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CONJUGATION AND HYPERCONJUGATION: A SURVEY WITH EMPHASIS ON ISOVALENT HYPERCONJUGATION

ROBERT S. MULLIKEN

Laboratory of Molecular Structure and Spectra, Department of Physics, The University of Chicago, Chicago 37, Illinois

Abstract—Various aspects and examples of conjugation and hyperconjugation are surveyed, and the desirability of an explicit classification of both conjugation and hyperconjugation into two major types, isovalent and sacrificial (ordinary) is emphasized. The existence of a third type, pluvalent conjugation, is also mentioned. Further, the desirability of a subclassification of isoconjugation and isohyperconjugation each into three sub-types (dative, non-dative, and homodative, in orderof increasing conjugative stabilization) is pointed out, with examples. Sacrificial conjugation and hyperconjugation are usually non-dative, but some examples of dative conjugation and hyperconjugation are cited. The intrinsic jointness of the inductive and mesomeric effects (both of which are forms of resonance) in homodative isoconjugation and isohyperconjugation is emphasized. Homodative alkyl isohyperconjugation in carbonium ions is discussed extensively, with especial reference to McCaulay's Conference paper. Some hitherto incompletely published theoretical evidence, supported by experimental spectroscopic evidence, that the ethylene positive ion is partially twisted in its ground state, is presented; the twist is due to incipient isohyperconjugation.

Definitions of the term hyperconjugation are considered with some care. It is suggested that the Baker–Nathan effect (in so far as it refers to differences between C–H and C–C hyperconjugation) should not itself be described as hyperconjugation, but rather as *differential* hyperconjugation. It is pointed out that there are no obvious theoretical reasons for expecting radical differences in stabilization energy or in magnitude of electron release between C–C and C–H hyperconjugation. Finally, the writer wishes to apologize if he has sometimes gone astray in this paper because of the superficiality of his acquaintance with the vast literature of organic chemistry.

I. INTRODUCTION

(*a*) *General remarks*

MULLER and the writer in a recent paper[1] have shown by modified Hückel-type LCAO–MO (LCAO molecular orbital) calculations how the observed relatively large stabilization energies in alkyl radicals and ions (relative to CH_3 and CH_3^+) can be understood in terms of hyperconjugative π-electron resonance. In seeking to understand the large size of the effects, they found it very illuminating to introduce a classification of hyperconjugative (and of conjugative) effects in terms of types of major VB (valence-bond) resonance structures. Although these structures are in general very familiar,[2] it was felt that a systematic classification and terminology would be of real value.

Although corresponding LCAO and VB structures are only roughly equivalent, the equivalence is probably usually good enough to form the basis for a qualitative classification which should be significant for both. Although the LCAO method is more useful for quantitative calculations, one can much more easily obtain fairly

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[1] N. Muller and R. S. Mulliken, *J. Amer. Chem. Soc.* **80**, 3489 (1958).

[2] G. W. Wheland, *Resonance in Organic Chemistry*. Wiley, New York (1955).

reliable qualitative[3] insight into the reasons for the magnitudes of π-electron resonance effects in various kinds of cases by writing corresponding VB resonance structures. (But see Section III(a), Notes added 20 November 1958).

The present paper contains a further development of the classification of conjugated and hyperconjugated molecules in terms of VB resonance structures, with examples. Since this paper was prepared in final form *after the Conference*, advantage has been taken of the opportunity to include in the discussion of examples commentaries[4] on some of the papers presented by others at the Conference.

In view of Dewar's strong advocacy at the Conference of the idea that the effects of π-electron resonance in ordinary conjugation, hence all the more so in ordinary hyperconjugation, are inconsequential, one might be persuaded that any further use of the idea of hyperconjugation has become superfluous. However, as is set forth in a separate complementary paper* the writer is very doubtful that such an extreme viewpoint can be justified. Moreover, a major point in the present paper is that isovalent hyperconjugation should be a much stronger effect than ordinary hyperconjugation, because of resonance akin to that in benzene. On the whole, it seemed best not to consider the impact of Dewar's new ideas in the present paper, except incidentally. Resulting doubts and reasonable modifications of usual ideas will be examined more carefully in the separate paper mentioned.

(b) *Definitions of conjugation and hyperconjugation*

A variety of phenomena in unsaturated and aromatic organic molecules, including those historically referred to as conjugation, have been explained in quantum-mechanical VB theory in terms of π-electron resonance between two or more classical VB structures. The use of the term conjugation has in recent years been increasingly extended to include all molecules believed to be stabilized by π-electron resonance; for example to benzene with its two equivalent Kekulé structures and to aniline with its quinoid in addition to Kekulé structures. In the present paper the word conjugation will be used in this broadened sense. *Conjugation* is then said to exist in a molecule when the principal classical structure or structures contain single bonds each interposed between two multiple bonds or having on one side a multiple bond and on the other a lone π electron, π-electron pair or quartet, or π-electron vacancy. (For conjugation in the cumulenes– see Section III(a)—a slight extension of this definition is needed.)

Hyperconjugated molecules can be defined similarly if we regard a pair or triplet of bonds from an atom e.g. $\left(\begin{array}{l} R\diagdown \\ \qquad C \\ R'\diagup \end{array}\right.$ or $\left.\begin{array}{l} R\diagdown \\ R'\!-\!C \\ R''\diagup \end{array}\right)$ as a quasi-double or quasi-triple bond $\left(\left.\begin{array}{l} R' \\ R \end{array}\right\} = C\right.$ or $\left.\left.\begin{array}{l} R \\ R' \\ R'' \end{array}\right\} \equiv C\right)$. *First-order hyperconjugation* can be said to exist when the

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* R. S. Mulliken, *Tetrahedron* (1959) in press.

[3] However, quantitative factors, which are automatically taken into account in the LCAO-MO method (though not very accurately unless refined forms of the method are used), can sometimes become so important as to seriously modify or even outweigh conclusions based on qualitative insight from VB structures.

[4] Thus the present paper incorporates (a) material prepared before the Conference; (b) responses to ideas and material presented by others at the Conference; (c) some improvements, refinements, and modifications resulting from the stimulus of the Conference papers and discussions. Finally (d) some additional comments believed important were inserted on 20 November 1958.

principal classical structure or structures contain single bonds interposed between one quasi-multiple bond and either an ordinary multiple bond, a lone π electron, π electron pair or quartet, or π-electron vacancy [with a slightly extended definition for cumulenes—see Section III(a)]. *Second-order hyperconjugation* involves single bonds interposed between two quasi-multiple bonds; recent calculations[5] indicate that the effects of second-order hyperconjugation should be quite small.

In the discussion of unsaturated or aromatic molecules with a planar skeleton of the unsaturated and directly attached atoms, the x direction will always be taken in this paper to be perpendicular to the skeletal plane. Then in any quasi-double bond, one is a quasi-σ and one a quasi-π_x or quasi-π_y. Hereafter these will be designated as $[\sigma]$ and $[\pi_x]$ or $[\pi_y]$ bonds.

For a group $H_2=$ or $R_2=$ (as for example in $H_2{=}CO$ or $R_2{=}CO$), let the bond orbitals of the two H atoms or of those R atoms which form the quasi-double bond be called a and b. Then the $[\sigma]$ GO (group orbital) has the form $a + b$, the $[\pi_x]$ or $[\pi_y]$ orbital the form $a - b$ (omitting a normalizing factor in each case).

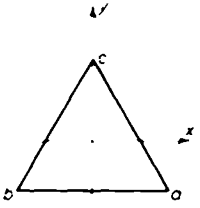

Fig. 1.

For a group $H_3\equiv$ or $R_3\equiv$, letting the three H_3 or R_3 bond orbitals of the quasi-triple bond be called a, b, c, the $[\sigma]$ GO has the form $a + b + c$, while the $[\pi_x]$ and $[\pi_y]$GOs are of the forms $a - b$ and $c - \frac{1}{2}(a + b)$, or *vice versa* (omitting normalization factors and neglecting overlap effects) or suitable orthogonal linear combinations of these, depending on how the triangle *abc* (see Fig. 1) is oriented with respect to rotation around the $R_3\equiv$ bond. However, the hyperconjugative action is independent of the angle of such rotation. (This is no longer quite true for composite groups $\left.\begin{matrix}R'\\R\end{matrix}\right\}=$ or $\left.\begin{matrix}R\\R'\\R''\end{matrix}\right\}\equiv$, insofar as the different R's are unlike in their hyperconjugative effectiveness.)

II. ISOVALENT CONJUGATION AND ISOVALENT HYPERCONJUGATION

(a) *General characteristics; subclasses; interrelations of inductive and mesomeric effects*

In *isovalent conjugation* (or *isoconjugation* if one wants a briefer term) there are two or more classical structures containing equal numbers of π bonds, also of σ and of total bonds. The writer feels that it is worth while, and important,[6] to distinguish

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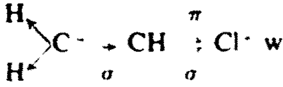
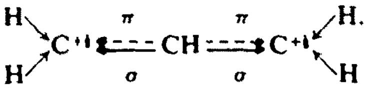
[5] C. A. Coulson and V. Crawford, *J. Chem. Soc.* 2052 (1953); A. Lofthus, *J. Amer. Chem. Soc.* 79, 24 (1957).

[6] Of course everyone knows these types, and perhaps most chemists will think it silly or presumptuous to give them names, but the writer is convinced that their overt recognition should make it easier to think clearly about them.

three main sub-classes of isovalent conjugation, namely (listing them in order of increasing expected resonance energy), (1), *dative*, (2), *non-dative*, and (3), *homodative*. Typical examples are the following: (1) for the dative subclass, chlorethylene: isovalent dative structure $H_2C^- {-} CH = Cl^+$ in addition to main structure $H_2C = CHCl$; or chloracetylene; (2), for the non-dative subclass, benzene and the allyl radical: *two equivalent* isovalent structures each; (3), for the homodative subclass, allyl ion or amidinium ion, or their derivatives: two equivalent isovalent structures each, with stabilization not only by resonance per se but also by *necessarily concomitant*[7] partial uniformization of π charge distribution, brought about by the dative action involved in a shift from one of the two isovalent resonance structures to the other (e.g. $H_2C^+ {-} CH = CH_2$ to $H_2C = CH - C^+H_2$). Two familiar further examples of dative isoconjugation (here *superposed* on benzenoid isoconjugation) are chlorobenzene and aniline, with dative isovalent structures $C_6H_5^- = Cl^+$ and $C_6H_5^- = N^+H_2$ respectively.

