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# BOND LENGTHS AND BOND ENERGIES IN CONJUGATION AND HYPERCONJUGATION*

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**Abstract**—Dewar's arguments to the effect that all evidence for the existence of appreciable effects of $\pi$-electron resonance in the ground states of conjugated and hyperconjugated molecules is inconclusive, and that all observed effects are explainable as a result of differences in hybridization in carbon $\sigma$ bond orbitals, are examined. It is shown that the C—C bond-length shortenings predicted by up-to-date $\pi$-electron theory are not as great as usually supposed, and that the corresponding predicted *lengthenings* of C═C and C≡C bonds are almost *nil*. It is concluded that Dewar is partly right in supposing that the lengths of conjugated and hyperconjugated C—C single bonds are determined, to a greater extent than previously supposed, by the states of hybridization of the carbon $\sigma$ bond orbitals. However, there seems to be no justification for Dewar's assumption that resonance shortenings are negligible. Tentative formulas for the contributions of resonance and hybridization are given, also a similar formula for the shortening of conjugated or hyperconjugated C═C bonds in the cumulenes. Bond angles and hybridization are discussed, and the probable existence of marked deviations from ideal trigonal and digonal hybridization, often in opposite directions for C—H and C—C or C═C carbon $\sigma$ orbitals, is emphasized. These differences may help to explain why C—H bonds are shortened less than C—C bonds involving supposedly similar hybrids.

Rather general bond energy formulas are given which assume additivity of bond energies but with a different bond energy for each hybrid type of C—H or C—C (or C═C) bond. It is shown that these reduce to the usual simple formula which ignores differences in hybrid type under not unplausible assumptions which, however, are at fault in neglecting polar energies (i.e. ionic-covalent resonance energies), especially in CH bonds. Dewar's assumption that CH bond energies are essentially independent of hybridization, and his consequent conclusion that observed stabilization energies in conjugated systems are due entirely to strengthened hybrid C—C bonds and not at all to $\pi$-electron resonance energy, is difficult to justify, especially in view of the expected importance of polar energies in CH bonds. A table of predicted polar energies for C—H and C—C bonds involving various hybrid C—C $\sigma$ orbitals is given. The estimation of $\pi$-electron energy in $C_2H_4$, and of $\pi$-electron conjugation energy in butadiene, based on some energy data for 90° twisting, are discussed. Diphenyl and *s-cis* butadiene are compared.

The relative importance of $\pi$-electron resonance and hybridization in determining the dipole moments of conjugated and hyperconjugated molecules are discussed. While any conclusive theoretical calculation would in most cases be extremely complicated, there seems to be no good reason to doubt that $\pi$-electron resonance makes important contributions. Very strong evidence from nuclear magnetic resonance data is cited in support of usual current beliefs as to the role of $\pi$-electron resonance in charge distribution in conjugated and hyperconjugated molecules. Other evidence, including dipole moments in agreement with $\pi$-electron resonance theory predictions for molecules like fulvene and azulene where no differential hybridization effects should contribute, is cited.

## INTRODUCTION

DEWAR and Schmeising[1] have argued that the physical evidence usually cited in proof of $\pi$-electron delocalization as the cause of ordinary (sacrificial) conjugation and hyperconjugation in ground states of unsaturated molecules is inconclusive; and have gone further in an effort to show that the effects of $\pi$-electron resonance are

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* This work was assisted under a grant from the National Science Foundation.

[1] M. J. S. Dewar and A. N. Schmeising, Report at Conference on Hyperconjugation, Bloomington, Indiana, June, 1958. *Tetrahedron* 5, 166 (1959).

*negligible* in these systems, and much smaller than usually believed even in systems involving isovalent conjugation, such as benzene or the allyl radical. (Burawoy[2] has long advocated the idea that there is no such thing as $\pi$-electron resonance).

Dewar cites the following types of evidence as inconclusive, for the reasons given:

(1) *Bond lengths.* Although conjugated and hyperconjugated C—C bonds are shortened (from 1·54 Å in $C_2H_6$ to 1·501 ± 0·002 in acetaldehyde, 1·48 ± 0·01 Å in butadiene,[3] 1·46 Å in $CH_3—C{\equiv}CH$, 1·38 Å in diacetylene, etc.) much more than (*about* 8/3 *as much as*) one would expect from observed C—H bond lengths with carbon atoms in supposedly corresponding states of hybridization (C—H lengths about 1·09 Å, 1·085 Å, and 1·06 Å in $C_2H_6$, $C_2H_4$, and $C_2H_2$ respectively), this can be accounted for by assuming that the shortening of the carbon atom covalent radius for trigonal or digonal hybridization is greater in C—C than in C—H bonds, so that $\pi$-electron resonance is not needed to explain the extra shortenings. (Hitherto,[4] it had been assumed that the shortening of the covalent radius of carbon, attributed to increased *s* character in the carbon bond orbital, is *the same* in C—C as in C—H bonds, and that a corresponding *part* of the C—C bond shortening observed in conjugation and hyperconjugation is due to this decrease in carbon orbital covalent radius.) Moreover, the lengths of such C—C bonds for a given hybrid type are remarkably constant (e.g. in $H_3C—C{\equiv}CH$, $F_3C—C{\equiv}CH$, $Me_3C—C{\equiv}CH$, $H_3C—C{\equiv}N$, etc.) Also, the lengths of C=C and C≡C bonds seem to be unaffected by ordinary conjugation or hyperconjugation. Finally, the trigonal-trigonal C—C bond in octatetraene is 1·46 Å although there can presumably be no appreciable $\pi$-electron delocalization since adjacent C=C bonds are twisted by 80°. (Further, there is convincing spectroscopic evidence that alternation of single and double bonds persists in, for example, the higher conjugated polyenes, without change from the lengths occurring in butadiene.[6]) Dewar concludes that the C—C lengths are completely explained by changes in covalent radius of carbon due to hybridization, and finds that the covalent radius is a "linear function of *s* character," meaning that the shortening from "$sp^3$" to "$sp^2$" carbon is equal to that from "$sp^2$" to "$sp$" carbon and so on.

(2) *Bond energies.* Although extra stabilities of conjugated and hyperconjugated systems, disclosed by energy or the like formulas based on addivity, are currently attributed to $\pi$-electron resonance stabilization, they can instead be consistently explained by assuming suitable increased strengths for C—C bonds whose bond orbitals are hybrids having more *s* character than in $C_4H_6$. However, the possibility of such an explanation depends on assuming that C—C bonds are strengthened *more* than C—H bonds by increased *s* character in the carbon bond orbitals; in fact Dewar assumes that C—H bonds are strengthened not at all (or negligibly), in for example $C_2H_2$ and $C_2H_4$ as compared with $C_2H_6$; he justifies this in terms of the conclusion reached in (1) that the carbon covalent radius is decreased much more in C—C bonds than in C—H bonds by increased *s* character in the bond orbital.

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[2] A. Burawoy, *Chem. & Ind.* **51**, 434 (1944); *Trans. Faraday Soc.* **40**, 537 (1944); *V. Henri Memorial Volume.* Desoer, Liège (1948).

[3] O. Bastiansen, Private communication.

[4] L. Pauling, H. D. Springall and K. J. Palmer, *J. Amer. Chem. Soc.* **61**, 927 (1929); R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941); C. A. Coulson, *V. Henri Memorial Volume* p. 15. Desoer, Liège (1948).

[5] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).

[6] J. R. Platt, *J. Chem. Phys.* **25**, 80 (1956); H. Krauch, *J. Chem. Phys.* **28**, 898 (1958); and references cited in these articles.

(3) *Dipole moments.* The existence of dipole moments in such molecules as propylene, toluene, and methylacetylene, usually attributed to hyperconjugation, can be fully explained by the fact that the C—C single bonds in these molecules involve orbitals differing in hybrid character, hence in electronegativity.

(4) *Electronic spectra.* Electronic spectra showing red shifts on methyl (or alkyl) substitution next to a multiple bond prove nothing about $\pi$-electron hyperconjugative delocalization in the *ground* state, since an excited state is also involved. They are of course consistent with real $\pi$-delocalization effects in the excited state.

(5) *Reaction rates.* Differences in reaction rates prove nothing about ground states, since they are likely to be due to peculiarities of transition states or reaction intermediates.

In a preceding paper,[7] the writer has pointed out the need to distinguish between ordinary (sacrifical) and isovalent conjugation and hyperconjugation, and the fact that relatively large effects are associated with isovalent hyperconjugation. The present paper, prepared in preliminary form in August and in final form in November, 1958, includes a considerable amount of further study carried out after the Conference. In it, Dewar's views as summarized above are examined critically in relation to the present state of $\pi$-electron resonance theory, taking up the several types of evidence considered by Dewar. The examination discloses no adequate reasons for believing, and some for disbelieving, that $\pi$-electron resonance is of negligible importance in causing the observed phenomena in ordinary conjugation and hyperconjugation (isovalent conjugation and hyperconjugation are not considered here). Rather, it appears that $\pi$-electron resonance and other causes may be of comparable importance. Dewar's challenge has in any event made clear the importance of a careful re-examination of the theoretical basis of conjugation, hyperconjugation, and related phenomena.

