addition of CF_3CN to ethylene was found[4] to be 2 × 10^2 at the same temperature.

It is striking, at first, that the free radical additions of CF_3CN to propylene and ethylene differ so markedly in the values of E_0, the energy of activation for the over-all reaction (51.5 kcal mol^{-1} with C_3H_6 and 27 kcal mol^{-1} with C_2H_4). Consideration of these systems in detail shows that an abstraction reaction, leading to an allyl radical is a feature of the propylene system and is not an inherent part of the ethylene system. The difference thus may be attributed, in large part, to the "allylic termination." The bimolecular initiation step undoubtedly involves a transition-state configuration in which there is considerable interaction between the π bonds of $C{\equiv}N$ and $C{=}C$, and the possibility of a charge-transfer species suggests itself. Without additional data this is, at best, speculative and further discussion is deferred accordingly.

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Methyl Group Inductive Effect in the Toluene Ions. Comparison of Hückel and Extended Hückel Theory[1]

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Abstract: An HMO perturbation analysis is made of the methyl group splitting of the unsubstituted benzene ion degeneracy and of the effective methyl group Q values in aromatic positive and negative ions. The necessity for including both hyperconjugative and inductive interactions between the ring and the methyl group is demonstrated; the inductive effect, in particular, is shown to be required to obtain an energy level ordering in agreement with esr data. These results are contrasted with extended Hückel calculations, which yield the correct level ordering and reasonable spin distributions with nonempirical (NEMO) parameters that are apparently very different from the usual HMO parameters and without explicit introduction of an inductive effect. When the nonorthogonal orbitals used in the extended Hückel theory are replaced by an orthogonalized (OAO) set, the NEMO and HMO Hamiltonian matrices are found to be very similar in form. Moreover, the substituted carbon (C^1) is shown to have a Coulomb integral (α_1) that differs from the unsubstituted carbon α values. This suggests that the overlap between C^1 and the methyl group is a source of the HMO inductive effect.

In spite of its approximate nature, Hückel molecular orbital (HMO) theory has proved itself extremely useful in elucidating problems concerned with the electronic structure of π-electron systems. A case in point is provided by the esr spectra of the toluene and related anion radicals. Although quantitative calculation of the hyperfine splitting constants of these radicals requires the inclusion of a complex set of factors due to the vibronic coupling of two near-degenerate electronic states,[4–7] it is well known that the dominant features of the spin distribution can be obtained from the simple HMO theory.[8] Moreover, by means of HMO theory it is possible to decompose the methyl group–aromatic orbital interaction into contributions from hyperconjugation and from an inductive effect, and thereby to understand the differences between the esr spectra of the positive and negative ions derived from the same neutral hydrocarbon.

A number of authors have concluded that in HMO theory, and in a Pariser–Parr ASMO–CI model, both hyperconjugation and the inductive effect are important for deriving the correct spin distribution[6,9,10] as well as other properties.[11,12] In particular, inclusion of the inductive effect appears to be essential for obtaining the correct ordering of the near-degenerate levels.[10,11] However, Hoffmann[13] has pointed out that if an extended Hückel theory calculation[14] is made for the toluene system, the correct level ordering is obtained without the need for explicit resort to an inductive effect. Corresponding results have been obtained by Newton[15] with SCF parameters in the extended Hückel theory (NEMO).[16] Moreover, since the parameters

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(15) M. Newton, private communication.

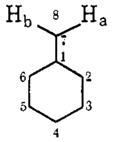
used bear no apparent relation to the normal (HMO) Hückel parameters, a resolution of this paradox appears to be required.

In section I, a HMO perturbation treatment that takes account of both the methyl group bonding and antibonding orbitals is presented for the methyl group splitting of the benzene ion degeneracy and for the effective methyl Q values in positive and negative ions. The importance of including both hyperconjugative and inductive contributions is demonstrated. Section II makes a detailed comparison of the SCF and HMO parameters for toluene. It is found that the Hückel parameters are consistent with the SCF Hamiltonian matrix elements for the corresponding orthogonalized atomic orbitals.

I. HMO Perturbation Treatment

In this section, we present a perturbation treatment of the methyl group–ring interaction to demonstrate the importance of hyperconjugation and induction in the removal of the benzene ion degeneracy and in the determination of the effective methyl group Q value.

Removal of the Benzene Ion Degeneracy. An approximate description of the toluene anion and cation spin distributions is obtained by assuming that the only effect of the methyl group is to lift the double degeneracy of the benzene ion ground state and that the unpaired electron is in the lower energy orbital. The benzene degenerate orbitals in question are



$$\psi_s^{(+)} = (12)^{-1/2}[2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6] \quad (1)$$
$$\psi_a^{(+)} = {}^1/_2[\phi_2 + \phi_3 - \phi_5 - \phi_6]$$

for the cation, and

$$\psi_s^{(-)} = (12)^{-1/2}[2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6] \quad (2)$$
$$\psi_a^{(-)} = {}^1/_2[\phi_2 - \phi_3 + \phi_5 - \phi_6]$$

for the anion, where the atomic orbitals ϕ_i are numbered as shown in the diagram. The MO's $\psi_a^{(+)}$ and $\psi_a^{(-)}$ are antisymmetric with respect to the perpendicular plane through C^1 and C^4; the orbitals $\psi_s^{(+)}$ and $\psi_s^{(-)}$ are symmetric with respect to this plane. The esr spectrum of the anion clearly shows that its unpaired electron orbital is closely approximated by $\psi_a^{(-)}$ of eq 2; although no corresponding data for the cation are available, the durene positive ion results indicate that in the cation the unpaired electron is located in $\psi_s^{(+)}$.[17] Consequently methyl substitution destabilizes the symmetric orbitals relative to the antisymmetric orbitals in both ions.