Dative isoconjugation involves *exclusively one-way* π dative action, which costs energy in creating an (often long) dipole, so that the dative structure, although isovalent with the main structure, is non-equivalent. On the other hand, homodative isoconjugation releases electrostatic energy by charge redistribution (equalization) as an *intrinsic part* of the total energy release by isovalent π-electron resonance. The resulting bond and charge distribution in the allyl ion may be summarized by $H_2C^{+\frac{1}{2}} {\cdots} CH {\cdots} C^{+\frac{1}{2}}H_2$.

But also, in the presence of either dative or homodative isoconjugation, *additional* "inductive" shifts of charge via both σ and π bonds must of course occur. In the dative case, they serve to lower the energy of the dative resonance structure very considerably and thus increase its importance for the molecule; for example in CH_2CHCl,  $H_2C^- \underset{\sigma}{\rightarrow} CH \overset{\pi}{\underset{\sigma}{;}} Cl^+$ would much better describe the dative structure than $H_2C^- {-} CH = Cl^+$; then in the actual molecule, when both the isovalent resonance structures have been included, the Cl atom has lost π charge but gained σ charge.

In the homodative case, inductive effects serve to distribute some σ and also some π-electron positive charge to *all* the atoms in the molecule; the resulting distribution might be described by  $H_2C^{+\frac{1}{2}} \underset{\sigma}{\overset{\pi}{\leftarrow\!-\!-\!-}} CH \underset{\sigma}{\overset{\pi}{-\!-\!-\!\rightarrow}} C^{+\frac{1}{2}}H_2$. A major part of the π-electron "inductive" redistribution, as compared with a single VB resonance structure, had, however, already been accomplished by isovalent resonance. Further, it should be especially noted that LCAO-MO π-electron calculations, in contrast to the usual VB formulations, automatically take into account *all* "inductive" as well as mesomeric *π-electron* charge shifts if allowance is made in the calculations for the effect of its charge on the π-electronegativity of each carbon atom.

In isovalent *hyperconjugation* (or isohyperconjugation), as in isoconjugation, there are in VB theory two or more resonance structures containing equal total numbers of bonds, and also containing equal numbers of σ and π bonds if one counts $[\sigma]$ and $[\pi]$ bonds as σ and π bonds. Further, three main sub-classes of isohyperconjugation can usefully be distinguished, namely, (1), dative, (2) non-dative, and (3)

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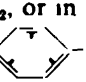
[7] L. Goodman and H. Shull, *J. Chem. Phys.* 23, 33 (1955). For discussion of the corresponding phenomena in *hyperconjugation*, see references 1 and 11.

homodative; the characteristics of these classes parallel those of the corresponding sub-classes of isoconjugation.

Isohyperconjugation differs from isoconjugation in that there are two (or in general two sets of) isovalent structures which differ (and hence are always non-equivalent) in a certain special way. Namely, the subordinate isovalent structures have *one more ordinary π bond and one less $[\pi]$ bond* than the predominant structures; that it is the former which are subordinate is indicated by experimental evidence and justified by the belief that $[\pi]$ bonds are very considerably stronger than ordinary π bonds.

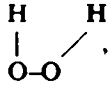
(b) *Dative isohyperconjugation (and some new notation)*

Let us first consider some examples from the dative sub-class, beginning with CH_3OH. The two isovalent structures are $H_3\overset{\perp}{\underset{\top\top}{-}}C{-}\ddot{O}H$ and $H_3^-\underset{\top\top}{-}C\stackrel{\perp}{-}O^+H$ The symbol $\perp$ represents a π_x bond and the symbol $\top\top$ represents a π_y bond.[1] This or equivalent symbolism is useful in keeping track of π_x and π_y bonds when both types are present, as is very frequently the case when one considers isovalent resonance structures in hyperconjugation.

Even in conjugation, such symbolism is useful for a clear understanding whenever triple bonds, or cumulated bonds, are present: for example $HC\overset{\perp}{\underset{\top\top}{-}}C\ddot{Cl}$, with two dative isovalent resonance structures $HC\ \underset{\top\top}{-}C\stackrel{\perp}{-}Cl^{\cdot}$, $HC\stackrel{\perp}{-}C\underset{\top\top}{-}\ddot{C}l$. of equal importance, and a third less important one; allene with the single structure $H_2C\stackrel{\perp}{-}C\underset{\top\top}{-}CH_2$, or in more detail, $H_2\underset{\top\top}{-}C\stackrel{\perp}{-}C\underset{\top\top}{-}C\stackrel{\perp}{-}H_2$; phenylacetylene with main structures like  $C\overset{\perp}{\underset{\top\top}{-}}CH$. This symbolism can of course be omitted whenever it is more trouble than it is worth.

Dative isohyperconjugation should occur in $(CH_3)_2O$ in a way similar to that in CH_3OH: $(H_3\equiv C{-})_2\ddot{O}$, $H_3\quad C{=}O^{\cdot}Me$, $MeO^{\cdot}{=}C\quad H_3^-$. CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ insofar as they may be treated as having a nearly planar arrangement of atoms bonded to the nitrogen present again a similar situation. Dative isohyperconjugation is again expected in CH_3Cl, the main structure being $H_3\equiv C{-}Cl$, the main subordinate structures $H_3^-\underset{\top\top}{-}C\stackrel{\perp}{-}Cl^+$ and $H_3^-\stackrel{\perp}{-}C\underset{\top\top}{-}Cl^+$. Dative isohyperconjugation here is closely analogous to dative isoconjugation in chloracetylene. The foregoing examples illustrate how conjugation or hyperconjugation can be either *one-dimensional* (π_x only), or *two-dimensional* (both π_x and π_y). Another interesting example is H_2CO, with isovalent structures $H_2\underset{\top\top}{-}C\stackrel{\perp}{-}O$ and $H^-{-}C\overset{\perp}{\underset{\top\top}{-}}O^+$.

In the foregoing examples the effects of isohyperconjugation are doubtless small, first because they are dative (and the effects even of dative *conjugation* are relatively moderate), and second because they are hyperconjugative. The writer sees no sufficient reason, however, to assume that they are entirely negligible.

Another interesting example is that of H_2O_2, where on the basis of spectroscopic evidence[8] the two H-O-O bonds are in planes nearly perpendicular to each other. It is easily shown that a planar structure, either *cis* or *trans*, offers no possibility of isovalent hyperconjugation; only ordinary hyperconjugation is then possible. If steric repulsions between the two H atoms were a determining factor, the planar *trans* form should be preferred. For a 90° twisted form, dative isohyperconjugation can occur to its maximum possible extent. Besides the main structure,  , two

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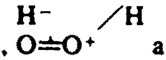
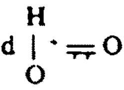
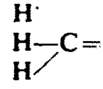
[8] E. Hirota, *J. Chem. Phys.* **20**, 136 (1958), and references cited therein.

dative isovalent structures,  $\overset{H^-}{O}\overset{+}{=}O^{+}{\diagup}H$ and  $\overset{H}{\underset{O}{|}}{}^{\cdot}\underset{\mp}{=}OH^-$ can be written. If we neglect the fact, whose effect here should be minor, that the HOO angles are somewhat greater than 90°, the left-hand OH bond is formed by a π_z oxygen electron leaving a π_y (and an *s*) lone pair on the atom, while the right-hand OH bond is formed by a π_y oxygen electron leave a π_z lone pair on that atom. By dative action, either a π_z or a π_y $O{=}O$ double bond can be formed, as indicated in the isovalent structures above. Unfortunately this example cannot be used as a proof of the decisive importance of isovalent hyperconjugation, since π-electron non-bonded repulsions *also* favor the twisted form.[9] Further, the actual twisted form according to Hirota's analysis[8] is only 1·29 kcal more stable than the planar *cis* form (and 0·59 kcal more stable than the planar *trans* form).[8] Another similar example is that of N_2H_4, where again the stable configuration is a twisted one which again is favored both by non-bonded repulsions[9,10] and by isovalent hyperconjugation. In contrast, the planar structure of C_2H_4 is strongly stabilized by π_x-electron bonding although the twisted form would be favored by isovalent hyperconjugation. In $C_2H_4{}^+$, the latter apparently becomes partially dominant, causing twist. (The cases of C_2H_4 and $C_2H_4{}^+$ will be discussed below.)

A final example of dative isovalent hyperconjugation where the effects may be larger is that of boron trimethyl. The main structure is $B(-C{\equiv}H_3)_3$, and there are three isovalent structures of the type $Me_2B\overset{+}{=}C\underset{\mp}{=}H_3{}^{\cdot}$. The fact that BMe_3 does not dimerize like BH_3 suggests that it has special stability in itself, due to isovalent hyperconjugation, which is not possible in BH_3. One may of course argue that the CH_3 group cannot replace an H atom in the diborane bridge, but, (a), there is no theoretical reason why it cannot and (b) in Al_2Me_6 with structure analogous to diborane, the methyl group does function as a bridging agent.[10] To be sure, $Me_2BH_2BMe_2$ is known, suggesting that H but not Me can function in a bridge bond; but the dimerization of Me_2BH might also be explained by the lesser amount of hyperconjugation possible here; and/or H may be a *better* bridging agent than Me. Theoretical computations on hyperconjugation in BMe_3, for example by the Hückel method using reasonable empirical parameters, and with due allowance for the presence of strong $B^+{-}C^-$ σ bond polarities ("inductive effect"), would be of much interest.

