Hyperconjugation*

BY ROBERT S. MULLIKEN, CAROL A. RIEKE AND WELDON G. BROWN

I. Theoretical Considerations

1. General Discussion.—It has occurred to several writers that a group such as CH_3 should have the power to conjugate with other groups containing double or triple bonds.[1,2,3,4] The name hyperconjugation has been proposed for this effect,[4] implying conjugation over and above that usually recognized. Previous discussions of hyperconjugation have been qualitative. Quantum-mechanical computations have now been carried through for typical molecules, using the molecular orbital (MO) method with numerical parameters derived from empirical data.[5]

It is natural from the MO viewpoint,[6,7,8] though not from the atomic orbital (AO) viewpoint,[6,9] to write for the methyl group the structure $-C \equiv H_3$, and to compare it with such groups as $-C \equiv N$ and $-C \equiv CH$. According to the analysis below, the differences in conjugating power among these groups are quantitative rather than qualitative and are expressible in terms of a numerical parameter related to the strength of the indicated triple bond. The triple $C \equiv H_3$ bond is much more saturated than the $C \equiv C$ bond, and has correspondingly much less tendency to conjugate. But the calculations, taken in connection with thermal and bond distance data, indicate that the conjugating power of $C \equiv H_3$ is still considerable.

In general, three ordinary single bonds from a carbon to any three other atoms may be regarded as constituting a quasi-triple bond whenever there is opportunity for conjugation, across an intervening C—C single bond, with a second (quasi or ordinary) multiple linkage. Some simple examples of conjugated systems, in the generalized sense, are the following:

$$
\left.
\begin{array}{ll}
\begin{array}{l} HC \equiv C - C \equiv CH \\ \text{or} \\ N \equiv C - C \equiv N \end{array} & \text{Ordinary (first-order) conjugation} \\[2em]
\begin{array}{l} H_3 \equiv C - C \equiv CH \\ \text{or} \\ H_3 \equiv C - C \equiv N \end{array} & \begin{array}{l}\text{Second-order conjugation (first} \\ \text{order hyperconjugation)} \end{array} \\[2em]
H_3 \equiv C - C \equiv H_3 & \begin{array}{l}\text{Third-order conjugation (second} \\ \text{order hyperconjugation).} \end{array}
\end{array}
\right\} (1)
$$

Nearly all saturated organic molecules, according to this viewpoint, are stabilized by third order conjugation, usually of a rather complicated character. For example, propane may be written as $H_3 \equiv C - C \equiv H_2 Me$ or $MeH_2 \equiv C - C \equiv H_3$. The two ways of writing the formula illustrate two different possibilities for hyperconjugation, both of which contribute toward the stability of the molecule.

With respect to strength and stability, the single and multiple bonds of a conjugated system may be labelled acceptor bonds and donor bonds, respectively. As especially Pauling and his collaborators have shown,[9] ordinary conjugation causes a shortening of the acceptor bonds and a slight lengthening of the donor bonds. It is also known from thermal data that there is a net energy of conjugation (resonance energy). One can show by quantum-mechanical calculations that this must be the sum of a positive or stabilization energy residing in the acceptor bonds and a smaller negative energy in the donor bonds. Characteristically the acceptor bonds gain more in stability than the donor bonds lose.

In third order conjugation in saturated hydrocarbons the C–H bonds play exclusively a donor role, the C–C bonds predominantly an acceptor role. The C–C bonds are entirely acceptor in ethane, simultaneously donor and acceptor in propane and larger molecules, but always more acceptor than donor. The computations given below indicate that whereas the gains in stability

* Presented at the Fifth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Columbia University, New York, December 30, 1940 to January 1, 1941. Assistance in the preparation of the materials was furnished by the personnel of Works Projects Administration Official Project no. 665-54-3-387.

(1) G. W. Wheland, *J. Chem. Phys.*, **2**, 478–479 (1934): AO method, free radicals.

(2) According to a private communication (see also reference 1, footnote 20), E. Hückel has also used the MO method in similar ways.

(3) L. Pauling, H. D. Springall and K. J. Palmer, THIS JOURNAL, **61**, 927 (1939): AO method applied to methylacetylenes, etc.

(4) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939): MO method applied to cyclic dienes, methylacetylenes, etc., and general discussion of hyperconjugation.

(5) If one wishes to consider hyperconjugation of CH_3 from the AO viewpoint, one must discuss resonance among a variety of bond structures (*cf.* reference 3). This approach is equally valid, but more cumbersome and less well suited to simple calculations.
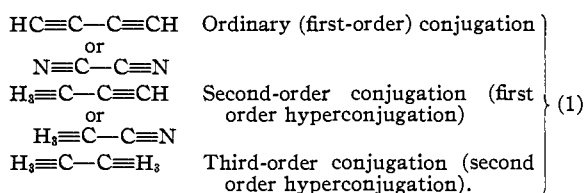
(6) See E. Hückel, *Z. Elektrochem.*, **43**, 752, 827 (1937), for a very excellent review of the application of both the AO and MO methods to unsaturated and aromatic compounds.

(7) *Cf.* R. S. Mulliken, *J. Chem. Phys.*, **3**, 375 (1935).

(8) *Cf.* R. S. Mulliken, *Phys. Rev.*, **41**, 49 (1932).

(9) *Cf.* L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., second edition, 1940.

by the acceptor bonds are appreciable, the losses by the donor bonds are extremely small. Similar conclusions are reached for second order conjugation, and for hyperconjugation in general.

The (first order) conjugation energy for conjugated polyenes has been computed quantum-mechanically, using the MO approximation, by Hückel and others,[10] and one notes that it is very nearly proportional to the number of C–C single bonds, or in other words to the number of acceptor bonds. This result appears to be in harmony with thermal data. It is then reasonable to postulate that the hyperconjugation energy of saturated hydrocarbons is to a good approximation a function only of the number of C–C bonds. The hyperconjugation energy per C–C bond should then be constant. This is in harmony with the constancy of the C–C bond length (1.54 Å.) in saturated molecules.

It is not feasible to make computations of third order conjugation energy except for relatively simple or symmetrical molecules. For saturated molecules we shall rely largely on our computations for ethane in order to establish the normal contributions of third order conjugation to the total bonding energy.

2. Rope and Ribbon (σ, π, x, and y) Bonds; Unsaturation Electrons.—Before proceeding further, it is advisable to review the nature of multiple bonds, and the forms of the AO's or MO's occupied by the electrons. In diatomic or linear molecules,[11] bonds are usually formed by electrons in σ or in π orbitals. A single bond is always formed by a pair of electrons each in a σ orbital, and can be called a σ bond. In the MO approximation, both electrons occupy a single, bonding, σ MO which unites the two atoms. The σ type of AO or MO is symmetrical with respect to rotation about the axis of the molecule.

A triple bond (as in N_2 or in C_2H_2) is composed of a σ bond plus a double π bond. The double π bond consists of two pairs of electrons in π AO's or MO's. If we assign axes x, y and z with the z axis along the symmetry axis of the molecule, then each π AO or MO occurs in two forms which may be called π_x and π_y, or briefly, x and y. If ϕ is the angle of rotation around the z axis, and π_x is of the form $f \cos \phi$, then π_y is of the form $f \sin \phi$, where f is some function of the cylindrical coördinates z and ρ ($\rho = \sqrt{x^2 + y^2}$). For σ orbitals, the form is a function of z and ρ only.

Using MO's, the σ bond may be described as rope-like, the x or y bond as double-ribbon-like. The double-ribbon-

form x or y MO (as also the rope-form σ MO) stretches along the z axis and so connects the two atoms. The two (thickened) ribbons of the x MO run along one on each side of the plane $x = 0$. Similarly the y MO lies partly on each side of $y = 0$.

The designations σ and π have been extended[12] to polyatomic molecules. For example, the C–C bond in C_2H_6 may be described as a σ bond, although the σ MO is now only approximately cylindrically symmetrical. Although in diatomic and linear molecules, the π_x and π_y orbitals (either AO's or MO's) are physically equivalent, in non-linear polyatomic molecules this is not always true.

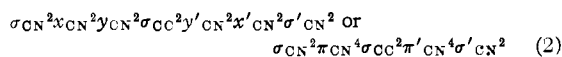In double-bonded polyatomic molecules, where the atoms surrounding the bond normally all lie in one plane, the double bond is formed by a pair of σ electrons together with a pair of x electrons, without y electrons. The designation π ought really not to be used for such planar molecules, since in its original definition the π type of AO or MO is one which includes two types π_x and π_y of equal energy (twofold degeneracy). This degeneracy occurs only when the bond-axis (z axis) is at least a threefold axis of symmetry, and we shall hereafter restrict the symbol π to such cases. For cases of lower symmetry we shall refer to σ, x and y orbitals or electrons.[13]

Electrons in x or in π orbitals give weaker bonds than those in σ orbitals. They may be called "unsaturation electrons," and the corresponding orbitals unsaturation AO's or MO's. Another designation proposed by Lennard-Jones[14] is "mobile electrons."

3. Conjugation Energy as Delocalization Energy.

—In terms of MO's, conjugation as in butadiene or cyanogen or resonance as in benzene corresponds to the passage from the crude approximation of localized MO's[12] to the better approximation of non-localized MO's.[7,15] The conjugation or resonance energy may therefore well be described as *energy of delocalization*.

4. Electron Configurations and LCAO Forms of MO's.

—In the qualitative description of MO's, and also for approximate quantitative calculations, it is convenient to use the crude but simple LCAO type of approximation; here the form of any MO is approximated by a linear combination of atomic orbitals (LCAO).[6,7]

It will be convenient to begin with cyanogen ($N{\equiv}C{-}C{\equiv}N$). Using localized MO's, the electron configuration for the valence electrons is

$$\sigma_{CN}{}^2 x_{CN}{}^2 y_{CN}{}^2 \sigma_{CC}{}^2 y'_{CN}{}^2 x'_{CN}{}^2 \sigma'_{CN}{}^2 \text{ or}$$
$$\sigma_{CN}{}^2 \pi_{CN}{}^4 \sigma_{CC}{}^2 \pi'_{CN}{}^4 \sigma'_{CN}{}^2 \quad (2)$$

This description corresponds to an *unconjugated* structure, the first six electrons (two in each of the

(10) *Cf.* J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, **35**, 811 (1939), and references given there. See Table VIII for computed resonance energies. This article gives the gist of the LCAO method as used by Hückel, Lennard-Jones, Wheland, Coulson and others for computing resonance energies, bond orders, etc.

(11) *Cf.* G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," Prentice-Hall, New York, N. Y., 1939.

