been large enough to produce an overall raising of the n orbital (relative to the parent compound). The secondary σ effect stabilizes the π^* orbitals of *trans*-HO-N=NH and -F—N=NH, with the result that they occur at lower energies than the π^* orbital in *trans*-HN=NH. Thus, although the order of the n $\rightarrow$ π^* transition energies in the trans compounds is identical with the order in the substituted carbonyls, the effect of substituents on the n and π^* orbitals is quite different for the two chromophores.

Conclusions

Ab initio minimal basis SCF–CI calculations have been performed on a series of small molecules possessing uv bands which may be attributed to n $\rightarrow$ π^* excitations. The calculated results show that this level of theory can give an adequate description of such transition energies. The changes of transition energy produced by substituents show very similar trends for four different chromophores and follow the order of the π-donating ability of the substituents. However, an analysis of each series suggests that this is somewhat misleading. There are two effects associated with both π donation and σ withdrawal, and the transition energy depends on a balance among these four effects. For molecules containing unsaturated substituents which can conjugate with the chromophore, inclusion of CI was found to be necessary for an adequate description of the n $\rightarrow$ π^* excited singlet states. The interaction between the two nitrogen lone pairs in azo compounds was found to be much larger in the trans isomers and consequently the two n $\rightarrow$ π^* states are split to a greater extent in the trans isomers than in the cis compounds.

Localized Molecular Orbitals in Methane and Ethane and the Transferability of the Chemical Bond between These Molecules

David Peters

Contribution from the Department of Chemistry, Royal Holloway College, University of London, Englefield Green, Surrey, England.

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Abstract: The localized molecular orbitals (MO's) of the self-consistent-field wave functions of methane and ethane are examined in order to compare the calculated carbon–hydrogen bonds of the two molecules and to see how nearly identical are these two bonds. The results show that in many ways the two carbon–hydrogen bonds are indeed very alike and not far removed from Pauling's description of them. The general question of the choice of the localization route is discussed and illustrated.

In some earlier work,[1] the localized molecular orbitals (MO's) which correspond to chemical bonds and lone pairs were examined in an effort to establish a simple but rigorous theoretical description of these bonds and lone pairs. It must not be felt that these results are final or definitive, because there are some improvements which could be made in them.

The two molecules methane and ethane are treated separately from the main group of molecules for several reasons. First, they are the prototype of the whole class of saturated organic compounds. Second, this pair of molecules is the natural testing ground for ideas about the transferability of the chemical bond from one molecule to another.[2] Third, these two molecules exemplify many of the ideas developed earlier[1] and, in particular, they are a useful exercise in some aspects of the localization problem. Fourth, it is interesting to see just how much information may be derived from such wave functions as these.

The wave functions at the all-electron, all-integral self-consistent field level of approximation were computed for methane and ethane by the writer[3] and by Pitzer and Lipscomb,[4] respectively. There are several other methane computations available.[5]

Summary of Procedure

The methane results may be taken directly from the literature.[3] The ethane results are obtained as follows. We consider a $2n$-electron, closed-shell molecule with n doubly occupied MO's which are taken in real form throughout. Then we follow Coulson, Lennard-Jones, and others[6] by replacing the Slater determinant Ψ' of delocalized MO's (ϕ') by the determinant Ψ of localized MO's (ϕ), where the row vector of the delocalized MO's and that of the localized MO's are related by[1a]

$$\boldsymbol{\phi} = \boldsymbol{\phi}'\mathbf{A} \qquad (1)$$

The matrix $\mathbf{A}$ is an $n \times n$ orthogonal matrix, and it is chosen in such a way as to localize the MO's into regions of space.

Given the forms of the localized MO's we can read off the hybridizations in the valence atomic orbitals

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(1) (a) D. Peters, *J. Chem. Soc.*, 2003 (1963); (b) 2015 (1963); (c) 4017 (1963); (d) 2901 (1964); (e) 2908 (1964); (f) 2916 (1964); (g) 3026 (1965); (h) 644 (1966); (i) 652 (1966); (j) 656 (1966).

(2) T. L. Allen and H. Shull, *J. Chem. Phys.*, 35, 1644 (1961); C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, 34, 457 (1963).

(3) D. Peters, *J. Chem. Phys.*, 51, 1559, 1566 (1969).