## *Bond Lengths*

Basically, the factors governing the exact values of bond lengths are not well understood theoretically. There is no good theoretical basis for the idea of an accurately constant covalent bond radius for an atom even when it is using a particular definite bond orbital (or orbitals). A survey of actual bond lengths shows that the concept of definite bond radii is on the whole justified as an approximateion, but that even when allowances are made for ionic character or other reasonably assignable structural causes, many anomalies remain. Consider for example the following values of the covalent radius $r_c$ obtained for the H atom in various bonds AH when the covalent radius of the A atom is taken as half the length of the bond in A—A:

| From | $r_c$ (Å) |
|---|---|
| $H_2$ | 0·37 |
| CH in $CH_4$ | 0·32* |
| LiH | 0·26 |
| HI | 0·27 |
| HCl | 0·28 |
| HF | 0·20 |

* Using the C—C bond length for $C_2H_6$

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[7] R. S. Mulliken, Report at Conference on Hyperconjugation, Bloomington, Indiana, June, 1958. *Tetrahedron* **5,** 253 (1959)

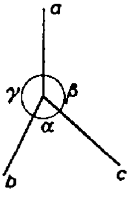
In view of the rather sketchy basis for the assumption that a given bond orbital should have a fixed "bond radius", Dewar's proposal that the bond radii of carbon for "trigonal" and "digonal" bond orbitals are considerably smaller in C—C than in C—H bonds cannot be considered very unreasonable.

*Hybridization and bond lengths*

A rather plausible alternative is the possibility that the actual state of hybridization is not the same for "trigonal" or "digonal" carbon in C—H as in C—C bonds. The observed bond lengths (those for C—C bonds should first be corrected for $\pi$-electron resonance, see below) might be consistently understood if in C—H and C—C bonds both deviate from true trigonal or digonal hybridization in the direction of tetrahedral hybridization, but with a *greater* deviation (less $s$ and more $p$ character) in the C—H bonds. The current widely accepted belief that carbon $\sigma$ orbitals are definitely either tetrahedral in $\gtrdot$C—, trigonal in $>$C=, or digonal in —C≡ or =C= situations, has little to recommend it beyond simplicity.

The belief in trigonal orbitals in $>$C= situations is based on the fact that observed bond angles around the C atom are near 120°. For 120° angles, *assuming* (1) that the carbon $\sigma$ orbitals extend out in the directions of the bonds and (2) that the overall valence structure is $sp^3$, and noting that the $\pi$ bond is formed by a pure $p$ orbital, one concludes that the carbon orbitals of the three $\sigma$ bonds are equivalent; and if so, they are necessarily trigonal hybrids. However, actual bond angles often deviate appreciably from 120°.

For the case of a planar molecule with bond angles $\alpha$, $\beta$, $\gamma$, Coulson[4] gives the following equations for the "hybridization ratio" $\lambda$ in a hybrid orbital of the form $s + \lambda p\sigma$:



$$\lambda_a = [-\cos\alpha/\cos\beta\cos\gamma]^{\frac{1}{2}}, \qquad \lambda_b = [-\cos\beta/\cos\alpha\cos\gamma]^{\frac{1}{2}},$$

$$\lambda_c = [-\cos\gamma/\cos\alpha\cos\beta] \tag{1}$$

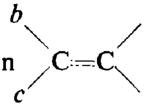
where $a$, $b$, $c$ refer to the carbon bond orbitals pointing in the directions indicated by the figure. According to recent careful determinations for ethylene, $\alpha$ is 117·37° ± 1°, $R$ C=C = C is 1·337 ± 0·003 Å, and $R_{\mathrm{CH}}$ is 1·086 ± 0·003 Å (Allen and Plyler[8]), or $\alpha = 116° \pm 1°$, $R_{\mathrm{CC}} = 1{\cdot}334 \pm 0{\cdot}003$ Å, $R_{\mathrm{CH}} = 1{\cdot}085 \pm 0{\cdot}005$ Å (Bartell and Bonham[9]). Taking $\alpha = 117°$, $\beta = \gamma = 121{\cdot}5°$, one obtains $\lambda_{\mathrm{CC}} = 1{\cdot}29$ and $\lambda_{\mathrm{CH}} = 1{\cdot}48$, as compared with 1·00, $\sqrt{2}$, and $\sqrt{3}$ for digonal, trigonal, and tetrahedral

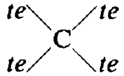
[8] H. C. Allen, Jr. and E. K. Plyler, *J. Amer. Chem. Soc.* **80**, 2673 (1958). Infrared spectrum.

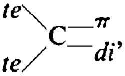
[9] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **27**, 1414 (1957). Electron diffraction.

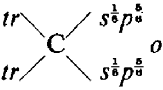
hybrids. This indicates that the C—H bond is intermediate between trigonal and tetrahedral, although nearer the former, and the C=C $\sigma$ bond between trigonal and digonal, although nearer the former.

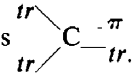
In ethylene *derivatives*, the literature indicates (although one should probably await verification with the best modern techniques before reaching final conclusions) that smaller values of $\alpha$ than 120°, and larger values of $\beta$ and $\gamma$, are the rule rather than the exception. For example, Pauling and Brockway[10] by electron diffraction obtained $\alpha = 110{\cdot}5 \pm 2°$ (hence $\beta = \gamma = 124°$) in tetramethylethylene. Equation (1) then gives $\lambda = 1{\cdot}08$ (close to digonal) for the C=C bond, and $\lambda = 1{\cdot}65$ (close to tetrahedral) for the C—C bonds.

These deviations from trigonal bond angles would correspond to a tendency of the carbon atom to have always four equivalent *te* (tetrahedral) bond orbitals. If this tendency were completely realized, the left-hand carbon in 

would use two equivalent *te* orbitals in the molecule plane for the bonds to *b* and *c* (angle *b*C*c* 109°28′) and two others perpendicular to the plane to form the double bond. This is the old original bent-bond model which uses two equivalent *te* orbitals from each atom to form the double bond. A single electron in a *te* orbital may conveniently be called an $s^{\frac{1}{4}}\, p^{\frac{3}{4}}$ electron, and two such electrons embody a population distribution $s^{\frac{1}{2}}p^{\frac{3}{2}}$. Quantum-mechanically an $s^{\frac{1}{2}}p^{\frac{3}{2}}$ bent-bond C= structure is completely equivalent to a $\sigma$, $\pi$ structure, provided (since the $\pi$ electron contributes 1·00 to the $p$ population) the $\sigma$ orbital is digonal ($s^{\frac{1}{2}}p^{\frac{1}{2}}$), and thus non-equivalent to the $s^{\frac{1}{4}}p^{\frac{3}{4}}$ $\sigma$ orbitals of the *b* and *c* bonds. The actual C= structures in ethylene and its derivatives apparently are compromises between the structure just discussed and the 120°-angle structure with three equivalent $\sigma$ orbitals. Using the symbols *tr* and *di* to represent $s^{\frac{1}{3}}p^{\frac{2}{3}}$ and $s^{\frac{1}{2}}p^{\frac{1}{2}}$ orbitals of $\sigma$ type, one may describe the first structure either as 

*or* as 

, and the second in a similar way as 

*or* as 

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The application of equation (1) to some recent microwave results[11] on the structure of $CH_3CHO$ is of interest. Identifying the angles HCC, CCO, and HCO of the HCO group with $\alpha$, $\beta$, $\gamma$ respectively, one finds $\lambda_{C=O} = 1{\cdot}315$, $\lambda_{CH} = 1{\cdot}59$, and $\lambda_{CC} = 1{\cdot}36$, as compared with $\lambda_{C=C} = 1{\cdot}29$ and $\lambda_{CH} = 1{\cdot}48$ for $C_2H_4$ (see above) and $\lambda = 1{\cdot}414$ for pure *tr* and 1·732 for pure *te*. The difference between the C—H and C—C bonds here is striking: the $\sigma$ bond orbital in CH seems to be nearer to *te* than to *tr*, while that in C—C has even a little more *s* character than *tr*.

In linear molecules of structures *a*—C≡*b*, bond angles can give no guidance (although perhaps force constants could). Equation (1) is here replaced by

$$\lambda_a \lambda_b = 1. \tag{2}$$

If the $\sigma$ bonds C—*a* and C—*b* are equivalent, then both are digonal ($\alpha = 1$). The

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[10] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.* **59**, 1223 (1937).

[11] R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *J. Chem. Phys.* **26**, 1695 (1957).

structure is $di{-}\underset{-\pi}{\overset{-\pi}{\mathrm{C}}}{-}di$, equivalent to $di{-}\mathrm{C}\left\langle\begin{matrix} s^{\frac{1}{6}}p^{\frac{5}{6}} \\ s^{\frac{1}{6}}p^{\frac{5}{6}} \\ s^{\frac{1}{6}}p^{\frac{5}{6}} \end{matrix}\right.$. On the other hand, the bent-bond model using tetrahedral orbitals $te{-}\mathrm{C}\left\langle\begin{matrix} te \\ te \\ te \end{matrix}\right.$ is equivalent to $te{-}\underset{-\pi}{\overset{-\pi}{\mathrm{C}}}{-}s^{\frac{3}{4}}p^{\frac{1}{4}}$, the $\sigma$ orbital of the C≡ bond having even more $s$ character than *di*. Although variations in bond angles are not available as a guide here, it seems likely that the hybrids in actual molecules lie between those of the two cases discussed.