The antisymmetric orbitals $\psi_a^{(+)}$ and $\psi_a^{(-)}$ belong to the A_2 representation of C_{2v}. The remaining four real benzene MO's, as well as the methyl group π-electron orbitals, belong to the B_2 representation and are symmetric with respect to the C^1–C^4 plane. Since the Hamiltonian is totally symmetric, there can be no mixing between the A_2 orbitals $\psi_a^{(+)}$ and $\psi_a^{(-)}$ and any of the other orbitals, in particular the methyl group orbitals. Moreover, if the methyl group perturbation is assumed to be limited to the substituted ring carbon (C^1), the matrix element between $\psi_a^{(+)}$ and $\psi_a^{(-)}$ also vanishes. Thus the two antisymmetric benzene orbitals, as well as their energies, remain unchanged in toluene. The esr data therefore require that the energy of the symmetric orbitals be raised in going from benzene to the toluene ions.

Methyl substitution can perturb the symmetric orbitals $\psi_s^{(+)}$, $\psi_s^{(-)}$ through hyperconjugation, through the inductive effect, or through a combination of both interactions. The hyperconjugation contribution to the energy of these orbitals is readily obtained by means of second-order perturbation theory. Instead of treating the toluene molecule as a single unit, one can consider it as benzene and the $C{=}H_3$ fragment coupled by the perturbation β_{17}.[18] To second order, the resulting changes in the energy of the benzene orbitals $\psi_s^{(+)}$ and $\psi_s^{(-)}$ are given by

$$E_s^{(2)}(\pm) = C_1^2\beta_{17}^2\left[\frac{C_{7b}^2}{E_s^0(\pm) - E_b^0} + \frac{C_{7a}^2}{E_s^0(\pm) - E_a^0}\right] \quad (3)$$

where C_1 is the coefficient of ϕ_1 in $\psi_s^{(\pm)}$ and the subscripts b and a refer to the usual methyl π-fragment bonding and antibonding orbitals

$$\begin{aligned}\psi_b &= C_{7b}\phi_7 + C_{8b}\phi_8\\ \psi_a &= C_{7a}\phi_7 + C_{8a}\phi_8\end{aligned} \quad (4)$$

The energy levels E_b^0, E_a^0 and the coefficients C_{7b}, C_{7a} can be obtained in terms of the methyl group parameters by performing an HMO calculation for the $C{=}H_3$ fragment. We define the required Hückel parameters in the usual manner[19]

$$\begin{aligned}\alpha_i &= \alpha_0 + h_i\beta_0\\ \beta_{ij} &= k_{ij}\beta_0\end{aligned} \quad (5)$$

where a_0 and β_0 are the benzene atomic Coulomb and resonance integral, respectively, and h_i and k_{ij} are proportionality constants selected by some fitting procedure. With the definitions of eq 5, we find

$$\begin{aligned}E_k^0 &= \alpha_0 - {}^1/_2[-\delta \mp (\delta^2 + 4)^{1/2}]k_{78}\beta_0\\ C_{7k} &= [{}^1/_4(-\delta \mp (\delta^2 + 4)^{1/2})^2 + 1]^{-1/2}\end{aligned} \quad (6)$$

where $\delta = h_8/k_{78}$ and it has been assumed that $h_7 = 0$.[20] The subscript k is either a or b and the upper sign corresponds to the bonding orbital.

From eq 3 it can be seen that $E_s^{(2)}(\pm)$ consists of two parts, the energy change due to interaction with the methyl bonding orbital ψ_b and that due to interaction with the antibonding orbital ψ_a. Labeling these contributions, respectively, by $E_b^{(2)}(\pm)$ and $E_a^{(2)}(\pm)$ and substituting eq 6 into eq 3, we find for the cation

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(17) R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, 1120 (1965).

(18) R. Bersohn, *J. Chem. Phys.*, 24, 1066 (1956).

(19) See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., Chapter 6.

(20) The value of h_7 has negligible effect on the energy level ordering.

$$E_b^{(2)}(+) = -{}^4/_3 k_{17}{}^2\beta_0[(\delta^2 + \delta(\delta^2 + 4)^{1/2} + 4)(-2 + k_{78}\delta + k_{78}(\delta^2 + 4)^{1/2})]^{-1}$$

$$E_a^{(2)}(+) = -{}^4/_3 k_{17}{}^2\beta_0[(\delta^2 - \delta(\delta^2 + 4)^{1/2} + 4)(-2 + k_{78}\delta - k_{78}(\delta^2 + 4)^{1/2})]^{-1}$$

and for the anion

$$\begin{aligned} E_b^{(2)}(-) &= -{}^4/_3 k_{17}{}^2\beta_0[(\delta^2 + \delta(\delta^2 + 4)^{1/2} + 4)(2 + k_{78}\delta + k_{78}(\delta^2 + 4)^{1/2})]^{-1} \\ E_a^{(2)}(-) &= -{}^4/_3 k_{17}{}^2\beta_0[(\delta^2 - \delta(\delta^2 + 4)^{1/2} + 4)(2 + k_{78}\delta - k_{78}(\delta^2 + 4)^{1/2})]^{-1} \end{aligned} \qquad (8)$$