(12) F. Hund, *Z. Physik*, **73**, 565 (1931); **74**, 429 (1932).

(13) If the reader prefers consistency in notation he may wish to use the Greek letters ξ and η instead of x and y.

(14) J. E. Lennard-Jones, *Proc. Roy. Soc.*, **A158**, 280 (1937).

(15) *Cf.* R. S. Mulliken, *J. Chem. Phys.*, **3**, 517 (1935): structures of methane, ethane, ethylene, acetylene.

localized C–N bonding MO's called σ_{CN}, x_{CN} and y_{CN}) giving the triple bond in the first CN group, the next two (in the C–C bonding σ_{CC} orbital localized between the two C atoms) giving the C–C single bond, and the last six giving the second C≡N bond. The symbol π includes both x and y MO's. In LCAO approximation, the forms of the π and π' MO's are as follows

$$x = k_N x_N + k_C x_C; \quad x' = k_C x'_C + k_N x'_N \quad (3)$$

with analogous equations for y and y'. The symbols x_N and x_C refer to $2p_x$ AO's[9] of atoms N and C.

In the LCAO MO method, the Schrödinger equation is set up for each electron separately, assuming the electron to be moving in the "self-consistent field" given by the nuclei together with the other electrons. The solution of this equation gives the energies of the MO's, also the values of the coefficients such as k_N and k_C. The energy of the molecule is then given, with sufficient accuracy for our purpose, by adding the energies of all the individual electrons, each in its own MO.

Using non-localized MO's, thus taking conjugation into account, the electron configuration (2) is replaced by

$$\sigma_1{}^2 \sigma_2{}^2 \sigma_3{}^2 x_1{}^2 y_1{}^2 x_2{}^2 y_2{}^2 \quad \text{or} \quad \sigma_1{}^2 \sigma_2{}^2 \sigma_3{}^2 \pi_1{}^4 \pi_2{}^4 \quad (4)$$

where, in LCAO approximation

$$x_i = k_{ai} x_a + k_{bi} x_b + k_{ci} x_c + k_{di} x_d \quad (5)$$

with a corresponding equation for $y_i (i = 1$ or $2)$. Here x_a, x_b, x_c, x_d mean the same as x_N, x_C, x'_C, x'_N in Eq. (3). When the fourteen electrons are assigned to the seven non-localized MO's of (4) and the total energy is computed, it is found to be somewhat lower than when they are assigned to the seven localized MO's of (3). The difference is the conjugation energy. Essentially this procedure will be used throughout the following computations.

We have not yet given LCAO expressions for the σ MO's in (3) and (4). This can be done, at least qualitatively,[15] but the quantum-mechanical problem of determining the energies and coefficients is much more difficult than for the π MO's, because the LCAO forms for the σ MO's involve unknown mixtures of $2s$ and $2p_z$ AO's, whereas the x or y MO's involve only $2p_x$ or $2p_y$ AO's, respectively. Moreover, there are good reasons for believing that the energy of delocalization is much smaller for the relatively tightly bound σ electrons than for the unsaturation electrons. Hence, while recognizing σ conjugation as a

problem deserving future attention, we shall in the following ignore σ hyperconjugation energy, as others also have always done.

5. The Secular Equation for Non-localized MO's.—The first step[6,10] in obtaining the coefficients k_{ni} in Eq. (5) is the solution of the secular equation[16]

$$\begin{vmatrix} \alpha^* - E & \gamma^* - S^*E & 0 & 0 \\ \gamma^* - S^*E & \alpha - E & \gamma - SE & 0 \\ 0 & \gamma - SE & \alpha - E & \gamma^* - S^*E \\ 0 & 0 & \gamma^* - S^*E & \alpha^* - E \end{vmatrix} = 0 \quad (6)$$

In Eq. (6), the following abbreviations have been used

$$\alpha^* = H_{aa} = H_{dd}, \quad \alpha = H_{bb} = H_{cc}, \quad \gamma^* = H_{ab} = H_{cd}, \quad \gamma = H_{bc}, \quad S^* = S_{ab} = S_{cd}, \quad S = S_{bc} \quad (7)$$

where

$$H_{ij} = \int x_i H x_j d\tau, \quad S_{ij} = \int x_i x_j d\tau \quad (8)$$

H being the Hamiltonian operator. The α's are called Coulomb integrals, the γ's resonance integrals, the S's overlapping integrals.

In discussions[6,10] of problems of this type it is customary to "neglect S," i. e., assume $S_{ij} = 0$, in order to simplify the computations. If, also, we put $\alpha^* = \alpha$ and $\gamma^* = \gamma$ as an approximation, and replace the symbol γ by β for reasons to be discussed later, Eq. (6) becomes

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (9)$$

6. Computation of Conjugation Energy.—This equation is readily solved for E in terms of α and β. Four solutions are obtained, of which we use the two lowest.[17] Identically the same equations and energy solutions apply for the y MO's. The conjugation energy is then

$$\text{C.E.} = 4[2E(\pi) - E(\pi_1) - E(\pi_2)] \quad (10)$$

The factor 4 occurs because there are four electrons in each π MO. $E(\pi) = E(\pi')$ is the energy per electron in the localized π MO's π_{CN} and π'_{CN} of (2), while $E(\pi_1)$ and $E(\pi_2)$ refer to the non-localized π MO's of (4).

Equation (9) and its solutions are the same as those obtained by Hückel for the x electrons of butadiene.[6] In this approximation, Eq. (9) applies equally to butadiene, cyanogen, diacetylene,

(16) In obtaining Eq. (6), we have replaced six terms $H_{ac} - S_{ac}E$, $H_{ad} - S_{ad}E$, and so on, by zero. The terms so neglected are relatively small, since they do not involve neighboring atoms.

(17) Eq. (5) really covers four MO's, x_1, x_2, x_3, x_4, of which only the bonding MO's x_1 and x_2 are occupied in the normal state of the molecule (electron configuration (4)). The other MO's, x_3 and x_4, which have anti-bonding characteristics, are of importance for excited electronic states and ultraviolet spectra.

and other molecules having first-order conjugation across a single acceptor bond. Equation (10) likewise applies equally to all such molecules, except that the factor 4 is replaced by 2 in the case of double bond conjugation.

The energies in Eq. (10) are[6]

$$E(\pi) = \alpha + \beta$$
$$E(\pi_1) = \alpha + 1.618\beta \qquad (11)$$
$$E(\pi_2) = \alpha + 0.618\beta$$

The expression here for $E(\pi)$ is obtained by solving the secular equation

$$\begin{vmatrix} \alpha^* - E & \gamma^* - S^*E \\ \gamma^* - S^*E & \alpha - E \end{vmatrix} = 0 \qquad (12)$$

related to Eq. (3), after making the same simplifications as were used in Eq. (9).

Using Eq. (11), Eq. (10) gives for C_2N_2 or diacetylene

$$\text{C.E.} = -0.944\beta; \text{ or } -0.472\beta \qquad (13)$$

for butadiene. The experimental conjugation energy may then be compared with Eq. (13), and this gives an empirical value of β which is then customarily identified as the "resonance integral" γ, i. e., H_{ab}, of Eqs. (7) and (8). As expected from the theory the empirical β is negative; it is of the order of magnitude of one electron volt.[10,18] No attempt has been made to compute β theoretically.

7. A Reinterpretation of the Empirical Parameter β.—Now let us re-examine the legitimacy of neglecting S in Eq. (6). It is known from theoretical computations that S is fairly large (0.27 for a C=C bond,[19] and probably as much as 0.4 in C≡N). Further, α can be estimated as roughly -50 electron volts.[20] Now referring to Eq. (11), since β is empirically about -1 e. v., it is seen that E is always approximately equal to α. Hence SE in Eq. (6) is in the neighborhood of -15 to -20 e. v. The neglect of this quantity would seem to invalidate the whole procedure, and seems not to have been considered hitherto, the idea having been that *somehow* the calculation works, since the resonance energies of different compounds lead to a rather constant empirical β.

Fortunately, the atmosphere of unreality about these results can be dissipated easily. As we have just seen, $-SE$ in Eq. (6) should amount to 15 or 20 e. v. A little consideration of the form of the resonance integral γ shows that its value

ought to be just of the order of magnitude of SE.[21] Hence $\gamma - SE$ could well be much smaller in magnitude than either γ or SE. One then sees that β of Eq. (9) is not approximately γ as hitherto supposed, but must be identified with a very much smaller quantity $\gamma - SE$ with E treated as a constant. In short, the β of Eq. (9) and of experiment is really $\gamma - S\alpha$ (since α is the average value of E for the several solutions of (6)). This still leaves some questions,[21] since with $| \gamma - SE |$ much smaller than $| SE |$, the quantity $\beta = \gamma - SE$ should vary by a considerable fraction of its average value for different solutions E; but it appears that Eq. (9) with β taken as a constant may well be a tolerable though rough approximation to Eq. (6). We need, however, perhaps not be so much surprised as formerly if empirical values of β obtained from different types of data (e. g., spectroscopic and chemical) do not agree very well.

8. Effects of Bond Length and Polarity.—Now dropping the assumption $\gamma^* = \gamma$ but treating E in $\gamma - SE$ as a constant, Eq. (9) reads

$$\begin{vmatrix} \alpha - E & \beta^* & 0 & 0 \\ \beta^* & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta^* \\ 0 & 0 & \beta^* & \alpha - E \end{vmatrix} = 0 \qquad (14)$$

As Lennard-Jones has pointed out,[10,14] the resonance integral γ should vary considerably with bond length. It should also be somewhat altered if other atoms than carbon are involved.

Similar remarks obviously apply to β. We shall deduce the approximate mode of variation of β with bond length for carbon–carbon bonds from empirical evidence. In a similar way we shall deduce an empirical β (our β^*, see below) for hyperconjugated carbon–hydrogen bonds as in $H_3≡C—C≡H_3$.

In our computations below, we have retained the assumption that $\alpha^* = \alpha$ for the C–H bond. Preliminary computations showed that the use of an α^* not equal to α for the H atoms has an effect on energies and bond orders which is inappreciable compared with that of the change from β for carbon–carbon bonds to β^* for hyperconjugated carbon–hydrogen bonds.

9. Secular Equations for Hyperconjugation in Ethane and Methylacetylene.—Equation (14) was deduced for the π electrons of cyanogen. Referring to (1), one sees that if the H_3 group can be treated like a nitrogen atom, and suitable H_3-

(18) G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935).

(19) R. S. Mulliken, *J. Chem. Phys.*, **7**, 20 (1939).

(20) Using Slater AO's, α for a 2-quantum electron in a free *carbon atom* is -36 e. v.; the same quantity for a free nitrogen atom is -51 e. v. For a bound atom, $-\alpha$ should be considerably greater.