We may ask *why* carbon atom $\sigma$ orbitals forming C—H and C—C single bonds in unsaturated systems should depart to different extents from the trigonal or digonal ideal. Such differences could perhaps occur because of the different electronegativities of H 1*s* and C 2*s* and 2*p* orbitals, or because of failure of the two assumptions made at the outset of the foregoing discussion. Assumption (1) is essentially that single bonds are never bent bonds, with the obvious exception of cyclic systems, of which *cyclo*propane is a notable example. But if strongly bent bonds are tolerated in *cyclo*propane and in double and triple bonds when the description in terms of equivalent bond orbitals is used, it is not clear why they cannot occur also in ordinary single bonds. For example, in ethylene the principle of maximum overlap of bond orbitals would, it is true, cause the H atoms to be located on the symmetry axes of the appropriate hybrid carbon $\sigma$ orbitals, but nonbonded repulsions between H atoms might displace them from these locations, and there seems to be no reason why the hybridizations should change to accommodate fully to these changed locations. With regard to assumption (2), we know that actual carbon valence atom states are partially $s^2p^2$ (and $p^4$), not all $sp^3$, and there is also a little $s^2p^3$, $p^5$, and $sp^4$ due to polarity of CH bonds.[12] It seems entirely possible that failure of the two assumptions just discussed may be responsible for quite appreciable effects, which also may differ for C—H and C—C bonds and lead to differences in carbon orbital hybrid character and bond lengths in the two cases.

While the preceding discussion has led to little in the way of positive conclusions, it underlines the dangers of oversimplified explanations which do not consider all factors. A really full and clear understanding of bond lengths will probably not be available until accurate wave functions have been obtained by extensive quantum-mechanical calculations.

However, it does seem possible to reach some fairly definite conclusions about the effect of $\pi$-electron resonance on bond lengths. Fortunately, the particular hybrid character of accompanying $\sigma$ bonds does not enter into the theory of $\pi$-electron resonance, except only in so far as it affects the "natural" lengths of $\sigma$ bonds: shorter $\sigma$ bonds result in somewhat stronger $\pi$-electron resonance.

### *Effects of $\pi$-electron resonance on bond lengths*

Dewar's account of C—C bond lengths, as summarized in the Introduction, has the advantages (and the dangers) of simplicity, but he apparently also feels that the empirically observed *constancies* of C—C, and of C=C and C≡C, bond lengths within specific types of conjugated and hyperconjugated compounds contradict what one would expect from $\pi$-electron resonance theory. A careful examination of the

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[12] H. H. Voge, *J. Chem. Phys.* **4,** 581 (1936); **16,** 984 (1948); M. Kotani and K. Siga, *Proc. Phys. Math. Soc. Japan* **19,** 471 (1937).

theory in its present state fails to support this view. If the predicted effects of $\pi$-electron resonance were as large as in the early calculations of the simple Hückel theory, the observed constancies *would* be very difficult to understand, but on the basis of calculations by the LCAO-SCF, Pariser–Parr, Pople and similar methods, they are entirely consistent with $\pi$-electron theory, as will be shown below. The observed constancies remain surprising only in view of the unreliability *in general* of predictions from fixed covalent radii; one would not have been surprised at considerable departures from constancy as a result of *other* causes than $\pi$-electron resonance.

Let us first consider *conjugated* C—C bonds. As a result of numerous computations on 1:3-butadiene, one can arrive at rather definite conclusions. In a single-determinant wave function, the two occupied $\pi$ MOs of butadiene have the forms:

$$\phi_1 = a_1\chi_a + b_1\chi_b + b_1\chi_c + a_1\chi_d; \quad \phi_2 = a_2\chi_a + b_2\chi_b - b_2\chi_c - a_2\chi_d, \tag{3}$$

where *a, b, c, d* refer to the four carbon atoms. Table 1 contains the results obtained for these coefficients by various authors, and also the corresponding Coulson LCAO bond orders. The first three computations listed were by the semiempirical Hückel method, neglecting overlap; they differ through varying assumptions about how the resonance integral $\beta$ varies with carbon–carbon distance $R$. Hückel assumed it constant, Lennard-Jones, and Mulliken *et al.* used empirical evidence to determine a functional relation $\beta(R)$. Parr and Mulliken[13] made an LCAO–SCF Slater–AO $\pi$-electron computation assuming a Goeppert–Mayer–Sklar type of $\sigma$-electron-core field. In Table 1, their coefficients (which take account of overlap) have been renormalized (as have those of Berry) in such a way that $2(a_i^2 + b_i^2) = 1$ ($i = 1$ or 2), since this is necessary in order to obtain Coulson bond orders (Table 1, footnote*). Later computations (Pople, Kon, Moser, Berry AIM, (atoms-in-molecules)) by the Pariser–Parr and similar methods (all formally neglect overlap), designed to correct by semiempirical procedures for the faults of the LCAO–SCF method, give

TABLE 1. LCAO–MO COEFFICIENTS AND BOND ORDERS BASED ON COMPUTATIONS BY VARIOUS AUTHORS (COEFFICIENTS NORMALIZED CORRESPONDING TO ZERO OVERLAP)

| Author | Coefficients | | | | Bond orders* | | $R$ Values assumed |
|---|---|---|---|---|---|---|---|
| | $a_1$ | $b_1$ | $a_2$ | $b_2$ | *ab* or *cd* | *bc* | |
| Hückel | 0·372 | 0·601 | 0·601 | 0·372 | 0·894 | 0·447 | equal |
| Lennard-Jones | 0·401 | 0·582 | 0·582 | 0·401 | 0·934 | 0·356 | 1·44, 1·35 |
| Mulliken, Rieke and Brown[a] | 0·411 | 0·576 | 0·576 | 0·411 | 0·945 | 0·325 | 1·46, 1·35 |
| Pople[b] | 0·4246 | 0·5655 | 0·5655 | 0·4246 | 0·960 | 0·279 | |
| Parr and Mulliken[c] | 0·426 | 0·564 | 0·543 | 0·452 | 0·972 | 0·227 | 1·46, 1·35 |
| Kon[d] | | | | | 0·974 | 0·227 | |
| Moser[e] | 0·426 | 0·564 | 0·536 | 0·461 | 0·975 | 0·211 | 1·46, 1·35 |
| Berry LCAO-SCF[f] | 0·410 | 0·576 | 0·541 | 0·455 | 0·965 | 0·251 | 1·46, 1·35 |
| Berry AIM[f] | 0·466 | 0·534 | 0·561 | 0·429 | 0·978 | 0·202 | 1·46, 1·35 |

* $2(a_1b_1 + a_2b_2)$ for bond *ab* or *cd*; $2(b_1^2 - b_2^2)$ for bond *bc*.

[a] Ref. 4. [b] J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953). [c] Ref. 13. [d] H. Kon, *Bull. Chem. Soc. Japan* **28**, 275 (1955). [e] C. M. Moser, *J. Chem. Soc.* 3455 (1954). [f] Ref. 14.

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[13] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.* **18**, 1338 (1950).

coefficients, and in particular bond orders, which agree well with those of Parr and Mulliken. Since all these methods take account specifically of electronic interactions, it would seem that one can place considerable reliance on the resulting bond orders as substantially correct; Moser's result of 0·975 for the C=C bonds and 0·21 for the C—C bond may be taken as representative.

Further refinements in the theory might of course alter one's opinion somewhat. Dewar has suggested that more accurate allowance for interelectronic repulsions and for correlation energy (as shown e.g. by configuration interaction) than in the Parr and Mulliken calculation might reduce the C—C bond order to nearly zero. However, the results of the various subsequent calculations listed in Table 1, indicate that these effects are of minor importance. In fact, a recent as yet unpublished analysis by Berry of wave functions he had previously obtained[14] shows that configuration interaction actually increases the amount of double bond character in the central bond in butadiene, as compared with a single-determinant wave function.

Given the Coulson bond orders, one can use a standard bond-order bond-length curve to estimate the effects of $\pi$-electron resonance on bond lengths. (More properly, one should use a somewhat shifted curve (cf. e.g. Coulson[4]) for each state of hybridization; but since these curves are probably nearly parallel, this makes no real difference for present purposes.) For the C—C bond lengths, one obtains a predicted shortening of 0·04 Å using the C—C end of the curve (based on $C_2H_6$), or perhaps 0·035 Å in view of the evidence that the "natural length" of the *tr-tr* C—C bond is somewhat shorter than for a *te-te* C—C bond. (Here and from this point on, the symbols *te*, *tr*, and *di* should be taken as merely conventional, subject to all the qualifications and uncertainties outlined in the paragraphs above on "Hybridization and Bond Lengths.") With correct values of the actual C—C and C=C bond lengths in butadiene ($1{\cdot}483 \pm < 0{\cdot}01$ and $1{\cdot}337 \pm 0{\cdot}0005$ Å)[3] instead of those assumed in the calculations summarized in Table 1, the calculated C—C $\pi$ bond order would be a little smaller, and the predicted $\pi$ delocalization shortening reduced perhaps to 0·03 Å. The "natural length" of a *tr-tr* C—C bond then comes out to be 1·51 ± 0·01 Å.

In the absence of any Pariser–Parr or LCAO–SCF calculations for diacetylene, one can only estimate roughly, by assuming a parallelism to Table 1, how the earlier results (Hückel, Mulliken–Rieke–Brown) would be modified in such a calculation. The so estimated $\pi$ bond orders are, 0·43 for the C—C bonds and 1·947 for the C≡C bonds. Using the bond-order bond-length curve, the predicted $\pi$-delocalization shortening for the C—C bond is then about 0·07 Å. With an *observed* length of 1·38 Å, one obtains a "natural length" for a *di-di* C—C bond of about 1·45 Å, as compared with about 1·51 Å for a *tr-tr* and 1·54 Å for a *te-te* C—C bond.*

In a similar way for *hyperconjugation*, the following rough estimates can be made. For the C—C bond in propylene, $\pi$ bond order 0·066, predicted shortening 0·01 Å; for the C—C bond in methylacetylene, $\pi$ bond order 0·154, shortening 0·025 Å. Using observed bond lengths, one then obtains 1·51 and 1·485 Å for the "natural lengths" of the respectively *te-tr* and *te-di* C—C bonds in these molecules.