(c) *Non-dative isohyperconjugation*

If its geometry conforms approximately to its conventional formula, as seems probable, the ethyl radical is a typical example of non-dative isohyperconjugation.[1] The main structure is then $H_3\overset{+}{\underset{\mp}{\equiv}}C{-}\dot{C}H_2$, with an odd π_x electron on the CH_2 carbon. The hyperisovalent resonance structure is $\dot{H}_3\underset{\mp}{=}C\overset{+}{=}CH_2$, with a quasi-$\pi_x$ odd electron on the H_3. (This is equivalent to  $\overset{H^{\cdot}}{\underset{H}{H{-}C}}{=}CH_2$, as the hyperconjugation resonance structure is often written, provided, of course, suitable resonance among three such forms is understood.) The isopropyl and *t*-butyl radicals furnish similar examples.[1] Another example, ethylene twisted through 90°, will be discussed below. Alkyl-substituted triphenylmethyl radicals, on the other hand, furnish examples where

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[9] W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.* 2, 492 (1934).

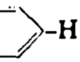
[10] R. S. Mulliken, *Chem. Rev.* 41, 207 (1947).

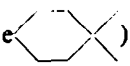
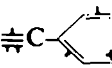
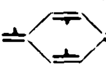
isohyperconjugation, though theoretically expected, is apparently unimportant, but for reasons which appear understandable (see footnote 33).

(d) *Homodative isohyperconjugation*

The alkyl and the aromatic carbonium ions furnish numerous examples of homodative isohyperconjugation. In agreement with experimental evidence, the energy effects of isovalent hyperconjugation should be at a maximum in the homodative subclass. LCAO-MO computations on the alkyl ions (assuming conventional geometry) have been presented by Muller and the writer.[1] Taking the ethyl cation as a typical example, the main structure is $H_3\overset{\rightarrow}{\underset{\pi}{\equiv}}C \rightarrow C^{+}\underset{\pi}{\leftrightarrows}H_2$, the hyperisovalent resonance structure is $H_3^{+}\underset{\pi}{\leftrightarrows}C\overset{+}{\underset{-}{=}}C\cdot H_2$. Arrowheads have been added to indicate inductive effects; for the π_x electrons, these are automatically included in the LCAO computations (cf. Section II (a) for a fuller discussion in the analogous case of homodative isoconjugation). In our paper, we also included π_y inductive effects because we allowed for π_y as well as π_x hyperconjugation. (Here π_y hyperconjugation is of the ordinary, not isovalent type.)

A related example would be that of the ethyl anion.

The carbonium ions derived from benzene and alkylated benzenes by addition of a proton have been extensively studied by McCaulay and by Kilpatrick, and their collaborators, and those from polycyclic aromatic hydrocarbons by Mackor *et al.*[11] Semi-empirical LCAO computations on the simplest of these, the benzenium ion $C_6H_7^{+}$, indicate that homodative isohyperconjugation between three ring-positive isovalent structures of the type  $\overset{+}{\underset{-}{=}}H_2$ and two hyperisovalent Kekulé-type structures  $-H_2^{+}$ should strongly stabilize the ion.[12] Let us call this Kekulé hyperconjugation.

In all the methylated (or alkylated) benzene carbonium ions, the same type of isohyperconjugation should occur, *plus* methyl (or alkyl) isohyperconjugation involving homodative transfer of π-electron positive charge to the methyl (or alkyl) groups.[13] The simplest case is that of the toluenium ion. This should exist in six *isomeric forms*[14] depending on which of ring atoms 1 to 6 accepts the proton. Let us consider the 4-toluenium ion (Me)$^{+}$, with its three isovalent ring-positive structures such as $H_3\underset{\pi}{\overset{+}{\equiv}}C-$$\overset{+}{\underset{-}{=}}H_2$ and two isovalent Kekulé-hyperconjugation structures, just as in the benzenium ion, and *in addition* one isovalent methyl-hyperconjugation structure $H_3^{+}\underset{\pi}{\equiv}C\overset{+}{\underset{-}{=}}$$=H_2$. Isovalent methyl hyperconjugation is possible in toluenium ions for 2, 4, or 6 addition of the proton; less stable isomers with the added

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[11] E. L. Mackor, G. Dallinga, J. H. Kruizinga and A. Hofstra, *Rec. Trav. Chim. Pays-bas* 75, 836 (1956); E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.* 54, 66, 186 (1958); and numerous other papers.

[12] N. Muller, L. W. Pickett and R. S. Mulliken, *J. Amer. Chem. Soc.* 76, 4770 (1954). Note that all π-electron inductive effects are automatically included (cf. discussion in Section II(b) of the analogous situation in homodative isoconjugation).

[13] D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.* 73, 2013 (1951); D. A. McCaulay's, *Tetrahedron*. This issue.

[14] The word "isomeric" is not strictly appropriate here, since some of the forms are indistinguishable. But its use, in this section, will be very helpful in making things clear.

proton in the 1, 3, or 5 position should exist but without methyl isohyperconjugation, hence with stability about like the benzenium ion. Attribution of the observed increasing base strengths of increasingly methylated benzenes to methyl hyperconjugation, as proposed by McCaulay,[13] by no means necessarily implies that this is more effective than Kekulé hyperconjugation. The latter (which is equally present[15] in *all* the methylated benzenes, and for *all six* isomers of each) should be present as a more or less constant background factor in all, supplemented by methyl hyperconjugation to an extent which depends on the numbers and positions of the substituted methyl groups. Although the basicity of benzene is very low, it seems entirely likely that the Kekulé hyperconjugation may be of predominant importance in creating a *minimal* basicity in benzene which is then *enhanced* to notable levels of strength by successive increments of methyl hyperconjugation. Theoretical computations by the LCAO-MO method on methylated benzenes would be of great interest in this connection.

As already noted, each carbonium ion derived from benzene or any methylated benzene by protonation can exist in six isomeric forms. For *each* of these isomers, methyl isohyperconjugation with some definite number M of methyl groups, from zero to a maximum of three, can occur, as one can see by drawing VB structures and keeping only those which are isovalent with the ring-positive and Kekulé-hyperconjugated structures.[16] If isohyperconjugative stabilization is the main determining factor, the basicity of any methylated benzene should depend primarily on the *largest M value* possessed by *any of the isomers* of its carbonium ion, and should be greater for larger maximum M; isomers with less than the largest M for that particular molecule should count very little for its basicity, because of their lower stability. On the other hand, the basicity should be greater the greater the *number* N of isomers of *maximum* M.

Table 1 lists the numbers of isomers of each M type for each of the methylated benzenes, and also gives the relative basicity as reported by McCaulay in his Conference paper. It will be seen that the various molecules fall into groups in which the basicity is indeed primarily governed by the maximum M which appears for any of its isomeric forms, and also increases somewhat with the N value for maximum M. The striking increases in basicity from *p*- and *o*-xylene to *m*-xylene and to mesitylene parallel an increasing maximum M.

Inspection of Table 1 shows that an additional factor also somewhat influences basicity. In parentheses following the number N of isomers for any M type for any carbonium ion, in Table 1, is a number (say n) which says how many of these isomers have the added proton attached to the same ring atom as a methyl group. It will be seen that basicity increases somewhat as n/N for the *maximum-M* isomers increases. For example, the mesitylene, isodurene, and pentamethylbenzene carbonium ions all have the same N(3) for the same maximum M (3) but with $n = 0$, 1, and 2 respectively; and the basicity increases with n/N. The hexamethylbenzene carbonium ion has $N = 6$ for its maximum M (again 3) but now $n/N = 1$ since the added proton is necessarily attached to a methyl-bearing ring carbon in *all* isomers. Both effects evidently

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[15] Except that proton addition to methylated ring atoms (which should certainly occur) may be somewhat more (or less) effective than to non-methylated ring atoms: half-CC instead of all-CH hyperconjugation.

[16] Additional hyperconjugated structures having one less valence bond (*ordinary* hyperconjugation) although left out of account here, may perhaps also have *some* influence in determining basicity.

TABLE 1. NUMBERS N OF ISOMERS OF METHYLATED-BENZENE CARBONIUM IONS BELONGING TO VARIOUS M TYPES (first four columns of numbers; see text for explanation of M).

Each number N is followed by a second number n in parentheses which tells how many of the N isomers have the proton attached to a methyl-bearing ring carbon. The basicity (last four columns of numbers from McCaulay's Conference paper[13]) is seen to be determined essentially only by those isomers which have maximum M (indicated in the first four columns by bold face type).

					Basicity (McCaulay) and Type			
	$M = 0$	$M = 1$	$M = 2$	$M = 3$	$M = 0$	$M = 1$	$M = 2$	$M = 3$
Benzene	**6(0)**				(very small)			
Toluene	3(1)	**3(0)**				(0·01)		
p-Xylene		**6(2)**				1		
o-Xylene		**6(2)**				2		
m-Xylene	3(2)		**3(0)**				20	
Mesitylene	3(3)			**3(0)**				2800
Pseudocumene		3(2)	**3(1)**				40	
Durene			**6(4)**				120	
Prehnitene			**6(4)**				170	
*iso*Durene		3(3)		**3(1)**				5600
Pentamethylbenzene			3(3)	**3(2)**				8700
Hexamethylbenzene				**6(6)**				89000

increase the basicity. The enhancement of basicity associated with attachment of a proton to a methyl-bearing ring carbon may reasonably be explained as due to inductive stabilization of isomers of this type, consequent on release of some negative charge by the methyl carbon to the ring carbon to which it is attached.

Further minor factors somewhat influencing the basicity of aromatic carbonium ions perhaps include steric effects, ordinary hyperconjugation,[16] the presence of isomers with less than maximum M values, differences in solvation effects, and perhaps others.

It is of interest that Table 1 indicates that the basicity of toluene, too small to be accurately determined but estimated as 0·01 by McCaulay, should be considerably larger (say about 0·3) to be consistent with the rest of Table 1.