(21) We hope to discuss these matters in more detail in later papers. *Cf.* also R. S. Mulliken, *J. Chem. Phys.*, **3**, 573 (1935), especially Eq. (14) and foot of p. 379, where the symbol γ was used with the same meaning as $\beta - \gamma = S\alpha$ here.

group MO's be formulated which behave like N atom AO's, then the entire preceding discussion for N≡C—C≡N can be applied equally to $H_3≡C—C≡H_3$.

If the three hydrogen atom $1s$ AO's of an H_3 group, arranged in an equilateral triangle, are called a, b, and c, with atom c in the yz plane, then the following linear combinations of these[22] resemble AO's of the kinds mentioned at the right

$$\begin{array}{l} [\sigma] = (a + b + c)/\sqrt{3}: \text{ like } 2p_s \\ [x] = (a - b)/\sqrt{2}: \text{ like } 2p_z \\ [y] = (a + b - 2c)/\sqrt{6}: \text{ like } 2p_y \end{array} \Bigg\} \quad (15)$$

MO's such as $[x]$ and $[y]$ of (15) may be called *quasi-x* or *quasi-y* MO's. The $[x]$ and $[y]$ MO's, even though different in form, are strictly equal in energy; in view of this degeneracy, any two mutually orthogonal linear combinations of $[x]$ and $[y]$ of (15) could be taken as $[x]$ and $[y]$.

Equations (2), (3), (4), (5) and so on, and the discussion accompanying them, then apply to C_2H_6 just as well as to C_2N_2 if we substitute "H_3" and its $[x]$ and $[y]$ MO's everywhere for "N" and its x and y AO's.[23]

The final secular equations are Eq. (14) for the non-localized or hyperconjugated π MO's, and Eq. (12), with α^* put equal to α and $\gamma^* - S^*E$ written as β^*, for the localized (unconjugated) π MO's of each CH_3 group. Analogous to $E(\pi)$ of Eq. (11) we now have[24] $E(\pi) = \alpha + \beta^*$. To obtain $E(\pi_1)$ and $E(\pi_2)$, and the hyperconjugation energy, we now need to find the two lowest-energy solutions of Eq. (14). We have done this for various values of β^*; the results are reported in a later section.

Similar considerations apply to methylacetylene and methyl cyanide, where we have second-order conjugation. For methylacetylene, Eq. (14) is replaced by

$$\begin{vmatrix} \alpha - E & \beta^* & 0 & 0 \\ \beta^* & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta' \\ 0 & 0 & \beta' & \alpha - E \end{vmatrix} = 0 \quad (16)$$

Also, in analogy to $E(\pi)$ in Eq. (11), we find

$$E(\pi_{CH_3}) = \alpha + \beta^*; \quad E(\pi_{C≡C}) = \alpha + \beta' \quad (17)$$
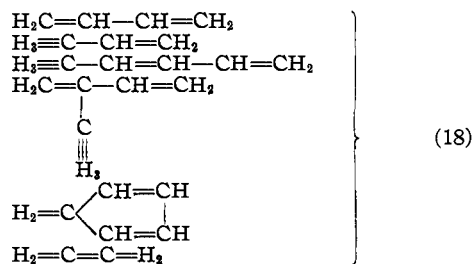
Solutions of Eq. (16) have been obtained for

(22) Cf., e. g., R. S. Mulliken, *J. Chem. Phys.*, **1**, 495 (1933), Fig. 1a and Eqs. (1). Eqs. (3) show how these are combined with carbon AO's to form CH_3 MO's (in LCAO approximation).

(23) This is true whether we assume D_{3h}, D_{3d}, or D_3 symmetry for ethane (i. e., opposed, intermediate, or staggered arrangement of the two H_3 groups). However, for D_{3d} symmetry, $[y]$ of Eq. (15) must be taken with opposite signs for the two CH_3 groups, while for D_3, $[x]$ and $[y]$ must be replaced by certain linear combinations (cf. ref. 4, pp. 349-50, fine print).

(24) For further discussion of ethylene, see reference (15). Localized MO's are used there for the y electrons.

various assumed relations of β^* and β' to β, and are reported in a later section. The two lowest roots of Eq. (16) correspond to $E(\pi_1)$ and $E(\pi_2)$ of Eq. (11), and from them and Eq. (17) the hyperconjugation energy is obtained.

10. Conjugation and Hyperconjugation in Molecules Containing Double Bonds.—Some simple examples of conjugation and hyperconjugation in molecules containing double bonds are the following

$$\left. \begin{array}{l} H_2C{=}CH{-}CH{=}CH_2 \\ H_3{≡}C{-}CH{=}CH_2 \\ H_3{≡}C{-}CH{=}CH{-}CH{=}CH_2 \\ H_2C{=}C{-}CH{=}CH_2 \\ \qquad | \\ \qquad C \\ \qquad {\parallel\!\!\!\parallel} \\ \qquad H_3 \\ H_2{=}C{\Big\langle}\!\!\!\begin{array}{l} CH{=}CH \\ \quad | \\ CH{=}CH \end{array} \\ H_2{=}C{=}C{=}H_2 \end{array} \right\} \quad (18)$$

In molecules such as these, we shall always take the x-axis perpendicular to the plane of the molecular skeleton. The indicated $C{=}H_2$ quasi double bonds in the last two examples have a significance analogous to that of the quasi triple bonds in (1).

Butadiene is the simplest example of ordinary (first-order) x conjugation. For this the secular equation (14) applies.[6,10] In propylene the C–C single bond can act as acceptor for second-order x conjugation between the x electrons of the C≡C double bond and the x electrons of the $C{≡}H_3$ quasi triple bond. The secular equation is the same as for methylacetylene (Eq. (16)). The y electrons of the $C{≡}H_3$ bond are inactive in second-order conjugation, hence for this purpose the $C{≡}H_3$ bond acts like a double bond. However, the y electrons of CH_3 in propylene are active in third-order conjugation (see below).

The pentadienes in (18) introduce a combination of first-order x conjugation as in butadiene with second-order x conjugation as in propylene. There is also third-order conjugation (see below). The methylbutadienes have one second-order and one first-order C–C acceptor bond; cyclopentadiene has two second-order and one first-order acceptors. In the MO computations, the first- and second-order x conjugations are treated as a single whole, exactly the same (except quantitatively) as first-order x conjugation in $H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$ or

$$H_2C{=}C{\Big\langle}\!\!\!\begin{array}{l} CH{=}CH \\ \quad | \\ CH{=}CH \end{array}$$
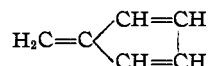
However, the computations (see Table VIII) show that the total resonance energy is practically the same as if the first-order and second-order conjugation energies had been computed separately and added. The computed x conjugation energy per second-order acceptor bond is found to be always nearly the same as in propylene.

In the case of cyclopentadiene, the quasi double bond between C and H_2 involves one σ bond and one x bond, with MO's formed (in LCAO localized MO approximation) by combination of a σ and an x carbon AO, respectively, with the following MO's, or quasi AO's, of the H_2 group

$$[\sigma] = (a + b)/\sqrt{2}; \quad [x] = (a - b)/\sqrt{2} \quad (19)$$

Here a and b refer to the two H atoms, with a on the positive, b on the negative side of the yz plane (cf. the H_3 MO's in (15)).

In ethylene only third-order conjugation is present. For each H_2 group there are quasi AO's as follows

$$[\sigma] = (a + b)/\sqrt{2}; \quad [y] = (a - b)/\sqrt{2} \quad (20)$$

Here $[y]$ is of course just like $[x]$ in (19), except that a and b are now located on opposite sides of the xz instead of the yx plane.

The $[y]$ electrons of the two CH_2 groups of ethylene can give third-order conjugation across the $C=C$ bond, which here acts as acceptor, in the same way that the $[y]$ and $[x]$ electrons of the two CH_3 groups conjugate across the single bond in ethane.[24] (In both cases the acceptor bond takes on partial triple bond character.) This one-dimensional (four-electron) hyperconjugation in ethylene is found to be stronger than the two-dimensional (eight-electron) hyperconjugation in ethane. This is because the hyperconjugation energy per electron is greater for the shorter bond.

The y MO's in ethylene are formally identical with those of ethane. In LCAO approximation (cf. Eqs. (3), (5)) they are as follows, using $[y]$ from (20)

Localized: $y = k_1[y] + k_2 y_C; \quad y' = k_2 y'_C +$
$$k_1[y'] \quad (21)$$

Non-localized: $y_i = k_{ai}[y] + k_{bi} y_C + k_{ci} y'_C +$
$$k_{di}[y'] \quad (22)$$

The secular equation corresponding to (22) is of exactly the same form as (14).

11. Third-order Conjugation in General.— One may generalize as follows from the foregoing discussion: (1) Every C–C and every $C=C$ bond in every carbon compound is a y conjugation acceptor, of first, second, or third order according

to whether the C–C bond has two, one, or zero adjacent triple bonds. (2) Every C–C bond is an x acceptor of first, second, or third order according to whether the C–C bond has two, one, or zero adjacent multiple bonds, either double or triple. (3) Carbon–hydrogen bonds, and triple bonds ($C\equiv C$, $C\equiv N$, $N^+\equiv N$, or other), can be donors, but never acceptors; double bonds ($C=C$ or other) can be x donors, but never x acceptors, may be y acceptors, but never y donors; single bonds (C–C or other) may be donors or acceptors, x or y. The foregoing statements may perhaps need some modification or qualification if one tries to consider every conceivable case. Some of them are essentially valid but need rephrasing if they are applied to cases like benzene or H_2N— $CH=CH$—$CH=NH_2^+$ where delocalization of the double bonds is complete.

The application of the concept of third-order conjugation to molecules with more than one carbon–carbon (or other multivalent-atom) bond presents difficulties since, except in linear molecules and except for the x direction in planar molecules, no unique choice of x, y, and z axes can be made. The only recourse is to use local x, y, and z axes. One then considers each bond in turn in the role of a third-order conjugation acceptor, and for this purpose one takes the bond direction as z axis.

As examples, let us consider propylene and propane. In propylene there is no third-order x conjugation, but both the C–C bond and the $C=C$ bond should be acceptors for y hyperconjugation. For the $C=C$ bond in the y acceptor role, propylene may be written $H_2=C=C=(HMe)$, with the $C=C$ direction as z axis. Non-localized y MO's exactly like y of $H_2=C=C=H_2$ (cf. Eq. (22)) may be formulated, except that the quasi-AO $[y']$ of the right-hand H_2 group (cf. Eq. (20)) is modified by the substitution of a valence AO of the methyl carbon atom for one of hydrogen in (20). This AO can best be taken as a tetrahedral AO, directed along the C–C single bond. The secular equation (14) now applies just as for hyperconjugation in ethane, provided we neglect the difference between β^* for $H_2=C$ and for $(HMe)=C$.