The foregoing estimates of $\pi$-electron resonance shortening in ordinary conjugation and hyperconjugation suggest that observed shortenings should be expressible

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* Incidentally, the shortenings thus obtained from *te-te* to *tr-tr* and *di-di* agree very closely with values computed theoretically by Coulson[4] by considering the charge centroids of *te*, *tr*, and *di* hybrid $\sigma$ AO's.

[14] R. S. Berry, *J. Chem. Phys.* **26** 1660 (1957).

as a sum of resonance and hybridization shortenings of comparable magnitude. Table 2 shows that formulas based on this idea give good agreement with observed shortenings, especially when allowance is made for the fact that molecules having the same bond pattern do *not* always show the same shortening within experimental error. The coefficients in the formulas used in Table 2 attribute roughly 40 per cent of observed shortenings to $\pi$-electron resonance, 60 per cent to hybridization. The observed shortenings in Table 2 A are respectively somewhat higher or lower than the calculated for the hyperconjugated type *te-tr* and the conjugated type *tr-tr*. However, the observed values in each case are based on a single molecule. In the hyperconjugated case, the bond angles for $CH_3HCO$ indicate *more* than *tr s* character in the "*tr*" orbital (see discussion in an earlier paragraph), which perhaps explains the large observed $\Delta R$. (Already earlier,[15] Mulliken suggested 0·03 Å hybridization shortening in butadiene.)

TABLE 2. SHORTENINGS (Å.U.) OF CONJUGATED BONDS

| Bond patterns | Calculated $-\Delta R$(Å.U.)[a] | | | | | Observed[b,c] | |
|---|---|---|---|---|---|---|---|
| | $an_{tr}$ | $bn_{di}$ | $cN_{CJ}$ | $dN_{HCJ}$ | Total | $-\Delta R$ | Molecules |
| A. C—C *Bonds* | | | | | | | |
| $H_3C$—CH= (*te-tr*) | 0·02 | | | 0·015 | 0·035 | 0·043 ± 0·002 | $H_3CCHO$ only |
| $H_3C$—C≡ (*te-di*) | | 0·05 | | 0·03 | 0·08 | 0·084 | $CH_3CN$, $CH_3C$≡CH |
| —HC—CH= (*tr-tr*) | 0·04 | | 0·035 | | 0·075 | 0·061 ± <0·01 | Butadiene |
| =HC—C≡ (*tr-di*) | 0·02 | 0·05 | 0·035 | | 0·105 | 0·098 ± 0·001 | O=CH—C≡CH |
| | | | | | | 0·119 ± 0·001 | $H_2C$=CH—C≡N |
| ≡C—C≡ (*di-di*) | | 0·10 | 0·07 | | 0·17 | 0·166 ± 0·001 | N≡C—C≡CH,<br>etc. |
| B. C=C *Bonds* | | | | | | | |
| $H_2C$=C= (*tr-di*) | | 0·018 | | 0·01 | 0·03 | 0·027 ± 0·001 | Allene |
| =C=C= (*di-di*) | | 0·035 | 0·025 | | 0·06 | 0·058 | $C_3O_2$ |

[a] For case A(C—C bonds), from $-\Delta R = 0{\cdot}02n_{tr} - 0{\cdot}05n_{di} + 0{\cdot}035N_{CJ} + 0{\cdot}015N_{HCJ}$, where $n_{tr}$ and $n_{di}$ are the numbers of "trigonal" or "digonal" atoms, and $N_{CJ}$ and $N_{HCJ}$ are the numbers of dimensions of conjugation or first-order hyperconjugation. For case B(C=C bonds), from $-\Delta R = 0{\cdot}018n_{di} + 0{\cdot}025N_{CJ} + 0{\cdot}01\,N_{HCJ}$.

[b] For C—C bonds, relative to 1·544 Å assumed for $R_{CC}$ in $C_2H_6$. For C=C bonds, relative to 1·337 Å for $R_{CC}$ in $C_2H_4$ (cf. ref. 8).

[c] From selected $R_0$ values believed by B. Stoicheff to be good to ±0·005 Å.U. or better. Butadiene and $C_3O_2$ from unpublished $R_0$ values by O. Bastiansen.

Part B of Table 2 deals with the fact that conjugative (for internal) and hyperconjugative (for $=CH_2$ terminal) shortenings of cumulated C=C bonds are expected and observed. Both resonance and hybridization shortenings might reasonably be expected to be smaller than for C—C bonds, because the $\sigma$ bond in a C=C bond is already under compression by the $\pi$ bond. A plausible formula in line with this expectation reproduces observed shortenings.

It appears likely that observed conjugation and hyperconjugation shortenings, even after all have been brought to the highest possible accuracy, will not in themselves provide definitive evidence as to the relative importance of resonance and

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[15] R. S. Mulliken, *J. Chem. Phys.* **23**, 2343 (1955); **23**, 1841 (1955).

hybridization. We will probably have to be guided by theory. But in any event there seems to be no inconsistency between observed shortenings and present predictions of theory. However, LCAO–SCF calculations on $\pi$ bond orders will be desirable in the several cases, other than =C—C= in butadiene, where they have not yet been made.

Although the symbols *te*, *tr*, and *di* in Table 2 refer ostensibly to tetrahedral, trigonal, and digonal hybrids, it is well to keep constantly in mind that the actual hybrids involved may be rather different.

Turning now from the inner or acceptor bonds to the outer or donor bonds in conjugation and hyperconjugation, the usual $\pi$-electron theory predicts that if the former are shortened by resonance, the latter should be somewhat lengthened. For the case of butadiene, one may refer to the *ab* bond orders in Table 2, and then use the bond-order bond-length curve to find the predicted lengthening of the C=C bonds. With the Mulliken–Parr or Moser bond order, the predicted lengthening is only 0·004 Å, as contrasted with 0·02 Å if one had used the bond order from the Hückel calculation. Similarly, the C≡C bond order 1·947 estimated above for diacetylene corresponds to a predicted lengthening of only 0·006 Å from the C≡C length in acetylene. Thus the presently predicted bond order changes for *multiple* bonds in conjugation (all the more so in hyperconjugation) are comparable with experimental error, in contrast to the Hückel predictions which were large enough to furnish Burawoy[2] with what seemed a serious objection to $\pi$-electron resonance theory.

But even the small predicted increases just indicated for the lengths of *multiple* bonds should in fact be reduced (or possibly even changed to small decreases) in a more accurate $\pi$-electron theory treatment. Very briefly, the argument runs as follows.* In a conjugated molecule such as butadiene, if there were no $\pi$-electron resonance, the juxtaposition of two double bonds would introduce according to VB theory a nonbonded repulsion between the adjacent $\pi$ electrons at opposite ends of the single bond. As compared with an isolated double bond as in ethylene, this would increase the $\pi$-electron density within each double bond somewhat, and so strengthen and no doubt shorten it correspondingly. Although no VB calculations are available, LCAO–MO calculations show that in the assumed absence of $\pi$-electron resonance, the "overlap populations" in the C=C bonds in butadiene are distinctly greater than those in ethylene.[15] This result appears to confirm the statement just made in terms of VB theory. However, $\pi$-electron resonance tends to reverse this shortening effect on the C=C bonds by transferring some $\pi$-electron density into the C—C bond, and the net result of both effects may well be either a slight shortening or a slight lengthening, or almost no change, of the C=C bond length as compared with ethylene. Similar considerations apply for the lengths of conjugated triple bonds as compared with the C≡C bond in acetylene.

In all of the preceding discussion, nothing has been said about $\sigma$-electron delocalization effects. These of course must have had some effect on the "natural" lengths of all C—C bonds, but this point need not seriously concern us if we are interested primarily in $\pi$-electron delocalization (resonance) effects. Also, there is no obvious reason why $\sigma$-delocalization effects should be much different for different kinds of C—C bonds.

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* A full explanation of the small but interesting effect in question would be rather lengthy, and will be reserved for a separate paper.

More relevant is the fact that second-order $\pi_x$ and/or $\pi_y$ hyperconjugative resonance should be universally present for C—C bonds whenever corresponding conjugative or first-order hyperconjugative resonance is absent. This must be kept in mind in connection with "natural lengths" of C—C bonds discussed above following Table 1. To be consistent, the true natural length of *te-te* C—C bonds, as in $C_2H_6$, must be considered slightly greater than the actual C—C bond length in $C_2H_6$. However, the $\pi$ bond orders due to second-order hyperconjugative delocalization are small according to the more recent computations.

## CONCLUSIONS

The foregoing review of $\pi$-electron theory predictions indicates that Dewar is partly right in supposing that, to a greater extent than previously supposed, the lengths of conjugated and hyperconjugated C—C bonds are determined by the states of hybridization of the carbon bond orbitals rather than by $\pi$-electron resonance. However, there seems to be no justification for Dewar's assumption that the $\pi$-delocalization shortenings in conjugation and hyperconjugation are negligible. The observed approximate constancy of C—C bond lengths for carbon atoms with orbitals in particular states of hybridization is not inconsistent with $\pi$-electron delocalization predictions, except apparently in the case of *cyclo*octatetraene. (However, twisting of two adjacent double bonds so that their planes become perpendicular (as is approximately true in *cyclo*octatetraene), although it destroys conjugation, creates first-order hyperconjugation at *both* ends of the C—C bond: each —C= after twisting functions, like a —$CH_3$ group in propylene, to give hyperconjugation across the C—C bond with the C=C $\pi$ electrons of the other =CH— group. Thus some resonance shortening is still expected.*) But in any event the observed C—C bond lengths in *cyclo*octatetraene (1·46 Å as compared with 1·48 Å for butadiene) are anomalous even in terms of Dewar's proposals.

