most part less than 0.5 ev, although a few of the approximate off-diagonal elements were found to be in error by 1–2 ev. The approximate eigenvalues of the occupied MO's are found to differ from the accurate values by less than 1 ev.

In spite of the generally good agreement of energy quantities from the two methylacetylene calculations, the respective charge distributions show appreciable differences. As one might expect, the approximate results, which were not obtained by a self-consistent procedure, show an exaggerated amount of charge transfer. The gross atomic charges from the approximate calculation,[7b,25] corresponding to those listed in Table III, are −0.57, +0.22, −0.04, +0.21, and +0.06.[26,27] Similarly, the total dipole moment of the approximate wave function is 1.71 D. Having pointed out the quantitative discrepancies between the two methylacetylene charge distributions, we stress that certain qualitative features are common to both wave functions: the total dipole moment is essentially a π-electron effect, the gross atomic charges indicate the same bond polarities, in both cases the methyl group is somewhat electron deficient, and the π-electron overlap population for the C–C single bond is negligible.

We shall not attempt here a detailed rationalization of the differences among the accurate values of α listed in Table IV. The differences between the α's for the two acetylenic carbon atoms seem at first sight to be consistent with the shielding argument used to justify the ω technique:[28] the terminal carbon atom has a larger negative charge than that of −0.188 in free acetylene,[5a] and hence has less negative values of α (relatively to acetylene); correspondingly, the other acetylenic carbon atom has a less negative charge and more negative values of α than the corresponding values in free acetylene. However, this is fortuitous, since shielding effects from the other centers have similar magnitudes. Furthermore, the methyl carbon atom, although more negative than the ethane carbon atom,[5a] has considerably more negative values of α than does ethane.[5a] This situation arises because the methylacetylene carbon atom is adjacent to strongly positive hydrogen atoms and to an almost neutral carbon atom. It is thus clear that if the approach of the ω technique is to be reliable, it must take into account, among other factors, shielding effects from neighboring centers.[29] Finally, the fact that the α's of the acetylene carbon atom adjacent to the methyl group are *more* negative than the α's of the terminal acetylenic carbon atom suggests that the inductive model of charge transfer is not compatible with the present calculation.

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(23) The ethane and acetylene α's were taken from ref 5a; in the approximate methylacetylene calculation,[7b] some averaging of these α's was performed to reduce the number of parameters; *i.e.*, single values of α for the carbon 1s, carbon 2s, and hydrogen 1s orbitals, and a single value for the α of the methyl 2p orbitals were used.

(24) R. S. Mulliken, *J. Chem. Phys.*, **46**, 497, 675 (1949), and ref 7.

(25) We wish to correct two misprints in ref 7b: in Figure 1, $q_{H_3} = +0.118$; in Table VIII, $q_R^{\pi} = +0.074$ for methylacetylene.

(26) The extended Hückel theory (R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963)) yields values of gross atomic charge which lie between the two sets discussed here: C_1, −0.351; C_2, +0.043; C_3, −0.273.

(27) We wish to point out that the quantities referred to as net atomic charges in ref 7 should properly be called gross atomic charges, in accord with ref 6.

(28) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949); N. Muller, L. W. Pickett, and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 4770 (1954); and A. Streitwieser, Jr., *ibid.*, **82**, 4123 (1960).

(29) See, *e.g.*, A. Streitwieser, Jr., A. Heller, and M. Feldman, *J. Phys. Chem.*, **68**, 1224 (1964).

Table V. Hamiltonian Matrix (au)

	1C1s	1C2s	1C2p$_z$	1C2p$_x$	1C2p$_y$	2C1s	2C2s	2C2p$_z$
1C1s	−11.266	−2.639	−0.005	0.000	0.000	−0.003	−0.775	1.298
1C2s	−2.639	−1.444	−0.187	0.000	0.000	−0.776	−0.937	0.774
1C2p$_z$	−0.005	−0.187	−0.733	0.000	0.000	−1.300	−0.784	0.262
1C2p$_x$	0.000	0.000	0.000	−0.157	0.000	0.000	0.000	0.000
1C2p$_y$	0.000	0.000	0.000	0.000	−0.157	0.000	0.000	0.000
2C1s	−0.003	−0.776	−1.300	0.000	0.000	−11.289	−2.643	0.005
2C2s	−0.775	−0.937	−0.784	0.000	0.000	−2.643	−1.490	0.129
2C2p$_z$	1.298	0.774	0.262	0.000	0.000	0.005	0.129	−0.824
2C2p$_x$	0.000	0.000	0.000	−0.367	0.000	0.000	0.000	0.000
2C2p$_y$	0.000	0.000	0.000	0.000	−0.367	0.000	0.000	0.000
3C1s	0.000	−0.021	−0.037	0.000	0.000	0.000	−0.444	−0.753
3C2s	−0.022	−0.121	−0.162	0.000	0.000	−0.442	−0.661	−0.604
3C2p$_z$	0.037	0.163	0.211	0.000	0.000	0.749	0.604	0.294
3C2p$_x$	0.000	0.000	0.000	−0.033	0.000	0.000	0.000	0.000
3C2p$_y$	0.000	0.000	0.000	0.000	−0.033	0.000	0.000	0.000
1H1s	−0.853	−0.765	0.427	0.000	0.000	−0.059	−0.204	0.251
2H1s	−0.007	−0.036	−0.045	−0.003	0.000	−0.083	−0.217	−0.228
3H1s	−0.007	−0.036	−0.045	0.002	−0.003	−0.083	−0.217	−0.228
4H1s	−0.007	−0.036	−0.045	0.002	0.003	−0.083	−0.217	−0.228

