

deprotonation of the formyl cation can be expected to be much more extensive at equilibrium than that for the other acylium ions, just as has been observed in solution.

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Calculations of Proton Shieldings in Conjugated Hydrocarbons

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Abstract: In this paper a theory for the calculation of ^1H chemical shifts of planar conjugated hydrocarbons with sp^2 - and sp -hybridized atoms is given. All nonlocal ring current (RC) and local anisotropic (LA) contributions are calculated in the framework of an extended π theory using the coupled Hartree-Fock perturbation theory. The σ core is approximated by localized two-center bonds. Therefore, it gives only LA contributions which are calculated by applying the uncoupled Hartree-Fock perturbation theory. The method can be successfully applied to cyclic and noncyclic conjugated hydrocarbons containing double and triple bonds. The anisotropic long-range shielding of the double and the triple bond is discussed.

In recent years the ring-current concept^{1,2} has been used extensively to calculate ^1H chemical shifts of cyclic conjugated hydrocarbons. These ring currents (RC) can be obtained quantum mechanically by using the Pople³ and McWeeny⁴ modifications of the London² theory or their extensions to the SCF method.^{5,6} Also a classical formulation of ring currents has been applied to account for the deshielding of the protons in polycyclic hydrocarbons.⁷ It was shown,^{8,9} however, that the RC contributes only about 50% to the observed deshielding in benzene. The remaining part has to be attributed to local anisotropic (LA) shielding effects. Only a consideration of the combined LA and RC effects provides a useful explanation of the chemical shifts of the inner and outer protons of annulenes.^{9,10}

All mentioned theoretical methods can only be applied to cyclic conjugated hydrocarbons which consist only of sp^2 -hybridized carbon atoms. Most of the known annulenes contain, however, sp -hybridized atoms in triple or in cumulated double bonds. The conformational mobility in these dehydroannulenes is considerably reduced against the annulenes. This fact facilitates the comparison of experimental and theoretical

shifts. Therefore, a quantum mechanical method is presented in this study at which all local and nonlocal contributions to the shielding of any conjugated planar hydrocarbon can be calculated. The size of the studied molecules forces one to adopt the π -electron approximation in order to derive the wave function.

Quantum Mechanical Formulation

A. π -SCF Procedure. Hell¹¹ proposed a modified PPP method¹² which allows the study of conjugated molecules with sp^2 - and sp -hybridized carbon atoms. For the benefit of the reader we shall review this method. The atomic orbital basis set consists of the $2p_{z_A}$ functions on each carbon atom A as in ordinary PPP theory. On each sp -hybridized atom A we have an additional $2p_{y_A}$ function defined as linear combination of $2p_{x_A}$ and $2p_{y_A}$ functions: $2p_{y_A} = a_A 2p_{x_A} + b_A 2p_{y_A}$. The coefficients a and b are defined as $a_A = a_B = (y_A - y_B)r_{AB}^{-1}$ and $b_A = b_B = (x_B - x_A)r_{AB}^{-1}$. A and B are two adjacent sp -hybridized atoms with internuclear separation r_{AB} . Bond angles on sp -hybridized atoms are always taken as 180° . The Hartree-Fock operator F^0 is defined as in ordinary PPP theory.

Table I. PPP Parameters¹¹ (All Integral Values in eV)

A	B	U_A	β_A	γ_{AA}	$\bar{\gamma}_A$	γ_{AA}^a	ζ_A^b	a_{AB}^c	b_{AB}^c
Csp ²	Csp ²	-10.00	-11.42	10.07		6.00	1.625	1.541	-0.216
Csp ²	Csp							1.498	-0.208
Csp	Csp	-18.33	-11.84	10.07	0.87	6.00	1.625	1.453	-0.126

^a Monocentric repulsion integrals used for the γ_{AB} integrals. ^b Orbital exponents used for the overlap integrals $S_{SA'IB}$. ^c In Å.