The observed constancy of C—C bond lengths in such hyperconjugated systems as $Me_3C—C{\equiv}CH$, $Cl_3C—C{\equiv}CH$, $H_3C—C{\equiv}CH$, $F_3C—C{\equiv}N$, $H_3C—C{\equiv}N$ is not inconsistent with reasonable expectations from $\pi$-electron theory which, contrary to the ideas of Baker and Nathan, would not suggest radically diverse degrees of hyperconjugative delocalization for $CH_3$, $CMe_3$, $CCl_3$, etc. Finally, the observed constancy of C=C and C≡C bond lengths in conjugated systems and their close agreement with the lengths in $C_2H_4$ and $C_2H_2$ are precisely what would be expected from a correct application of $\pi$-electron theory.

### *Bond Energies*

### *Significance of bond energy formulas*

Central to any consideration of "empirical resonance energies" is a standard formula for heats of formation, or atomization energies, or heats of combustion.[17] For atomization energies, taking energy given out as positive, such a formula for any hydrocarbon may be written as follows:

$$B = HN_{CH} + SN_{C-C} + DN_{C=C} + TN_{C\equiv C} + \Delta \qquad (4)$$

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* On the other hand, data cited[16] indicate a progressive lengthening of the C—C bond in substituted diphenyls with progressive increase in twist angle caused by steric repulsion of *o*-substituents. However, perhaps the lengthening here is a by-product of the steric repulsion.

[16] D. Cook, *J. Chem. Phys.* **28**, 1001 (1958).

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

The "bond energies" $H$ and $S$ are first chosen so as to fit with $\Delta \approx 0$ the experimental $B$ for diamond and for two or three light unbranched paraffins, say propane, $n$-butane, and $n$-pentane.* $D$ and $T$ are then determined as follows:

$$D \equiv B(\mathrm{C_2H_4}) - 4H; \quad T \equiv B(\mathrm{C_2H_2}) - 2H \tag{5}$$

$H$, $S$, $D$, and $T$ chosen in the manner just specified are now assumed to be constant for all hydrocarbons. After deducting any systematic deviations which are believed assignable to causes other than $\pi$-electron resonance (e.g. branching in paraffins, or steric effects; obviously this is a matter of judgment), the remainder of $\Delta$ is commonly interpreted as due to stabilization by $\pi$-electron resonance ("vertical delocalization energy" minus the "compression energy" required to change $\sigma$ bond lengths from their "natural" values to observed values).

Equations (4) and (5) seem to imply that all C—H bonds have the same strength $H$ and all C—C bonds the same strength $S$. Actually, as many people who have worked with equation (4) have doubtless realized, no such implication is necessarily involved.

To see this, let us first generalize equation (4) by assuming different values of $H$ and $S$ depending on the states of hybridization believed to exist in the carbon $\sigma$ orbitals involved. If $H_1$, $H_2$, and $H_3$ refer to "*te*", "*tr*", and "*di*" C—H bonds, and $S_{11}$, $S_{12}$, $S_{13}$, $S_{22}$, $S_{23}$, and $S_{33}$ to *te-te*, *te-tr*, *te-di*, *tr-tr*, *tr-di*, and *di-di* C—C bonds, we have (letting $i$ and $j$ take on values 1, 2 and 3):

$$B = \sum_{i} H_i \mathrm{N}_i\,(\mathrm{CH}) + \sum_{i,j} S_{ij}\mathrm{N}_{ij}(\mathrm{C{-}C}) + D_{22}\mathrm{N}(\mathrm{C{=}C}) + T_{33}\mathrm{N}(\mathrm{C{\equiv}C}) + \Lambda \tag{6}$$

The various coefficients $H_1$, $H_2$, $H_3$, $S_{11}$, and so on, are now assumed to be constants valid for all hydrocarbons. (For cumulenes, $D_{22}\mathrm{N}(\mathrm{C{=}C})$ should be replaced by $\sum_{i,j} D_{ij}\mathrm{N}_{ij}(\mathrm{C{=}C})$, with $i, j$ having values 2, 3 only). $\Lambda$ of equation (6) plays the same role as $\Delta$ of equation (4), but need not be equal to $\Delta$; since equation (6) should have greater validity than equation (4), $\Lambda$ should be a better measure of $\pi$-electron resonance energy than $\Delta$, if they differ. $H_1$ and $S_{11}$ of equation (6) are identical with $H$ and $S$ of equation (4), and $D_{22}$ and $T_{33}$ are related to $D$, $T$, and $H$ of equations (4) and (5) by

$$\begin{aligned} D_{22} &\equiv B(\mathrm{C_2H_4}) - 4H_2 = D - 4(H_2 - H); \\ T_{33} &\equiv B(\mathrm{C_2H_2}) - 2H_3 = T - 2(H_3 - H). \end{aligned} \tag{7}$$

Without necessarily assuming that the $H$'s and $S$'s are independent of hybridization, equations (6), (7), reduce to equation (4) under certain not unplausible assumptions. This can be more readily understood by considering two specific examples, 1:3-butadiene and propylene. For these, using equations (6) and (7), we have:

$$\left.\begin{aligned} B(\mathrm{C_4H_6}) &= 6H_2 + S_{22} + 2D_{22} + \Delta \\ &= 6H + S + 2D + \{[(S_{22} - S) - 2(H_2 - H)] + \Lambda\} \\ B(\mathrm{C_3H_6}) &= 3H + 3H_2 + S_{12} + D_{22} + \Delta \\ &= 6H + S + D + \{[S_{12} - S) - (H_2 - H)] + \Lambda\} \end{aligned}\right\} \tag{8}$$

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* Actually, absolute $B$ values are still not accurately known, but this uncertainty involves only an additive constant and does not matter here. However, corrections to eliminate thermal and zero-point energy should be, but usually are not, made.

Note that the quantities in curly brackets in equations (8) correspond to Δ of equation (4).

*If it it assumed* that the quantities in *square* brackets in equations (8), and similar quantities in other cases, are equal to zero, then equation (4) always holds for hydrocarbons (other than cumulenes), with Δ equal to Λ of equation (6). This assumption would be correct if (a), hybrid orbitals of each kind (*te*, *tr*, or *di*) are the same in C—H and C—C bonds, and (b), C—H and C—C bond strengths are equally altered for any given change in hybridization of any one carbon bond orbital. (For a C—C bond, two carbon bond orbitals are of course involved). Those who have used equation (4) to determine "resonance energies" Δ have had, knowingly or not, the justification that this apparently oversimplified equation is equivalent to the much more acceptable equation (6) coupled with the at first sight not unplausible assumption just discussed (but see next section).

Dewar, on the other hand, arguing from the fact that carbon covalent radii seem to be shortened much more in conjugated C—C bonds than in C—H bonds involving supposedly the same hybrid carbon bond orbitals, assumes that the *bond energy* differences for C—C bonds also are much greater, and in fact to such an extent that he assumes $H_3 - H_1 = H_2 - H_1 = 0$. This, combined with the assumption that the π-electron resonance energy is negligible, i.e. $\Lambda = 0$ in equations (6) and (8), permits him (cf. equations 8) to identify the deviations Δ from equation (4) with C—C bond energy changes such as $S_{22} - S_{11}$ for butadiene or $S_{12} - S_{11}$ for propylene. He believes that these and certain other assumptions are justified by the self-consistency of the results obtained.

Until Dewar's paper is published, it is not possible to pass judgment on the strength of these arguments of self-consistency. A priori, however, Dewar's assumptions certainly appear to be at least as arbitrary as those involved in the supposition that Δ of equation (4) (after correction for steric effects, etc.) represents exclusively π-electron resonance energy. In proposing that the quantities Δ shall be called "stabilization energies", rather than resonance energies, Dewar is certainly right in principle. But there seem to be no sufficient reasons to deny that π-electron delocalization may make an important contribution to observed Δ's in conjugated and hyperconjugated systems.

### *Expected polar contributions to bond energies*

In fact, reasons can be given for believing that π-electron delocalization energies Λ may often be *larger* than observed Δ's, rather than smaller. Namely, as will be shown below, one might reasonably expect considerable *negative* contributions to Δ to be present corresponding to the *polar excess bond energies* (Pauling's Δ quantities as used in the empirical basis of his electronegativity scale) of $C^{di}$—H and $C^{tr}$—H as compared with $C^{te}$—H bonds. For example, in equations (8), the greater polarity of *tr*—H as compared with *te*—H should result in a net polar contribution increasing $H_2 - H_1$ (partially compensated in propylene by a polar contribution from $S_{12} - S$). This increase tends to make Δ smaller than Λ. Similar but *larger* effects are expected for conjugation or hyperconjugation involving triple bonds.

Even on quite general grounds, it seems unsafe to argue that because C—H bond *lengths* show relatively small changes with state of hybridization of the carbon orbital, one must expect C—H bond *energies* to be equally insensitive to hybridization. Such a parallelism would seem possible, but not particularly probable.