In deriving eq 7 and 8 we have used the fact that $C_1{}^2 = {}^1/_3$ in both $\psi_s{}^{(+)}$ and $\psi_s{}^{(-)}$ and that $E_s{}^0(+) = \alpha_0 + \beta_0$ while $E_s{}^0(-) = \alpha_0 - \beta_0$. For $\delta < 0$ ($h_8 < 0$; $k_{78} > 0$) and $k_{78} > {}^1/_2[-\delta + (\delta^2 + 4)^{1/2}]$, both $E_b{}^{(2)}(+)$ and $E_b{}^{(2)}(-)$ are positive while $E_a{}^{(2)}(+)$ and $E_a{}^{(2)}(-)$ are negative. It follows that the energy of the orbitals $\psi_s{}^{(+)}$ and $\psi_s{}^{(-)}$ is raised by interaction with the methyl bonding orbital but lowered by interaction with the antibonding orbital. For a positive $E_s{}^{(2)}$, the contribution of the bonding orbital must therefore predominate. Combining $E_b{}^{(2)}$ and $E_a{}^{(2)}$, we find for the cation

$$E_s^{(2)}(+) = {}^1/_3 k_{17}{}^2\beta_0(1 - k_{78}\delta)/(1 - k_{78}\delta - k_{78}{}^2) = -{}^1/_3 k_{17}{}^2\beta_0(1 - h_8)/(k_{78}{}^2 + h_8 - 1) \qquad (9)$$

and for the anion

$$E_s^{(2)}(-) = -{}^1/_3 k_{17}{}^2\beta_0(1 + k_{78}\delta)/(1 + k_{78}\delta - k_{78}{}^2) = -{}^1/_3 k_{17}{}^2\beta_0(1 + h_8)/(1 + h_8 - k_{78}{}^2) \qquad (10)$$

From eq 9 and 10 it can be seen that both $E_s{}^{(2)}(+)$ and $E_s{}^{(2)}(-)$ are positive if $k_{78}{}^2 > (1 - h_8)$ and $|h_8| > 1$.

To illustrate this perturbation equation, typical results of calculations with the purely hyperconjugative model ($h_1 = 0$) are shown in Table I. The condition for a positive $E_s{}^{(2)}(+)$ is easily satisfied ($k^2{}_{78} > (1 - h_8)$), since k_{78} has been assumed to be between 2 and 3 in all previous HMO treatments of the methyl group.[21] However, if h_8 is assigned its usual value (between -0.3 and -0.5),[21] $E_s(-)$ is negative, contrary to experiment. As is evident from eq 10, for $h_8 = -1$ the two anion levels become degenerate, and for the $|h_8| > 1$, $E_s(-)$ is shifted above $E_a(-)$. A value of $h_8 \simeq -1.5$ is required to yield an energy difference ($E_s(-) - E_a(-)$) of the right sign and of the right magnitude ($0.0126\beta_0$ or about 0.03 eV).[7]

Table I. Toluene Cation and Anion Unpaired Electron Energy Levels in the Hyperconjugative Model[a]

$-h_8$	$(E_s(+) - \alpha_0)^{b,c}$	$(E_s(-) - \alpha_0)^{b,d}$
0.50	0.9520	−0.9860
0.80	0.9396	−0.9946
1.00	0.9307	−1.0000
1.30	0.9160	−1.0077
1.50	0.9054	−1.0126
2.00	0.8751	−1.0242

[a] With $h_7 = 0.1h_8$; $k_{17} = 0.8$; $k_{78} = 2.80$. [b] In units of β_0. [c] Compare with $E_a(+) = \alpha_0 + \beta_0$. [d] Compare with $E_a(-) = \alpha_0 - \beta_0$.

The parameter value $h_8 = -1.5$ is considerably larger than estimates based on other properties.[21] Moreover, this implies a change in the Huckel Coulomb integral of about 3.5 eV in going from carbon to the H_3 group. Since the Huckel parameter α is approximately related to the ionization potential and one-center Coulomb integral of an atom by the equation[22]

$$\alpha_i = -I_i + {}^1/_2\langle ii|ii\rangle \qquad (11)$$

such a large difference between α_8 and α_0 is inconsistent with the estimated electronegativity of the H_3 group; *e.g.*, for $I(H_3) = 10.659$ eV and $A(H_3) = 0.541$ eV, the calculated difference ($\alpha_8 - \alpha_0$) is 0.4 eV.[23,24] Thus HMO calculations based on the purely hyperconjugative model of the methyl group with standard parameter values fail to yield toluene anion results in agreement with experiment.

To resolve this difficulty, the most reasonable alternative appears to be the introduction of a parameter associated with the methyl group inductive effect acting at the substituted carbon. If we define the perturbation due to the inductive effect as

$$\int \phi_1{}^* \mathcal{H}' \phi_1 d\tau = h_1\beta_0 \qquad (12)$$

first-order perturbation theory yields

$$E_s^{(1)}(+) = E_s^{(1)}(-) = \int \psi_s{}^* \mathcal{H}' \psi_s d\tau = C_1{}^2 h_1\beta_0 = {}^1/_3 h_1\beta_0 \qquad (13)$$

The change in the symmetric orbital energy resulting from a combination of the inductive effect and hyperconjugation is found by adding eq 9 and 13 for the cation and eq 10 and 13 for the anion; that is

$$\begin{aligned} \Delta E_s(+) &= E_s^{(1)}(+) + E_s^{(2)}(+) = {}^1/_3\beta_0[h_1 - (1 - h_8)k_{17}{}^2/(k_{78}{}^2 + h_8 - 1)] \\ \Delta E_s(-) &= E_s^{(1)}(-) + E_s^{(2)}(-) = {}^1/_3\beta_0[h_1 - (1 + h_8)k_{17}{}^2/(h_8 + 1 - k_{78}{}^2)] \end{aligned} \qquad (14)$$

Substitution of some acceptable values of the methyl group parameters into the expression for $\Delta E_s(-)$ shows that for $h_1 \simeq -0.05$ the two anion levels are degenerate, and that for $h_1 \simeq -0.1$, $\Delta E_s(-)$ is of the required order of magnitude, about 0.03 eV. An inductive effect corresponding to $h_1 = -0.1$ is consistent with estimates based on other properties.[21] Equations 14 also show that for the usual range of methyl group parameters, the hyperconjugative and inductive contributions to $E_s(+)$ have the same sign, while the two contributions to $E_s(-)$ have the opposite signs and therefore tend to cancel. Thus methyl substitution is expected to result in a larger energy splitting between the two benzene cation levels than between the anion levels. In this regard, it would be of interest to have comparison measurements of the temperature dependence of the hyperfine splitting for some methyl-substituted benzene anion and cation pair.