For the C–C bond of propylene in the acceptor role, the suitable formulation is $(H_2C,H)\equiv C$—$C\equiv H_3$, with the C–C direction as z axis. The second-order x conjugation here, and its secular equation, have already been discussed. The third-order y conjugation differs from that in $H_3\equiv C$—$C\equiv H_3$ in much the same way that the y hyperconjugation across the $C=C$ bond in $H_2=C=C=(HMe)$ differs from that in $H_2=C=C=H_2$. In constructing the $[y]$ quasi AO for the left-hand group, a carbon trigonal σ AO directed along the $C=C$ bond must be substituted for two of the hydrogen AO's in (15). The corresponding secular equation is of the same form as Eq. (16), but probably Eq. (14) would be a good practical approximation (cf. preceding paragraph).

The foregoing type of procedure can be applied to x and y third-order conjugation in propane by

successively considering the two structures $H_3 \equiv$ C—C≡(H₂Me) and (MeH₂)≡C—C≡H₃. It can be further generalized for third-order conjugation in molecules of any degree of complexity, by dividing the whole molecule into units (which are not mutually exclusive but partially overlapping), with one ethylene-like unit for each double bond, one ethane-like unit for each single bond. It appears likely that this procedure, whereby each acceptor bond is treated like a separate problem and the resulting computed hyperconjugation energies added, represents a tolerably correct approximation.

II. Results of Computations

12. Empirical Conjugation Energies from Heats of Combustion.—Our procedure for deriving conjugation energies from thermal data is similar to that of Pauling and Sherman[9] who, assuming additivity of bond energies (with corrections for special groups), compute energies of formation and interpret deviations therefrom as resonance energies. However, we shall work with heats of combustion rather than bond energies. The following formula fits the available good data for gaseous saturated hydrocarbons except methane (including branched and six-membered and higher ring compounds) with considerable accuracy (mostly better than ±1 kcal.)[25,26]

$$-\Delta H_{298°} = 54.625 N_{CH} + 48.25 N_{CC} - 1.5 N_{Me} + 22.18 N_{C-C} + 56.6 N_{C≡C} \quad (23)$$

The last two terms are added to make Eq. (23) fit ethylene and acetylene. N_{CH}, N_{CC}, N_{Me}, $N_{C=C}$, $N_{C≡C}$ refer to the numbers of C–H bonds, C–C bonds (counting each bond of a multiple bond separately), methyl groups, C=C double bonds, and C≡C triple bonds, respectively. Equation (23) gives 218.5 kcal. in the exceptional case of methane as against 212.79 observed; for diamond, it gives 96.5 per atom as against 94.44 observed.

With additional corrections if needed (e. g., about +5 kcal. for each 5-ring), Eq. (23) may be used as

(25) The data which form the basis of Eq. (23) are taken from new critical tables of heats of combustion being prepared by M. S. Kharasch and W. G. Brown. In a number of cases, the best heats of combustion have been obtained indirectly, using data on heats of hydrogenation.

(26) Strictly speaking, all ΔH values ought to be corrected to those for gaseous substances at 0°K., and further than this, for zero-point energy. As Zahn has pointed out (C. T. Zahn, *J. Chem. Phys.*, **2**, 671 (1933)) the latter correction is much the larger. We have not attempted to make these corrections, since for the calculation of conjugation energies they probably would largely cancel out. This ought, however, to be verified.

a standard formula for gaseous hydrocarbons.[27] Negative departures from the heats of combustion it predicts will be interpreted in most cases as energies of conjugation or hyperconjugation or resonance. For the most part, the resonance energies so computed agree rather well with those of Pauling and Sherman.

13. Corrections for Compression and Extension of Bonds.—As Lennard-Jones has shown,[10] empirical conjugation or resonance energies need to be corrected, before they are compared with corresponding theoretically computed values, to take into account the energy required to shorten acceptor bonds and lengthen donor bonds from their normal to their observed conjugated lengths against their normal restoring forces. This correction always increases the empirical resonance energies, sometimes very considerably. As a result, the empirical parameter β which we deduce proves to be more than twice as large as the values which Hückel, Wheland, Pauling, and others obtained; in fact we arrive at β values somewhat larger even than those of Lennard-Jones.

The magnitudes of the resonance energies and of the compression energy corrections as estimated by us for benzene, butadiene, and diacetylene are given in Table VI. Our corrections for compression and extension are based on new

(27) The comparatively large deviation for CH₄ may be interpreted to mean that the C–H bonds there are each about 1.4 kcal. stronger than in most hydrocarbons. Similarly, the term $-1.5 N_{Me}$ in Eq. (23) would mean that the C–H bonds are each 0.5 kcal. stronger in CH₃ groups than in CH₂ or CH groups. G. B. Kistiakowsky, *J. Phys. Chem.*, **41**, 180 (1937), has expressed similar ideas.

The term $-1.5 N_{Me}$ may also be interpreted as a correction for branching, corresponding to some kind of change in the total energy which may not necessarily inhere exclusively in the C–H bonds. It should be mentioned that the correction $-1.5 N_{Me}$ fits the data well for cases of simple branching, as in isopentane, but that for cases of double branching as in neopentane a larger correction (about $-2.4 N_{Me}$) would fit better. It is then possible that we ought to have used a numerically smaller coefficient than 1.5 for N_{Me} for unbranched chains, with correspondingly somewhat altered coefficients for N_{CH}, N_{CC}, and N_{C-C}. But the latter changes would make Eq. (23) fit the data on diamond, also on polycyclic hydrocarbons, less well. [The 2.1 kcal. discrepancy between Eq. (23) and the observed ΔH for diamond is of a magnitude that can plausibly be attributed to excess branching as in neopentane, plus perhaps some excess of third-order hyperconjugation energy per C–C bond as compared with hydrocarbons.] Furthermore, the choice of $-1.5 N_{Me}$ yields conjugation and hyperconjugation energies which together with observed bond distances give about maximum self-consistency within the framework of our theory.

Strictly speaking, one cannot hope to determine an equation like Eq. (23) by means of which one can with certainty separate off exact conjugation and hyperconjugation energies from the whole delocalization energy of which they form a part; nor to separate out the whole delocalization energy sharply from the total energy. [Exactly the same limitations exist in the procedure used by Pauling and Sherman.]

Morse curves constructed by us for normal single and double bonds.[28]

14. The $\rho(r)$ Curve and the Parameter η.—In setting up the secular equation (14) or (16), we need suitable values of several β's for each molecule (e. g., β, β', and β^* in Eq. (16)). In general, the β's may be expected to increase with the strengths of the bonds to which they belong. Taking methylacetylene as an example, β^* refers to the $H_3 \equiv C$ bond, β to the C–C bond (empirically 1.462 Å. ± 0.005 long)[29],[3] β' to the $C \equiv C$ bond (1.20 Å. long).[3]

It is desirable to have a curve for β as a function of r. Lennard-Jones has given such a curve based on bond-energies and force-constants; but, especially in view of our reinterpretation of β, we have modified this curve to fit additional empirical evidence. For our computations, it is convenient to let

$$\beta_r = \rho_r \beta_{1.33}; \quad \text{also } \beta^* = \eta \beta_{1.33} \qquad (24)$$

We take $\beta_{1.33}$, i. e., β for $r = 1.33$ Å., equal to the double-bond distance in ethylene, as a standard of reference; we shall determine its value by trial and error to fit the empirical data. Table I gives our values of ρ_r.[28]

TABLE I

r (Å.)	ρ_r
1.20	1.40
1.33	1.00
1.35	0.95
1.39	0.84
1.46	0.65
1.54	0.47

To get some idea of the size of η of Eq. (24), let us compare the bond-energy for a C–H bond with the average energy for a C–C π bond in acetylene. According to Pauling the C–H, C–C, and $C \equiv C$ energies are, respectively, 87, 59, and 123 kcal.[9] The energy per π bond in $C \equiv C$ is then 32 kcal.

If $\beta_{1.20}$ and β^* are proportional to the bond energies, β^* should then be about 2.7 times[30] $\beta_{1.20}$, i. e., $\eta = 2.7\rho_{1.20}$. Actually, our analysis of the conjugation energy data in relation to our calculations gives $\eta = 4 = 2.9\rho_{1.20}$.

15. Computation of Conjugation Energies and LCAO Coefficients.—The immediate problem is now the solution of the secular equation for various assumed values of β^*, β, and β'. Making the substitution (24), also letting

$$\epsilon = (\alpha - E)/\beta_{1.33} \qquad (25)$$

and then dividing through by $\beta_{1.33}$, Eq. (14) or (16), after expanding the determinant and rearranging, takes one of the following forms

$$
\begin{aligned}
(a) \quad & (\epsilon^2 + \rho_1\epsilon - \rho_2^2)(\epsilon^2 - \rho_1\epsilon - \rho_2^2) = 0 \\
(b) \quad & \epsilon^4 - (\rho_1^2 + \rho_2^2 + \eta^2)\epsilon^2 + \rho_2^2\eta^2 = 0 \qquad (26) \\
(c) \quad & (\epsilon^2 + \rho_1\epsilon - \eta^2)(\epsilon^2 - \rho_1\epsilon - \eta^2) = 0
\end{aligned}
$$

Form (a) applies to the π MO's of diacetylene and to the x MO's of butadiene; form (b) to the π MO's of methylacetylene and to the x MO's of propylene; form (c) to the π MO's of ethane and to the y MO's of ethylene. In the equations, ρ_1 is for the acceptor bond (C–C, or, in the case of ethylene, $C = C$), ρ_2 for the $C \equiv C$ or $C = C$ donor bond; ρ_2 is nearly equal to 1 for $C = C$ and distinctly larger for $C \equiv C$ bonds. For cyanogen and methyl cyanide, (a) and (b) are, respectively, applicable after a suitable η_{CN} has been substituted for ρ_2.