If we denote with s_A the $2p_{z_A}$ orbital and with $s_{A'}$ the $2p_{y_{A'}}$ orbital, we obtain the following matrix elements of F^0 :

$$F_{SA'IB}^0 = H_{SA'IB}^0 + (\delta_{st} - 1/2)P_{SA'IB}^0\gamma_{AB} \\ + \delta_{st} \left[\sum_{C \neq A} (P_{tC}^0 + \delta_{C,sp}P_{tC'}^0)\gamma_{AC} \right. \\ \left. + \delta_{A,sp}P_{SA'SA'}^0(\gamma_{AA} - 5\bar{\gamma}_A/2) \right] \\ H_{SASA}^0 = U^{sp^2} - \sum_{B \neq A} (1 + \delta_{B,sp})\gamma_{AB}$$

$H_{SA'IB}^0 = \beta S_{SA'IB}$ if A and B are next neighbors; otherwise $H_{SA'IB}^0 = 0$ ($F_{SA'IB}^0$ and $H_{SA'IB}^0$ are analogous). $\delta_{A,sp} = 1$ if A is sp-hybridized; otherwise $\delta_{A,sp} = 0$. All one-center integrals are considered in F^0 as in the INDO theory.^{11,13} The electron-repulsion integrals γ_{AB} are calculated according to Mataga and Nishimoto.¹⁴ Self-consistent bond lengths are obtained using the relationship $r_{AB} = a_{AB} + b_{AB}(P_{SA'IB}^0 + \delta_{A,sp}\delta_{B,sp}P_{SA'IB}^0)$ in each SCF iteration. All necessary parameters are given in Table I. The ordinary π -molecular orbitals are linear combinations of the $2p_z$ functions, $i^0 = \sum_s c_{is}^0 s$, and likewise the π' -molecular orbitals are linear combinations of the $2p_y$ functions, $i'^0 = \sum_{s'} c_{i's'}^0 s'$. The corresponding orbital energies are ϵ_i^0 and $\epsilon_{i'}^0$. It is possible to treat these π' orbitals together with the π orbitals only if we consider the σ core to be composed of localized σ -molecular orbitals instead of canonical ones. Since these localized orbitals have the symmetry of the correspondent bonds, we have around a triple bond a local C_{2v} symmetry and we obtain in our basis set σ , π , and π' orbitals.¹¹

B. π - and π' -Electronic Contributions to the Chemical Shift. The Hartree-Fock operator F^0 can be written as $F^0 = H^0 + G^0$ with the electron interaction operator G^0 , $H^0 = T^0 + V^0$, $T^0 = -\hbar^2(2m)^{-1}\Delta$ being the kinetic energy operator. Now consider an external magnetic field \mathbf{h} and the field of an infinitesimal "test" dipole \mathbf{m} introduced at the proton whose chemical shift shall be calculated. The new Hartree-Fock operator F is written as $F = H + G$ with $H = T + V^0$. The kinetic energy operator $T = \hbar^2(2m)^{-1}(-i\nabla + e(\hbar c)^{-1}\mathbf{A})^2$ contains the vector potential $\mathbf{A} = \mathbf{A}^h + \mathbf{A}^m = (\mathbf{h} \wedge \mathbf{r})/2 + R^{-3}(\mathbf{m} \wedge \mathbf{R})$ of the fields \mathbf{h} and \mathbf{m} . The origin of \mathbf{r} can be chosen arbitrarily.^{15,16} The origin of \mathbf{R} is fixed at the proton in question. Since we are only interested in the trace of the chemical shift tensor, we need merely to consider the special cases $\mathbf{h} = (h_x, h_y, h_z)$ with $h_x = h, h_y = h_z = 0$ ($k = x$), $h_y = h, h_x = h_z = 0$ ($k = y$) or $h_z = h, h_x = h_y = 0$ ($k = z$) and the similar equations for \mathbf{m} . In the fields gauge invariant orbitals² $\omega_{sA}^{(1)} = s_A^{(1)} \exp[-ie(\hbar c)^{-1}(\mathbf{A}_A^h \mathbf{r} + \mathbf{A}_A^m \mathbf{R})]$ are introduced. \mathbf{A}_A^h and \mathbf{A}_A^m are the vector potentials at the atom A. For all two-center integrals the London approximations^{2,17} are applied:

$$\mathbf{r} \rightarrow (\mathbf{r}_A + \mathbf{r}_B)/2 \quad R^{-3} \rightarrow |\mathbf{R}_A + \mathbf{R}_B|^{-3}/8, = K_{AB}/2$$