(4) R. M. Pitzer and W. Lipscomb, *ibid.*, 39, 1995 (1963).

(5) *Cf.* O. Sinanoğlu and D. F. Tuan, *Annu. Rev. Phys. Chem.*, 15, 260 (1964); J. Sinai, *J. Chem. Phys.*, 39, 1575 (1963).

(6) C. A. Coulson, *Trans. Faraday Soc.*, 38, 433 (1942); J. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, 198, 1, 14 (1949).

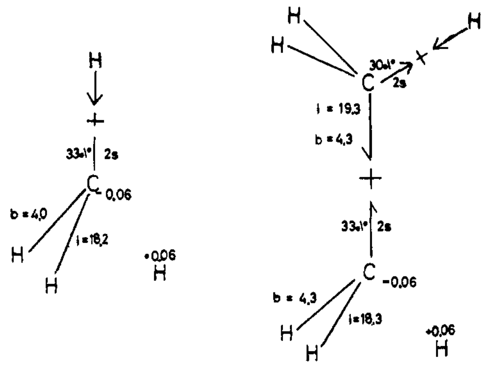

Figure 1. Hybridization, atomic charge, ionization energy, and binding energy for methane and ethane. Symbols are defined in ref 1a,b. The symbol *i* is the ionization energy or energy parameter of the bond and *b* is the binding energy.

and in the lone-pair orbitals[1a] and also the atomic charges.[1b] With each molecular orbital there is associated an energy parameter which represents the ionization energy of this MO (Koopmans' theorem).[7] Notice carefully that this ionization energy is *not* the observable ionization energy of the molecule: this latter quantity is the energy parameter of the delocalized MO's.[8] These ionization energies of the localized MO's[1d] are the diagonal elements of the **e** matrix, which is related to the **e′** matrix, which is diagonal by the transformation

$$\mathbf{e} = \tilde{\mathbf{A}}\mathbf{e}'\mathbf{A} \tag{2}$$

where $\tilde{\mathbf{A}}$ is the transposed (reciprocal) matrix of **A**.

From the ionization energy of the bond, we can derive the binding energy of the bond[1e] from the equation

$$b = (-\delta e^{\mu}) = (-e^{\mu}) - \{l_{\mathrm{a}}(-e_{\mathrm{a}}) + l_{\mathrm{b}}(-e_{\mathrm{b}})\} \tag{3}$$

The theory shows[1f] that the bond energy is given, to a well-defined approximation, by twice the binding energy plus a repulsive term which is written as C. That is

$$E^{\mu} = 2b - C \tag{4}$$

It often turns out that the repulsive term is about equal to b, so the bond energy is roughly equal to b itself. There is no theoretical justification for this last result.

Finally, we can go back to the localization step of eq 1 and notice that perfect localization is rarely achieved.[1g] Then we may ask how nearly localized the bonds and lone pairs are. The simplest way to estimate this is to evaluate the overlap integral $S(\mu^*, \mu)$ between the exact, slightly delocalized bond μ and the perfectly localized bond μ^*. A more sophisticated way of estimating this "σ conjugation" energy is a direct calculation of it,[3] but we cannot easily do the same thing for ethane.

When all these steps have been completed, we have a quite thorough picture of the electron organization in the molecule itself and also in the bonds and lone pairs. These results are expressed in terms of well-defined quantities which are closely related to those commonly used in chemical valence theory.[9] There are in all seven pieces of information for the general bond.

The final step is to compare the results for methane with those for ethane, particularly those for the two carbon–hydrogen bonds.

Methane. In this section, the results for the methane molecule are written down. Methane is a ten-electron molecule, so that, in the electronic ground state, there are five doubly occupied MO's. In the delocalized picture, two of these MO's are a_1 MO's which are close to spherically symmetrical; the other three MO's are the triply degenerate t_2 MO's which resemble a 2p atomic orbital in general shape.

The localization of the methane MO's has been reported,[10] but, as pointed out earlier, the localized MO's of methane may be calculated directly.[3] We use the results of ref 3 in this work. Some of these results are reproduced in Figure 1 and others are summarized in the next paragraph.

