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Strong or Isovalent Hyperconjugation in Some Alkyl Radicals and their Positive Ions[1]

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We have used a procedure based on the semi-empirical LCAO MO method to calculate hyperconjugation or conjugation energies for the ethyl, isopropyl, *t*-butyl and allyl radicals and their positive ions. An important feature of the method is the introduction of a parameter which allows for a linear dependence of the coulomb integral, α, of a given atom upon the charge on that atom. The large magnitudes in the present and other related cases of the observed and computed hyperconjugation energies (comparable for the radicals with ordinary conjugation energies, and still larger for the ions) are qualitatively explained in terms of valence-bond resonance theory. On this basis they are here classified as examples of the new category of "strong hyperconjugation" or "isovalent hyperconjugation." This differs from ordinary or "sacrificial" hyperconjugation in the same way that resonance or "strong (or "isovalent") conjugation" in for example benzene or the allyl radical or ion differs from ordinary or "sacrificial" conjugation. Some new valence bond symbols for multiple and quasi-multiple bonds are introduced as an essential aid in making clear the roles of π_x and π_y bonds in various resonance structures in conjugation and hyperconjugation. The extra-large stabilization energies in ions as compared with radicals, in both strong conjugation and strong hyperconjugation, are attributable to a joint effect of conjugation and charge redistribution.

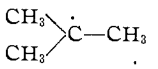
Introduction

Recent measurements by electron impact methods have led to experimental stabilization energies for a number of gaseous hydrocarbon radicals and their positive ions.[2] Table I shows these stabilization energies for four of the simplest radicals and their ions.

In the series ethyl, isopropyl, *t*-butyl, the stabilization energy of the radicals increases approximately linearly with the number of methyl groups, each of which contributes about 5 kcal./mole. Perhaps the most striking feature of the data, however, is that the stabilization energies of the ions are almost an order of magnitude larger than those of the radicals, and that this is true not only for such ions as the allyl ion, where there are two obvious resonance forms, but also for the ions of the saturated radicals, where there seems to be no scope for resonance in the usual sense. This led Franklin and his co-workers[2a,c,3] to maintain that the observed stabilization cannot be due to resonance in either case; but no satisfactory alternative origin for it was proposed. On the other hand, Halpern[2b] and authors cited by him have attrib-

TABLE I

OBSERVED STABILIZATION ENERGIES OF SOME SIMPLE RADICALS AND THEIR IONS[a]

Radical	Stab. energy (radical), kcal./mole	Stab. energy (pos. ion), kcal./mole
$\dot{C}H_3$	0	0
$CH_3{-}\dot{C}H_2$	5	36
$CH_3{-}\dot{C}H{-}CH_3$	11	66
 $(CH_3)_2\dot{C}{-}CH_3$	16	84
$CH_2{=}CH{-}\dot{C}H$	24[b]	58

[a] Values are taken from ref. 2c, except for the allyl radical and ion; the latter values are from ref. 2b. See ref. 2c and Section 12 for a critical discussion of the applicability of these values. [b] Franklin and Field in ref. 3 cite evidence in favor of a value of 19 kcal./mole for allyl radical.

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[1] The major part of the calculations (by N.M.) was done in 1952/1953 while N.M. was a National Research Postdoctorate fellow at Magdalen College, Oxford, and R.S.M. a Fulbright Research Scholar at St. John's College, Oxford.

[2] (a) J. L. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **19**, 1073 (1951); (b) J. Halpern, *ibid.*, **20**, 744 (1952); (c) J. L. Franklin and H. E. Lumpkin, *ibid.*, **20**, 745 (1952); (d) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957; (e) questions have been raised as to the absolute accuracies of the appearance potentials of fragment ions on which these resonance energies are based. However, since the resonance energies themselves involve only *differences* of appearance potentials for closely related molecules, it seems *probable* that these resonance energies can be relied on to 0.1–0.3 e.v. The writers are greatly indebted to Dr. James D. Morrison for discussions on the reliability of the mass-spectrometrically determined stabilization energies.

[3] H. L. Franklin and F. H. Field, THIS JOURNAL, **75**, 2819 (1953).

uted the effect to hyperconjugation, and have offered qualitative arguments to show that hyperconjugation should be more effective in stabilizing the ions than the radicals.

Recently, arguments of considerable force have been advanced which indicate that the experimentally observed ions may be *isomers* of those here and heretofore assumed. If so, the stabilization energies of the ions in Table I may represent energies of these isomers. Nevertheless (see Section 12) we believe that existing evidence still indicates stabilization energies at least near those of Table I so that the relevance of our calculations is not seriously altered. The following discussion proceeds on this basis. However, in Section 12 we shall consider critically the interesting question of the actual structures and stabilities of the alkyl ions and their possible isomers.

In a previous paper,[4] we developed a procedure based on the semi-empirical linear-combination-of-atomic-orbitals molecular orbital (LCAO MO) method, for calculating the hyperconjugation energies (HCJE's) of carbonium ions. We found an unusually large HCJE, about 17 kcal./mole, for the benzenium ion, $C_6H_7^+$, and suggested that HCJE's (strictly speaking, joint induction-hyperconjugation energies) comparable in magnitude with usual conjugation energies might be expected in general for positive ions having an odd number of centers bearing π or quasi-π electrons. (Reasons are discussed in section 13.)

The ethyl, isopropyl and *t*-butyl ions are of this type, and the present paper describes calculations using the method of reference 4 which show that the large stabilization energies of these ions may indeed be attributed to the joint effects of hyperconjugation and charge redistribution. Application of the same method to the neutral radicals gives HCJE's also in good agreement with the observed stabilization energies, and with results of earlier HCJE calculations of Roberts and Skinner.[5]

More recent calculations on vertical conjugation energies of unsaturated hydrocarbon radicals and ions by Brickstock and Pople,[6] using a self-consistent MO method including electron interaction explicitly instead of a semi-empirical method as we have, show results for conjugation energies similar to ours for hyperconjugation energies. These will be discussed further in section 11.

Here and in the following discussion we shall for simplicity spoak for the most part of conjugation and hyperconjugation energies, even when we ought more properly to refer to stabilization energies resulting from the joint effect of charge redistribution (or induction) and conjugation or hyperconjugation.

The Calculations

1. General Considerations.—We consider the ethyl, isopropyl and *t*-butyl radicals and their ions as derived from a planar methyl radical or ion by successive substitutions of hydrogen atoms by methyl groups. The configurations and numbering of the atoms are shown in Fig. 1.

The delocalization energy arises principally from the interaction of π-AO's (atomic orbitals) and quasi-π GO's (group orbitals) having their nodes in the plane of the carbon atoms. Thus for example the isopropyl ion is treated as if it had four π-electrons, assigned to LCAO MO's obtained as linear combinations of the three $2p\pi_C$ AOs and two quasi-π GOs on the two H_3 quasi-atoms.[7]

In this example, the *vertical* HCJE is the difference between the total energy of the four electrons in these delocalized MOs and the energy of four electrons in localized quasi-2-center bond MOs formed from CH_3 carbon π and H_3 quasi-π orbitals.