We have obtained numerical solutions of Eqs. (26) for a variety of assumed combinations of ρ_r and η values, but shall record the results (cf. Tables II–V) only for $\eta = 4.0$, with each ρ_r taken from Table I for the best observed r value for the particular bond of the particular molecule in question.[31]

On solving Eqs. (26), the energy of each of four MO's of the form of Eq. (5) is obtained in terms of $\beta_{1.33}$ and α. These energies are recorded in Tables II and IV, together with the LCAO coefficients (i. e., the k's of Eq. (5)) for the first two MO's. These coefficients can be obtained, once the energies are known, by standard quantum

(28) The Morse curves were drawn using force constants from infrared spectral data and reasonable estimated x_e values (cf. reference 11, page 108). For C–C, we used 4.50×10^5 (Stitt, J. Chem. Phys., **7**, 297 (1939)), for $C = C$, 8.2×10^5 (Bonner, THIS JOURNAL, **58**, 34 (1936)), and for $C \equiv C$, 17.2×10^5 dynes/cm. (Wu and Kiang, J. Chem. Phys., **7**, 178 (1939)). Changing from these force constants to others given in the literature would have an inappreciable effect on our results.

These same Morse curves were used also as a guide in determining the ρ_r curve of Table I; for this purpose the three curves were plotted on a single diagram, with ordinates adjusted with respect to each other so as to make $\rho_{1.46}$ consistent with the observed butadiene conjugation energy of Table VI. (At any r in such a diagram, the vertical distance from the $C \equiv C$ to the $C = C$ curve, or from the $C = C$ to the C—C curve, should according to theory be approximately $2\beta_r$.) Other values of ρ_r were then determined directly as differences in ordinates of the three curves.

(29) G. Herzberg, F. Patat and H. Verleger, J. Phys. Chem., **41**, 123 (1937).

(30) The reasoning just given is subject to several large corrections (reference 21) which on the whole decrease the estimate. The tacit assumption that the bond energy for a quasi π bond in $C \equiv H_3$ is the same as for a localized C–H bond is probably not badly in error; actually, the quasi σ bond is expected to be stronger, the quasi π bonds somewhat weaker, than a localized C–H bond.

(31) In most cases we have used electron diffraction r values (errors ±0.02 to ±0.03 Å.) as given in reference 3 and by V. Schomaker and L. Pauling, THIS JOURNAL, **61**, 1769 (1939). For methylacetylene (reference 29), ethylene and acetylene, we have used the spectroscopic values, where the errors are smaller.

TABLE II

FORMS AND ENERGIES[a] OF NON-LOCALIZED π MO'S; CONJUGATION ENERGIES R[a]

Molecule	i	LCAO coefficients (k_{ni}) and energies (ϵ_i)[b]					Total π energy[c]		R
		k_{ai}	k_{bi}	k_{ci}	k_{di}	ϵ_i	$\pi_1{}^4\pi_2{}^4$	$\pi^4\pi'^4$	
Methylacetylene	1	0.695	0.706	0.129	0.044	−4.060	−21.758	−21.600	0.158
	2	.129	.044	− .695	− .706	−1.379			
	3	.129	− .044	− .695	.706	1.379			
	4	.695	− .706	.129	− .044	4.060			
Ethane	1	.485	.515	.515	.485	−4.244	−32.056	−32.000	0.056
	2	.515	.485	− .485	− .515	−3.770			
Diacetylene	1	.412	.575	.575	.412	−1.900	−11.505	−10.896	0.609
	2	.575	.412	− .412	− .575	−0.977			

[a] All energies are in units of $-\beta_{1.33}$ (note that $-\beta$ is positive). The computation is based on $\eta = 4.0$ and ρ_r as in Table I, with r values as in Table VI, also 1.54 Å. for ethane and 1.33 Å. for ethylene.

[b] The coefficients and energies in methylacetylene are given for all of the four non-localized π MO's π_1, π_2, π_3, π_4 (cf. reference 17) which belong to Eqs. (5), (16). For the remaining molecules the coefficients and energies are given only for π_1 and π_2; the coefficients and energies for π_3, π_4 are related to these in the same sort of way as in methylacetylene.

[c] The energy of each localized π MO is simply η for each π_{Me} and 1.4 for each $\pi_{C\equiv C}$ (cf. Eq. (11)).

theory procedure.[6,10] They will be used in a later section.

In order to obtain conjugation energies, the total energy of the four or eight electrons in the

TABLE III

BOND ORDERS OF π ELECTRONS (EIGHT ELECTRONS)[a]

Molecule	Electrons	ab	Bond bc	cd
Methylacetyl-	π_1	1.963	0.364	0.023
ene	π_2	0.023	− .123	1.963
	π_1 and π_2	1.986	.241	1.986
	Same normalized[b]	1.886	.229	1.886
Ethane	π_1	0.998	1.059	0.998
	π_2	0.998	− .941	0.998
	π_1 and π_2	1.997	.118	1.997
Diacetylene	π_1	0.947	1.321	0.947
	π_2	.947	− .679	.947
	π_1 and π_2	1.894	.642	1.894

[a] The partial bond order contributed to the ab bond by each π_1 electron is given by the product $k_{a1}k_{b1}$ of the k's of Table II; the number given in Table III is four times this, corresponding to the four π_1 electrons. Similarly for the π_2 electrons, and for the bc and cd bonds. [b] Here the figures in the preceding line have been multiplied by a suitable factor so that the sum of the partial bond orders is equal to the conventional number of π and/or [π] bonds, i. e., four.

occupied x or π MO's (x_1, x_2 or π_1, π_2), as computed using non-localized MO's, must be subtracted from the corresponding energy in terms of localized MO's (see Table II, footnote). The results, in units of $\beta_{1.33}$, are given in Tables II and IV. Tables III and V, referring to bond orders, will be explained in a later section.

16. Comparison of Computed and Observed Conjugation Energies.—In order to make comparisons between the observed conjugation energies and the computed ones of Tables II and IV, it is necessary to deduct from the "computed" conjugation energies such quantities of third-order conjugation energy as must, according to our analysis, be present in the normal molecules to which Eq. (23) applies.

To understand these deductions, it is useful first to write

$$- \Delta H_{298^\circ} = Q_{CH}N_{CH} - dN_{Me} + Q_{CC}N_{CC} + A_{C=C}N_{C=C} + A_{C\equiv C}N_{C\equiv C} - \Delta \quad (27)$$

This is merely Eq. (23) plus a correction $- \Delta$, Δ being "observed conjugation energy" or "observed resonance energy." [In computing Δ in cases where there is ring-strain, a correction for this is first deducted.] Q_{CH} and Q_{CC} are supposed to be the normal heats of combustion

TABLE IV

FORMS AND ENERGIES[a] OF NON-LOCALIZED x OR y MO'S; CONJUGATION ENERGIES R[a]

Molecule	MO type	LCAO coefficients k_{ni} and energies ϵ[b]						R[c]
		k_{a1}	k_{b1}	k_{c1}	k_{d1}	ϵ_1	ϵ_2	
Butadiene	x	0.411	0.576	0.576	0.411	−1.332	−0.678	0.219
Propylene	x	.701	.707	.092	.023	−4.032	− .992	.048
Ethylene	y	.468	.530	.530	.468	−4.531	−3.531	.124

[a] See Table II, note a.

[b] The coefficients are given only for the first of the four non-localized MO's x_1, x_2, x_3, x_4 (or y_1, y_2, y_3, y_4), and the energies only for the first two. In regard to the remaining coefficients and energies, cf. Table II, note b.

[c] This is obtained by subtracting the total energy of $x_1{}^2x_2{}^2$ (or $y_1{}^2y_2{}^2$) from that of $x^2x'^2$ (or $y^2y'^2$), where x (or y) refers to a localized bonding MO of C=C, $H_3\equiv C$, or $H_2\equiv C$, and x' (or y') to one of C=C, C=C, or C=H$_2$, for the three respective molecules; the energy per localized MO is $\rho(1.35)$, η, η, $\rho(1.35)$, 1, η for the six MO's in the order named.

TABLE V

BOND ORDERS OF x OR y ELECTRONS (FOUR ELECTRONS)[a]

Molecule	Electrons	ab	Bond bc	cd
Butadiene	x_1 and x_2	0.945	0.325	0.945
Propylene	x_1 and x_2	.995	.098	.995
Ethylene	y_1 and y_2	.992	.124	.992

[a] Cf. Table III, note a.

of C—H and C—C single bonds.[32] The term $-dN_{M_0}$ has been interpreted[27] tentatively as a correction to $Q_{CH}N_{CH}$ corresponding to a slight increase above normal bond strength for C–H bonds in methyl groups.

The discussion will be clearer if we can refer to an equation for heats of formation from atoms, D. The D equation corresponding to Eq. (27) is obviously

$$D = D_{CH}N_{CH} + dN_{M_0} + D_{CC}N_{CC} - A_{C=C}N_{C=C} - A_{C≡C}N_{C≡C} + \Delta \quad (28)$$

Now according to reasoning given in earlier sections, D must include third-order conjugation energy in amounts approximately proportional, for *saturated compounds*, to the number of C–C bonds. This may be expressed by writing

$$D_{CH} = D^0_{CH}; \quad d = d^0; \quad D_{CC} = D^0_{CC} + 2\delta_{1.54} \quad (29)$$

Here $2\delta_{1.54}$ represents the average or normal hyperconjugation energy per C–C single bond of length 1.54 Å. The factor 2 is introduced because this third-order conjugation is two-dimensional (x and y), and it is convenient to let $\delta_{1.54}$ stand for the hyperconjugation energy per bond per dimension. In accordance with discussion in earlier sections, we shall *assume that $2\delta_{1.54}$ is equal to the hyperconjugation energy of ethane.*[33]

On analysis, it is seen that the terms in $N_{C=C}$ and $N_{C≡C}$ correspond each to the sum of several corrections which enter when multiple bonds are present: (a) they correct from $2D^0_{CC}$ or $3D^0_{CC}$, respectively, to $D^0_{C=C}$ or $D^0_{C≡C}$; (b) they correct for possible changes in D_{CH} for hydrogens attached to multiply as compared with singly bonded carbon atoms; (c) they correct from $4\delta_{1.54}$ or $6\delta_{1.54}$ to $\delta_{1.33}$ or $\delta_{C≡C}$, where $\delta_{1.33}$ represents the average normal one-dimensional (y) hyperconjugation energy per C=C double bond of length 1.33 Å., and $\delta_{C≡C}$ is zero since there is no hyperconjugation energy in acetylene. We shall *assume $\delta_{1.33}$ equal to the hyperconjugation energy of ethylene.*[34] The A's may now be written

$$A_{C=C} = A^0_{C=C} + (\delta_{1.33} - 4\delta_{1.54});$$
$$A_{C≡C} = A^0_{C≡C} - 4\delta_{1.54} \quad (30)$$

where the A^0's include the corrections to D^0_{CC} and D_{CH}.

(32) On analysis of what these mean, one finds $Q_{CH} = (\frac{1}{2}D_{CO_2} + \frac{1}{2}D_{H_2O} - \frac{1}{2}D_{O_2}) - D_{CH}$; $Q_{CC} = (\frac{1}{2}D_{CO_2} - \frac{1}{2}D_{O_2}) - D_{CC}$, where the D's are energies of dissociation into atoms.