It has been suggested[25] that hyperconjugation and the inductive effect result in equivalent energy changes in the aromatic orbitals. Equations 7–14 show that this

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(21) See ref 19, pp 131–134.

(22) I. Fischer-Hjalmars, *J. Chem. Phys.*, **43**, 1962 (1965).

(23) D. Lazdins and M. Karplus, *ibid.*, **44**, 1600 (1966).

(24) P. Nordio, M. V. Pavan, and G. Giacometti, *Theoret. Chim. Acta*, **1**, 302 (1963).

(25) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

conclusion is valid only if the methyl group antibonding orbital can be neglected; that is, the two factors operate in the same direction only in the special case when the contribution of the bonding orbital predominates. In general, the energy of the unpaired electron orbital is raised by interaction with the bonding orbital as well as by the inductive effect, while interaction with the antibonding orbital tends to lower the energy. The total effect of hyperconjugation can therefore be opposite to that of induction.[26]

Methyl Group Q Values in Positive and Negative Aromatic Ions. Bolton, Carrington, and McLachlan[25] have shown that hyperconjugation leads to larger methyl proton splittings in the positive than in the negative ion, if the methyl group is approximated as a single orbital fragment. On the basis of $\sigma-\pi$ spin polarization alone, on the other hand, the positive and negative ion splittings are expected to be nearly identical.[26] Since the former is found to be the case experimentally,[25,26] the treatment of Bolton, *et al.*, has been advanced as an argument for existence of hyperconjugation. Because the heteroatom model of the methyl group is valid only under special conditions, we reexamine the generality of their conclusion.

Application of the perturbation treatment of the preceding section shows that (to first order) the methyl proton spin density is given by

$$\rho_8^{(1)} = C_1^2\beta_{17}^2\left[\frac{C_{7\mathrm{b}}C_{8\mathrm{b}}}{(E^0 - E_\mathrm{b}^0)} + \frac{C_{7\mathrm{a}}C_{8\mathrm{a}}}{(E^0 - E_\mathrm{a}^0)}\right]^2 \tag{15}$$

where E^0 is the energy of the singly occupied aromatic orbital, C_1 is the coefficient of the substituted carbon in this orbital, and the remaining quantities have been defined in eq 3 and 4. Substitution of the HMO expressions for the methyl orbital coefficients and energies into eq 15, with E^0 given by

$$E^0 = \alpha_0 + \epsilon\beta_0 \tag{16}$$

yields

$$\rho_8^{(1)} = C_1^2k_{17}^2k_{78}^2/[\epsilon^2 - \epsilon h_8 - k_{78}^2]^2 \tag{17}$$

Since the effective Q is proportional to the ratio ρ_8/ρ_1 and since to first order $\rho_1 = C_1^2$, we find

$$Q_{\mathrm{CCH_3}}{}^{\mathrm{H}} \propto k_{17}^2k_{78}^2/[\epsilon^2 - \epsilon h_8 - k_{78}^2]^2 \tag{18}$$

If the parameters h_8, k_{17}, and k_{78} are assumed to be the same in the positive and negative ion, the only difference is introduced by changes in ϵ in the denominator of eq 18. In the polycyclic aromatic ions of interest, ϵ is of the order of unity, and identical in absolute value in the positive and negative ions, but positive in the cation and negative in the anion. Since the value of k_{78} is between 2 and 3,[21] the quantity $(\epsilon^2 - k_{78}^2)$ is negative; h_8 is also negative, so the $-h_8\epsilon$ has the sign of ϵ. Thus from eq 18 the effective Q for the cation is expected to be larger than that for the anion. Although this result is in agreement with the conclusion of Bolton, *et al.*,[25] it should be noted that it depends explicity on the sign of h_8 as well as on the relative magnitudes of ϵ and k_{78}. For $h_8 = 0$, the Q's for the positive and negative ions become identical, in agreement with the prediction of Hückel theory that the positive and negative ions of alternant hydrocarbons have identical spin densities. For $h_8 > 0$ (*i.e.*, an electron attracting group), the relative values of the effective Q's should be reversed. An observational test of this prediction would be very worthwhile.

For the toluene ions a set of HMO parameters consistent with the usual values[19] can be selected by fitting the toluene anion experimental hyperfine splittings. An analogous procedure to that described for the ASMO–CI parameters in the Appendix of ref 7 was used; the set of parameters[27] are $h_8 = -0.5$, $h_7 = -0.05$, $k_{17} = 0.86$, and $k_{78} = 2.50$. Since the methyl group splitting depends on (k_{17}/k_{78}) and not on their individual values, the parameter k_{78} was chosen so that it falls in the range previously used for the methyl group; k_{17} is close to that estimated from methylquinone hyperfine splittings ($k_{17} = 0.93$).[18] With these parameters, the effective $Q_{\mathrm{CCH_3}}{}^{\mathrm{H}}$ for the cation and anion symmetric states, $Q_{\mathrm{eff}}(+) = 41.1$ and $Q_{\mathrm{eff}}(-) = 30.3$, are in reasonable agreement with those usually suggested.[28]

II. Comparison of Huckel and Extended Huckel (NEMO) Parameters

Newton, Boer, and Lipscomb[16] have performed extended Hückel calculations for a number of methyl group containing molecules, using parameters determined by nonempirical SCF–MO minimum basis set calculations for suitably chosen reference compounds. In contrast to the HMO results these authors find that the extended Hückel theory α associated with the H_3 group pseudo π orbital is not less negative, but considerably *more negative*, than the α appropriate for an aromatic carbon $2p\pi$ orbital. Moreover, the correct energy level ordering is obtained without the introduction of the methyl group inductive effect. Corresponding results had been obtained previously by Hoffmann.[13]