There is an additional small contribution to the HCJE resulting from hyperconjugation in the plane of the carbon atoms[7a]; we made separate computations for the ethyl ion including such a contribution and leaving it out, and found that the total net HCJE is almost the same, provided the charge distribution is suitably adjusted (see section 6 below).

2. Illustration of the Method; Secular Determinant for the Ethyl Ion: "Complete" or "Two-Dimensional" Calculation Including Both x and y Hyperconjugation.—As indicated in Fig. 1a, we assume the two carbon atoms, the hydrogen atoms of the CH_2 group, and the center of gravity of the H_3 group to lie in one plane, which we call the plane of the molecule. We shall call the π (or quasi-π) orbitals that have a node in this plane π_x (or $[\pi]_x$) orbitals, and those that have a node in the plane passing through the carbon atoms perpendicular to the plane of the molecule π_y (or $[\pi]_y$) orbitals. For brevity, we shall sometimes call all these simply x or y orbitals.

Using the numbering of Fig. 1 it may be seen that quasi-atom 1 and atoms 2 and 3 are centers for x GOs or AOs, while all four atoms or quasi-atoms are centers for y GOs or AOs. The ion has two electrons in the energetically lowest of the three x MOs obtainable from the x GOs and AOs, and two more electrons in each of the two lowest y MOs obtainable from the y GOs and AOs. To evaluate these energies, and the coefficients in the respective linear combinations, a system of linear equations, and the resulting secular equation, must be set up and solved in the usual way.

Making the usual approximation of neglecting interactions except between nearest neighbors, the secular determinant for the y MOs of the ethyl ion may be written

$$\begin{vmatrix} x_1 & \beta_{12} + S_{12}\dfrac{(x_1 + x_2)}{2} & 0 & 0 \\ \beta_{12} + S_{12}\dfrac{(x_1 + x_2)}{2} & x_2 & \beta_{23} + S_{23}\dfrac{(x_2 + x_3)}{2} & 0 \\ 0 & \beta_{23} + S_{23}\dfrac{(x_2 + x_3)}{2} & x_3 & \beta_{34} + S_{34}\dfrac{(x_3 + x_4)}{2} \\ 0 & 0 & \beta_{34} + S_{34}\dfrac{(x_3 + x_4)}{2} & x_4 \end{vmatrix} \quad (1)$$

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[4] N. Muller, L. W. Pickett and R. S. Mulliken, THIS JOURNAL, **76**, 4770 (1954); see also *J. Chem. Phys.*, **21**, 1400 (1953).

[5] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949). In their calculations, considerably different parameters from ours were used, the overlap integrals being neglected.

[6] A. Brickstock and J. A. Pople, *ibid.*, **50**, 901 (1954); J. A. Pople, *J. Phys. Chem.*, **61**, 6 (1957).

[7] (a) R. S. Mulliken, C. A. Ricke and W. G. Brown, THIS JOURNAL, **63**, 45 (1941); (b) C. A. Coulson, "Valence," Oxford, 1952, Fig. 12.4, p. 312.

That for the x MOs is identical except that the last row and column should be deleted.

In (1), $x_i = \alpha_i - E$, where $\alpha_i = \int \psi_i H \psi_i^* d\tau$ and E is the eigen value of the energy; $\beta_{ij} = \int \psi_i H \psi^*_j d\tau - S_{ij}[(\alpha_i + \alpha_j)/2]$, and $S_{ij} = \int \psi_i \psi_j^* d\tau$. ψ_i is an AO or GO on atom or quasi-atom i. The method of assigning numerical values to these quantities will be discussed in the following sections.

The energies of the electrons in the *localized* MOs are given by the roots of two second-order secular determinants. For the CH_3 group the determinant is the same for the x and the y localized MOs and is obtained, formally, by striking out the last two rows and columns of (1). The numerical values of the terms occurring in this determinant, which we will refer to as (2), will not, however, be the same as those in (1). For the CH_2 group the determinant is obtained by striking out the *first* two rows and columns of (1).

3. Numerical Values of the α's.—α_1 for an uncharged carbon atom is taken as a reference value, and called α_0. The numerical value of α_0 may be left undefined, since it always cancels out in calculating conjugation energies. For an uncharged H_2 or H_3 quasi-atom, the value of α is taken as $\alpha_0 + \delta\beta_0$, where β_0 is an energy unit (see section 4) and δ is a proportionality constant; the choice of a negative value for δ is equivalent to the assumption that the hydrogen GO's are more electropositive than the $2p\pi_C$ AO's. We made separate calculations with $\delta = 0$ and $\delta = -0.50$. (See reference 4 for a discussion as to the best *a priori* value of δ.)

Following reference 4, we now assume that if the i^{th} atom or quasi-atom has a charge q_i, its α value will depend linearly on q_i, so that we may write it as $\alpha_0 + \omega\beta_0 q_i$, where ω is a proportionality constant which, since it cannot readily be determined *a priori*, may be chosen to give the best agreement with experiment. We chose ω to reproduce the experimental resonance energy of the isopropyl ion; for $\delta = 0$ this required setting $\omega = 1.47$; for $\delta = -0.50$, $\omega = 1.25$. ω is the only new adjustable empirical parameter in the treatment here described; the others are determined by the requirement that the method should become equivalent to those used in previous HCJE and CJE computations[8] when the q's vanish.

We computed the q_i's from the coefficients of the occupied MO's as described in section 5 of ref. 4; as there, the normalizing condition imposed on the coefficients of each MO was $\Sigma c_i^2 = 1$, which is sufficiently accurate for this purpose even though it ignores overlap effects. [This of course does not mean that we neglected overlap where its effects are important: note the S_{ij} in (1).] The q's were then adjusted to self-consistency as follows. For each ion, we began by guessing a first trial set of q's and calculated the energy levels, LCAO coefficients, and thence a new set of q's. These were used as a guide in picking new trial values, and the operation was repeated until the "output" set of q's agreed with the "input."

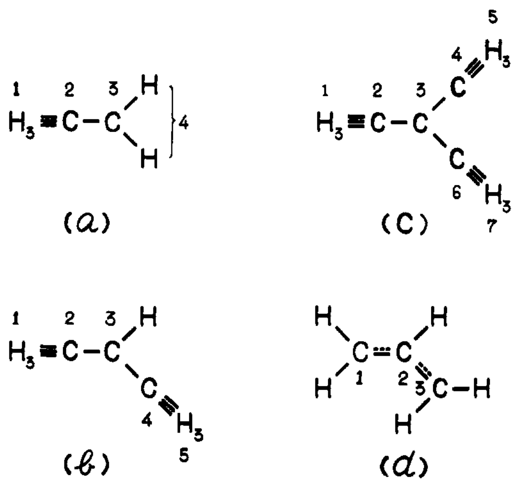

Fig. 1.—Assumed configurations and numbering of atoms and quasi-atoms for the radicals and their ions.