(33) This assumption implies that the hyperconjugation energy per acceptor bond is independent of whether the donor bonds are all C–H as in ethane or partly C–C as in the higher hydrocarbons. While theoretically $\delta_{1.54}$ should be somewhat larger in the latter case, the empirical evidence discussed in an earlier section supports our assumption as at least a rough approximation.

(34) The correction items (b) and (c), being based on ΔH data on C_2H_4 or C_2H_2, should presumably be roughly but not exactly correct for double or triple bonds in general. Thus if we have one or more *carbons* attached by single bonds to C=C or C≡C, instead of *all hydrogens* as in C_2H_4 or C_2H_2, item (b) ought presumably be slightly altered. Similarly, item (c) should be slightly in error, when carbons instead of hydrogens are attached to C=C, since it assumes $\delta_{1.33}$ in general to be equal to $\delta_{1.33}$ of C_2H_4.

Eq. (28) may now be rewritten

$$D = (D_{CH}N_{CH} + dN_{M_0} + D^0_{CC}N_{CC} - A^0_{C=C}N_{C=C} - A^0_{C≡C}N_{C≡C}) + (2\delta_{1.54}N_{C-C} + \delta_{1.33}N_{C=C} + \Delta) \quad (31)$$

where N_{C-C} is the number of carbon–carbon single bonds (e. g., three in benzene) as contrasted with N_{CC} which is the total number of carbon–carbon bonds (e. g., nine in benzene).

Eq. (31) shows that the *total resonance or conjugation energy R*, of all orders, is

$$R = \Delta + C + 2\delta_{1.54}N_{C-C} + \delta_{1.33}N_{C=C} \quad (32)$$

where C is the energy correction for changes in bond length by conjugation (cf. section 13). In using Eq. (32), $\delta_{1.54}$ and $\delta_{1.33}$ are always to be taken for the bond lengths 1.54 Å. and 1.33 Å., respectively,[35] *but R refers to the total conjugation energy at bond lengths equal to the actual ones in the molecule.*

The total conjugation energy as given by Eq. (32), in which Δ and C are essentially empirical, is now to be compared with the same quantity computed entirely theoretically. For the latter, we may write

$$R = R_x + R_y \quad (33)$$

When R_x and R_y are equal and of the same conjugation order, as in methylacetylene, diacetylene, or ethane, we have computed them directly. In cases where R_x is of higher order than R_y, as in benzene, butadiene, or propylene, we have computed only R_x directly.

In the latter cases R_y is third-order conjugation energy, which we shall estimate by assuming that the contribution to it for each C–C or C=C bond is the same as the computed value of R_y for C_2H_6 or C_2H_4, respectively. It is to be noticed that R_y here must be estimated corresponding not to normal C–C and C=C bond lengths, but to the lengths of the bonds in the actual molecules. Now R_y is obtained for both C_2H_6 and C_2H_4 on the basis of solutions of the same secular equation (28c), the only difference being in the value of ρ_1, which depends on the bond lengths.[36] Values of R_y per bond corresponding to bond lengths of 1.54, 1.53, 1.46, 1.39, 1.35, and 1.33 Å. have been computed and recorded in Table VII opposite the headings $\delta_{1.54}$, $\delta_{1.53}$, $\delta_{1.46}$, $\delta_{1.39}$, $\delta_{1.35}$, and $\delta_{1.33}$; the first and last of course agree with R_y for C_2H_6 and for C_2H_4, respectively.

Letting δ_s and δ_d stand for the values of R_y for a single or for a double bond, respectively, we have for molecules containing double bonds

$$R_y = \delta_s N_{C-C} + \delta_d N_{C=C} \quad (34)$$

(In benzene, $\delta_s = \delta_d = \delta_{1.39}$, and $R_y = 6\delta_{1.39}$.)

Now combining Eqs. (32) and (33), we find

$$\Delta + C = R_x + R_y - 2\delta_{1.54}N_{C-C} - \delta_{1.33}N_{C=C} \quad (35)$$

(35) C automatically includes any needed changes in $\delta_{1.54}$ N_{C-C} + $\delta_{1.33}$ $N_{C=C}$ which accompany compression or stretching.

(36) We are tacitly making the simplifying assumption that η of Equation (28) is the same for —C≡H₃ as for >C=H₂.

In the following tables, we shall consider $\Delta + C$ as an empirical quantity, and compare it with the corresponding theoretically computed expression on the right of Eq. (35).

In obtaining the following tables, computations were first made for a variety of assumed values of $\beta_{1.33}$ and of η, and of assumed forms of the ρ_r curve between 1.20 and 1.54 Å. By trial and error, values of the parameters were found such as to give good agreement between the observed and computed $\Delta + C$ for the molecules benzene, butadiene, methylacetylene, and dimethylacetylene in Table V. In determining $\rho_{1.20}$, weight was given to the location of the methylacetylene and diacetylene points in Fig. 1. The computed hyperconjugation energies for dimethylacetylene, obtained after solving a suitable secular equation, are almost exactly twice those for methylacetylene so that we have treated this molecule and methyl-

acetylene together, seeking to match the observed $\Delta + C$ *per methyl group* averaged for the two molecules.

In obtaining $\beta_{1.33}$, benzene was our main reliance, since it is relatively insensitive to η and ρ_r. On the other hand, diacetylene and butadiene are particularly sensitive to ρ_r, and the methylacetylenes to η. Using $\beta_{1.33}$, η, and ρ_r, obtained from the other molecules, the computations for propylene were made last, and have significance as an independent check. The computations for C_2H_4, C_2H_6, and the δ's in Table VII were made collaterally with those for benzene, butadiene, and methylacetylene, since they are needed in making the R_y estimates for benzene and butadiene and in the "deductions" in Table VI for all three molecules.

The final values of $\beta_{1.33}$, η, and ρ_r which cause agreement between experiment and theory in

TABLE VI

CONJUGATION ENERGIES[a]

| Molecule | Carbon–Carbon distances assumed[c] | Computed[c,d] | | | | | Observed | | |
		R_x[e]	R_y[f]	R[e]	Deduction	$\Delta + C$	Δ[b]	C[g]	$\Delta + C$
Benzene	1.39	74.94	23.60	98.54	24.08	74.46	39.4 ± 0.3	35.0	74.4
1,3-Butadiene	1.35	9.74	12.37	22.11	13.56	8.55	5.7 ± 0.2	2.8	8.5
	1.46								
Diacetylene[h]	1.21	13.55	13.55	27.09	2.49	24.6	13　± 10(?)	6	19
	1.36								
Propylene	1.33	2.15	6.89	9.04	8.03	1.01	1.3 ± 0.2	0.0	1.3
	1.53								
Methylacetylene	1.20	3.51	3.51	7.01	2.49	4.52	3.6 ± 0.2	1.1	4.7
	1.46								
Dimethylacetylene	1.20	7.01	7.01	14.03	4.98	9.04	6.4 ± 0.2	2.2	8.6
	1.46								

[a] The first three molecules are examples of first-order (ordinary) conjugation, the second three of second-order conjugation.

[b] The observed Δ values are based on Eq. (23).

[c] The computed energies assume $\beta_{1.33} = -44.5$ kcal., $\eta = 4.0$, and ρ_r as given in Table I, with r values as given in the second column. These r values are based mainly on electron diffraction data,[31] except for methylacetylene and dimethylacetylene, where the spectroscopic value for methylacetylene[29] has been used for the C–C distance. For the triple bond in diacetylene, the electron diffraction value (1.19 ± 0.02 Å.) seems in error in view of the considerable amount of first-order conjugation present. Guided by our bond order curve (Fig. 1), we have therefore assumed 1.21 for the calculations, and similarly 1.53 for propylene instead of the electron diffraction value of 1.54 Å.

[d] See Eq. (35) and Table VII.

[e] R_x for butadiene and propylene was computed using the R_x expressions from Table IV; R for methylacetylene and diacetylene using the R expressions of Table II. In the case of dimethylacetylene, a procedure similar to that of Table II was used, after setting up a suitable secular equation for the non-localized MO's.

[f] For the molecules with double bonds, see Eq. (34) and Table VII.

[g] See section 13; in computing C values, the r values of column two were used. In diacetylene and the methylacetylenes, respectively, C was computed corresponding to shortenings of $(1.54 - 0.06 - 1.36 = 0.12$ Å.) and $(1.54 - 0.03 - 1.46 = 0.05$ Å.), a portion of the shortening being deducted as due to decreased single bond radius of acetylenic carbon (*cf.* section 16).

[h] No observational data exist on diacetylene itself. Instead, ΔH data on dimethyldiacetylene have been used, and from the resulting values of Δ, a deduction for each methyl group has been made, equal to the average of the values of Δ per methyl group obtained from methylacetylene and dimethylacetylene. The observed $-\Delta H$ of 847.8 kcal. for dimethyldiacetylene is not very reliable; since other data of the same observer average about $1/2\%$ high, we have used $-\Delta H$(solid) = 844, or $-\Delta H$(gas) = 853.

TABLE VII

COMPUTED THIRD-ORDER CONJUGATION ENERGIES[a]

Molecule or bond	R_x	R_y[b]	R[c]
Acetylene	0	0	0
Ethylene	0	5.54	5.54
Ethane	1.25	1.25	2.50
$\delta_{1.54}$			1.25
$\delta_{1.53}$			1.35
$\delta_{1.46}$			2.37
$\delta_{1.39}$			3.93
$\delta_{1.35}$			5.00
$\delta_{1.33}$			5.54

[a] See Table VI, note c, regarding β, η, and ρ_r. The r values assumed here are 1.20 Å. for acetylene, 1.33 Å. for ethylene, 1.54 Å. for ethane. [b] R_y for ethylene was computed using the expression obtained in Table IV. [c] R for ethane was obtained using the expressions in Table II.

Table VI and Fig. 1 have already been discussed. The final value of 44.5 kcal. or 1.93 e. v. for $\beta_{1.33}$ is larger than previous values (15–20 kcal. per mole according to Hückel, Wheland, and Pauling, or 35 kcal. according to Lennard-Jones). It is much nearer than before to β values deduced from spectroscopic data.[21]

17. Second-order Conjugation between Methyl or Methylene Groups and Double Bonds.—In addition to the computations in Tables VI and VII, computations of R_x in terms of $\beta_{1.33}$ have been made for a considerable number of other double-bonded molecules with second-order conjugation (see Table VIII). These were made before the final ρ_r and η values were obtained. They serve, however, to show that the computed contribution to the total x conjugation energy per bond is practically the same for —CH₃ linked to C=C as for —CH₂— with either one or with two links to a C=C, and is independent of the number of —CH₃ per C=C; and that the computed hyperconjugation energy of a CH₃ or CH₂ group is nearly the same with an unconjugated C=C, a conjugated C=C, or with resonating C=C's as in toluene.