Newton's **H** matrix for the toluene π-electron system is shown in Table II.[15] In order to separate the σ- and π-electron problems exactly, the methyl group is assumed to be oriented so that the line joining two of hydrogens is perpendicular to the plane of the ring. (We note that because of the assumed CH_3 configuration the molecule no longer has a symmetry plane through C^1 and C^4.) The H_3 group pseudo π orbital, ϕ_8, is a linear combination of two of the hydrogen 1s orbitals.

$$\phi_8 = 0.781097(h_\mathrm{a} - h_\mathrm{b}) \tag{19}$$

Two sets of matrix elements involving the methyl carbon $2p\pi$ orbital (ϕ_7) are shown in columns 7a and 7b. These have been obtained, respectively, by treating the methyl carbon as aliphatic ($k_{i7} = 0.731$) or as aromatic ($k_{i7} = 1.099$).[16] From Table II it is clear that the diagonal SCF matrix elements for the toluene π orbitals do not at all resemble the HMO matrix elements. In particular, α_8 is more than twice as large as α_0; also $\alpha_1 = \alpha_0$, so that there appears to be no methyl group inductive effect. Nevertheless, calculation of the

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[26] This has also been pointed out by J. P. Colpa and E. de Boer, *Mol. Phys.*, 7, 333 (1964).

[27] If vibronic coupling of the near-degenerate levels is included, better results are obtained with $h_1 = -0.125$ and $k_{17} = 0.65$.[7] The larger inductive effect is required to yield a sufficiently large splitting between the two vibronic states to reduce the thermal mixing to the required extent. Since the methyl proton spin density is larger in the antisymmetric vibronic state than in the antisymmetric electronic state, a smaller k_{17} value is required to yield the experimental methyl proton spin density.

[28] For the ethyl radical, $Q_{\mathrm{CCH_3}}{}^{\mathrm{H}} = 30$ G (D. G. Chesnut, *J. Chem. Phys.*, **29**, 43 (1958); A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); see also ref 23. For the durene positive ion, $Q_{\mathrm{CCH_3}}{}^{\mathrm{H}} = 44$ G (ref 17).

Table II. Extended Huckel (NEMO) **H** Matrix for Toluene π Electrons[a,b]

	1	2	3	4	5	6	7a[c]	7b[d]	8
1	−3.9727	−8.3064	−1.5779	−0.7461	−1.5779	−8.3064	−4.6437	−7.7796	−4.1084
2	−8.3064	−3.9727	−8.3067	−1.5779	−0.7461	−1.5779	−0.9477	−1.3760	−0.5113
3	−1.5779	−8.3067	−3.9727	−8.3064	−1.5779	−0.7461	−0.0612	−0.0838	−0.0403
4	−0.7461	−1.5779	−8.3064	−3.9727	−8.3064	−1.5779	−0.0190	−0.0256	−0.0182
5	−1.5779	−0.7461	−1.5779	−8.3064	−3.9727	−8.3067	−0.0612	−0.0838	−0.0762
6	−8.3064	−1.5779	−0.7461	−1.5779	−8.3067	−3.9727	−0.9477	−1.3760	−1.1736
7a[c]	−4.6437	−0.9477	−0.0612	−0.0190	−0.0612	−0.9477	−9.9044		−15.1666
7b[d]	−7.7796	−1.3760	−0.0838	−0.0256	−0.0838	−1.3760		−9.9044	−20.0236
8	−4.1084	−0.5113	−0.0403	−0.0182	−0.0762	−1.1736	−15.1666	−20.0236	−8.7856

[a] Row i, column j gives the matrix element between atomic orbitals ϕ_i and ϕ_j. [b] In units of electron volts. [c] With $k_{i7} = 0.731$ (see ref 16). [d] With $k_{i7} = 1.099$ (see ref 16).

Table III. Orthogonalized Atomic Orbitals (OAO'S) for Toluene π Electrons[a]

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
ϕ_1^{or}	1.06475	−0.13181	0.00818	−0.00557	0.00821	−0.13192	−0.10942	0.00341
ϕ_2^{or}	−0.13182	1.04816	−0.13066	0.00823	−0.00548	0.00833	0.00489	0.00058
ϕ_3^{or}	0.00817	−0.13065	1.04805	−0.13065	0.00822	−0.00548	0.00059	−0.00028
ϕ_4^{or}	−0.00557	0.00823	−0.13064	1.04805	−0.13070	0.00824	0.00056	−0.00014
ϕ_5^{or}	0.00820	−0.00548	0.00822	−0.13065	1.04804	−0.13067	−0.00020	0.00112
ϕ_6^{or}	−0.13193	0.00834	−0.00548	0.00823	−0.13067	1.04827	0.00991	−0.00951
ϕ_7^{or}	−0.10954	0.00487	0.00057	0.00056	−0.00022	0.00983	1.22056	−0.41921
ϕ_8^{or}	0.00350	0.00061	−0.00029	−0.00013	0.00115	−0.00946	−0.41889	1.20384

[a] $\phi_j^{or} = \sum_{i=1}^{8} C_{ji}\phi_i$, where ϕ_i is the Slater 2pπ orbital on atom i, and C_{ji} is the coefficient in the jth row and ith column of the table.

energy levels yields $(E_s(-) - E_a(-)) = 0.409$ eV and $(E_s(+) - E_a(+)) = 1.708$ eV; although too large in magnitude, both energy differences have the correct sign. Moreover, the spin density distributions turn out to be similar to the Hückel results (see below).