When the α's are determined in this manner, it follows that $x_i = \alpha_0 - E + \omega q_i \beta_0$ for carbon atoms and $x_i = \alpha_0 - E + \delta\beta_0 + \omega\beta_0 q_i$ for hydrogen quasi-atoms. Writing $x = \alpha_0 - E$, these expressions become $x_i = x + \omega\beta_0 q_i$ and $x_i = x + \delta\beta_0 + \omega\beta_0 q_i$, respectively. Finding the eigenvalues of x is then tantamount to finding the energy eigenvalues; the energies so obtained will be in units of β_0, and are converted to kcal./mole using the value $\beta_0 = -60.0$ kcal./mole.[4]

4. The Off-diagonal Terms of the Secular Determinant.—To fix the values of β_{ij} and S_{ij} we used for the C–C bonds a self-consistency procedure as in section 8 of ref. 4. For simplicity we used the constant values $S = 0.50$ and $\beta = 2\beta_0$ for bonds between C and H_2 or H_3 (1–2 and 3–4), although here too the use of a self-consistency procedure would have been somewhat better. For the carbon–carbon bonds we used the approximate formulas $S(p) = 0.080p + 0.115$ and $\beta(p) = \beta_0 S \cdot (p)/0.25$, where p is the total bond order. The $\beta(p)$ formula expresses the assumption that β is proportional to S. The S value obtained from the formula usually was rounded off to two significant figures. For the ethyl ion including both x and y hyperconjugation we arrived at $S_{23} = 0.26$, $\beta_{23} = 1.04\beta_0$; β_0 is the value of β for a C–C bond of length 1.39 Å.[4]

To keep the treatment as simple as possible, we made no allowance for any effect of q_i and q_j on S_{ij} or β_{ij}. The only effect of the q's on the off-diagonal terms in the secular equation arises therefore from the occurrence of x_i and x_j in the ij^{th} term.

5. Results for the Ethyl Ion.—Table II shows the q's, bond orders, LCAO MO energies and HCJE obtained when the elements of the secular determinant were fixed as indicated above. It should be noted that in computing the *localized* CH_3 and CH_2 energies the q's are all zero when $\delta = 0$, while for $\delta = -0.50$ small charge separations

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(8) See Mulliken, Rieke and Brown, ref. 7a above and THIS JOURNAL, **63**, 1770 (1941); C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953); also R. S. Mulliken and C. C. J. Roothaan, *J. Chem. Phys.*, **16**, 118 (1948), in which the parameters used were most similar to those used here; further, A. Lofthus, THIS JOURNAL, **79**, 24 (1957). The parameters used in the present paper are slightly different from those later arrived at by Lofthus, but the effects of these differences are not important. See also Y. I'haya, *Bull. Chem. Soc. Japan*, **28**, 369, 376 (1955).

arise (with $q_1 = -q_2$, $q_3 = -q_4$) so that a self-consistency procedure was necessary.

TABLE II

RESULTS OF COMPLETE "TWO-DIMENSIONAL" CALCULATIONS FOR THE ETHYL ION

		$\delta = 0, \omega = 1.47$	$\delta = -0.50, \omega = 1.25$
Charges on the atoms:	q_1	+ 0.246	+0.392
	q_2	+ .157	+ .044
	q_3	+ .453	+ .344
	q_4	+ .144	+ .220
Energies of occupied delocalized π-type MOs	y MOs (1)	$-1.9779\beta_0$	$-1.9686\beta_0$
	y MOs (2)	$-1.4569\beta_0$	$-1.1383\beta_0$
	x MO	$-1.7793\beta_0$	$-1.5237\beta_0$
Total delocalized π-energy		$-10.4282\beta_0$	$-8.7212\beta_0$
Total localized π-energy		$-9.5322\beta_0$	$-7.8636\beta_0$
Vertical hyperconjugation energy		$0.8960\beta_0$ = 53.76 kcal./mole	$0.8576\beta_0$ 51.46 kcal./mole
Total bond orders	(1–2)	2.752	2.720
	(2–3)	1.829	1.893
	(3–4)	1.977	1.954
Compressional energy corrn. (kcal./mole)		11.60	13.36
Net HCJE (kcal./mole)		42.16	38.10

The C. E. (compressional energy), in kcal./mole, corrections were evaluated using the formulas[4]

$$\text{C. E. (C–C single bond)} = 323.7(0.29 - 0.33p + 0.04p^2)^2$$
$$\text{C. E. (C=C double bond)} = 688.5(0.50 - 0.33p + 0.04p^2)^2$$
$$\text{C. E. (C}\equiv\text{H}_3\text{ "triple bond")} = 165.6(1 - p/3)^2$$
$$\text{C. E. (C=H}_2\text{ "double bond")} = 110.4(1 - p/2)^2 \quad (2)$$

where p is the total (σ plus π_x plus π_y) bond order, calculated from the LCAO coefficients, again as in ref. 4.

The net HCJE is seen to be in fair agreement with the observed value of the stabilization energy; just as for the benzenium ion,[4] it is an order of magnitude larger than HCJE's in neutral molecules previously studied. The π bond order for the C–C bond is correspondingly very large.

6. The Ethyl Ion without y Hyperconjugation: "One-dimensional" (x Only) Calculation.—It was apparent during the calculations that the HCJE of the ethyl ion resulted almost entirely from delocalization of the x orbitals, and we therefore repeated the calculations leaving the y orbitals out of consideration. It soon became evident that if we used the same ω value as before and $q_1 + q_2 + q_3 = 1.00$ the computed HCJE would be considerably larger than that computed including y hyperconjugation. This is a consequence of the fact that although the y delocalization contributed little to the HCJE directly, it made a considerable difference to the charge distribution, by placing an appreciable part of the positive charge of the ion on the H_2 quasi-atom 4. Actually, this charge q_4 which appears through our allowing y delocalization is essentially a result not of y HCJ but of a largely localized shift of positive charge from atom 3 to quasi-atom 4 (*cf.* discussion in section 12).

Assuming q_4 to have the same values as found in the complete calculations, we now recalculated the HCJE using the LCAO's to determine the ratio $q_1{:}q_2{:}q_3$ after setting $q_1 + q_2 + q_3 = 1.00 - q_4$, which is 0.856 for $\delta = 0$ and 0.780 for $\delta = -0.50$, and obtained HCJE values in quite close agreement with those of the preceding section.