Contrary to earlier qualitative considerations,[3] the cyclic conjugated dienes do not show an especially large computed hyperconjugation energy per C–C acceptor bond. (In regard to their observed Δ's, cf. Table VIII, end of note c.) In obtaining the R_x per bond for cyclohexadiene-1,3, we first deducted from the gross computed R_x an amount equal to the computed R_x of ethane. The agreement of the resulting value with the others in Table VIII supports our assumption that $\delta_{1.54}$ in general is equal to R_x of ethane.

The foregoing computed results, and the fact that the computed R per methyl group is practically the same in Table VI for methylacetylene and dimethylacetylene, are the foundation for our belief that conjugation energies of different orders are approximately additive, and that the x or y hyperconjugation energy of any given type is approximately a constant per bond independent of the size or structure of the particular molecule.

Computed and observed $\Delta + C$ values have not been worked out in detail as in Table VI for the molecules in Table VIII. From the constancy of R_x per bond in Table VIII, however, it can be seen that the computed $\Delta + C$ values per C–C acceptor bond would in all cases be nearly the same as the value for propylene in Table VI. This, therefore, may be compared with the observed Δ values as given in Table VIII (in these molecules, C is practically zero). One sees that the results for propylene are fairly typical.

Our Table VIII gives an explanation of observations of Kistiakowsky and his colleagues, who found that the heat of hydrogenation of unsaturated compounds decreases with increasing methylation of the compounds. This is now explained, in part, by hyperconjugation (cf. Table VIII, footnote c, for further details), in harmony with an earlier suggestion.[4]

It is of interest that Schomaker and Pauling[36a] have assigned a conjugation energy (our Δ) of 1.5 kcal. for interaction of a methyl or ethyl group with unsaturated rings of the pyrrole type. This is not far different from our Δ values in the last column of Table VIII.

Accurate Δ values are available for aldehydes and ketones. Using Eq. (23), supplemented by a standard $-\Delta H$ value (namely zero) for the C=O bond, based on $\Delta = 0$ for formaldehyde, we obtain the Δ values

Acetaldehyde: observed Δ = 6
Acetone: observed Δ = 12

Formaldehyde, acetaldehyde, and acetone are, respectively, analogous in structure, as regards hyperconjugation, to ethylene, propylene, and isobutylene, but the net hyperconjugation energy Δ per methyl group is much larger. This is confirmed by the shortening of the C–C bond to 1.50 Å. in acetaldehyde, which Stevenson, Burnham and Schomaker attribute mainly to hyperconjugation.[37] We have recently made computations

(36a) Reference 31, p. 1778, just under their Table IX.
(37) D. P. Stevenson, H. D. Burnham and V. Schomaker, THIS JOURNAL, 61, 2922 (1939).

SECOND-ORDER CONJUGATION ENERGIES OF METHYL AND
METHYLENE GROUPS

Molecule	No. conj. bonds[a]	Computed R_x per conj. bond[b]	Obsd. net Δ per conj. bond[c]
Propylene	1	0.108β	1.21
Butene-2, cis	2	$.108\beta$	0.62
Butene-2, trans	2	$.108\beta$	1.05
Isobutylene	2	$.107\beta$	1.46
Trimethylethylene	3	$.108\beta$	0.97
Tetramethylethylene	4	. . .	0.80
Pentadiene-1,3	1	$.112\beta$	1.46
Isoprene	1	$.114\beta$	2.96 ± 0.5
Pentadiene-1,4	2	. . .	0.92
Cyclopentadiene	2	$.118\beta$	1.60
Cyclohexadiene-1,3[d]	2	$.119\beta$	−0.65
Ethylbenzene	1	$.108\beta$	0.98
o-Xylene	2	. . .	1.27
Mesitylene	3	. . .	0.73

[a] This is the number of *single* bonds connecting CH_3 or CH_2 groups with C=C groups, and so subject to *second-order* conjugation.

[b] The total x conjugation energy R_x for each molecule was computed (*cf.* Table IV) in terms of $\beta_{1.33}$ after setting up the appropriate secular equation for the non-localized x MO's for the entire molecule. In the conjugated dienes and the methylbenzenes, these non-localized MO's take into account the combined first-order and second-order conjugation; the value of R_x tabulated above was obtained by subtracting, from this total R_x, the value of R_x computed for butadiene or benzene, respectively, then dividing by the number of second-order acceptor bonds in the second column. The computations were made assuming $\eta = 3$ and the following ρ_r (different from that in Table I): $\rho_r = 1.00, 0.904, 0.779, 0.664$ for $r = 1.33$, 1.39, 1.46, and 1.54 Å., respectively.

[c] Δ for the methylethylenes here is the usual Δ divided by the number of methyl groups in each case. For the methylbutadienes and methylbenzenes, the Δ's given above are *net*, obtained from usual Δ's by subtracting from the latter the observed Δ's of butadiene or benzene, respectively, and, further, dividing by the number of methyl groups or in general of second-order C–C acceptors.

With the exception of isoprene, the gross total Δ values were obtained directly from heats of hydrogenation (Kistiakowsky, *et al.*, THIS JOURNAL, **61**, 1868 (1939); **60**, 440 (1938); **59**, 831 (1937); **58**, 146 (1936); **57**, 876 (1935); **57**, 65 (1935)), in the following way. Taking propylene as an example, let H_1 and H_2 be the heats of hydrogenation of ethylene and propylene, respectively. Now applying Eq. (23) or (27) to these molecules and to their hydrogenation products, one finds $\Delta = (H_1 - H_2) -$ 1.5, the 1.5 being the coefficient of N_{Me} in Eq. (23). An analogous procedure was used for the other molecules.

In the case of cyclopentadiene, this procedure has the effect of automatically assuming the same ring strain correction for cyclopentadiene as for its hydrogenation product cyclopentane. The approximate correctness of this assumption receives support from the fact that, if we had used the ring strain correction for cyclopentane but not for cyclopentadiene, the tabulated net Δ per bond in

Table VIII would be about −1.1 instead of +1.60. On the other hand, Δ for cyclohexadiene appears to be inexplicably negative anyway (but some of its derivatives, not tabulated, give positive Δ's).

[d] The total computed R_x for cyclohexadiene-1,3 included first-, second-, and third-order conjugation energy; the last corresponds to the C–C bond between the two CH_2 groups. In obtaining the listed R_x, the first order R_x as computed for butadiene and the third-order R_x as computed for ethane were first subtracted.

which indicate that there is in all >C=O compounds a new remarkably energetic type of hyperconjugation involving the C=O bond as acceptor, with the non-bonding pair of oxygen y electrons together with the C–C or C–H bonds as donors. The observed Δ's seem to be too large to be explained by propylene-like hyperconjugation alone.

18. Bond Orders.—In connection with his analysis of bond distances and the character of bonds,[9] Pauling drew a curve connecting bond distance with percentage of double-bond character applicable to molecules containing conjugated or resonating double bonds. Penney and Coulson[38] have further discussed this problem, have introduced the term "bond order," and have drawn curves relating bond distance to bond order. These differ somewhat from Pauling's curve, because the "bond order" is a quantity which is proportional to bond energy, so that the sum of the bond orders in a conjugated molecule is fractionally greater than the total number of conventional bonds. This difference can of course be removed if the bond order is "normalized" through multiplication by a suitable factor (*cf.* Table III, note *b*). In the following we shall usually use the unnormalized bond order.

Coulson has pointed out that the bond order for any bond in a conjugated molecule can be computed theoretically in LCAO MO approximation in a simple way. (Similar results are obtained by the AO approximation, as Penney has shown.) Namely, in addition to a contribution of 1 for each σ bond, the total bond order for any given bond is the sum of partial bond orders, each partial bond order being the contribution made by a particular pair of unsaturation electrons in a particular non-localized MO. The sum is taken over all the unsaturation electrons involved in the conjugated system. The partial bond orders are obtained from the LCAO coefficients in the non-

(38) See especially, C. A. Coulson, *Proc. Roy. Soc.* (London), **169A**, 419 (1939).

localized MO's in a manner illustrated in Tables III and V.
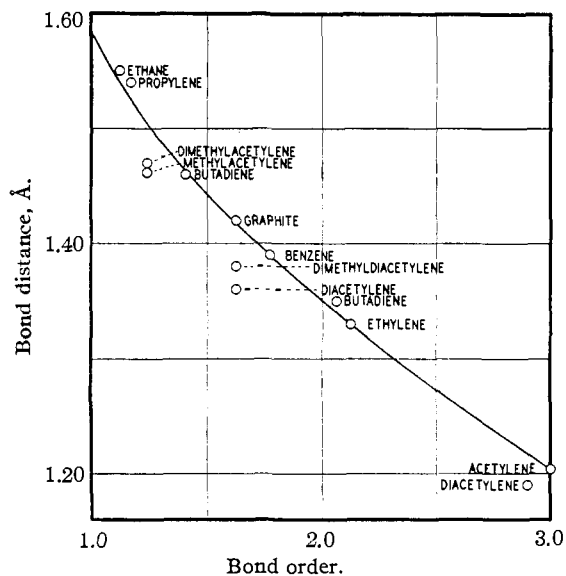

Fig. 1.—The relation between bond distance and bond order. The bond orders were obtained using Tables III and V, in the manner explained in section 18. For methylacetylene, ethylene and acetylene, the bond distances are obtained from spectroscopic data and are relatively accurate; other distances are mostly from electron diffraction data (errors ±0.02 to ±0.03, cf. ref. 31). The departures from the curve for the acetylenes and diacetylenes are in agreement with expectation (see section 18).

In the accompanying figure the total unnormalized bond order for carbon–carbon acceptor bonds in various molecules has been plotted against the experimental bond distance. The total bond order for the C–C bond in ethane, methylacetylene, and diacetylene is obtained by adding 1 (for the σ bond) to the figures for "π_1 and π_2" in the bc columns of Table III. For the C=C bond in ethylene, the total bond order is 1 for the σ bond plus 1 for the x bond, here unconjugated, plus a contribution for y hyperconjugation (see the bc column in Table V). For the C≡C bond in acetylene the bond order is just 3, since there is no conjugation. For propylene, butadiene, benzene, and graphite, the x bond order is known, in the first two cases from Table V, while for benzene and graphite we may refer to Coulson[38]: the x order is 2/3 for benzene and 0.53 for graphite. To this in each case must be added 1 for the σ bond, and also a computed allowance for y hyperconjugation.