One positive reason *against* it lies in the existence of familar examples where bond energy increases markedly with increasing polarity, without notable corresponding effects on bond lengths. Thus, $R_{\mathrm{HI}} = 1/2(R_{\mathrm{HH}} + R_{\mathrm{II}}) - 0{\cdot}10$ Å and $B_{\mathrm{HI}} = \frac{1}{2}(B_{\mathrm{HH}} + B_{\mathrm{II}}) + 2$ kcal, while $R_{\mathrm{HCl}} = \frac{1}{2}(R_{\mathrm{HH}} + R_{\mathrm{ClCl}}) - 0{\cdot}09$ Å and $B_{\mathrm{HCl}} = \frac{1}{2}(B_{\mathrm{HH}} + B_{\mathrm{ClCl}}) + 22$ kcal. Because of its greater polarity perhaps even more than because of its greater *s* character, one might expect $H_2$ to exceed $H_1$. On the other hand, if the *s* character of the carbon bond orbital in $C^{tr}$—H is less than in $C^{tr}$—$C^{tr}$, as seems likely on the basis of the discussion earlier in this paper, the magnitude of $H_2 - H_1$ would be less for both reasons; also it may well vary from case to case. Still, there seems to be no reason why it should be negligible.

Equations (8) are special cases of the following general equation which can be obtained by systematically substituting equations (7) into equation (6):

$$\begin{aligned} B = {} & H\mathrm{N(CH)} + S\mathrm{N(C{-}C)} + D\mathrm{N(C{=}C)} + T\mathrm{N(C{\equiv}C)} \\ & + \sum_{i \neq 1} (H_i - H)\mathrm{N}_i(\mathrm{C{-}H}) + \sum_{i \neq 1, j \neq 1} (S_{ij} - S)\mathrm{N}_{ij}(\mathrm{C{-}C}) \\ & - 4(H_2 - H)\mathrm{N}_{22}(\mathrm{C{=}C}) - 2(H_3 - H)\mathrm{N(C{\equiv}C)} + \Lambda \end{aligned} \tag{9}$$

(For cumulenes, add $(D_{23} - D)\mathrm{N}_{23}(\mathrm{C{=}C}) + (D_{33} - D)\mathrm{N}_{33}(\mathrm{C{=}C})$. Equation (9) consists of the same major terms as equation (4), plus correction terms.

It will be recalled that Pauling found that the bond energies of polar bonds between atoms Y and Z can be represented rather well by

$$B(\mathrm{Y{-}Z}) = \tfrac{1}{2}[B(\mathrm{Y{-}Y}) + B(\mathrm{Z{-}Z})] + \Gamma_{\mathrm{YZ}}; \quad \Gamma_{\mathrm{YZ}} = \gamma(X_{\mathrm{Y}} - X_{\mathrm{Z}})^2, \tag{10}$$

$\gamma$ being a universal constant and $X_{\mathrm{Y}}$ and $X_{\mathrm{Z}}$ being identified as the electronegativities of atoms Y and Z. (The symbol $\Gamma$ is used here, rather than Pauling's $\Delta$, to avoid confusion with $\Delta$ of equation 4.) As various people have pointed out, different carbon hybrid $\sigma$ orbitals should differ in electronegativity,[18] hence $H_i$ (including $\mathrm{H} \equiv \mathrm{H}_1$) and $S_{ij}$ in equation (9) should be expressible as

$$H_i = \tfrac{1}{2}[S_{ii}' + B(\mathrm{H}_2)] + \Gamma_{i\mathrm{H}}'; \quad S_{ij} = \tfrac{1}{2}(S_{ii}'' + S_{jj}'') + \Gamma_{ij}''. \tag{11}$$

Here *i*, *j* refer to *te*, *tr*, or *di* hybrid carbon orbitals (1 for *te*, 2 for *tr*, 3 for *di*). Indices ′ and ″ have been added to provide for the fact that the actual hybrids probably differ considerably from pure *te*, *tr*, and *di*, *and in different ways* for C—H and C—C bonds. The distinction can of course easily be dropped later. From equations (11), recalling that $H$ means $H_1$, the following equations are readily obtained:

$$\left.\begin{aligned} H_i - H &= \tfrac{1}{2}(S_{ii}' - S) + (\Gamma_{i\mathrm{H}}' - \Gamma_{1\mathrm{H}}) \\ S_{ij} - S &= \tfrac{1}{2}(S_{ii}'' - S) + \tfrac{1}{2}(S_{jj}'' - S) + \Gamma_{ij}'' \\ D_{ij} - D &= \tfrac{1}{2}(D_{ii} + D_{jj}) - D + \Gamma_{ij} \text{ (for cumulenes)} \end{aligned}\right\} \tag{12}$$

Substituting equations (12) into equation (9), one obtains *for the correction terms*

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[18] R. S. Mulliken, *J. Chem. Phys.* **2**, 782 (1934); *J. Phys. Chem.* **41**, 318 (1937).

(Equation (9) minus equation (4)):

$$\left.\begin{aligned}
&[\tfrac{1}{2}(S_{22}' - S) + (\Gamma_{2H}' - \Gamma_{1H})]\mathrm{N}_2(\mathrm{CH}) + [\tfrac{1}{2}(S_{33}' - S) + (\Gamma_{3H}' - \Gamma_{1H})]\mathrm{N}_3(\mathrm{CH})\\
&\quad + [\tfrac{1}{2}(S_{11}'' - S) + \tfrac{1}{2}(S_{22}'' - S) + \Gamma_{12}'']\mathrm{N}_{12}(\mathrm{C{-}C}) + (S_{22}'' - S)\mathrm{N}_{22}(\mathrm{C{-}C})\\
&\quad + [\tfrac{1}{2}(S_{11}'' - S) + \tfrac{1}{2}[S_{33}'' - S) + \Gamma_{13}'']\mathrm{N}_{13}(\mathrm{C{-}C}) + [\tfrac{1}{2}(S_{22}'' - S)\\
&\quad + \tfrac{1}{2}(S_{33}'' - S) + \Gamma_{23}'']\mathrm{N}_{23}(\mathrm{C{-}C}) + (S_{33}'' - S)\mathrm{N}_{33}(\mathrm{C{-}C})\\
&\quad - 4[\tfrac{1}{2}(S_{22}' - S) + (\Gamma_{2H}' - \Gamma_{1H})][N_{22}(\mathrm{C{=}C}) + \tfrac{1}{2}\mathrm{N}_{23}(\mathrm{C{=}C})]\\
&\quad + [\tfrac{1}{2}(D_{33} - D) + \Gamma_{23}]\mathrm{N}_{23}(\mathrm{C{=}C}) + (D_{33} - D)\mathrm{N}_{33}(\mathrm{C{=}C})\\
&\quad -2[\tfrac{1}{2}(S_{33}' - S) + (\Gamma_{3H'} - \Gamma_{1H})]\mathrm{N}(\mathrm{C{\equiv}C}) + \Lambda.
\end{aligned}\right\}\quad(13)$$

Now the numbers of bonds of various types in equation (13) are not entirely independent, but obey the relations

$$\left.\begin{aligned}
&\mathrm{N}_2(\mathrm{CH}) + \mathrm{N}_{12}(\mathrm{C{-}C}) + 2\mathrm{N}_{22}(\mathrm{C{-}C}) + \mathrm{N}_{23}(\mathrm{C{-}C})\\
&\qquad\qquad = 4\mathrm{N}_{22}(\mathrm{C{=}C}) + 2\mathrm{N}_{23}(\mathrm{C{=}C})\\
&\mathrm{N}_3(\mathrm{CH}) + \mathrm{N}_{13}(\mathrm{C{-}C}) + 2\mathrm{N}_{33}(\mathrm{C{-}C}) + \mathrm{N}_{23}(\mathrm{C{-}C} = 2\mathrm{N}(\mathrm{C{\equiv}C}).
\end{aligned}\right\}\quad(14)$$

*If* now we make the simplifying assumption that the hybrids "*te*", "*tr*", "*di*" are really pure *te*, *tr*, and *di* in both C—H and C—C bonds, so that $S_{ii}' - S_{ii}''$, and so on (including $S''_{11} - S) = 0$, expression (13) for the correction terms in equation (9) reduces with the help of equations (14) to

$$\begin{aligned}
&(\Gamma_{2H} - \Gamma_{1H})[\mathrm{N}_2(\mathrm{CH}) - 4\mathrm{N}_{22}(\mathrm{C{=}C}) - 2\mathrm{N}_{23}(\mathrm{C{=}C})] + \Gamma_{12}\mathrm{N}_{12}(\mathrm{C{-}C})\\
&\quad + (\Gamma_{3H} - \Gamma_{1H})[\mathrm{N}_3(\mathrm{CH}) - 2\mathrm{N}(\mathrm{C{\equiv}C})] + \Gamma_{13}\mathrm{N}_{13}(\mathrm{C{-}C}) + \Gamma_{23}[\mathrm{N}_{23}(\mathrm{C{-}C}) \qquad (15)\\
&\quad + \tfrac{1}{2}\mathrm{N}_{23}(\mathrm{C{=}C})] + (D_{33} - D)[\tfrac{1}{2}\mathrm{N}_{23}(\mathrm{C{=}C}) + \mathrm{N}_{33}(\mathrm{C{=}C})] + \Lambda
\end{aligned}$$

*If further*, we ignore the polar terms (i.e. the Γ's) in (15), nothing but Λ remains, except for cumulenes. This verifies for the general case the statement made immediately following equation (8), that equation (9) reduces to equation (4) with $\Delta = \Lambda$ if certain plausible assumptions are made.