(e) *Isohyperconjugation in 90°-twisted ethylene and in* $C_2H_4^+$.

Ethylene with the two CH_2 planes twisted to perpendicularity ("perp. C_2H_4") was perhaps the first recognized example of hyperconjugation, although the name was not then used. Later Roothaan and the writer made a series of LCAO-MO computations on ethylene in its ground state and three excited states, and on $C_2H_4^+$, for angles of twist ϕ ranging from 0° (planar) to 90°.[17] Semiempirical parameter values similar to those used in more recent computations[5] were used, and the effect of π-electron overlap was included. Both π_x and π_y hyperconjugation were taken into account, as becomes obviously necessary as $\phi \to 90°$. Our 1947 paper was intended to be preliminary, and failed to report certain details of our computations. Some of the results on C_2H_4 which are of particular interest in the present connection will be reported below.

For planar C_2H_4, the VB structure is $\mathrm{H_2C\doteq CH_2}$, or if one wishes to consider π_y hyperconjugation (which is second-order, and *not* isovalent), $\mathrm{H_2\equiv C\doteq C\equiv H_2}$. For perp. C_2H_4, the main VB structure $\mathrm{H_2\equiv \dot{C}-\underset{\cdot}{C}\doteq H_2}$ is in resonance with the two

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[17] R. S. Mulliken and C. J. Roothaan, *Chem. Rev.* **41**, 219 (1947). Note that the symbol δ is generally used to mean what is here called δ/β.

isovalent hyperconjugated structures $\underset{\cdot}{H}_2-\dot{C}\equiv C\doteq H_2$ (π_x hyperconjugation) and $H_2\equiv C\doteq \underset{\cdot}{C}-\dot{H}_2$ (π_y hyperconjugation).

For planar $C_2H_4^+$ the VB structure may be represented as $H_2\equiv C^{+\frac{1}{2}}\doteq C^{+\frac{1}{2}}\equiv H_2$. For perp. $C_2H_4^+$, the electronic state would be ^2E of symmetry D_{2d}, for which there are two independent though equivalent orbital wave functions (twofold orbital degeneracy). For *one* of these (in the other, the · and + would be interchanged), the main VB structure $H_2\equiv\dot{C}-\underset{+}{C}\doteq H_2$ is in resonance with the homodatively isovalent hyperconjugated structure $H_2-\dot{C}\equiv C\doteq C-H_2$ and with the neutrally isovalent structure $H_2\equiv C\doteq C-H_2$. (Note that these three structures correspond to those of perp. C_2H_4 if one replaces one · by a + in each.)

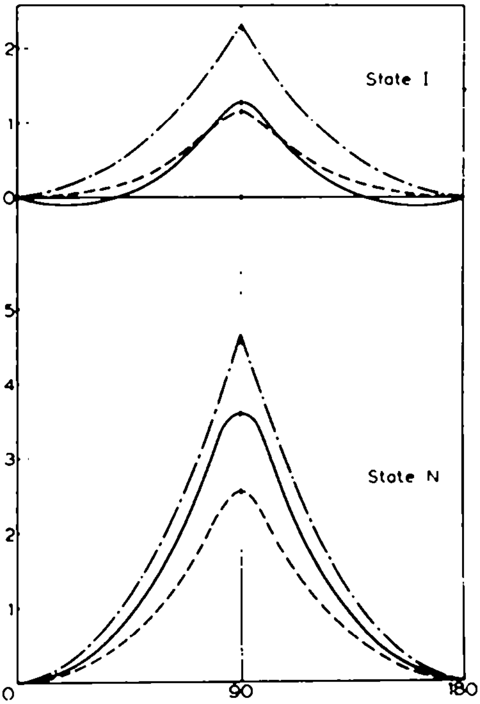

FIG. 2. Theoretically computed orbital energies (in eV) of ground states of C_2H_4 (state N, below) and $C_2H_4^+$ (state I, above) as functions of angle of twist ϕ. From unpublished work of Mulliken and Roothan (cf. reference 18). Full line curves are for best parameter values used ($\beta^* = 2\beta$, $\delta = 0$, $\beta = -3$ eV; dot–dash curves are for the case of *no hyperconjugation*; dashed curves for $\beta^* = 1.5\beta$, $\delta = \beta$, $\beta = -3$ eV.

Fig. 2 shows the computed curves that we obtained for C_2H_4 and $C_2H_4^+$, but did not publish in 1947, for each of three choices of semiempirical parameters:[17] (a) no hyperconjugation ($\beta^* \gg\!> \beta$); (b) $\beta^* = 1{\cdot}5\beta$, $\delta = \beta$; (c) $\beta^* = 2\beta$, $\delta = 0$. Of these, the third choice is the most nearly correct according to recent views (β^*/β measures the degree of reluctance of an H_2 to give up its quasi-π bond in favor of a C C bond, while δ measures the tendency of H_2 to release an electron to carbon; values of β^*/β of 2·0 and of δ about $-0{\cdot}3\beta$ to $-0{\cdot}5\beta$, corresponding to electropositive behavior of the H_2 group, have been currently accepted.[5]) Our curve for case (c) shows about 20 kcal stabilization by isovalent hyperconjugation in case (c); with $\delta/\beta < 0$, this would be somewhat increased.

For $C_2H_4^+$, allowance should have been made, as in later papers,[1, 11] for an additional parameter to take account of the increase in electronegativity of positively charged atoms, but it is probable that this and $\delta/\beta < 0$ would give for $C_2H_4^+$ an energy-angle curve of the same qualitative character as in case (c) but with intensified departure from cases (a) and (b). It will be noted that curves (a) and (b) have a flat minimum at $\phi = 0°$ corresponding to stability of planar $C_2H_4^+$, while case (c)—evidently as a result of incipient isovalent hyperconjugation—shows a low maximum at $\phi = 0°$ and shallow minima at perhaps about $\phi = 30°$; but still a fairly high barrier at $\phi = 90°$. This partial twisting may be understood by considering the following pair of VB structures for planar $C_2H_4^+$: $\underset{+}{H_2}\text{–C}\overset{+}{=}\text{C}\underset{+}{=}H_2$ and $H_2\underset{+}{=}\text{C}\overset{+}{=}\text{C–}H_2$. As long as $C_2H_4^+$ remains planar, these *cannot mix* with the main VB ground state structure given above, because they belong to excited states with wave functions sharply different in symmetry from the latter. But if twisting occurs, the symmetry distinctions are relaxed, and they can begin to mix in. (It may be remarked that description and understanding are easier using LCAO-MO theory.)[17]

It is now of great interest that experimental vacuum-ultraviolet spectroscopic data[18] on Rydberg states of C_2H_4 and C_2D_4 (which are essentially states of the ethylene positive ion plus an electron in an orbital so large that it has scarcely any influence on the molecular geometry) show unusual features which seem to be impossible to reconcile with a planar structure for $C_2H_4^+$, but which seem to be just about what might be expected for an energy-angle curve like the computed one for case (c) in Fig. 2. While an alternative interpretation of the spectroscopic data, involving excitation of a low-frequency out-of-plane bending instead of twisting frequency in the upper state, cannot be excluded with certainty, it seems much less probable. However, it is planned to make further experimental studies as soon as feasible which it is hoped may settle this question definitely, since there seems to be here an important probable confirmation of predicted effects of hyperconjugation.

III. SACRIFICIAL (ORDINARY) CONJUGATION AND HYPERCONJUGATION

(a) *General discussion*

Ordinary conjugation and hyperconjugation are *sacrificial*, in the sense that π-electron resonance stabilization is effected only by structures in which, as compared with the single dominant VB structure, one π bond has been lost. In the following discussion in this Section the qualifying adjective "ordinary" or "sacrificial" will usually be assumed to be understood when "conjugation" or "hyperconjugation" is used.

In the familiar example of 1,3-butadiene, with the dominant structure $H_2C{=}CH{-}CH{=}CH_2$, there are three minor structures which may collectively be symbolized by $H_2\overset{\circ}{C}{-}CH{=}CH{-}\overset{\circ}{C}H_2$. The two $\circ$ here represent either two $\cdot$ (odd electrons, between which there is a "long bond"), or $+$ and $-$, or $-$ and $+$ (two equivalent ionic structures of opposite polarity).

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[18] P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.* 23, 1895 (1955); P. G. Wilkinson, *Canad. J. Phys.* 34, 643 (1956). Stretching of the molecule in the ionized state also occurs; the twisting effect is approximately independent of this according to the spectroscopic data. When these papers were written the present Fig. 2, buried in the files, had been forgotten. In the first of these papers, an effort was made to explain the Rydberg spectra using a planar model with a very flat minimum for $C_2H_4^+$. However, as time went on, we felt more and more convinced that the data pointed to a twisted model. Finally, only recently, the earlier calculated curves here reproduced as Fig. 2, were rediscovered.

Very likely (although this point seems usually not to be recognized) the two ionic structures are much less important than the long-bond structure, since much more energy would be needed to create them. One should also especially note that this pair of structures involves *two-way π* dative action, as contrasted with the one-way π dative action involved in the subordinate VB structures in dative isoconjugation.

[*Note added* 20 *November* 1958. Recent calculations on butadiene by Berry[19] based on LCAO-MO wave functions throw light on this question. He finds that the VB structures $C{=}C{-}C{=}C$, $\dot{C}{-}C{=}C{-}\dot{C}$, and $\overset{\pm}{C}{-}C{=}C{-}\overset{\mp}{C}$ make up roughly 35, 5, and 0·6 per cent of the wave function, while simple ionic structures $C{=}C{-}C^{+}{-}C^{-}$ and $C^{\pm}{-}C^{\mp}{-}C{=}C$ make up 29 per cent and dispersion-type structures[20] $C^{+}{-}C^{-}{-}C^{+}{-}C^{-}$ and $C^{-}{-}C^{+}{-}C^{-}{-}C^{+}$ 30 per cent. These figures substantiate the unimportance of $C^{\pm}{-}C{=}C{-}C^{\mp}$, but indicate that other ionic structures may be more important even than $C{-}C^{\cdot}{=}C{-}\dot{C}$ in contributing to the π-electron resonance energy in conjugation. It seems likely that analogous ionic structures are important in all forms of conjugation and of hyperconjugation, both sacrificial and isovalent.]