The inner-shell MO was held fixed at the 1s atomic orbital in ref 3. There is 0.96% of the carbon 1s atomic orbital in the valence orbital of the carbon atom. This is rather larger than the values found earlier for the amount of 1s atomic orbital in a valence atomic orbital. The energy parameter of the carbon–hydrogen bond is 18.2 eV, and this is the diagonal element of the **e** matrix of eq 2. The binding energy of the bond is obtained from eq 3 and is 4.0 eV. The experimental bond energy of methane is 3.6 eV if this quantity is simply defined as one quarter of the atomization energy. So the bond energy is again close to the "binding energy" of the bond. The ionic bond energy[11] of the carbon–hydrogen bond is effectively zero. In the earlier work, an ionic bond energy of about 0.5 eV was obtained for the carbon–hydrogen bond of hydrogen cyanide and acetylene, so it seems that this latter carbon–hydrogen bond is more polar than the methane bond. This agrees with general experience for these bonds. The dipole–dipole interaction energy between two of the carbon–hydrogen bonds of methane is known[3] to be −0.04 eV, the minus sign denoting that the molecule is destabilized by this interaction.

Ethane. The localization of the MO's of this molecule has been examined by Pitzer[11] using Reudenberg's criterion of localization.[2] In the present work we examine the localization from the beginning without selecting any one criterion of localization.

There are 18 electrons in the ethane molecule and, in the delocalized description of the electronic ground state, these electrons occupy three a_1' MO's, two a_2'' MO's, one doubly degenerate e' MO and one doubly degenerate e'' MO. This is the eclipsed case of symmetry D_{3h}. One of the a_1' MO's is close to $(1s + 1s')/\sqrt{2}$ and one of the a_2'' MO's is close to $(1s - 1s')/\sqrt{2}$. These latter are essentially the inner-shell MO's. We now have altogether four parameters to dispose of, but it turns out that three of these are restricted parameters and only the fourth one is a freely disposable parameter. Of the three restricted parameters, one is contained in a 2 × 2 transformation between the two a_2'' MO's, and this parameter is used to remove the 1s

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[7] T. Koopmans, *Physica*, **1**, 104 (1933).

[8] D. Peters, *J. Chem. Phys.*, **45**, 3474 (1966).

[9] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

[10] G. G. Hall and J. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, **205**, 360 (1951).

[11] R. M. Pitzer, *J. Chem. Phys.*, **41**, 2216 (1964).

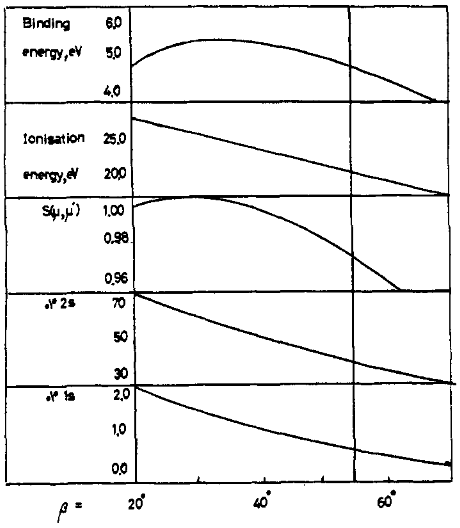

Figure 2. Properties of the carbon–carbon bond as a function of the parmeter β. (*Cf.* footnote *a*, Table I.)

atomic orbital of the hydrogen atoms from the inner-shell type a_2'' MO. The second of the three restricted parameters is used to remove the 1s atomic orbital of the hydrogen atoms from the inner-shell type a_1' MO. The third restricted parameter cannot be used constructively and is arbitarily set equal to unity.

This procedure generates an a_1' MO and an a_2'' MO whose sum and difference give the two inner-shell MO's in the form

$$\phi(\text{k shell}) = 0.99830(1s_C) + 0.05418(2s_C) - 0.00234(1s_{C'}) + 0.00363(2s_{C'}) - 0.00137(2p_{z_C} - 2p_{z_{C'}}) \quad (5)$$

The partner inner-shell atomic orbital of the primed carbon atom is obtained by exchanging the primed and unprimed carbon atoms. The inner shell of methane is $1.0000(1s_C)$. The similarity between the analytical form of the inner shell of methane and that of ethane (5) suggests that these portions of the wave functions may be transferable between the two molecules. In addition, the energy parameters of the k-shell MO's are virtually identical (308.33 eV for methane and 308.21 eV for ethane). This result is like that of Ruedenberg and his colleagues,[12] in which they show that the k shells, expressed in a natural orbital expansion, are invariant on molecule formation both for LiH and for BH.