The apparent discrepancy between the SCF and HMO matrix elements can be resolved, however, if we note that the SCF matrix elements for nonorthogonal π orbitals are not really appropriate for comparison with HMO matrix elements. The secular equation corresponding to the **H** matrix of Table II is

$$|\mathbf{H} - E\mathbf{S}| = 0 \tag{20}$$

where **S** is the nondiagonal overlap matrix for the toluene π orbitals. In the HMO calculation, however, it is assumed that **S** is diagonal, so that the secular equation simplifies to

$$|\mathbf{H} - E\mathbf{I}| = 0 \tag{21}$$

In order to have a meaningful comparison between the two sets of matrix elements, eq 20 must be transformed so that it reduces to eq 21. This can be best accomplished by obtaining the extended Hückel matrix elements for the symmetrically orthogonalized orbitals (Lowdin orbitals or OAO's).[29]

Table III lists the toluene OAO's, each one of which is dominated by the contribution of one atomic orbital. The ring carbon OAO's are approximated rather well by the 2pπ atomic orbitals; the methyl group OAO's, however, contain significant contributions from both the methyl carbon 2pπ orbital and the H_3 group pseudo-π orbital due to their large overlap. Table IV gives the SCF Hamiltonian matrix corresponding to the toluene OAO's. Considering the diagonal elements (the α values of the OAO extended Hückel matrix), we note that they resemble the Hückel α's in several important respects. There is a methyl inductive effect (α_1 is less negative than the "normal" ring α's, $\alpha_2, \ldots, \alpha_6$) and the methyl group α values (α_7 and α_8) are more positive than the ring carbon values. Quantitatively, the Hückel and extended Hückel α values still look quite different, as do the two alternative complete OAO **H** matrices.

Since the eigenvectors and the structure of the eigenvalue spectrum depend only on the form of the **H** matrix, we can further reduce the extended Hückel formulation by dividing all of the elements by an effective β_0^{EH}. In complete analogy with the ordinary Hückel formulation, the elements can then be expressed as products of certain factors (h_i, k_{ij}) times β_0^{EH}. Choosing $\beta_0^{EH} = -8.17545$ eV (the value of β_{34}), we obtain the matrix shown in Table V. Except for the fact that there are nonzero matrix elements between orbitals on nonnearest neighbors and that $\alpha_0 \simeq 0$ (which corresponds to a particular zero of energy), the **H** matrix of Table V is very similar to the Hückel Hamiltonian matrix for toluene. The terms of particular interest are

$$\alpha_1 = \alpha_0 - 0.104\beta_0^{EH} \qquad \beta_{17} = 0.411\beta_0^{EH}$$
$$\alpha_7 = \alpha_0 - 0.005\beta_0^{EH} \qquad \beta_{78} = 1.853\beta_0^{EH}$$
$$\alpha_8 = \alpha_0 - 0.101\beta_0^{EH}$$

if the methyl carbon is considered to be aliphatic ($k_{i7} = 0.731$), or, alternatively

$$\alpha_1 = \alpha_0 - 0.191\beta_0^{EH} \qquad \beta_{17} = 0.927\beta_0^{EH}$$
$$\alpha_7 = \alpha_0 - 0.714\beta_0^{EH} \qquad \beta_{78} = 0.848\beta_0^{EH}$$
$$\alpha_8 = \alpha_0 - 0.701\beta_0^{EH}$$

if the methyl carbon is considered to be aromatic ($k_{ij} = 1.099$). The corresponding Huckel matrix elements

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(29) P. O. Lowdin, *J. Chem. Phys.*, **18**, 365 (1950).

Table IV. Extended Huckel (NEMO) H Matrix for Toluene OAO'S[a,b]

	1	2	3	4	5	6	7	8
				$k_{i7} = 0.731$[c]				
1	0.8489	−8.2835	0.6430	−0.5146	0.6433	−8.2796	−3.3608	−1.4377
2	−8.2835	0.0000	−8.1758	0.6455	−0.5060	0.6577	0.3625	0.0667
3	0.6430	−8.1758	−0.0141	−8.1755	0.6445	−0.5057	0.0387	−0.0210
4	−0.5146	0.6455	−8.1755	−0.0145	−8.1755	0.6455	0.0468	−0.0080
5	0.6433	−0.5060	0.6445	−8.1755	−0.0138	−8.1777	−0.0329	0.1128
6	−8.2796	0.6577	−0.5057	0.6455	−8.1777	0.0121	0.7669	−0.7804
7	−3.3608	0.3625	0.0387	0.0468	−0.0329	0.7669	0.0422	−15.1476
8	−1.4377	0.0667	−0.0210	−0.0080	0.1128	−0.7804	−15.1476	0.8243
				$k_{i7} = 1.099$[c]				
1	1.5586	−8.2951	0.6399	−0.5175	0.6435	−8.3129	−7.5787	0.5613
2	−8.2951	−0.0003	−8.1758	0.6455	−0.5060	0.6573	0.3267	0.0543
3	0.6399	−8.1758	−0.0141	−8.1754	0.6445	−0.5056	0.0536	−0.0291
4	−0.5175	0.6455	−8.1754	−0.0145	−8.1755	0.6458	0.0606	−0.0156
5	0.6435	−0.5060	0.6445	−8.1755	−0.0138	−8.1777	−0.0284	0.1122
6	−8.3129	0.6573	−0.5056	0.6458	−8.1777	0.0123	0.8031	−0.8428
7	−7.5787	0.3267	0.0536	0.0606	−0.0284	0.8031	5.8358	−23.2872
8	0.5613	0.0543	−0.0291	−0.0156	0.1122	−0.8428	−23.2872	5.7289

[a] Row i, column j gives the matrix element between ϕ_i^{or} and ϕ_j^{or} of Table III. [b] In units of electron volts. [c] See ref 16.