Conjugation in diacetylene, according to π-electron theory, is entirely analogous to that in butadiene, except that it is *two-dimensional* instead of one-dimensional: predominant structure $HC\overset{+}{\underset{\pi\pi}{=}}C{-}C\overset{+}{\underset{\pi\pi}{=}}CH$, secondary structures $\overset{\circ}{H}C\underset{\pi\pi}{=}C\overset{+}{=}C\underset{\pi\pi}{=}\overset{\circ}{C}H$, $H\underset{\circ}{C}\overset{+}{=}C\underset{\pi\pi}{=}C\overset{+}{=}\underset{\bullet}{C}H$, and (very minor) $H\overset{\circ}{\underset{\bullet}{C}}{-}C\overset{+}{\underset{\pi\pi}{=}}C{-}\overset{\circ}{\underset{\bullet}{C}}H$.

Examples of a structural situation which on the basis of quantum theory should also be described as conjugation occur in the cumulenes, for example one-dimensional conjugation for $H_2C\overset{+}{=}C\underset{\pi\pi}{=}C\overset{+}{=}CH_2$ with secondary structures $H_2\overset{\circ}{C}{-}C\overset{+}{\underset{\pi\pi}{=}}C{-}\overset{\bullet}{C}H_2$ and two-dimensional conjugation for $H_2C\overset{+}{=}C\underset{\pi\pi}{=}C\overset{+}{=}C\underset{\pi\pi}{=}CH_2$ with secondary structures $H_2\overset{\bullet}{C}{-}C\overset{+}{\underset{\pi\pi}{=}}C{-}\overset{\circ}{C}\underset{\pi\pi}{=}CH_2$ and $H_2C\overset{+}{=}\underset{\circ}{C}{-}C\overset{+}{\underset{\pi\pi}{=}}C{-}\underset{\circ}{C}H_2$.

Ordinary *first-order hyperconjugation* is similar to ordinary conjugation in that there is one principal VB structure, and one bond is lost in the subordinate structures. It differs, however, in that the lost bond is a [π] instead of a π bond. For example, in propylene (one-dimensional hyperconjugation) with main structure $H_3\overset{+}{\underset{\pi\pi}{=}}C{-}CH\overset{+}{=}CH_2$, the subordinate structures are $H_3^{\circ}\underset{\pi\pi}{=}C\overset{+}{=}CH{-}\overset{\bullet}{C}H_2$. In methylacetylene (two-dimensional hyperconjugation) with main structure $H_3\overset{+}{\underset{\pi\pi}{=}}C{-}C\overset{+}{\underset{\pi\pi}{=}}CH$, the major subordinate structures are $H_3^{\circ}\underset{\pi\pi}{=}C\overset{+}{=}C\underset{\pi\pi}{=}\overset{\bullet}{C}H$ and $\underset{\circ}{H_3}\overset{+}{=}C\underset{\pi\pi}{=}C\overset{+}{=}\underset{\bullet}{C}H$. Another example of two-dimensional hyperconjugation is found in allene, with main structure $H_2\underset{\pi\pi}{=}C\overset{+}{=}C\underset{\pi\pi}{=}C\overset{+}{=}H_2$ and secondary structures $H_2^{\circ}{-}C\overset{+}{\underset{\pi\pi}{=}}C{-}\overset{\bullet}{C}\overset{+}{=}H_2$ and $H_2\underset{\pi\pi}{=}\underset{\circ}{C}{-}C\overset{+}{\underset{\pi\pi}{=}}C{-}\underset{\circ}{H_2}$. Here the term hyperconjugation is used to describe a situation analogous to conjugation in the cumulenes.

First-order hyperconjugation, like conjugation in butadiene and diacetylene, involves *two-way* dative action in the ionic subordinate VB structures. However, this may be slightly polar, in the sense that, for example in propylene, the structures $H_3^{+}\underset{\pi\pi}{=}C\overset{+}{=}CH{-}C^{-}H_2$ may be a little more prominent than $H_3^{-}\underset{\pi\pi}{=}C\overset{+}{=}CH{-}C^{+}H_2$, leading to a slight over-all polarity and dipole moment. But there is no theoretical justification for assuming that *only* the former of these two structures is important. In fact it is by no means clear theoretically that *either* of the two ionic structures should be comparable in importance with the long-bond structure $H_3^{\bullet}\underset{\pi\pi}{=}C\overset{+}{=}CH{-}\overset{\bullet}{C}H_2$. It seems

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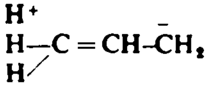
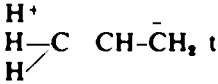
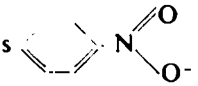
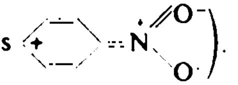
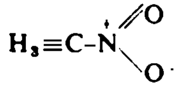
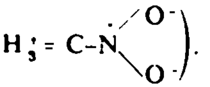
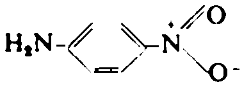
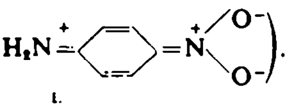
[19] R. S. Berry, *J. Chem. Phys.* (1959); based on wave functions obtained by him previously [*J. Chem. Phys.* **26**, 1060, (1957)]. For certain rather esoteric qualifications on the meaning of the percentages quoted, reference must be made to his new article.

[20] W. T. Simpson, *J. Amer. Chem. Soc.* 73, 5363 (1951); *Ibid.* 77, 6164 (1955).

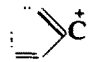
to the writer that the customary use of a symbolism such as  $\overset{H^{+}}{H}{-}C=CH{-}\bar{C}H_2$ and corresponding emphasis on electron release, without any mention of an oppositely polarized ionic structure and, especially, of the long-bond structure, may be seriously misleading.

[*Note added* 20 *November* 1958. Berry's calculations on butadiene lend strong support, by analogy, to these remarks. At the same time the probable importance of dispersion-type ionic structures offers a reasonable mechanism for appreciable electron release, through mild predominance of $H_3{}^{+}\equiv C\cdot{-}C^{\cdot}H{-}C^{-}H_2$ over $H_3{}^{\cdot}\equiv C^{+}{-}C^{-}H{-}C^{\cdot}H_2$.]

In this connection, the fact, emphasized by Dewar, that the observed dipole moments in propylene and other hyperconjugated molecules can be explained without assuming such structures as  $\overset{H^{+}}{H}{-}C\;\;CH{-}\bar{C}H_2$ to be of appreciable importance, is significant. It seems then entirely possible that *both* the above-indicated ionic structures are of minor importance in typical cases of ordinary hyperconjugation. This, however, would not necessarily imply that the *long-bond* structure is also unimportant, nor that ionic structures are *always* unimportant in hyperconjugation. [*Note added* 20 *November* 1958. It seems likely that π-electron resonance may contribute appreciably to the dipole moment through a mild preponderance of $H_3{}^{\cdot}=C^{-}{-}C^{+}{-}C^{-}$ over $H_3{}^{-}=C^{+}{-}C^{-}{-}C^{\cdot}$. (The structures $H_3{}^{\cdot}\;\;C^{-}{-}C{=}C$ and $H_3{}^{-}\cdot C^{\cdot}{-}C{=}C$ with the former preponderant need not be considered here, since they would also be present in the CH_3 group in the absence of π-electron hyperconjugation resonance.)]

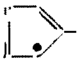
Before going further, an important difference between isovalent and sacrificial conjugation and hyperconjugation should be emphasized: while in the isovalent cases three important subclasses (dative, non-dative, and homodative) need to be distinguished, in the sacrificial case most examples (including all those thus far discussed) belong to the non-dative (or two-way dative) subclass. However, there is also a dative sacrificial subclass, whose most familiar examples are the nitro-compounds, for example nitrobenzene (four isovalent main structures such as  with four π_y bonds, and three sacrificial one-way dative structures such as . Nitroethylene, nitroacetylene, and the like, would belong to the same subclass. Similarly, nitromethane is an example of dative sacrificial hyperconjugation (main structure , sacrificial one-way dative structure . On the other hand, *p*-nitroaniline, like aniline, is an example of dative isovalent conjugation (main structures such as , isovalent dative structure .

in stabilizing respectively the allyl and methyl derivatives of aldehydes and ketones.

In fulvene, the presence of polar conjugation to an extent sufficient to create a dipole moment of about 1·2 D, and in the theoretically expected direction, seems to have been definitely established.[21] Besides the predominant VB structure  CH_2, there should here be five sacrificial structures, for example  $\overset{+}{C}H_2$, together with five corresponding structures with the charges reversed, and four long-bond structures such as  $\dot{C}H_2$. [*Note added* 20 *November* 1958. Again, dispersion-type ionic structures, for example,  $\dot{C}H_2$, are doubtless important.]