	2C2p$_x$	2C2p$_y$	3Cls	3C2s	3C2p$_z$	3C2p$_x$	3C2p$_y$	1H1s	2H1s	3H1s	4H1s
1C1s	0.000	0.000	0.000	−0.022	0.037	0.000	0.000	−0.853	−0.007	−0.007	−0.007
1C2s	0.000	0.000	−0.021	−0.121	0.163	0.000	0.000	−0.765	−0.036	−0.036	−0.036
1C2p$_z$	0.000	0.000	−0.037	−0.162	0.211	0.000	0.000	0.427	−0.045	−0.045	−0.045
1C2p$_x$	−0.367	0.000	0.000	0.000	0.000	−0.033	0.000	0.000	−0.003	0.002	0.002
1C2p$_y$	0.000	−0.367	0.000	0.000	0.000	0.000	−0.033	0.000	0.000	−0.003	0.003
2C1s	0.000	0.000	0.000	−0.442	0.749	0.000	0.000	−0.059	−0.083	−0.083	−0.083
2C2s	0.000	0.000	−0.444	−0.661	0.604	0.000	0.000	−0.204	−0.217	−0.217	−0.217
2C2p$_z$	0.000	0.000	−0.753	−0.604	0.294	0.000	0.000	0.251	−0.228	−0.228	−0.228
2C2p$_x$	−0.180	0.000	0.000	0.000	0.000	−0.191	0.000	0.000	−0.085	0.043	0.043
2C2p$_y$	0.000	−0.180	0.000	0.000	0.000	0.000	−0.191	0.000	0.000	−0.074	0.074
3C1s	0.000	0.000	−11.327	−2.652	0.003	0.000	0.000	−0.002	−0.776	−0.776	−0.776
3C2s	0.000	0.000	−2.652	−1.503	0.056	0.000	0.000	−0.016	−0.745	−0.745	−0.745
3C2p$_z$	0.000	0.000	0.003	0.056	−0.461	0.000	0.000	0.023	−0.138	−0.138	−0.138
3C2p$_x$	−0.191	0.000	0.000	0.000	0.000	−0.400	−0.000	0.000	−0.426	0.213	0.213
3C2p$_y$	0.000	−0.191	0.000	0.000	0.000	0.000	0.400	0.000	0.000	−0.369	0.369
1H1s	0.000	0.000	−0.002	−0.016	0.023	0.000	0.000	−0.553	−0.005	−0.005	−0.005
2H1s	−0.085	0.000	−0.776	−0.745	−0.138	−0.426	0.000	−0.005	−0.523	−0.274	−0.274
3H1s	0.043	−0.074	−0.776	−0.745	−0.138	0.213	−0.369	−0.005	−0.274	−0.523	−0.274
4H1s	0.043	0.074	−0.776	−0.745	−0.138	0.213	0.369	−0.005	−0.274	−0.274	−0.523

Thomas H. Dunning and Mr. Robert E. Frank for bringing to our attention an error in the computer program used to calculate dipole moment integrals.[30] The authors also benefited from a discussion with Mr. B. J. Nicholson.

Appendix

The development of transferable parameters among related molecules is facilitated by use of the one-electron Hamiltonian (F) matrix, which is given in Table V for this SCF calculation on methylacetylene.

(30) The error involved the two-center dipole moment integrals between s and p Slater orbitals. We wish to make the following corrections to published dipole moment values. The value for NH_3 reported in ref 5a should be changed to 1.76 D. The values for H_2CO reported by M. D. Newton and W. E. Palke (*J. Chem. Phys.*, **45**, 2329 (1966)) should be 0.598 D. (H exponent, 1.0) and 1.006 D. (H exponent, 1.2). The magnitudes of the total dipole moments reported in ref 7b should generally be increased by ~0.05–0.10 D. The program error had no significant effect on the dipole moment directions. It did, however, cause considerable exaggregation of the π-electron components of the dipole moments reported in ref 7b for molecules containing an alkyl group bonded to an unsaturated carbon atom, and these values should be disregarded.