Having dealt with the inner shells, we are left with seven valence-shell MO's, two a_1', one a_2'', one e′, and one e′′ MO. From these we make one carbon–carbon bond and six carbon–hydrogen bonds. We have one freely disposable parameter, the angle β say, which we can use in a 2 × 2 transformation between the two a_1' MO's. That is

$$[\mu_{CC'}, a_1'] = [1a_1', 2a_1']\begin{bmatrix} \cos\beta & -\sin\beta \\ \sin\beta & \cos\beta \end{bmatrix} \quad (6)$$

One of the resulting MO's is the carbon–carbon bond $\mu_{CC'}$ and the other a_1' MO is to be used with the other MO's to generate the six carbon–hydrogen bonds. This is done with the fixed transformation

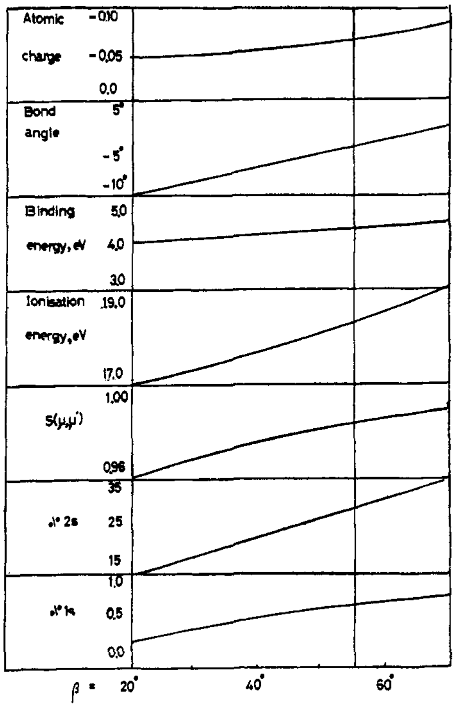

Figure 3. Properties of the carbon–hydrogen bond as a function of the parameter β. (*Cf.* footnote *a*, Table I.)

$$[\mu_1\mu_2\mu_3\mu_4\mu_5\mu_6] = [a_1'a_2''e'e'e''e''] \times \begin{bmatrix} p & p & p & -p & -p & -p \\ p & p & p & p & p & p \\ q & -r & -r & -q & r & r \\ 0 & s & -s & 0 & -s & s \\ q & -r & -r & q & -r & -r \\ 0 & s & -s & 0 & s & -s \end{bmatrix} \quad (7)$$

where $p = 6^{-1/2}$, $q = 3^{-1/2}$, $r = 12^{-1/2}$, and $s = 0.5$. Both the forms and the energy parameters of both the carbon–hydrogen bond and the carbon–carbon bond depend on the value of the parameter β. This parameter has been varied over a range and the values of the various quantities which depend on β are shown in Table I and in Figures 2 and 3. These values are useful in showing how sensitive are the various properties to this parameter. For reasons which are explained below, we choose the value of 55° for β and then everything is fixed. Some of the results are as follows.

The MO of the carbon–carbon bond is

$$\mu_{CC'} = 0.30084(hy_C + hy_{C'}) - 0.0752(h_1 + h_2 + h_3 + h_4 + h_5 + h_6) \quad (8)$$

where the hybrid on carbon is the normalized hybrid

$$hy_C = -0.07353(1s_C) + 0.5727(2s_C) + 0.8165(2p_C) \quad (9)$$

This hybrid corresponds to 33% 2s character, which is an sp^2 hybrid rather than the sp^3 hybrid which is widely assumed for the carbon hybrid orbitals in ethane. The overlap integral between the exactly localized MO and the MO of (8) is 0.973, and this is well below the

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[12] E. L. Mehler, K. Ruedenberg, and D. M. Silver, *J. Chem. Phys.*, **52**, 1181 (1970).