This case differs in an important way from that of butadiene or acrylaldehyde in which there is only *one* structure of each type (- ∔ ∔ -, and · ·). Namely, isovalent resonance (homodative, moreover, in the cases of the ionic structures) can occur *within* each group of sacrificial structures, causing pronounced extra stabilization. Under these circumstances, one may reasonably expect conjugation to have much more important effects than in butadiene or acrylaldehyde. But further, in view of the special, benzene-like, stability of the *cyclo*pentadienyl anion, it is reasonable to expect the ring-negative structures to predominate over the others. This result is confirmed theoretically by LCAO-MO computations and experimentally by the observed dipole moment.[21]

Similar results and conclusions have been found[21] for azulene. Here there is a *large number* of sacrificial conjugated structures, resonance among which should make conjugation important here. Further, the known benzene-like stability of the *cyclo*pentadienyl anion and the tropylium cation lead one to expect an over-all negative charge on the five-ring and positive charge on the seven-ring, and a dipole moment of corresponding polarity. The observed dipole moment is 1·0 D, which (although its sign has not been demonstrated experimentally) seems to be in reasonable agreement with the results of LCAO-MO computations.[21]

*cyclo*Pentadiene is the hyperconjugative analogue of fulvene, with a main structure  H_2 and five sets of sacrificially hyperconjugated VB structuressuch as  $-H_2^{+}$, of which ring-negative members may be expected to predominate for the same reason as in fulvene.[22]

IV. HYPERCONJUGATION IN POSITIVE MOLECULE-IONS

Particularly in mass spectroscopy, there is increasing interest in the structure of positive ions. In even-electron ions (radical ions), homodative isovalent conjugation or hyperconjugation appears to have an important stabilizing effect [cf. Sections II(b) and II(d)]. In odd-electron ions (molecule ions) we encounter also homodative situations which are half-way between isovalent and sacrificial. Observed ionization

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[21] G. W. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 264 (1949). The measurements were actually made on several derivatives, rather than on fulvene itself, but the reasoning back to fulvene seems convincing. Azulene: see also R. Pariser, *J. Chem. Phys.* **25**, 1112 (1956); W. G. Schneider, H. J. Bernstein and J. A. Pople, *J. Amer. Chem. Soc.* **80**, 3497 (1958).

[22] For results of LCAO-MO calculations, cf. G. Berthier and B. Pullman, *Bull. Soc. Chim. Fr.* **15**, 788 (1948); B. Pullman and A. Pullman, *Les Theories Electroniques de la Chimie Organique*, Masson et Cie, Paris (1952).

In non-dative sacrificial conjugation and hyperconjugation, one may of course distinguish between non-polar and polar cases (i.e., symmetrical or unsymmetrical two-way dative action), but the distinction is one of degree rather than kind. For example, conjugation in butadiene is necessarily non-polar, by symmetry, while first-order hyperconjugation in propylene must be polar, though perhaps only slightly so.

At this point something should be said about ordinary *second-order hyperconjugation*. This is now believed[6] to be a very small effect, and because of its universality it is difficult or impossible to isolate experimentally, but there seems to be no adequate reason to dismiss it as entirely negligible. Typical examples are found in ethylene (principal VB structure $H_2\underset{\pi}{=}C\pm C\underset{\pi}{=}H_2$, hyperconjugative structures $\underset{\circ}{H}_2-C\overset{+}{\underset{\pi}{=}}C-\underset{\circ}{H}_2$) and ethane (principal structure $H_3\overset{+}{\underset{\pi}{=}}C-C\overset{+}{\underset{\pi}{=}}H_3$, main hyperconjugative structures $H_3^{\circ}\underset{\pi}{=}C\pm C\underset{\pi}{=}H_3$ and $\underset{\circ}{H}_3\pm C\underset{\pi}{=}C\pm\underset{\circ}{H}_3$). It will be noticed that second-order hyperconjugation is one-dimensional in ethylene, two-dimensional in ethane; also that is non-polar in both cases.

Characteristic of second-order hyperconjugation as described by VB structures is the fact that *two* [π] bonds are sacrificed, while one π bond is gained. There is, however, a net loss of one (π or [π]) bond just as in ordinary conjugation or first-order hyperconjugation; but it should be noted that this occurs in a way which differs from hyperconjugation in the same way that hyperconjugation differs from conjugation, so that the effect might well be called *hyper-hyperconjugation*.

An example in which the LCAO-MO treatment of second-order hyperconjugation differs considerably from the usual VB treatment is found in the ethyl ion.[1] Here (in addition to isovalent hyperconjugation) we have second-order hyperconjugation involving in the VB method just the main structure $H_3\overset{+}{\underset{\pi}{=}}C-C^{+}\underset{\pi}{=}H_2$ and the subordinate structures $\underset{\circ}{H}_3\pm C\underset{\pi}{=}C^{+}-\underset{\circ}{H}_2$. The LCAO-MO treatment[1] (provided suitable electronegativity-difference parameters are introduced) automatically includes also an important amount of the structure $H_3\overset{+}{\underset{\pi}{=}}C-\overset{+}{\underset{-}{C}}-\underset{+}{H}_2$ in which the right-hand carbon atom as a whole is neutral. From the VB standpoint, the inclusion of this structure would be called an inductive effect. This is a rather extreme example of a characteristic feature of the LCAO-MO method which automatically includes any inductive effects which may occur in the π-electron system (σ-electron inductive effects—cf. Section II(a)—are of course not included).

(b) *Polar effects in conjugation and hyperconjugation*

As has been emphasized in Section III(a), the ionic secondary structures in ordinary "non-dative" conjugation and hyperconjugation occur in pairs of opposite polarity. The result may be non-polar, but if the atoms or groups between which, in these ionic structures, charge transfer takes place, differ in electronegativity, then some net polarity results. For conjugation, a simple example is H_2C CH–CH O, in which the secondary structure H_2C^{+}-CH -CH–O obviously would predominate over H_2C –CH - CH–O^{+}. [*Note added* 20 *November* 1958. Probably much more important is predominance of H_2C^{+}–C H–$C^{\cdot}$H–O^{-} over H_2C^{-}-C^{+}H–C^{-}H–$O^{\cdot}$.][2] For hyperconjugation, a similar example is $H_3\equiv C$–CH -O, where H_3^{+} C - CH–O^{-} must predominate over H_3 C CH–$O^{\cdot}$. [*Note added* 20 *November* 1958. Probably much more important is predominance of H_3^{+}= C –$C^{\cdot}$H–O^{-} over H_3^{-} C^{+}–C H–$O^{\cdot}$.] It seems possible that the polar effects in these cases may be of appreciable importance potentials suggest that these ions also are rather strongly stabilized by conjugation and hyperconjugation.

The $C_2H_4^{\cdot}$ ion has already been discussed in Section III(e). For planar $C_2H_4^{+}$, isovalent resonance between the two main structures $H_2C^{\cdot}-\dot{C}H_2$ and $H_2\dot{C}-\overset{+}{C}H_2$, each a single-bonded structure, results in the equivalent of a half π bond. This may be summarized as $H_2C'\doteq C'H_2$, where C′ means $C^{\cdot\frac{1}{2}}$.

The ionization potential of 1,3-butadiene is 1·45 V smaller than that of ethylene. This fact can be understood[23] in terms of much greater π_x-electron resonance stabilization by conjugation in the positive ion than in the neutral molecule. In the positive ion, the main VB structures may be described as $H_2C=CH-C'H\doteq C'H_2$ and $H_2C'\doteq C'H-CH\ \ CH_2$ (that is, $H_2C=CH-C^{\cdot}H-\dot{C}H_2$, $H_2C\ CH-\dot{C}H-C^{\cdot}H_2$ with resonance, and $H_2C^{\cdot}-\dot{C}H-CH=CH_2$, $H_2\dot{C}-C^{\cdot}H-CH=CH_2$ with resonance). Isovalent resonance between these is supplemented by resonance with the half-sacrificial structures $H_2\dot{C}-CH=CH-C^{\cdot}H_2$ and $H_2C^{\cdot}-CH=CH-\dot{C}H_2$, the over-all result being a much stronger conjugative effect than in the butadiene molecule. [*Note added* 20 *November* 1958. Probably dispersion-type structures such as $H_2C^{\cdot}-C\ \ H-C^{\cdot}H-\dot{C}H_2$ are also important.]

Homodative resonance within the π_x-electron system here distributes the positive charge fairly evenly over the carbon atoms, but a small amount of σ charge redistribution, by inductive effects in the σ bonds, must occur to alleviate in part an excess π_x positive charge on the two outer carbon atoms. Some further redistribution of charge by inductive electron release from the hydrogen atoms, via the C–H bonds, must of course also occur, and thereby contribute somewhat to the stabilization energy. But it seems likely that the major part of the stabilization energy is due to π_x-electron resonance.

In the positive ion of propylene, $C_3H_6^{+}$, with main structure $H_3\underset{\pi\pi}{\equiv}C-C'H\overset{+}{=}C'H_2$ one has homodative isovalent half-hyperconjugation with $H'_3\underset{\pi\pi}{\overset{+}{\equiv}}C'-CH\overset{+}{=}CH_2$ and homodative half-sacrificial hyperconjugation with $H_3^{\cdot}\underset{\pi\pi}{=}C\overset{+}{=}CH-\dot{C}H_2$ and $\dot{H}_3\underset{\pi\pi}{=}C\overset{+}{=}CH-C^{\cdot}H_2$ (altogether two main and four subordinate VB structures). The minimum ionization potential of propylene is 0·79 V lower than that of ethylene.[24] The difference may reasonably be ascribed largely to stabilization of the positive ion in consequence of methylation. (There is no reasonable doubt that it is a π_x electron which has been removed in the ground states of both the ethylene and the propylene ion.) Further, the stabilization energy can reasonably be identified in considerable part with homodative hyperconjugation energy, the situation being similar to that in the ethyl ion and in the toluenium ion [cf. Section III(d)]. However, electron release from the several hydrogen atoms by non-π_x (i.e. σ, [σ], and [π_y]) inductive effects must contribute very considerably to the stabilization energy (as also, though to a lesser extent, in the alkyl and methylated-benzene carbonium ions).

Observed further lowerings of ionization potential by further methylation or alkylation of ethylene[24] may be accounted for in the same way. A similar explanation can be given for the fact[24] that alkylation considerably lowers the ionization potentials of unsaturated and aromatic hydrocarbons in general.

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[23] J. Fain and A. L. Matsen, *J. Chem. Phys.* **26**, 376 (1957).