Table V. Extended Huckel (NEMO) H Matrix for Toluene OAO's in Units of β_0^{EH} [a,b]

	1	2	3	4	5	6	7	8
				$k_{77} = 0.731$[c]				
1	−0.1038	1.0132	−0.0786	0.0629	−0.0786	1.0127	0.4111	0.1759
2	1.0132	0.0000	1.0000	−0.0789	0.0619	−0.0804	−0.0443	−0.0082
3	−0.0786	1.0000	0.0017	1.0000	−0.0788	0.0619	−0.0047	0.0026
4	0.0629	−0.0789	1.0000	0.0018	1.0000	−0.0790	−0.0057	0.0010
5	−0.0786	0.0169	−0.0788	1.0000	0.0017	1.0003	0.0040	−0.0138
6	1.0127	−0.0804	0.0619	−0.0790	1.0003	−0.0015	−0.0938	0.0955
7	0.4111	−0.0443	−0.0047	−0.0057	0.0040	−0.0938	−0.0052	1.8528
8	0.1759	−0.0082	0.0026	0.0010	−0.0138	0.0955	1.8528	−0.0008
				$k_{17} = 1.099$[c]				
1	−0.1906	1.0146	−0.0783	0.0633	−0.0787	1.0168	0.9270	−0.0687
2	1.0146	0.0000	1.0000	−0.0790	0.0619	−0.0804	−0.0400	−0.0066
3	−0.0783	1.0000	0.0017	1.0000	−0.0788	0.0618	−0.0066	0.0035
4	0.0633	−0.0790	1.0000	0.0018	1.0000	−0.0790	−0.0074	0.0019
5	−0.0787	0.0619	−0.0788	1.0000	0.0017	1.0003	0.0035	−0.0137
6	1.0168	−0.0804	0.0618	−0.0790	1.0003	−0.0015	−0.0982	0.1031
7	0.9270	−0.0400	−0.0066	−0.0074	0.0035	−0.0982	−0.7138	2.8484
8	−0.0687	−0.0066	0.0035	0.0019	−0.0137	0.0131	2.8484	−0.7007

[a] Row i, column j gives the matrix element between ϕ_i^{or} and ϕ_j^{or} of Table III. [b] $\beta_0^{EH} = -8.1745$ eV. [c] See ref 16.

Table VI. π-Electron Energy Levels of Toluene[a]

	Extended Hückel[b]				
	$k_{i7} = 0.731$[e]		$k_{i7} = 1.099$[e]		
Energies	I	N	I	N	Hückel[c,d]
E_1	2.033	2.058	2.379	2.441	2.501
E_2	1.757	1.785	1.806	1.862	1.888
$E_a(+)$	1.019	1.001	1.109	1.001	1.000
$E_s(+)$	0.932	0.952	0.900	0.874	0.893
$E_a(-)$	−0.853	−1.000	−0.853	−1.000	−1.000
$E_s(-)$	−0.910	−1.021	−0.903	−1.059	−1.018
E_7	−1.877	−1.860	−2.184	−2.013	−1.970
E_8	−2.308	−2.121	−3.765	−3.708	−2.956

[a] I, with nonnearest neighbor terms of Table V; N, without nonnearest neighbor terms of Table V. [b] In units of $\beta_0^{EH} = -8.17545$ eV. [c] In units of $\beta_0^{H} = -2.36$ eV; with $h_8 = -0.5$; $h_7 = -0.05$; $h_1 = -0.120$; $k_{17} = 0.86$; $k_{78} = 2.50$. [d] Relative to α_0 as zero. [e] See ref 16.

given in section II are

$$\alpha_1 = \alpha_0 - 0.120\beta_0^{H} \qquad \beta_{17} = 0.86\beta_0^{H}$$

$$\alpha_7 = \alpha_0 - 0.05\beta_0^{H} \qquad \beta_{78} = 2.5\beta_0^{H}$$

$$\alpha_8 = \alpha_0 - 0.5\beta_0^{H}$$

The Hückel parameters fall between the set of extended Hückel parameters obtained assuming that the methyl carbon is aromatic and that obtained assuming it to be aliphatic. Intuitively, this is a reasonable and consistent result.

To complete the analysis of the relationship between Hückel and extended Hückel theory, consideration must be given to the presence of nonnearest neighbor H matrix elements in Table V. Also, there is some question about the validity of approximating the OAO's by one-center atomic orbitals in calculating the spin and charge densities.

Table VI compares the toluene energy levels obtained with and without the nonnearest neighbor matrix elements of Table V; also included are the corresponding Huckel energies. Both with and without the nonneighbor terms, the ordering of the unpaired electron energy levels of the positive and negative ions is correct; however, the splitting in the anion is $0.057\beta_0^{EH}$ ($k_{i7} = 0.731$) or $0.050\beta_0^{EH}$ ($k_{i7} = 1.099$) as compared with the Hückel value of $0.018\beta_0^{H}$. Since $\beta_0^{EH} = -8.175$ eV, while $\beta_0^{H} = -2.36$ eV, the splitting in the extended Hückel calculation is about ten times as large as in the

Table VII. Toluene Anion Spin Densities[a]

	Extended Huckel[b]				
	AO		OAO[e]		
	spin density[d]		spin density		
i	I	N	I	N	Huckel[c]
	Symmetric State (ψ_s)				
1	0.3057	0.3174	0.3062	0.3179	0.3194
2	0.0825[f]	0.0634[f]	0.0826[f]	0.0635[f]	0.0743
3	0.0979[g]	0.0937[g]	0.0979[g]	0.0937[g]	0.0828
4	0.2960	0.3326	0.2960	0.3325	0.3198
7	0.0007	0.0005	0.0010	0.0005	0.0019
8	0.0367	0.0353	0.0360	0.0347	0.0447
	Antisymmetric State (ψ_a)				
1	0.0233	0.0001	0.0234	0.0001	0.0000
2	0.2363[f]	0.2503[f]	0.2364[f]	0.2503[f]	0.2500
3	0.2379[g]	0.2497[g]	0.2379[g]	0.2497[g]	0.2500
4	0.0227	0.0000	0.0227	0.0000	0.0000
7	0.0010	0.0000	0.0009	0.0000	0.0000
8	0.0045	0.0000	0.0044	0.0000	0.0000