This "renormalization" of the q's in effect allows for the "leakage" of positive charge out of the x-orbital system which arises from y delocalization. Since it is necessary to have the complete calculations to determine the extent of this leakage, there would no be advantage in a "one-dimensional" (x only) treatment with allowance for leakage if the ethyl ion were the only one being considered. However, we can use the results obtained for this ion to estimate the effect of an analogous leakage in the isopropyl ion, where computations including y hyperconjugation would be quite cumbersome, and the one-dimensional ethyl ion calculations were carried out with this in mind. [A complete understanding of the charge distribution in the alkyl ions would require consideration not only of x and y but also of σ delocalization, but this would fall outside the framework of our scheme of semi-empirical calculations. We feel, however, that the procedure used here, which allows for leakage of charge to atoms which are *not represented in the x-electron system* (namely the two H atoms called 4 in $C_2H_5^+$ and the H atom on carbon atom 3 in the isopropyl ion) should give reasonably satisfactory HCJE's.]

The calculated C–C bond order was somewhat smaller in this approximation than in the preceding one; accordingly we used $S_{23} = 0.24$ and $\beta_{23} = 0.96\beta_0$. The same S and β values were used for the remaining ions, the calculated C–C bond order being nearly the same for all.

The secular determinant for the delocalized x LCAO MO's is now

$$\begin{vmatrix} x + \delta\beta_0 + \omega\beta_0 q_1 & 0.5x + \beta_0[2 + 0.25(\delta + \omega q_1 + \omega q_2)] & 0 \\ 0.5x + \beta_0[2 + 0.25(\delta + \omega q_1 + \omega q_2)] & x + \omega\beta_0 q_2 & 0.24x + \beta_0[0.96 + 0.12(\omega q_2 + \omega q_3)] \\ 0 & 0.24x + \beta_0[0.96 + 0.12(\omega q_2 + \omega q_3)] & x + \omega\beta_0 q_3 \end{vmatrix} \quad (3)$$

The total *localized* energy is given by twice the negative root of the two-by-two determinant (2) of section 2 above.

The results are displayed in Table III, and show that the change in the vertical HCJE as compared with the two-dimensional calculation is nearly compensated by a change in the compressional energy correction; the net HCJE is hardly altered when y hyperconjugation is not explicitly included, provided that allowance is made for its effect on the charge distribution.

7. The Isopropyl Ion (One-dimensional Calculation).—If hyperconjugation is neglected, the four quasi-π_x electrons are localized in CH_3 bonding orbitals whose energy is the same as in the ethyl ion, so that the total localized energy is four times the negative root of determinant (2) of section 2.

In consequence of the symmetry of the ion, the delocalized MO's that can be obtained as linear combinations of the five x AO's and GO's must be either symmetrical, in the sense that the coefficients obey the relations $c_1 = c_5$ and $c_2 = c_4$, or else antisymmetrical, that is, with $c_1 = -c_5$, $c_2 = -c_4$, and $c_3 = 0$. Substituting these conditions into

TABLE III

RESULTS OF ONE-DIMENSIONAL CALCULATIONS FOR THE ETHYL ION (OMITTING *y*-HYPERCONJUGATION)[a]

		$\delta = 0, \omega = 1.47$	$\delta = -0.50, \omega = 1.25$
Charges on the atoms	q_1	+ 0.236	+ 0.324
	q_2	+ .103	+ .036
	q_3	+ .517	+ .420
	(q_4)	(+ .144)	(+ .220)
Energy of occupied delocalized π-type MO		$-1.7322\beta_0$	$-1.4879\beta_0$
Energy of corresponding localized MO		$-1.3333\beta_0$	$-1.0875\beta_0$
Vertical HCJE		$0.7978\beta_0$ = 47.87 kcal./mole	$0.8008\beta_0$ = 48.48 kcal./mole
Total bond orders	(1–2)	2.7976	2.7458
	(2–3)	1.5906	1.6642
Compressional energy corrn. (kcal./mole)		6.54	8.32
Net HCJE (kcal./mole)		41.33	40.16
Net HCJE with *y*-hyperconjugation (from Table II)		42.16	38.10

[a] But with allowance for charge redistribution effects of *y* hyperconjugation.

the linear equations which lead to the secular determinant brings about a transformation to symmetry orbitals and reduces the order of the determinant.

This leads, for the symmetrical MO's, to

$$\begin{vmatrix} 2D_{11} & 2D_{12} & 0 \\ 2D_{21} & 2D_{22} & D_{23} \\ 0 & D_{32} & D_{33} \end{vmatrix} = 0$$

where D_{ij} is the ij^{th} element of determinant (3) of the preceding section, but with a new set of q's. The secular determinant for the antisymmetrical MO's is

$$\begin{vmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{vmatrix}$$

Since $c_3 = 0$, these orbitals do not contribute to the C–C bonding, and they would be identical in energy with the localized CH_3 orbitals except that a different set of q's is involved for the delocalized ones. The lowest-energy MO of each class is doubly occupied.

As indicated in the last section, it is to be expected that some of the charge will leak out of the x-orbital system onto the central hydrogen atom in the plane of the ion. We estimated that the charge on this atom would be perhaps a little less than half as great as the charge on the H_2 quasi-atom of the ethyl ion, and accordingly used q's whose ratio was determined from the LCAO coefficients but with the total charge normalized to 0.94 for $\delta = 0$ and to 0.90 for $\delta = -0.50$. The results of the two separate calculations are shown in Table IV.

TABLE IV

RESULTS OF ONE-DIMENSIONAL CALCULATIONS FOR THE ISOPROPYL ION[a]

		$\delta = 0$	$\delta = -0.5$
Charges on the atoms	q_1 or q_5	+0.176	+0.274
	q_2 or q_4	+ .078	+ .002
	q_3	+ .432	+ .348
Energies of occupied delocalized π-type MOs		$-1.7696\beta_0$	$-1.5535\beta_0$
		$-1.5214\beta_0$	$-1.2574\beta_0$
Total delocalized π energy		$-6.5820\beta_0$	$-5.6218\beta_0$
Total localized π energy		$-5.3332\beta_0$	$-4.3500\beta_0$
Vertical HCJE		$1.2488\beta_0$	$1.2718\beta_0$
Vertical HCJE (kcal./mole)		74.93	76.31
Total bond orders	(1–2) or (4–5)	2.8554	2.8238
	(2–3) or (3–4)	1.4902	1.5360
Compressional energy corrn. (kcal./mole)		9.02	10.85
Net HCJE (kcal./mole)		65.91	65.46

[a] With allowance for charge redistribution effects of *y* hyperconjugation.

8. The *t*-Butyl Ion (One-dimensional Calculation).—The total localized energy is now six times the negative root of (2) of section 3. After delocalization, the six π_x electrons are to be assigned to the three most favorable MOs derived from the seven x AOs and GOs.

The lowest-energy LCAO MO will be symmetrical, with $c_1 = c_5 = c_7$ and $c_2 = c_4 = c_6$. Its energy is the lowest root of the determinant

$$\begin{vmatrix} 3D_{11} & 3D_{12} & 0 \\ 3D_{21} & 3D_{22} & D_{23} \\ 0 & D_{32} & D_{33} \end{vmatrix}$$

where D_{ij} is again the ij^{th} element of (3) above, with new q's.