Returning to (15), it is remarkable that (except for cumulenes) *only* polar terms and Λ remain as corrections to equation (4). However, if "*te*", "*tr*". and "*di*" hybrids are commonly quite different in C—H and C—C bonds, as seems likely from our earlier discussion, expression (13) is required, and it becomes almost impossible to draw any reliable conclusions from observed Δ values based on equation (4).

That the expected Γ's and Γ differences in (13) and (15) are often not small, especially where C—H bonds are concerned, can be seen from Table 3.

### *Possible usefulness of theory*

All things considered, one is inclined to agree that Dewar and Schmeising are right in being skeptical about identifying Δ's from equation (4) with π-electron delocalization energies, but one is equally inclined to feel skeptical about accepting Dewar's new assumptions. Rather, it appears that a more thoroughgoing review of the whole situation is in order.

One now begins to wonder whether theoretical computations may not be a more reliable guide to actual delocalization energies than empirical Δ values. As we have seen in the previous Section, the purely theoretical LCAO-SCF calculations of Parr and Mulliken[13] on butadiene and the somewhat more empirical but more securely

TABLE 3. CALCULATED POLAR ENERGIES OF BONDS INVOLVING HYBRID $\sigma$ CARBON ORBITALS

| Electronegativity differences[a] | Polar energies $\Gamma$[b] (kcal/mole) |
|---|---|
| $x_{te} - x_{H} = 0{\cdot}39$ | $3{\cdot}7 = \Gamma_{1H}$ |
| $x_{tr} - x_{H} = 0{\cdot}67$ | $10{\cdot}4;\ \Gamma_{2H} - \Gamma_{1H} = 6{\cdot}7$ |
| $x_{di} - x_{H} = 1{\cdot}22$ | $34;\ \Gamma_{3H} - \Gamma_{1H} = 30$ |
| $x_{tr} - x_{te} = 0{\cdot}28$ | $1{\cdot}8 = \Gamma_{12}$ |
| $x_{di} - x_{tr} = 0{\cdot}55$ | $6{\cdot}9 = \Gamma_{23}$ |
| $x_{di} - x_{te} = 0{\cdot}83$ | $15{\cdot}9 = \Gamma_{13}$ |

[a] Using Mulliken's electronegativity scale (ref. 18), multiplied by a suitable factor to reduce the $x$'s to Pauling's thermal scale.

[b] $\Gamma$ values from equation (10), using a value of $\gamma$ based on Pauling's work.

based calculations by the Pariser–Parr and similar methods are in close agreement with each other as to wave functions and bond orders. This agreement justifies placing considerable confidence in the values computed by Mulliken and Parr[17] (since they were based on the results of Parr and Mulliken on butadiene, and on similar results for benzene) for the vertical delocalization energies of butadiene and benzene. In other words, perhaps these purely theoretical quantities are more to be trusted than the empirical $\Delta$'s. It is noteworthy also that, after deducting estimated compression energies, these theoretical quantities are rather close to the empirical $\Delta$'s, giving some support to the belief that, in double-bonded systems at least, the empirical $\Delta$'s are really by good luck approximately equal to $\pi$-electron resonance energies. (It is only in triple-bonded systems that really *large* polar anomalies in the $\Delta$'s would be anticipated.)

Whatever may be the final conclusions as to the interpretation of $\Delta$ values, the work of Dewar and Schmeising has made it fairly certain that "natural" C—C bond lengths are somewhat shorter than hitherto supposed, when trigonal or digonal carbon $\sigma$ AO's are involved. This means that, in correcting theoretically computed vertical delocalization energies to allow for compression energies, the latter will often be considerably smaller than hitherto estimated. Existing comparisons between theory and experiment will need some revision on this account, and particularly so in the case of semi-empirical computations on hyperconjugation. With reference to the latter, the uncertainties discussed above in the interpretation of empirical $\Delta$'s will need particular attention. It would be highly desirable that some hyperconjugation computations based on Pariser–Parr or SCF–LCAO methods be made. Nevertheless, there are a number of indications that recent computed values of $\pi$-delocalization energies in hyperconjugation are not very far wrong.

### *Rotation barriers and $\pi$ bond energies*

The safest way to determine an empirical value of the bond energy of a $\pi$ bond would seem to be from the energy required to twist it through 90°, with, however, the following corrections:

(1) *add* the $\pi$-electron hyperconjugation energy of the twisted bond;

(2) *add* the energy of decompression of the bond, which should stretch considerably when the $\pi$ bond is largely destroyed;

(3) correct for any barrier energy which would be associated with twisting through 90° in the absence of any $\pi$ bonding. For $C_2H_4$ the energy required for a 90° twist is 61·3 ± 1·2 kcal (2·66 eV).[19] Roothaan and Mulliken[20] have computed the (vertical) hyperconjugation energy of 90° twisted ethylene to be about 1 eV, but for the somewhat stretched bond this may be, say, 0·8 eV. If $R$ for the twisted bond is, say, 1·42 Å, the decompression correction, if the natural $C^{tr}$—$C^{tr}$ length is 1·51 Å, may be 0·3 eV, while correction (3) may be, perhaps, −0·15 eV. The total (which of course is rather rough) is 3·6 eV.

For 1:3-butadiene one has a careful determination by Aston and collaborators[21] of the barrier height for a 90° twist of 1:3-butadiene, whose stable form is *s-trans*,[22] about the C—C single bond; their value is 5 kcal. Before setting up a theoretical counterpart, it is necessary first to recognize that in the absence of any $\pi$-electron (i.e. $\pi_x$-electron) delocalization there would be, (1), a considerable $\pi$-electron (i.e. $\pi_x$-electron) nonbonded repulsion across the C—C bond and further (2), an approximately equal $\pi_y$-electron nonbonded repulsion; also that, (3), on twisting, the sum of these two nonbonded repulsions (also the $\sigma$-electron nonbonded repulsions) should remain invariant according to usual VB theory (except for slight decreases in H—H interactions). The effect of $\pi_x$ delocalization in butadiene must be viewed against this background. The vertical $\pi_x$ delocalization energy (which, be it noted, depends on the delocalization-produced changes in *all* the bonds, not just in the C—C bond), as computed by Mulliken and Parr,[17] is 6·5 kcal. On twisting through 90°, this $\pi_x$-delocalization energy should be destroyed. It thus plays the same role here as the total $\pi_x$ bond energy in ethylene. Also, just as in ethylene, hyperconjugation in the 90° twisted form restores some of the lost $\pi$-electron delocalization energy. Finally, there is a small correction for decompression of the $\sigma$ bond on twisting. To estimate the total height of the barrier for 90° twisting, one may add to Mulliken and Parr's 6·5 kcal an estimated 0·9 kcal for second-order $\pi_y$ hyperconjugation[23] in planar butadiene and then subtract an estimated 3·2 kcal for $\pi_x$ and $\pi_y$ first-order hyperconjugation[13] in 90°-twisted butadiene and 0·3 kcal for decompression, leaving 4 kcal for the net barrier height. If lack of complete invariance to rotation around a $\pi$-delocalization-free C—C single bond adds 1 kcal to the barrier, the result agrees with Aston's empirical barrier height of 5 kcal.

This agreement is consistent with the idea that the typical stability of planar forms in conjugated systems, and the corresponding stabilities of conjugated double bonds toward twisting, are due to $\pi_x$-electron delocalization. However, Dewar suggests that, since we do not understand the rather considerable barrier (3 kcal) toward rotation in ethane (where the same sort of nonbonded $\pi_x$ and $\pi_y$ repulsions should exist as discussed above for butadiene,[24] and with their sum invariant to rotation—but

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[19] J. E. Douglas, B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.* **20**, 1807 (1952); **23**, 315 (1955).

[20] C. J. Roothaan and R. S. Mulliken, *Chem. Rev.* **41**, 219 (1947). The value 1 eV corresponds to $\beta_{\mathrm{CH}} = 2\beta_{\mathrm{CC}}$, $\delta = 0$, $\beta_{\mathrm{CC'}} = -3$ eV.

[21] J. G. Aston, G. Szasz, H. W. Woolley and F. C. Brickwedde, *J. Chem. Phys.* **14**, 67 (1946). See also C. M. Richards and J. R Nielsen, *J. Opt. Soc. Amer.* **40**, 438 (1950), who say that certain frequencies estimated by Aston *et al* "have been examined critically and found essentially correct."

[22] Not only the vibrational spectrum, but also the intensity relations in the ultraviolet absorption spectrum, give assurance that 1:3-butadiene in liquid or solution is at least very predominantly in the *s-trans* form at room temperature.

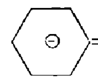
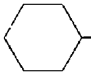
[23] Based on A. Lofthus' estimates [*J. Amer. Chem. Soc.* **79**, 24 (1957)] of the $\pi$ delocalization energies for hyperconjugation in similar situations.

[24] The variation of the intergroup H—H nonbonded repulsions in ethane on rotation cannot reasonably be large enough to account for the observed barrier.

weaker than in butadiene because of the greater C—C distance), a barrier of similar origin and comparable (or larger) magnitude might exist in butadiene. On the other hand, the theory in its present state gives a reasonable explanation of what is observed, and is not contradicted by anything which is observed; so why borrow trouble?