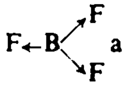
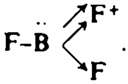
[24] W. C. Price, *Chem. Rev.* **41**, 257 (1947) lists the ionization potentials of a large number of compounds and their alkyl deratives (but see K. Watanabe, *J. Chem. Phys.* **26**, 542, 1773 (1957) for better values of some of the ionization potentials). He explains the lowering of ionization potentials by methylation in much the same way as here.

The alkyl derivatives of HCl, H_2O, H_2S, NH_3 and like molecules constitute another class of molecules in which substitution of alkyl groups for hydrogen atoms gives rise to lowered ionization potentials.[24] Here again, as in the alkylated aromatic and unsaturated compounds, hyperconjugation should help to stabilize the molecule ions. However, it is of a different and probably weaker type than in the unsaturated systems.

As examples, let us consider CH_3OH and CH_3Cl. In the ground electronic state of ionized CH_3OH, the main VB resonance structure is $H_3\equiv\!\!\rightarrow C \rightarrow \overset{+}{\ddot{O}}H$. The most important subordinate structures are $\dot{H}_3\rightrightarrows C\rightrightarrows O^{\cdot}H$ (involving isovalent hyperconjugation without charge transfer, i.e. *non-dative*) and $H'_3\equiv C'\text{–}OH$ (involving homodative half-sacrificial half-hyperconjugation: i.e. half of one $[\pi_x]$ bond is lost, but homodative transfer of positive charge from the O atom to the CH_3 group is accomplished). For CH_3Cl^+, the ground electronic state must be two-fold degenerate (^2E state), corresponding to removal of *either* a π_x or a π_y chlorine electron. The two substates are equivalent but independent; let us then consider just the one with a π_x electron removed. This is completely similar to CH_3OH^+: the main structure is $H_3\equiv\!\!\rightarrow C\rightarrow \dot{Cl}^{\cdot}$ and the chief subordinate structures are $H_3\rightrightarrows C\rightrightarrows Cl^+$ and $H'_3\equiv C'\text{–}Cl$.

It will be noted that *homodative isovalent* hyperconjugation, the strongest type of hyperconjugation, present in the ions of propylene and other alkylated aromatic or unsaturated compounds, is no longer present in CH_3OH^+, CH_3Cl^+, and the like. Hence it is reasonable to expect that non-π inductive effects may be more largely responsible for charge equalization and resulting stabilization in the latter than in the former. For the alkyl halides RCl, RBr, and RI, there is indeed strong spectroscopic evidence[25] indicating that hyperconjugation makes only relatively minor contributions to the structure of their positive ions; in other words, that the actual structure is not far from being $H_3\equiv\!\!\rightarrow C\rightarrow Cl^+$ alone.[26] However, it is generally believed that π bonding is weaker in higher-row than in first-row atoms, so that the conclusions derived from the spectroscopic evidence just cited may not apply with full force to $(CH_3F)^+$ and the ions of alkyl derivatives of H_2O and NH_3.

V. PLUVALENT CONJUGATION

Besides sacrificial and isovalent conjugation, there are a few cases in which conjugation occurs which may be described as *pluvalent* (one *more* bond in the secondary than in the main VB structure). Only *dative* pluvalent conjugation is to be expected. An example is BF_3 with main structure  $F\leftarrow B\begin{smallmatrix}\nearrow F\\ \searrow F\end{smallmatrix}$ and three equivalent pluvalent structures of the type  $F\text{–}\ddot{B}\begin{smallmatrix}\nearrow\!\!\!\nearrow F^+\\ \searrow F\end{smallmatrix}$. As is well known, resonance here causes strong stabilization.

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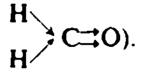
[25] R. S. Mulliken, *Phys. Rev.* **61**, 277 (1942): see especially footnote 9 and Table II, second column.

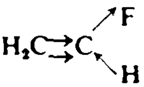
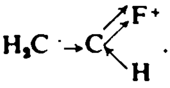
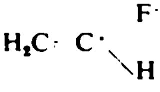
[26] This would be in accord with views earlier expressed by the writer, in which (a), the relatively low ionization potentials for example of H_2O as compared with O and of HCl as compared with Cl, and (b), the still lower values for $(CH_3)_2O$, CH_3Cl, C_2H_5Cl, etc., were attributed to accumulation of negative charge on the O or Cl atom by transfer from the H atoms or alkyl group. [R. S. Mulliken *J. Chem. Phys.* **3**, 514 (1935)—but see K. Watanabe *J. Chem. Phys.* **26**, 542, 1773 (1957) for more reliable ionization potentials (which give a more consistent picture than the earlier values).]

Another example in which pluvalent conjugation may be of non-negligible importance is HF with main structure $H\rightarrow F$ and pluvalent conjugated structure $H^{-}\rightrightarrows F^{+}$. Similar structures may be of appreciable importance in hydrides in general,[25] at least where the H atom has become distinctly positive, enabling it to some extent to hold an electron in the excited H^{-} state $1s\,2p\pi$.

VI. THE RELATIONS BETWEEN INDUCTIVE AND MESOMERIC EFFECTS

Inductive effects, and their interaction with mesomeric effects, have been referred to several times in the preceding Sections. Since the two effects cannot always be sharply separated, especially in hyperconjugation, and since confusion (more of language than of understanding) can and does arise, it seems desirable to survey the relations between them.

To begin with, it may be worth while to remind the reader that ordinary inductive effects correspond, in VB theory, to resonance between covalent and ionic structures. It will simplify the discussion if at first we ignore hyperconjugation with its quasi-σ and quasi-π bonds, and think only in terms of σ and π bonds (including both π_x and π_y in the case of triple bonds) in the usual sense. Both σ and π bonds can be polar, that is, can exhibit the inductive effect. From what is known of the polarizabilities of σ and π electrons, one expects the π bonds to be more strongly polar than the σ bonds, but both polarized in the same direction, in unconjugated polar double or triple bonds (example  $H_2C\rightrightarrows O$). Polarity is expected when the atoms connected by a multiple bond belong to different elements, or when, if they both belong to the same element, they differ in charge or (in the case of σ bonds) in degree of s–p hybridization. In conjugated systems, *provided* the conjugation is not dative or homodative, the inductive or polarity effect is not essentially different quantum-mechanically than in unconjugated systems such as for example, $H_2C\rightrightarrows CH\rightarrow C\rightrightarrows O$.

In dative and homodative isovalent conjugation, however, there is either a strong cooperative, or a strong joint, inductive-mesomeric effect [here see also Section II(a)]. In dative conjugation the dative charge shift in one direction in the π-electron system should be accompanied typically by an *oppositely* directed "inductive" shift in the σ bonds; through this cooperative action, a *larger* "mesomeric" π-electron charge shift should occur than would be possible without it. [Example:  $H_2C\rightleftarrows C\begin{smallmatrix}\nearrow F\\ \nwarrow H\end{smallmatrix}$ with subordinate structure  $H_2C^{-}\rightarrow C\begin{smallmatrix}\nearrow F^{+}\\ \nwarrow H\end{smallmatrix}$. Here, in terms of quantum-mechanical theory, the arrowheads are shorthand for a variety of ionic structures of which  $H_2C^{-}\;C^{+}\begin{smallmatrix}F^{-}\\ \diagdown H\end{smallmatrix}$ is the most important. In total, the F atom gives a fraction of a π_x electron (dative conjugation), but receives a rather different, probably larger fraction of a σ electron (inductive effect).]

In homodative isoconjugation, the mesomeric effect already *intrinsically* involves a considerable amount of π_x electron shifting, in such a way as to partially but by no means entirely even out the π_x charge distribution as compared with that in a single one of the isovalent structures. One may reasonably describe the result as a *joint* mesomeric-inductive effect. *Further* charge equalization can then take place by the ordinary inductive effect in the π and especially in the σ bonds. The polarity re-adjustments in the σ bonds may here be described as *cooperative* in the same sense as in dative conjugation, and just as in that case should make possible larger mesomeric effects than would occur otherwise.

In summary, both mesomeric and π-electron inductive effects are resonance effects according to VB theory. In ordinary semi-empirical LCAO-MO theory, both *resonance* parameters β and *inductive* parameters δ (and ω, if there are charged atoms[1])—or the equivalent of these if the self-consistent-field method is used (either in its original form or in the Pariser–Parr or the Pople modification) –are introduced at the outset. It is then in general scarcely feasible to say, except qualitatively, how much of the total computed effect is due to covalent resonance, how much to bond-polarities (inductive effect), and how much to a mutual interaction of the two.

Turning now to hyperconjugation, we first replace some sets of σ bonds by $[\sigma]$, $[\pi_x]$, and $[\pi_y]$ GO (group orbital) bonds [cf. Section I(b)]. This procedure represents a partial adoption of the LCAO-MO viewpoint, after which, however, we can then carry the discussion further using the VB method. This last has been done in the present classification of hyperconjugation into types and subtypes. The $[\pi_x]$ bonds are now treated in the same way as π_x bonds, and all that was said above about the inductive and mesomeric effects in conjugation becomes directly applicable also to hyperconjugation.

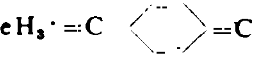
In all cases where the hyperconjugation is intrinsically *two-dimensional*, $[\pi_y]$ and $[\pi_x]$ hyperconjugation must be treated alike, and what has been said about $[\pi_x]$ hyperconjugation then applies equally to the $[\pi_y]$ bonds. But otherwise, it is a matter of choice as to whether one wishes to consider $[\pi_y]$ hyperconjugation. In particular, second-order hyperconjugation is a form of $[\pi_y]$ hyperconjugtaion which for many purposes can be ignored, since it must usually be a relatively small effect and since, because of its universal background presence, it probably does not lead to appreciable observable differences in molecular properties [cf. last paragraphs of Section III(a)].