The other two occupied delocalized MO's are a degenerate pair, each having $c_1 + c_5 + c_7 = 0, c_2 + c_4 + c_6 = 0$, and $c_3 = 0$. The energy is again the negative root of

$$\begin{vmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{vmatrix} = 0$$

with appropriate new q's. The total contribution of these two orbitals to the carbon–hydrogen bonding may be found, after determining the ratio of $q_1{:}q_2$ in the usual manner, by applying as a normalizing condition the requirement $c_1^2 + c_2^2 = {}^1/_3$, whereupon the contribution to each $C{\equiv}H_3$ bond will be $4c_1c_2$. Again since $c_3 = 0$, these orbitals do not contribute to the C–C bonding.

Since the *t*-butyl ion has no atoms or quasi-atoms which are not part of the x-orbital system, there is no possibility of a charge leakage in the sense discussed above, and the charges must therefore be normalized to unity. The results, for each of the trial values of δ, are shown in Table V.

TABLE V

RESULTS OF ONE-DIMENSIONAL CALCULATIONS FOR THE *t*-BUTYL ION

		$\delta = 0$	$\delta = -0.50$
Charges on the atoms	q_1 or q_5 or q_7	+0.144	+0.268
	q_2 or q_4 or q_6	+ .063	− .037
	q_3	+ .379	+ .307
Energies of occupied delocalized π-type MOs[a]		$-1.8136\beta_0$	$-1.6104\beta_0$
		$-1.4864\beta_0$	$-1.2732\beta_0$
Total delocalized π-energy		$-9.5728\beta_0$	$-8.3136\beta_0$
Total localized π-energy		$-7.9998\beta_0$	$-6.5250\beta_0$
Vertical HCJE		$1.5730\beta_0$	$1.7886\beta_0$
Vertical HCJE (kcal./mole)		94.38	107.32
Total bond orders	(1–2) or (4–5) or (6–7)	2.8848	2.8617
	(2–3) or (3–4) or (3–6)	1.4316	1.4622
Compressional energy corrn. (kcal./mole)		10.52	12.18
Net HCJE (kcal./mole)		83.86	95.14

[a] The second of the two listed energies belongs to a two-fold degenerate MO.

9. The Allyl Ion (One-dimensional Computation).—An interesting test of the method here proposed is to apply it to the evaluation of the conjugation energy (CJE) of the allyl ion. The delocalization energy of this ion is the difference between the energy of a pair of electrons in an ordinary

C–C double bond, and the energy of two electrons in a symmetrical three-center LCAO MO.

The energy of the *localized* π_x MO (double bond π MO) is the negative root of the determinant

$$\begin{vmatrix} x & \beta_0 + 0.25x \\ \beta_0 + 0.25x & x \end{vmatrix}$$

while the delocalized energy is the negative root of the determinant

$$\begin{vmatrix} 2(x + \omega\beta_0 q_1) & 2\{0.25x + \beta_0[1 + 0.125(\omega q_1 + \omega q_2)]\} \\ 2\{0.25x + \beta_0[1 + 0.125(\omega q_1 + \omega q_2)]\} & x + \omega\beta_0 q_2 \end{vmatrix}$$

In both cases, β and S have been assigned the specific values (β_0 and 0.25) appropriate to the interatomic distances calculated for the delocalized structure, where the bond order is 1.7 for both of the C–C bonds.

We evaluated the net CJE separately with $\omega = 0$, $\omega = 1.25$, and $\omega = 1.47$; the results are 19.47, 63.99 and 72.44 kcal./mole, respectively. It is noteworthy that unless the value of ω is of the order of that used to make the HCJE's of the other ions agree moderately well with experiment, the computed CJE of the allyl ion is badly out of line with the measured value. In other words, a single value of ω suffices to account for all the stabilization energies of the ions here considered to a reasonably good approximation, regardless of whether they originate from ordinary conjugation or hyperconjugation. The extent of charge redistribution effected by ω is as follows. For $\omega = 0$, 1.25, 1.47, respectively, q_2 (Fig. 1) = 0.000, +0.158, +0.170; while of course $q_1 = q_3 = +0.500(1 - q_2)$.

10. The Radicals.—As a further check on our method, we calculated the stabilization energy of the parent *radical* of each of the above ions. For each radical, the calculation is very nearly the same as for its ion. The *localized* energies are given by the same determinants as before, but there is now an additional electron in a $2p\pi_C$ AO. This AO will have $x = 0$, except that in the two-dimensional treatment of the ethyl radical with $\delta = -0.5$ one finds a small charge, q_2, on this atom and consequently $x = -\omega\beta_0 q_2$.

The determinants for the delocalized MO energies will have the same form for each radical as for its ion; the additional electron in each case goes into the second lowest symmetrical LCAO MO, which will have x equal to zero when $\delta = 0$ and nearly zero otherwise, so that this electron contributes little or nothing to the delocalization energy.

If ω were set equal to zero for both ions and radicals, the determinants, and hence the delocalized MO energies, of the radicals would be identical with those of their ions, and the HCJE of each radical and its ion would be the same. With non-zero ω's, the MOs differ strongly in energy because radical and ion have very different q_i's. For the radicals, every q_i is zero for $\delta = 0$, so that no self-consistency procedure for the charges is needed. For $\delta = -0.50$, there are small charge separations within each radical, and we adjusted these charges to self-consistency.

We treated the ethyl radical first as a "two-dimensional" and then as a one-dimensional system, and found that the calculated HCJE was again about the same. The bond orders are slightly different for the radical and ion, leading to somewhat different off-diagonal elements in the determinants. For the two-dimensional computations we used $S = 0.24$ and $\beta = 0.96\beta_0$, and for the one-dimensional treatment of all three saturated radicals, we used $S = 0.22$ and $\beta = 0.88\beta_0$. For the allyl radical, the bond order is so nearly the same as that of the ion that the same S and β were used for both.

The results are collected in Table VI. They are quite insensitive to the choice of δ, and in good agreement with both experiment and previous calculations.

TABLE VI

RESULTS OF CALCULATIONS FOR THE RADICALS

(All values are in kcal./mole)

		C_2H_5[a]	C_2H_5[b]	C_3H_7[b]	C_4H_9[b]	C_3H_5[c]
$\delta = 0$	Vert. HCJE	13.25	9.58	17.90	25.28	29.37
	Compr. energy	7.58	3.00	5.20	6.89	9.90
	Net HCJE	5.67	6.58	12.70	18.39	19.47
$\delta = -0.50$	Vert. HCJE	13.32	10.61	19.48	27.37	
	Compr. energy	8.35	3.96	6.49	8.33	
	Net HCJE	4.97	6.65	12.99	19.04	

[a] Values in this column calculated including both x and y hyperconjugation. [b] Values in this column calculated including only x hyperconjugation. [c] Values in this column are independent of the value of δ.