Our figure differs from a similar figure of Coulson[38] in that we have included all the first-, second-, and third-order conjugation contributions

to the bond order both x and y, while he included only the effects of first-order x conjugation. We have neglected only σ hyperconjugation. In Coulson's curve the bond orders for the central bond in ethane, ethylene, and acetylene are 1, 2, and 3; in ours they are 1.12, 2.12 and 3.

As a result of our inclusion of hyperconjugation energy, our curves do not reach bond order 1 at 1.54 Å.,[39] but at about 1.58 Å. This is to be interpreted as the normal bond length for an isolated or ideal C–C single bond with no hyperconjugation. Similarly our curves indicate 1.35 Å. for an isolated C=C bond. For an isolated C≡C bond, there is no change from the value in acetylene.[40]

In Fig. 1, it is seen that the propylene point at 1.54 Å. falls nearly 0.02 Å. above the curve. This indicates that the true bond length of the C–C bond in propylene is 1.52 or 1.53 Å., values which are not excluded by the experimental evidence.[3] Similarly, our curve indicates that the C≡C distance in diacetylene must be at least 1.21 Å., as compared with the observed 1.19 ± 0.02 Å.

The points for the C–C bonds of the methylacetylenes and for diacetylene and dimethyldiacetylene all fall considerably below the curve. The average departure is 0.035 Å. for the methylacetylenes, 0.05 Å. for the diacetylenes. These deviations are exactly what we should expect according to a suggestion of Pauling, Springall and Palmer.[3] They point out that the C–H bond in acetylene is 0.036 Å. shorter than in saturated compounds, and explain this as due to an unusually large amount of s character in the carbon valence AO which is used for the C–H bond when the carbon is part of a C≡C bond. They estimate that any C–C bond in the arrangement C—C≡C should be shortened by at least 0.02 Å. In diacetylene the total shortening should presumably be twice as great. We find an average shortening, per C—C≡C attachment, for the four molecules mentioned, of 0.03 Å.

The excess bond order, above the usually assumed values 1 and 2, indicated for normal C–C or C=C bonds by the computations on ethane

(39) The observed value (reference 9) for ethane is 1.55 ± 0.03 Å., but our analysis in general does not definitely indicate that ethane should have a greater C–C bond length than the usual value of 1.54 Å. in saturated molecules.

(40) It is interesting that an equation for bond length as a function of the number of bonds deduced for the C_2 molecule, from spectroscopic data, gives a value 1.62 Å. for the length of a single bond; also, 1.40 Å. for a double bond, and 1.18 Å. for a triple bond (R. S. Mulliken, *Phys. Rev.*, **56**, 778 (1939)).

and ethylene and plotted in our figure, may be expressed by saying that normal C–C bonds contain a certain percentage of double-bond character and normal C=C bonds a certain percentage of triple-bond character. This type of description is used by Pauling for bonds which are conjugated in the ordinary sense. Using normalized bond orders (*cf.* Table III, footnote *b*), our conclusion is that normal C–C bonds have 11% double-bond character and normal C=C bonds 12% triple-bond character.[41]

19. The Bond Order of C–H and Other Hyperconjugation Donor Bonds.

—The results of bond order computations such as those recorded in Tables III and V form the basis for our earlier statement that donor bonds are relatively little affected by conjugation. [This is of course no longer true in cases of complete resonance, as in benzene or H_2N—CH=CH—CH=CH—CH= $NH_2{}^+$, where all bonds become alike, or even in long conjugated chains where this condition is approached.[10]] The extent to which the donor bonds are affected in various simple molecules may be judged from the total π or x or y bond orders under the headings *ab* and *cd* in Tables III and V (using in Table III the results for "π_1 and π_2"). It is seen that, in cases with hyperconjugation only, these bond orders fall only very slightly below the values (2 in Table III, 1 in Table V) which would be expected for isolated or ideal bonds.

Our computations thus indicate that the acceptor bonds in hyperconjugation are very appreciably strengthened and shortened but that the donor bonds are almost inappreciably affected. Even in the relatively strong second-order conjugation in methylacetylene, where the order of the C–C acceptor bond has been increased from 1 to 1.24, the order of the $C≡H_3$ donor bonds has been decreased only from 3 to 2.99. If we assume a curve similar to Fig. 1 for the C–H bonds, we conclude that the C–H bonds in methylacetylene must be about 0.001 Å. longer than normal, an inappreciable amount. In other cases (*e. g.*, propylene and ethane) the effects should be still smaller. Hence actual C–H bonds should be practically identical with ideal C–H bonds.[42]

(41) We might also say that normal C–C bonds have 6% triple-bond character. According to our procedure, this is merely another phraseology. However, it may be that it would be more accurate if our analysis had made a distinction here, corresponding to the fact that *x* bonds in double and triple bonds are not quite identical (even for equal bond lengths).

(42) This, of course, does not exclude variations in length due to variations in the valence state of the carbon atom. Thus while the usual C–H bond length is 1.093 Å., in acetylene and HCN it is reduced to 1.057 Å. (*cf.* reference 3).

In large ring or chain molecules, according to our discussion in earlier sections, every C–C bond acts both as acceptor and as donor in third-order conjugation. It is now clear that only the acceptor role should affect the bond length and strength appreciably. It appears then that every C–C bond can act as hyperconjugation donor wherever this is needed, without appreciable cost.

20. Spectra of Methyl and Methylene Derivatives of Butadiene.

—The present work arose out of an attempt to explain why the first ultraviolet absorption regions of cyclopentadiene and of cyclohexadiene-1,3 are markedly shifted toward the red as compared with that of butadiene-1,3. Qualitatively, hyperconjugation gives a good explanation of these shifts.[4] It gives at the same time an explanation of the smaller red shifts and of the exaltation of refractivity which are universally associated with methyl substitution.

It was previously surmised[4] that hyperconjugation effects are much more pronounced for spectra and refractivities than for properties involving the ground states of molecules. Our quantitative computations, to be reported in a later paper, now indicate the reverse. Suffice it to say here that while they always agree qualitatively with observation, the computed spectrum shifts using the β, η, and ρ_r results of the present paper are now considerably smaller than the observed, even after dropping the assumption $\alpha^* = \alpha$, a procedure whose effects are relatively more pronounced for the spectra than for the ground states. While this is disappointing, it is no serious argument against our conclusions in the present paper, since other causes for spectrum red-shifts are known and might well account for shifts of the observed order of magnitude.[43]

21. Critical Discussion.

—The general consistency of the observed and computed quantities $\Delta + C$ in Table VI and the good fit of the points on the bond order curve indicate that our procedure has been essentially correct. Granting this, we may accept as real, at least as to order of magnitude, the computed hyperconjugation energies and bond orders for ethane and ethylene, and for C–C and C=C bonds in general, also our results on ideal bond lengths. The considerable magnitudes of the computed effects are striking.

From the MO viewpoint, simple bond formation, resonance or conjugation, and hyperconjuga-

(43) *Cf.*, *e. g.*, the discussion by W. C. Price and collaborators, *Proc. Roy. Soc.* (London), **A174**, 207, 220 (1940).

tion represent three successive orders of approximation for the electronic structure, or three successive stages of description in terms of orbital delocalization. It should be kept in mind, however, that the total energy of a molecule may include appreciable higher-order terms which would come under the general heading of delocalization energy yet not under that of hyperconjugation energy; and also terms under other headings such as exchange energy.

Strictly speaking, one cannot draw sharp lines in subdividing the total energy according to different orders and different types. Perhaps the most uncertain feature of our analysis is in the derivation of conjugation and hyperconjugation energies from thermal data. Consequently it may be that the best values of the empirical conjugation energies would differ considerably from our values in Table VI. Possibly these best values might even turn out to be twice as large as ours; or possibly they may be smaller than ours. Our empirical parameters, our bond order curve, and our numerical conclusions would then be strongly altered, since these are decidedly sensitive to variations in the empirical conjugation energies to which they are fitted. Nevertheless, their self-consistency gives distinct support to our numerical results, since we have found that such self-consistency is not easy to attain.

Our numerical conclusions are, of course, based on fitting bond distances as well as conjugation energies into a consistent scheme, and are in some respects fairly sensitive to small changes in bond distances. Although fortunately the empirical bond distances are on the whole reliable enough to make our results fairly definite, nevertheless more accurate bond distances would be very helpful.

Summary

1. It is shown by quantitative computations using the molecular orbital method that hyperconjugation (*i. e.*, conjugation with, or between, saturated groups) is a phenomenon of real importance for the structure of organic molecules. Observed conjugation and hyperconjugation energies from thermal data, and observed bond lengths, all fit into the theory if a suitable choice is made for the values of an empirical parameter β, of its mode of variation with bond length, and of a parameter β^* for C–H bonds (*cf.* Table VI and Fig. 1).

2. The parameter β is not the "resonance integral" as heretofore supposed. It is only about one-tenth as large as the latter should be. A satisfactory new interpretation is given for the observed β.

3. Our value of β (about 45 kcal. per mole for the C=C bond distance of 1.33 Å.) is larger than that obtained by others, and approaches consistency with β values obtained spectroscopically.

4. The terms donor and acceptor bonds in conjugation and hyperconjugation are introduced. It is shown that C–H bonds, which function exclusively as donor bonds in hyperconjugation, are not appreciably affected in strength or length by the latter. Isolated or ideal C–C bonds would have a bond length of perhaps about 1.58 Å., which is shortened to the normally observed 1.54 Å. by an omnipresent second-order hyperconjugation, or to smaller values when first-order hyperconjugation, ordinary conjugation, or resonance is present. Similarly the ideal C=C bond would have a length of about 1.35 Å., as compared with the normal C=C length of 1.33 Å. In agreement with a suggestion of Pauling, we conclude that, even without conjugation or hyperconjugation, a C–C single bond to a triple-bonded carbon atom is shorter than usual by about 0.03 Å.

5. About 2.5 kcal. per mole of the normal bond energy of the ordinary 1.54 Å. C–C bond comes from the omnipresent second-order hyperconjugation, and the ordinary 1.33 Å. C=C bond contains about 5.5 kcal. per mole of second-order hyperconjugation energy. (The exact figures are tentative.) Triple bonds contain no hyperconjugation energy.

6. The omnipresent hyperconjugation mentioned above implies that normal C–C bonds have about 11% double-bond character, and normal unconjugated double bonds about 12% triple-bond character.

7. An explanation is given for the observed decrease with methyl substitution in the heats of hydrogenation of unsaturated compounds.