[a] I, with nonnearest neighbor terms of Table V; N, without nonnearest neighbor terms of Table V. [b] With $k_{i7} = 1.099$. [c] With $h_8 = -0.05$; $h_7 = -0.05$; $h_1 = -0.120$; $k_{17} = 0.86$; $k_{78} = 2.50$. [d] Defined in eq 23. [e] Defined in eq 22. [f] Average of spin densities calculated for positions 2 and 6. [g] Average of spin densities calculated for positions 3 and 5.

HMO treatment. Thus the extended Hückel value is certainly too great to account for the temperature dependence of the toluene anion esr hyperfine constants and related phenomena. The two sets of extended Hückel energies are very similar; on the average, the excitation energies obtained in the two calculations differ by about $0.15\beta_0^{\mathrm{EH}}$, the lower excitation energies being larger and the higher energies smaller if the nonneighbor terms are neglected.

Toluene anion spin densities calculated from the extended Hückel theory functions are shown in Table VII, which includes the Hückel results for comparison. In the presence of nonzero overlap there is some uncertainty about what is the appropriate formulation, particularly when the spin densities are to be used for evaluating hyperfine constants. If the proper basis for a Hückel calculation with neglect of overlap is the set of OAO's, the Hückel spin densities are expected to correspond most closely to the results of the extended Hückel calculation with

$$\rho_i^{\mathrm{OAO}} = C_i^2 \tag{22}$$

where C_i is the coefficient of ϕ_i^{or} in the unpaired electron orbital. Alternatively, it is possible to define atomic orbital spin densities (ρ_i^{AO}) by

$$\rho_i^{\mathrm{AO}} = \sum_{j,k=1}^{8} C_j C_k \langle \phi_j^{\mathrm{or}} | \mathrm{O}_i | \phi_k^{\mathrm{or}} \rangle \tag{23}$$

In eq 23, the operator O_i is defined by

$$\langle \phi_i | \mathrm{O}_i | \phi_i \rangle = 1$$

$$\langle \phi_i | \mathrm{O}_i | \phi_j \rangle = {}^1\!/_2 S_{ij}$$

$$\langle \phi_j | \mathrm{O}_i | \phi_{j'} \rangle = 0 \qquad \text{if } j, j' \neq i$$

Comparison of eq 22 with eq 23 by the relation between the ϕ_j^{or} and the ϕ_j shows that ρ_i^{OAO} equals ρ_i^{AO} through first order in the overlap; thus the differences between these two definitions for the spin density are not expected to be large. From Table VII, it is evident that the ρ_i^{OAO} and ρ_i^{AO} values are very similar, although there are differences between the results obtained with and without the nonnearest neighbor terms. All of the different extended Huckel spin densities are also rather close to the Huckel values.

III. Conclusions

An HMO perturbation treatment of the energy splitting between the two lowest near-degenerate electronic states of the toluene anion and cation has been performed to demonstrate the importance of both hyperconjugation and the inductive effect in these systems. Hyperconjugation has been shown to lower the energy of the anion symmetric orbital relative to that of the antisymmetric orbital, but to raise the energy of the corresponding cation orbital. This is due to the fact that the interaction between the methyl antibonding orbital and the ring predominates in the anion, while in the cation interaction with the methyl bonding orbital provides the dominant term. Since the anion esr spectrum shows that the unpaired electron is located primarily in the antisymmetric orbital,[8] some additional factor is required to produce the correct ordering of the two levels. The methyl group inductive effect appears to be the simplest and most reasonable choice. It raises the energy of both the anion and the cation symmetric obtitals. The hyperconjugative and the inductive contributions to the energy splitting thus tend to cancel in the anion, but have the same sign in the cation. Consequently, the cation energy splitting is larger than the anion splitting, and thermal and vibrational coupling are expected to be less important in the former radical. This result, together with the calculation of Colpa and de Boer[26] which showed that σ–π spin polarization cannot account for the observed methyl proton hyperfine splittings, leads to the conclusion that the methyl group–aromatic ring interaction consists of both hyperconjugative and inductive contributions. This has also been suggested by studies of the spectra[11,12] and reactivities[30] of methyl-substituted aromatic molecules.

Recent extended Hückel calculations with empirical[13] and nonempirical SCF parameters[15,16] have cast some doubt on the above conclusions in that no inductive parameter appears to be required to obtain the level ordering consistent with the esr results. Moreover, the individual extended Hückel parameters are very different from their ordinary HMO counterparts. Since the extended Hückel theory includes all overlap terms while the HMO method assumes that the orbitals are orthogonal, a valid comparison of the two approaches requires that the former be reexpressed in terms of orthogonalized atomic orbitals (OAO). After the transformation, the extended Hückel and ordinary Hückel parameters are found to yield consistent Hamiltonian matrices. Moreover, the fact that the OAO value for the substituted carbon (C^1) is less negative than that for the unsubstituted carbons suggests that the C^1 orbital, methyl group orbital overlap of the extended Hückel theory may be the origin of the *ad hoc* inductive effect required in the ordinary Hückel method.

Acknowledgment. We wish to thank Professor Roald Hoffmann for first calling our attention to the fact that the extended Hückel theory did not require the explicit introduction of an inductive effect.

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(30) R. W. Taft and I. C. Lewis, *Tetrahedron*, 5, 210 (1959).