Discussion

11. Charge Redistribution Effects.—Table VII summarizes the calculated and experimental stabilization energies. In view of the drastic simplifications of the present treatment, the agreement between the computed and empirical values is quite satisfactory, and indicates that it is entirely reasonable to attribute the observed effects to hyperconjugation (or conjugation in the case of the allyl radical and its ion). It is gratifying that the MO calculations of Brickstock and Pople on odd alternant conjugated hydrocarbon radicals and ions have led them to a similar conclusion with respect to conjugation. The success of the present calculations reflects encouragingly on the procedure and assumptions involved, especially the use of a single new parameter, here called ω, to adapt the

TABLE VII

SUMMARY OF CALCULATED AND EXPERIMENTAL STABILIZATION ENERGIES

(All values are in kcal./mole)

		Calcd., $\delta = 0$	Calcd., $\delta = -0.50$	Obsd.
Ethyl ion "two-dimensional"		42.16	38.10	36
Ethyl ion "one-dimensional"		41.33	40.16	
Isopropyl ion		65.91	65.46	66
t-Butyl ion		83.86	95.14	84
Ethyl radical "two-dimensional"		5.67	4.97	5
Ethyl radical "one-dimensional"		6.58	6.65	
Isopropyl radical		12.70	12.99	11
t-Butyl radical		18.39	19.04	16
Allyl ion	with $\omega = 0$	19.47		
	with $\omega = 1.25$	63.99		58
	with $\omega = 1.47$	72.44		
Allyl radical		19.47		24[a]

[a] But see note *b*, Table I.

LCAO MO method as originally developed by Mulliken, Rieke and Brown[6a,8] to the computation of HCJE's of carbonium ions.

If ω is fixed so as to give agreement with observation for a single positive ion (here the isopropyl ion) the other data of Table I are made intelligible without the need of any further adjustment of parameters. It is interesting that the data could be fitted about equally well with any reasonable choice of δ, provided that δ was fixed first and the best ω then chosen. On the other hand, the best agreement for the allyl ion is obtained with $\omega = 1.25$, from a calculation in which δ is not involved, and this would tend to support $\delta = -0.50$ and $\omega = 1.25$ as the best pair of values within the present scheme.

For further discussion on the role of charge redistribution in enhancing stabilization energy[9] in hyperconjugated ions as compared with corresponding radicals, reference should be made to section 13 of ref. 4, which is just as applicable to the results of the present paper as to those there reported for the benzenium ion. However, it should be recognized (more definitely than in ref. 4) that the extra stability of the ions is a *joint* effect of hyperconjugation and charge redistribution. Reference should also be made to section 11 of ref. 4 for a discussion on charges and bond orders; see Fig. 1 and Tables II–V below for a listing of these quantities as obtained in the present work.

12. **The Configurations of Alkyl Ions.**—Reaction-kinetic studies on carbonium ions in solution[10] and, of more direct relevance here, mass spectroscopic studies of gas phase ions using isotopically labelled atoms,[11] indicate that the resonance energy data on ions in Table I may not refer to ions having the geometrical forms shown in Fig. 1, but to isomeric ions. For example, the ethyl ion may have a symmetrical protonated-ethylene hydrogen-bridged configuration rather than the unsymmetrical structure of Fig. 1. Existing evidence suggests that the two forms differ little in energy but leaves open the question as to which is the more stable. What is definite is that protons (and other groups in more complicated carbonium ions) can migrate rather freely from one carbon atom to neighbors; and presumably the reason is that bridged structures have small or possibly negative activation energies.

In the case of the isopropyl ion, Rylander and Meyerson have proposed that the $C_3H_7^+$ ion actually observed in mass spectroscopy has a protonated-cyclopropane structure[12] (cyclopropanium or[12] cyclonium ion). They point out that several investigators from data on appearance potentials have found the same ionization potential (7.43 ± 0.1 v.) for the $C_3H_7^+$ ion whether obtained from *n*-alkanes or isoalkanes, whereas a direct measurement of the ionization potential of the isopropyl radical by Farmer and Lossing[13] gives an appreciably higher value (7.90 ± 0.05 v.). "The discrepancy suggests that $C_3H_7^+$ ions produced by electron impact of hydrocarbon molecules and those produced by ionization of isopropyl radicals do not have the same structure." The implication is perhaps that the *n*-propyl ion is, or quickly becomes, a cyclopropanium ion, while the isopropyl ion may be produced as such by ionization of an isopropyl radical, but then may (and under rough treatment does) go over in the more stable cyclopropanium ion.

However, if we assume that the configurations at least of the *radicals* are correctly represented in Fig. 1, and if we accept the conclusions indicated by Rylander and Meyerson, the isopropyl ion is only 0.47 e.v., or 11 kcal., less stable than the cyclopropanium ion. This would reduce the resonance energy of the isopropyl ion in Table I from 66 to 55 kcal. Such a relatively moderate change would require only that the value of our empirical parameter ω be somewhat reduced. However, it would not affect our essential conclusion that the (without much question) very large resonance energies of the alkyl ions can be satisfactorily accounted for by strong hyperconjugation coupled with charge redistribution.

Further, Farmer and Lossing's ionization potential for the isopropyl ion should be essentially a *vertical* value and may be appreciably larger than the adiabatic value so that the latter might still be close to the 66 kcal. value of Table I. Our tentative conclusions from the foregoing discussion are (1) that even if bridged or cyclic structures are usually the stablest forms of alkyl ions, they are probably not *much* different in energy from the simple unsymmetrical structures of Fig. 1, which must then have remarkably large stabilization energies; and (2) that the latter are a result of strong hyperconjugation coupled with charge redistribution.

13. **"Strong" Conjugation and Hyperconjugation.**—As was pointed out in ref. 4, the observed HCJE's (hyperconjugation energies) for alkyl radicals are of the same order of magnitude as ordinary CJE's (conjugation energies), while in the ions (as also for aromatic carbonium ions) the joint effect of hyperconjugation and charge redistribution gives stabilization energies comparable with benzene-like resonance energies. Moreover, these large stabilization energies are satisfactorily accounted for theoretically using the same parameter values which yield,[8] in agreement with experiment, much smaller HCJE's for examples of ordinary hyperconjugation. Although the effect is greatly enhanced by charge readjustment in the ions, as discussed in Section 11 and in ref. 4, it is already noteworthy in the radicals—namely, the HCJE's in the radicals are comparable with ordinary CJE's. Likewise in the biradical obtained by twisting the planes of the two CH_2 groups in ethylene to perpendicularity, a similarly large computed HCJE is found.[8]

These facts can be understood in terms of VB

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[9] *Cf.* also L. Goodman and H. Shull, *J. Chem. Phys.*, **23**, 33 (1955), who discuss the related question of the mutual dependence of the inductive and resonance effects in substituted conjugated hydrocarbons.

[10] Work of Winstein, Roberts, Cram, Taft and others. L. G. Connell and R. W. Taft, Jr., THIS JOURNAL, **78**, 5812 (1956), give some of the references.