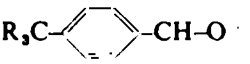
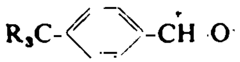
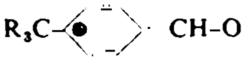
However, the *LCAO-MO treatment* of second-order hyperconjugation, because it includes an inductive parameter, yields a considerable stabilization energy in cases where transfer of a π_y electron can reduce charge inequalities, as for example in the ethyl ion.[1] From the VB standpoint, however, this LCAO-computed stabilization energy is nearly all due to an inductive effect in the π_y-$[\pi_y]$ electron system [cf. last paragraph of Section III(a)].

As already noted, $C\equiv R_3$ and $C=R_2$ σ bonds are treated in hyperconjugation *in part* like π_x bonds and in part like π_y bonds (and in part like σ bonds). In one-dimensional hyperconjugation (π_x and $[\pi_x]$ only), what would be classed as inductive effects if hyperconjugation were ignored are now classed *in part* as mesomeric (or as mixed inductive-mesomeric) effects. In two-dimensional hyperconjugation, a similar statement applies in double measure. Thus in speaking of inductive and mesomeric effects in hyperconjugated systems, it is desirable to take special care as to just what is meant by these terms. Perhaps it would be better if less emphasis than is customary were placed on trying to distinguish and separate them.

VII. HYPERCONJUGATION AND THE BAKER-NATHAN EFFECT

Baker and Nathan,[27] in first introducing the ideas which Baker identifies with hyperconjugation,[28] suggested that when a "methyl group is attached to a conjugated system, the duplet of electrons forming the C–H bond in this group are appreciably less 'localized' than are those in a similarly placed C–C bond," and referred to the effect as a "new mechanism of electron release" "which either cannot function or is greatly diminished in the higher alkyl groups." In later papers it was assumed to decrease from a maximum for Me to zero for *t*-Bu. They used it initially to explain data on the velocity of interaction, by a bimolecular (S_N2) mechanism, of various alkyl-substituted benzyl bromides with pyridine in dry acetone, where for a single *p*-alkyl substituent they found that the velocity decreased by small amounts in the order Me > Et > *i*-Pr > *t*-Bu > H. They then extended the application of the idea in various directions.

In their preceding paper,[29] they indicated a belief that the activated state in the bimolecular reaction with pyridine is one which involves incipient anionization of the bromine atom, and is therefore speeded by easier electron release from the *p*-alkyl (or other) substituent group (or groups) in the substituted benzyl bromide. *Complete* anionization of the bromine would create a benzyl carbonium ion in which *p*-alkyl substitution should give rise to homodative isovalent hyperconjugation (main structures  and three ring-positive structures; hyperconjugated structure ) closely similar to that in McCaulay's methylated-benzene carbonium ions [cf. Section II(d)].

The concept of hyperconjugation as defined by the present writer[30] referred to definite states of individual molecules, mainly ground states but also spectroscopically excited states; it was also obviously applicable to radicals and ions. In some of his later papers,[31] Baker adduced evidence that the Baker–Nathan order (Me > Et > *i*-Pr > *t*-Bu > H) holds for the ground as well as activated states of certain hyperconjugated systems. He concluded that, for example in *p*-alkyl benzaldehydes, in addition to stabilization of the main VB structure  by structures  (inductive effect, or polar character, of the C=O π bond) and  (ordinary or sacrificial conjugation in the present terminology), there is stabilization by  O (inductive effect or polar

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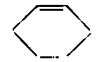
[27] J. W. Baker and W. S. Nathan, *J. Chem. Soc.* 1844 (1935).

[28] J. W. Baker, *Hyperconjugation.* Oxford University Press (1952).

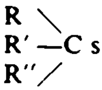
[29] J. W. Baker and W. S. Nathan, *J. Chem. Soc.* 1840 (1935).

[30a] R. S. Mulliken, *J. Chem. Phys.* 7, 339 (1939); cf. reference 3 in this paper with regard to the suggestion of the word "hyperconjugation" by W. G. Brown. In this paper (end of p. 345) it was concluded "that hyperconjugation changes (most likely decreases) the energy of the normal state", but that "the change is probably considerably smaller than for the [spectroscopically] excited states". [30b] Regarding some previous history of the concept of hyperconjugation (before the name was suggested), going back to Wheland (1934), see R. S. Mulliken, C. A. Rieke and W. G. Brown *J. Amer. Chem. Soc.* 63, 41 (1941). Regrettably, the papers of Baker and Nathan, and of Baker and other collaborators had not then come to our attention. [30c] A still earlier example, of what would here be called isovalent hyperconjugation, is contained in the writer's discussion of the theory of the structure of twisted ethylene in *Phys. Rev.* 43, 279 (1933).

[31] J. W. Baker, *J. Chem. Soc.* 191 (1942); *Ibid.* 445 (1938); 796 (1941); *Hyperconjugation.* Oxford University Press (1952).

character in the σ bond from R_3C to the ring), and finally by R_3^+C  $CH\text{-}O^-$ (ordinary or sacrificial hyperconjugation in the present terminology) but with a maximum effect of this last structure for $R = H$ and *no* effect for $R = CH_3$.

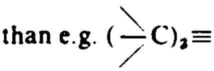
In two respects the quantum-mechanical theory of π-electron resonance in hyperconjugation seems to deviate strongly from the ideas presented by Baker.

(1) The theory gives no indication that the hyperconjugative π-electron resonance power of a group  $\begin{array}{l}R\diagdown\\R'-C\\R''\diagup\end{array}$ should depend in an essential way on how many of R, R', and R'' are H atoms. Qualitatively, bonds from H atoms, Me or other alkyl groups or indeed from any atom or group should be alike capable of participating in hyperconjugative resonance. Quantitative differences would be expected, of course; a C-C bond from Me might be less (or more) effective than a C-H bond from H,[32] but it would not be expected to be negligibly effective, nor is there any obvious reason why it should be radically different in effectiveness. This statement applies both to ordinary and to isovalent hyperconjugation.

In any event, the Baker-Nathan effect, in so far as it pertains to differences between C-H and C-C hyperconjugation, should not itself be called hyperconjugation, although it might be called *differential* hyperconjugation (for C-C relative to C-H).

Taft's Conference paper includes a thorough discussion of evidence of various kinds that π-electron resonance occurs for C-C as well as for C-H hyperconjugation although (in accord with the Baker-Nathan effect) more strongly for the latter. The evidence pertains both to ground state hyperconjugation and to activated state hyperconjugation (reaction rates, etc.).

(2) The theory [see detailed discussion of butadiene and propylene in Section III(a)] does not indicate that ordinary hyperconjugation should in general be an important electron-release mechanism (nor that, if it were, H should be better than Me—rather the contrary).

[*Note added* 20 *November* 1958. The probable importance of dispersion-type ionic states now furnishes a reasonable theoretical basis for appreciable electron release in hyperconjugation; and perhaps also for greater release in C-H than in C-C hyperconjugation, since H is more electropositive than C, and therefore $H_3\equiv$ or $H_2=$ than e.g.  $(\diagdown\!\!-\!\!\diagup C)_3\equiv$ or $(\diagdown\!\!-\!\!\diagup C)_2=$.] *Maximum strength* of hyperconjugative effects, including electron release, should occur in homodative isovalent hyperconjugation, as for example in McCaulay's alkylated aromatic carbonium ions [cf. Section II(d)].

In so far as the Baker-Nathan effect is concerned with activated states in chemical reactions, it is more difficult to say what might be expected theoretically than when one is concerned only with molecules or ions in ground (or definite spectroscopically excited) states. Presumably activated states are more affected by steric factors than ground states. Solvent effects can of course be important for any state, particularly for an ionic or highly polar state. However, when activated states involve incipient

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[32] R. S. Mulliken and R. G. Parr, *J. Chem. Phys.* **19**, 1271 (1951). Equation (23a) and footnote 26 of this paper attributed variations in heats of formation of variously branched hydrocarbons to *greater* C-C than C-H second-order hyperconjugation energies. However, especially in view of the theoretically expected smallness of all second-order hyperconjugation effects,[5] their attribution must be considered speculative.

carbonium ion formation, they should presumably involve incipient homodative isovalent hyperconjugation. Taft's Conference paper indicates that the relative importance of C–H and C–C hyperconjugation is similar in activated and ground states.

In connection with the role of hyperconjugation in reaction mechanisms, a survey by Wheland[33] of the explanation of the Markovnikov rule for the addition of reagents of type HX to a double bond is of interest. It is assumed that the reaction proceeds through a (perhaps only incipient) carbonium-ion-salt activated complex. The explanation is then essentially that, taking propylene as the simplest example, the isopropyl ion, with main structure $H_3\overset{\scriptscriptstyle |}{\equiv}C{-}CH{-}C\overset{\scriptscriptstyle |}{\equiv}H_3$, is stabilized by *two* (homodative isovalent) hyperconjugated structures ($H_3\overset{\scriptscriptstyle |}{\equiv}C{-}CH\overset{\scriptscriptstyle |}{=}C{-}\ H^+$ and $H^+{=}C\overset{\scriptscriptstyle |}{=}CH{-}C\overset{\scriptscriptstyle |}{\equiv}H_3$), whereas the propyl ion $H_3\overset{\scriptscriptstyle |}{\equiv}C{-}\underset{\substack{\Vert\!\vdash \\ H_2}}{C}{-}C^+\mathrel{\overset{-\,-}{-\,-}}H_2$ is stabilized only by one ($H_3\overset{\scriptscriptstyle |}{\equiv}C{-}C\overset{\scriptscriptstyle |}{=}\underset{\substack{| \\ H_2^+}}{C}{=}H_2$). Hence the *iso*propyl-type complex is more stable and the addition takes place accordingly. Mass spectroscopy as well as hyperconjugation theory furnishes evidence for the greater stability of the *iso*propyl than of the propyl ion; however, there are also questions of the geometry of the actual ions, but it would lead too far to attempt to discuss these questions further here.

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[33] G. W. Wheland, *Resonance in Organic Chemistry*, pp. 430 *et seq*. Wiley, New York (1955); C. K. Ingold, *Structure and Mechanism in Organic Chemistry*. Cornell University Press, Ithaca (1953).