Something should be added about diphenyl, which apparently is *not* planar (except in the crystal). This can be attributed to the fact that two pairs of H atoms on the two phenyl groups are rather close together and presumably exert local nonbonded repulsions which overcome the $\pi$-electron delocalization forces favoring planarity. It is of interest that the nearest H—H distances in planar diphenyl (1·80 Å) are the same as for the two adjacent H atoms in the *cis* form of planar butadiene (the *cis* perhaps also is twisted; at any rate it is less stable than the *trans* form,[21] very likely at least partly for this reason). Even more interesting is the fact that these distances are practically the same as those (1·78 Å) between H atoms in $CH_4$, or adjacent H atoms in $C_2H_6$. The computed overlap integrals between two H atom 1*s* orbitals at this distance are remarkably large (0·28) at 1·78 Å[25], and one might reasonably expect large nonbonded repulsions between two such H atoms (of the order of ½ eV energy, half the binding energy of two *bonded* H atoms in $H_2$ at the same distance apart).[*] The observed twist in diphenyl is not then surprising.

## *Dipole Moments and Other Properties*

The factors determining dipole moments in conjugated and hyperconjugated systems are so complicated that great caution is required in drawing structural conclusions from observed moments. One must include not only primary contributions $qR$ due to transfers of $\sigma$ or $\pi$ charge from a substituent to an adjacent unsaturated atom, but also covalent-dipole contributions whenever the transfer is between adjacent atoms whose participating orbitals are of unequal size, and also lone-pair dipole contributions in case hybrid lone-pair orbitals are present on substituent atoms. One must also include inductive contributions, both in the $\sigma$-electron system and in the $\pi$-electron system, especially the latter. Further, $\pi$-electron resonance should in general contribute. Finally, as Dewar and others have emphasized, one must take account of the fact that C—H or in general C—X $\sigma$ bond moments must differ for C atoms with $\sigma$ orbitals in different hybrid states, and that C—C $\sigma$ bonds should have moments if their $\sigma$ orbitals differ in hybrid state. In view of all this , one is inclined to agree with Dewar that the usual arguments for $\pi$-electron resonance as the cause of observed effects in conjugated systems are at present inconclusive. For example, it is incautious to conclude that $=X^+$ resonance is responsible for the fact that the moments of —X are smaller than for $CH_3X$ when X is more electronegative than carbon (more precisely, when the X $\sigma$ bond orbital is more electronegative than a tetrahedral $\sigma$ bond orbital of carbon).

However, a rough estimation of the effects of all the various modifying factors

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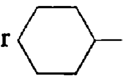
[*] In $C_2H_6$, the overlap integral at nearest approach (2·31 Å) between H atoms in the two methyl groups is 0·15, which by an estimate similar to that just mentioned would correspond to a nonbonded repulsion of 0·1 eV: not large enough, incidentally, to account for the observed barrier to free rotation in $C_2H_6$.

[25] R. S. Mulliken, *J. Amer. Chem. Soc.* 72, 4500 (1950).

mentioned above, except π-electron resonance, indicates that they may approximately cancel out as between $C_6H_5X$ and $CH_3X$ or perhaps even tend to *increase* the moment somewhat for —X, so that in the writer's opinion the usual conclusions could probably be justified by calculations taking all factors into account. But even if one agrees with Dewar that the usual arguments are not conclusive as they stand, one must concede that any argument that the observed effects are due solely to differences in hybrid states of carbon σ orbitals, and not to any appreciable extent to π-electron resonance is at least equally inconclusive. To be sure, Petro[27] has shown that the observed moments of conjugated and hyperconjugated systems can be explained quite well formally in terms of a set of bond moments differing for each different C—H and C—C hybrid σ case and assuming no contributions from conjugation or hyperconjugation. But the agreements obtained are no more conclusive than those obtained when contributions due to varying hybrid carbon orbitals are ignored and all effects associated with conjugation are attributed to π-electron resonance.

In view of the difficulty at the present time of correctly evaluating all relevant factors affecting dipole moments, it seems to the writer that one may place considerable reliance on theoretical calculations by the LCAO–SCF or Pariser–Parr or similar methods as giving approximately correct pictures of the effects of π-electron resonance on π-electron charge distributions in conjugated systems (compare paragraphs above on "Possible Usefulness of Theory"). However, more careful attention than hitherto should probably be given to the detailed interaction of σ-electron charge distributions on π-electron distributions.

In spite of what has been said about the difficulties of predicting bond moments, there do exist certain systems like azulene and the fulvenes where all carbon σ orbitals are "trigonal" so that C—H and C—C σ moments should cancel out, but π-electron resonance of the ordinary (sacrifical) conjugative type predicts dipole moments in agreement with observation. A similar situation exists for hyperconjugation in *cyclo*pentadiene. These cases are discussed in a separate paper.[7]

As to whether the observed dipole moments of such molecules as propylene, toluene, and methylacetylene are due to hyperconjugation, the writer believes, in accordance with remarks above about the usefulness of theory, that the most likely correct answer is "partly". In existing theoretical computations by the semiempirical LCAO–MO method, the extent and nature of hyperconjugation in such systems are determined by resonance paraments $\beta$ (for the C—C π bonds) and $\beta^*$ (for the C—H quasi-π bonds) and $\delta$ (the electronegativity of the H quasi-π orbitals relative to the carbon π orbitals): cf. Section II (e) of ref. 7. The now usually favored value of $\delta$ (about $-0{\cdot}5\beta$) is based on Coulson and Crawford's attribution of the dipole moment of toluene to hyperconjugation alone,[27] ignoring σ hybridization effects. The value of $\delta$ affects the computed hyperconjugation energy (the latter is considerably larger for $\delta = -0{\cdot}50\beta$ than for $\delta = 0$), and especially the charge distribution. It is clear that existing computations on hyperconjugation by the semiempirical method should be reviewed with respect to the best choice of $\delta$.

If possible, the contributions of hybridization differences to observed dipole

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[26] A. J. Petro, *J. Amer. Chem. Soc.* 80, 4230 (1958).

[27] C. A. Coulson and V. A. Crawford, *J. Chem. Soc.* 2052 (1953).

moments should first be calculated, but this may be difficult. However, it seems not unlikely on the basis of a rough estimation that these contributions are smaller than the observed moments but in the same direction, so that hybridization and hyperconjugation could share in explaining the observed dipole moments. This would make $\delta/\beta$ still negative but smaller than 0·5. From LCAO–MO theory a negative value of $\delta/\beta$ is understandable[28] but somewhat accidental. It should be pointed out that hyperconjugation would still be present if $\delta/\beta$ were zero, or positive, but its contribution *to the dipole moment* would then be zero, or reversed in sign. In other words, a dipole moment is not an essential inherent characteristic of ordinary hyperconjugation (although it is for dative isovalent hyperconjugation).

Turning to other types of information, nuclear magnetic resonance, although some authors have disagreed,[26] seems to give clear evidence for $\pi$-electron resonance effects in conjugation and hyperconjugation.[29,30] Particularly convincing is Taft's discussion[29] of Gutowsky's data on *m* and *p*-substituted fluorobenzenes. The fluortoluenes indicate that the $CH_3$ group produces a hyperconjugative resonance effect similar in magnitude and sign to the conjugative resonance effect of Cl or Br, and thus confirms the negative sign of $\delta/\beta$.

Strong experimental evidence for some important effects of hyperconjugation, predicted from semiempirical $\pi$-electron resonance theory, in the ultraviolet absorption spectrum of ethylene (relevant to the ground state of $C_2H_4^+$) was discussed in an earlier paper.[7] While in that case incipient isovalent, rather than ordinary sacrificial, hyperconjugation is involved, the fact that the effects were predicted using the same $\beta$ and $\beta^*$ parameters as in the usual semiempirical calculations on ordinary hyperconjugation supports the approximate correctness of the latter's predictions.

Dewar's argument (4) in the Introduction as to the irrelevance of the electronic spectra of hyperconjugated, and a similar argument for conjugated, systems can be answered as follows: the same LCAO–MO theory which approximately reproduces the observed excited state effects can be trusted in its predictions about ground state characteristics.

Dewar's argument (5) is certainly valid, but it is not an argument *against* $\pi$-electron resonance in ground states. It is of interest that Taft finds strong evidence for a close parallelism between activated and ground state properties in his comparison[29] of reactivity parameters with nuclear magnetic shielding parameters in substituted fluorbenzenes. Activated states, as noted in the companion paper[7], probably often involve isovalent conjugation or hyperconjugation in incipient carbonium ion structures.

An interesting ground state property which shows great sensitivity to conjugation is polarizability, as shown in the intensities of Raman lines.[31] This is in agreement with what is expected from $\pi$-electron resonance theory. One might, however, perhaps argue that polarizability is not a proper ground state property, since the theory makes it dependent on the strengths and frequencies in the electronic absorption spectrum of the molecule, it being the latter which, in agreement with $\pi$-electron theory, shows great changes in conjugation.

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[28] N. Muller, L. W. Pickett, and R. S. Mulliken, *J. Amer. Chem. Soc.* **76**, 4770 (1954); Y. I'Haya, *J. Chem. Phys.* **23**, 1165 (1955).

[29] R. W. Taft, Jr., *J. Amer. Chem. Soc.* **79**, 1045 (1957); R. W. Taft Jr. and I. C. Lewis, Report at Conference on Hyperconjugation, Bloomington, Indiana, June, 1958. *Tetrahedron* **5**, 210 (1959).

[30] R. A. Hoffman, *Molecular Phys.* **1**, 326 (1958).

[31] Private communication from W. T. Alexanjan, *U.S.S.R. Academy of Sciences* Moscow.