[11] P. N. Rylander and S. Meyerson, *ibid.*, **78**, 5779 (1956), and subsequent articles.

[12] J. D. Roberts, C. C. Lee and W. H. Saunders, *ibid.*, **76**, 4501 (1954), have proposed a similar structure for certain more complicated ions in solution.

[13] J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

(valence-bond) resonance theory. Let us, however, first look at *conjugation*, then afterwards at hyperconjugation. In ordinary conjugation, there is *one* predominant resonance structure with, say, N π bonds, while the other "excited" structures which give rise to conjugation have only $N - 1$ good π bonds. Typical examples are the following.

(1) Butadiene with predominant structure $H_2C\doteq CH—CH\doteq CH_2$ ($N = 2$) and three excited structures $H_2\overset{\circ}{C}—CH\doteq CH—\overset{\circ}{C}H_2$. The small circles over the outer carbons here indicate either odd electrons or ± charges. The symbol $\dot{-}$ in $\doteq$ signifies the π_x bond and the — the σ bond of the double bond; π_x means a π MO with nodal plane in the plane of the molecule. (2) Diacetylene with predominant structure $HC\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—C\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}CH$ ($N_x = 2$ and $N_y = 2$, with $\mathrel{\underset{\cdot\cdot}{-}}$ denoting a π_y bond), and excited structures $H\overset{\circ}{C}\mathrel{\underset{\cdot\cdot}{=}}C\doteq C\mathrel{\underset{\cdot\cdot}{=}}\overset{\circ}{C}H$, $H\underset{\circ}{C}\doteq C\mathrel{\underset{\cdot\cdot}{=}}C\doteq\underset{\circ}{C}H$, and $H\overset{\circ}{\underset{\circ}{C}}—C\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—\overset{\circ}{\underset{\circ}{C}}H$.

In contrast to these examples of ordinary conjugation one has various cases of *stronger* π-electron resonance which do not come under the classical idea of conjugation, but which because of their essential kinship in quantum-mechanical theory are now also frequently called conjugation. Familiar examples are benzene with two equivalent predominant resonance structures, the cyclopentadienyl anion $C_5H_5^-$ and the tropylium cation $C_7H_7^+$ with five and seven equivalent predominant resonance structures, and odd alternant ions of the type $(R_2N\dot{-}CH\dot{-}NH_2)^+$ with two equivalent resonance structures. Odd alternant radicals and ions such as the allyl radical and ion again have two equivalent predominant structures. In all these examples of *strong* π-electron resonance, resonance occurs between two or more structures with equal numbers of like π bonds, whereas in ordinary conjugation the best available resonance structures involve loss of one π bond. Hence ordinary conjugation is *weak* π-electron resonance. As a convenient terminology to distinguish the two cases yet show their relationship, we shall refer to "*strong conjugation*" and simply "*conjugation*."

An alternative terminology more explicitly indicating the VB-theory explanation of the distinction between these two cases would refer to the first as "*isovalent conjugation*" or perhaps "*non-sacrificial conjugation*," and to the second as "*sacrificial conjugation*" or just "*conjugation*." (In the first, the number of valence bonds is the same in two or more resonance structures, while in the second, one bond is sacrificed even in the most favorable resonance structures.)

It will now be recognized that ordinary hyperconjugation, like conjugation, is weak or "sacrificial" π-electron resonance with loss of one π-type bond in the excited resonance structures. However, hyperconjugation differs from conjugation in that the bond which is lost is a quasi-π instead of an ordinary π bond; and since quasi-π bonds are stronger than π bonds, the loss is greater, and as a result HCJE's are smaller than CJE's. To illustrate, we may consider propylene and methylacetylene. Each of these (like butadiene for conjugation) has only one predominant structure ($H_3\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—CH\doteq CH_2$ or $H_3\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—C\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}CH$, respectively). The hyperconjugative effect results from resonance with excited structures with one quasi-π bond less: $\overset{\circ}{H}_3\mathrel{\underset{\cdot\cdot}{=}}C\doteq CH—\overset{\circ}{C}H_2$, or $\underset{\circ}{H}_3\doteq C\mathrel{\underset{\cdot\cdot}{=}}C\doteq\underset{\circ}{C}H$ or $\overset{\circ}{H}_3\mathrel{\underset{\cdot\cdot}{=}}C\doteq C\mathrel{\underset{\cdot\cdot}{=}}\overset{\circ}{C}H$, respectively.

But for the radicals and ions discussed in the present paper and in ref. 4, which may now be described as cases of "*strong hyperconjugation*" or "*isovalent hyperconjugation*," π-electron resonance occurs with no decrease in the total number of π-type bonds. For example, the ethyl radical and the ethyl ion, with principal resonance structures $H_3\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—\overset{\circ}{C}H_2$ and $H_3\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—C^+H_2$, are stabilized by resonance with structures $\overset{\circ}{H}_3\mathrel{\underset{\cdot\cdot}{=}}C\doteq CH_2$ and $H_3{}^+\mathrel{\underset{\cdot\cdot}{=}}C\doteq CH_2$ in which there is no change in the number (here 1) of π_x-type bonds. However, there is here a substitution in the resonance structure of one ordinary π_x for one quasi-π_x bond, and it is for this reason that strong hyperconjugation gives smaller resonance energies than in analogous cases of strong conjugation. It is now qualitatively obvious why the resonance energies should be and are much larger in strong hyperconjugation than in (ordinary or "sacrificial") hyperconjugation.

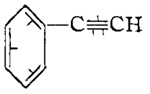
In the preceding paragraphs, only π_x resonance was considered for propylene and the ethyl radical and ion. For methylacetylene, an example of 2-dimensional first-order hyperconjugation,[7a] both π_x and π_y resonance were considered above because they contribute equally to the hyperconjugation there. In the case of propylene, π_x resonance gives first-order but π_y resonance only second-order hyperconjugation. The HCJE for second-order[7a] hyperconjugation (which might reasonably be called hyperhyperconjugation) is much smaller[8] than for first-order hyperconjugation. This is because, although in both cases (as also in conjugation) there is a net loss only of one π-type bond in the excited resonance structures, this loss involves in the case of second-order hyperconjugation the replacement of *two quasi-π* bonds by *one ordinary π* bond. This is most simply illustrated by a consideration of the second-order π_y type hyperconjugation which occurs in ethylene. If the principal structure is formulated as $H_2\mathrel{\underset{\cdot\cdot}{=}}C\doteq C\mathrel{\underset{\cdot\cdot}{=}}H_2$, the excited structures are of the type $\underset{\circ}{H}_2—C\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—\underset{\circ}{H}_2$. Further discussion of this case and of propylene π_y hyperconjugation is given in ref. 8.