Table I. Dependence of Bond Properties on the Parameter β[a]

β, deg	% 1s	% 2s	$S(\mu, \mu')$	Ionization energy, eV	Binding energy, eV		
			Carbon–Carbon Bond (Figure 2)				
20	2.0	77.5	0.9987	27.3	4.7		
30	1.5	65	0.9998	25.4	5.4		
40	1.1	52	0.9946	23.0	5.2		
50	0.7	39	0.982	20.5	4.8		
55	0.55	33	0.9735	19.3	4.6		
60	0.4	27	0.9630	18.2	4.4		
70				16.25	4.2		
			Carbon–Hydrogen Bond (Figure 3)				
						Bond angle, deg	Atomic charge
20	0.33	15.0	0.961	17.0	4.0	−9	−0.04
30	0.43	19.2	0.970	17.3	4.0	−7	−0.045
40	0.53	23.6	0.977	17.7	4.0	−5	−0.052
50	0.63	28.0	0.982	18.1	4.2	−2	−0.06
55	0.665	30.0	0.983	18.3	4.3	0	−0.066
60	0.70	31.95	0.984	18.5	4.3	2	−0.07
70	0.75	35.3	0.984	18.8	4.4	6	−0.08

[a] The % 1s and % 2s are the percentages of these atomic orbitals in the valence orbital used by the carbon atom to form the bond in question. $S(\mu, \mu')$ is the measure of how well localized the bond is. The bond angle is the angle between the hybrid atomic orbital on carbon and the carbon–hydrogen internuclear line. A negative sign for the bond angle means that the HCH angle is less than 109.5°. The atomic charge is the differential charge on the carbon atom which results from the polarity of one carbon–hydrogen bond.

recommended value of 0.995 for a well-localized bond. The energy parameter of the bond is 19.3 eV and the binding energy is 4.6 eV. All of these results except the low value of the overlap integral seem satisfactory.

The MO of the carbon–hydrogen bond is

$$\begin{aligned}\mu_1 = {} & 0.53997(\mathrm{h}_1) + 0.60226(\mathrm{hy_C}) + \\ & [-0.09336(\mathrm{h}_2 + \mathrm{h}_3) - 0.06596(\mathrm{h}_4) - \\ & 0.00839(1\mathrm{s}_{\mathrm{C}'}) - 0.05096(2\mathrm{s}_{\mathrm{C}'}) - \\ & 0.04688(2\mathrm{p}_{z_{\mathrm{C}'}}) - 0.01163(2\mathrm{p}_{\pi_{\mathrm{C}'}})] \qquad (10)\end{aligned}$$

where $\mathrm{hy_C}$ is the normalized hybrid orbital

$$\begin{aligned}\mathrm{hy_C} = {} & -0.08156(1\mathrm{s_C}) + 0.54803(2\mathrm{s_C}) + \\ & 0.83247(2\mathrm{p}_1) \qquad (11)\end{aligned}$$

and the 2p orbital is that which points straight at H(1). The hybridization corresponds to 30% 2s character, which is closer to sp^2 than to sp^3. The terms in the square brackets of (10) show the nature of the delocalization of the electron out of μ_1. The overlap integral between the perfectly localized MO and that of (10) is 0.984, and again this is low as compared with earlier experience.[1g] The energy parameter of 18.3 eV and the binding energy of 4.3 eV are much as expected for this bond. The ionic bond energy is effectively zero and the dipole–dipole interaction energy of the geminal carbon–hydrogen bonds is −0.01 eV per pair.

Some of the results for ethane are shown in Figures 1, 2, and 3 and all results are given in detail in Table I.

Discussion

We should perhaps begin with the discussion of the choice of the β value of 55°. It is simpler, for purposes of exposition, to assume this value in the first instance and return to the question at the end of the discussion.

Hybridization. The carbon hybrid atomic orbital of methane is a hybrid which contains 33% 2s character or $s^{1/3}p^{2/3}$ or sp^2. The ethane result is consistent with the methane one, and the fact that two independent computations of the two wave functions lead to the same result strengthens one's confidence in the result. Evidently, there is less than complete promotion of the carbon atom to the sp^3 state. The "total hybridization" of the carbon atom in methane is $s^{1.33}p^{2.67}$ and that of ethane is $s^{1.23}p^{2.66}$. Notice that this conclusion is sensitive to the chosen value of the parameter β, but it does seem that the traditional value of sp^3 for these carbon valence orbitals is an overestimate of the amount of promotion of the carbon atom.