For the ethyl ion when π_y (here second-order) as well as π_x (strong) hyperconjugation are to be considered (*cf.* section 2 above), the principal resonance structure should be formulated as $H_3\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—C^+\mathrel{\underset{\cdot\cdot}{=}}H_2$. The strong π_x hyperconjugation introduces the resonance structure $H_3{}^+\mathrel{\underset{\cdot\cdot}{=}}C\doteq C\mathrel{\underset{\cdot\cdot}{=}}H_2$, and the second-order π_y hyperconjugation then brings in $\underset{\circ}{H}_3\doteq C\mathrel{\underset{\cdot\cdot}{=}}C^+—\underset{\circ}{H}_2$ and (combined with strong π_x hyperconjugation) $\underset{\circ}{H}_3{}^+—C\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—\underset{\circ}{H}_2$. Closely parallel statements hold for the ethyl radical. However, in the ethyl ion, the resonance structure of major importance when we admit y delocalization (hence HCJ) is not one of the π_y HCJ structures just indicated, but the locally-polar structure $H_3C\mathrel{\underset{\cdot\cdot}{\dot{\equiv}}}C—\underset{\cdot\cdot}{C}\underset{-}{-}H_2$. It is *this* structure which accounts for the considerable charge q_4 which we found in sections 5 and 6.

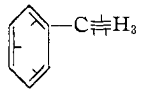
The foregoing discussion has been entirely in terms of VB theory. Our computations made in the framework of LCAO MO theory correspond of course to a somewhat different weighting of resonance structures, together with some additional ones. Nevertheless there is a sufficient degree of coincidence between the two theories so that our discussion of VB resonance structures has valid qualitative significance for the understanding of the distinctions between strong and ordinary conjugation and between strong and ordinary hyperconjugation.

Two further examples of VB resonance structures in conjugation and hyperconjugation may be instructive. For allene, π_x and π_y bonds are equally important. The principal resonance structure is $H_2\underset{\top\top}{=}C\overset{\perp}{=}C\underset{\top\top}{=}C\overset{\perp}{=}H_2$. The only π-type resonance here is (first-order) hyperconjugation involving excited structures $H_2\underset{\top\top}{=}\overset{\circ}{C}—C\underset{\top\top}{\overset{\perp}{=}}C—\overset{\circ}{H}_2$ and $\underset{\circ}{H}_2—C\underset{\top\top}{\overset{\perp}{=}}\underset{\circ}{C}\overset{\perp}{=}H_2$. In ethylene twisted until the two CH_2 planes are perpendicular, the principal resonance structure is $H_2\overset{\perp}{=}\underset{\circ}{C}—\overset{\circ}{C}\underset{\top\top}{=}H_2$. Here there is strong hyperconjugation with each of the two structures $\overset{\circ}{H}_2—\underset{\circ}{C}\overset{\perp}{=}C\underset{\top\top}{=}\underset{\circ}{H}_2$ and $H_2\overset{\perp}{=}C\underset{\top\top}{=}\overset{\circ}{C}—\underset{\circ}{H}_2$ (also, less important, with $\overset{\circ}{H}_2—C\underset{\top\top}{\overset{\perp}{=}}C—\underset{\circ}{H}_2$).

To illustrate further the new bond symbols introduced here, one might use (for one of the principal resonance structures in each case) the following symbols to make clearer the structures of phenylacetylene and of toluene from the point of view of conjugation or hyperconjugation



and



As another example, the VB formulation of CO_2 involves resonance between two equivalent structures $O\overset{\perp}{=}C\underset{\top\top}{=}O$ and $O\underset{\top\top}{=}C\overset{\perp}{=}O$.

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[CONTRIBUTION (N.R.C. NO. 4770) FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL AND THE DEPARTMENT OF THEORETICAL CHEMISTRY, CAMBRIDGE UNIVERSITY]

The Proton Magnetic Resonance Spectra of Azulene and Acepleiadylene

BY W. G. SCHNEIDER, H. J. BERNSTEIN AND J. A. POPLE[1]

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The proton resonance spectra of the non-alternant hydrocarbons, azulene and acepleiadylene, have been measured under conditions of high resolution. A satisfactory assignment of the spectra to individual protons in the molecules was possible and proton chemical shifts and spin coupling constants were evaluated. The chemical shifts are much larger in the non-alternant hydrocarbons, compared to the corresponding shifts in alternant hydrocarbons. The observed spin coupling constants between adjacent protons, increase with the size of the carbon ring, being of the order of 3.5, 7 and 12 c./sec. for the 5, 6 and 7-membered rings. The "ring current" model, which gave a fairly satisfactory interpretation of the proton shifts in the spectra of alternant hydrocarbons, is inadequate for the non-alternant hydrocarbons. This failure of the model is attributed to the highly asymmetric nature of the electron charge distribution in the non-alternant molecules. Surprisingly large shifts of the proton resonances were observed on dilution in various solvents. These dilution shifts were anomalous; the protons on the 7-membered carbon ring gave rise to a much larger dilution shift than the 5-membered carbon ring on the same molecule. This behavior is discussed in terms of an intermolecular interaction characteristic of these hydrocarbons.

The relative chemical shifts of protons bonded to different carbon atoms in polynuclear aromatic hydrocarbons are of some interest. Previous work[2] had shown that the proton chemical shifts of alternant aromatic hydrocarbons can be satisfactorily accounted for in terms of the "ring current" model.[3] An earlier proton resonance spectrum of the non-alternant hydrocarbon azulene, which was measured under conditions of moderate resolution,[2] did not permit a complete assignment of the spectrum. Moreover, the range of chemical shifts indicated by the spectrum did not appear to be reproduced by the spectrum calculated by the ring current model. The proton spectra of the non-alternant hydrocarbons, azulene and acepleiadylene, which are isomeric with naphthalene and pyrene, respectively, have now been measured under conditions of higher resolution. A complete assignment of the spectra has been made on the basis of which individual chemical shifts and spin-coupling constants could be evaluated.

Experimental

The proton magnetic resonance spectra were measured with a Varian V-4300 NMR spectrometer operating at a fixed frequency of 40 Mc./sec. and equipped with a Varian Field Stabilizer. The frequency separation of the signals in the spectra was measured by the side-band technique in the usual manner.

A sample of purified azulene and 1- and 2-methylazulene were kindly provided by Dr. E. Heilbronner. The spectra of the methylazulenes provided a useful confirmation of the proton assignment. Another sample of azulene was obtained from K. and K. Laboratories, Long Island, N. Y. The sample of acepleiadylene was provided by Professor V. Boekelheide. It had been purified by chromatographic methods and recrystallization and had a sharp melting point at 160–161°.

The spectrum of azulene was measured, above its melting point, at 125° and that of acepleiadylene at 175°. Heating of the samples was accomplished by means of an apparatus previously described[2] which had been modified to permit simultaneous spinning of the sample by the stream of hot nitrogen gas used to heat the sample. The samples were contained in a 5 mm. o.d. glass tube together with a sealed

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[1] Visiting Research Associate, National Research Council, Summer 1957.

[2] H. J. Bernstein, W. G. Schneider and J. A. Pople, *Proc. Roy. Soc. (London)*, **A236**, 515 (1956).

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