The situation is not quite as clear as this, however, because although this result is consistent with some earlier work[13] it is contradicted by other work.[14] If the same minimum basis set of Slater atomic orbitals is used together with the Ruebenberg criterion of localization,[13] then the same result is obtained as in the present work—the hybridization in the carbon atom's valence atomic orbital is about sp.[2] But if the basic atomic orbitals used are of about "double ζ" quality,[14] then the hybridization is close to sp^3. And this is so not only for the traditional sp^3 molecules but also for ethylene and acetylene. So it seems that the hybridization is sensitive to small changes in the forms of the basic atomic orbtials. This is a disappointing conclusion, because if one is to use hybridization as a rough guide to the electron organization in a molecule then one wants it to be insensitive to minor changes in such technical points as the localization route and the forms of the basic atomic orbitals.

Bond Polarity. The calculated values for the formal charges in the carbon–hydrogen bonds of methane and ethane are virtually identical, and this result is not sensitive to the value of the parameter β. So the carbon–hydrogen bond localized orbital is clearly similar in the two molecules as far as bond polarity is concerned.

It is interesting at this stage to construct a table of the hybridizations and bond polarities for the various carbon–hydrogen bonds which have been examined

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(13) C. Edmiston and K. Ruedenberg in "Quantum Theory of Atoms, Molecules and Solid," P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1966, p 263.

(14) S. Rothenberg, *J. Chem. Phys.*, 51, 3389 (1969).

Table II

Molecule	CH	CH_4	C_2H_6	CH_2O	HCN	HCCH
Hybridization % 2p	100	67	69	72	50	50
Atomic charge C^-H^+	0.00	0.06	0.06	0.12	0.23	0.22

in this work;[1] this is done in Table II. The trends in both hybridization and bond polarity are as expected, and it is clear that, as the amount of 2s in the valence orbitals increases, so does the amount of charge on the carbon atom increase. This agrees with general expectation.

Ionization Energies and Binding Energies. These two energies are closely similar in the carbon–hydrogen bonds of methane and ethane. Again we can construct a table (Table III) showing these energy quantities for the carbon–hydrogen bonds of the molecules dealt with so far. From these results, there is clearly a tendency for both the ionization energy and the binding energy to increase with increasing s content of the valence orbital of the carbon atom. This is often supposed to be so, but it must be stressed that there is no sound theoretical reason for supposing that this will happen.

Table III

Molecule	CH	CH_4	C_2H_6	CH_2O	HCN	HCCH
Bond orbital	p	sp^3	sp^3	sp^2	sp	sp
$(-e^{\mu})$	16.6	18.2	18.3	19.0	21.1	21.1
Binding energy	3.3	4.0	4.3	3.9	4.6	4.6

Carbon–Carbon Bond. We cannot make comparisons here until we have a molecule such as propane whose wave function is available to us. All we can say at this stage is that the hybridization is about sp^2 in the carbon valence orbital and that the binding energy is close to but rather larger than the bond energy.

Choice of the Parameter β. There is no hard and fast way of making this choice in the present method. The value of 55° is a compromise reached while trying to produce (1) good localization, (2) reasonable hybridizations, (3) straight bonds, (4) reasonable amounts of the 1s atomic orbital in the valence orbitals, and (5) reasonable ionization and binding energies. Clearly, one cannot optimize all of these quantities simultaneously, and the choice of 55° is partly a subjective one at this stage.

Summary

This work illustrates in some detail the localization method used in this series of papers.[1] The localized MO's are quite similar to those obtained by Pitzer[11] using a different localization technique. The nature of the carbon–hydrogen MO's in the SCF approximation has been discussed and clarified. It should be noted that we have not demonstrated the transferability of a bond between two molecules, but only the similarity of two bonds in different molecules. Actual transferability has been demonstrated by Shull and his colleagues[15] when they transferred the k shell, the lone pair, and the OH bond between H_2O and H_2O_2 with a marked degree of success.

Acknowledgments. I am indebted to R. M. Pitzer for a copy of the integrals over atomic orbitals which were used in this work and to two referees for helpful comments and references.

(15) M. Levy, W. J. Stevens, H. Shull, and S. Hagstrom, *J. Chem. Phys.*, **52,** 5483 (1970).