Expanding the operator H in powers of h , and m , $H^k = \sum_{p,q=0}^{\infty} h^p m^q H^k(pq)$ with $H^k(00) = H^0$, we get the following matrix elements in respect to the basis functions s_A and $s_{A'}$:

$$H_{SS}^k(10) = H_{SS}^k(01) = 0 \\ H_{SASA'}^k(10) = e\hbar(2mc)^{-1} \langle s_A | L_A^k | s_{A'} \rangle \\ H_{SASA'}^z(01) = e\hbar(2mc)^{-1} [\langle s_A | R^{-3} L_A^z - i(R^{-3} - R_A^{-3}) \\ \times (X_A \partial / \partial y - Y_A \partial / \partial x) | s_{A'} \rangle + c.c.]$$

$$H_{SA'IB}^k(10) = ie(\hbar c)^{-1} S_{AB}^k H_{SA'IB}^0$$

$$H_{SA'IB}^k(01) = ie(\hbar c)^{-1} \bar{S}_{AB}^k K_{AB} H_{SA'IB}^0$$

$$H_{SASA}^z(11) = e^2(4mc^2)^{-1} \langle s_A | (X_A(x - x_A) + Y_A(y - y_A)) \\ \times (R^{-3} - R_A^{-3}) + R^{-3}((x - x_A)^2 + (y - y_A)^2) | s_A \rangle$$

$$H_{SA'IB}^k(11) = -e^2(\hbar c)^{-2} S_{AB}^k \bar{S}_{AB}^k K_{AB} H_{SA'IB}^0$$

$$(H_{SA'IB}^k(10), H_{SA'IB}^k(01), H_{SASA'}^k(11), \\ \text{and } H_{SA'IB}^k(11) \text{ are analogous})$$

$$S_{AB}^z = (x_A y_B - x_B y_A)/2 \quad \bar{S}_{AB}^z = (X_A Y_B - X_B Y_A)/2$$

L_A^k is the k component of the operator of the angular momentum at atom A. All missing formulas for $k = x$ or y are obtained by cyclic permutation of the coordinates.

Adopting the coupled Hartree-Fock perturbation theory,⁵ we get the following π - and π' -electronic contributions to the second-order energy $E^k(11) = E_{11}^k + E_{011}^k$:

$$E_{11}^k = 2 \sum_I^{\text{occ}} \langle i^0 | H^k(11) | i^0 \rangle + 2 \sum_I^{\text{occ}} \langle i'^0 | H^k(11) | i'^0 \rangle$$

$$E_{011}^k = 4 \sum_i^{\text{occ}} \langle i^0 | H^k(01) | i^k(10) \rangle \\ + 4 \sum_{i'}^{\text{occ}} \langle i'^0 | H^k(01) | i'^k(10) \rangle$$

$i^k(10)$ and $i'^k(10)$ are the first-order molecular orbitals. Now it is possible to divide E_{11}^k as follows: $E_{11}^k = E_{11}^{k,l} + E_{11}^{k,n} + E_{11}^{k,n'}$, with the local contribution $E_{11}^{k,l} = \sum_A [P_{SASA}^0 H_{SASA}^k(11) + \delta_{A,sp} P_{SA'SA'}^0 H_{SA'SA'}^k(11)]$, the nonlocal contribution $E_{11}^{k,n}$ of the π -electron system $E_{11}^{k,n} = 2 \sum_{A < B} P_{SA'IB}^0 H_{SA'IB}^k(11)$, and a similar contribution $E_{11}^{k,n'}$, of the π' -electron system. The first-order orbitals are obtained iteratively from the equations¹⁶

$$i^k(10) = \sum_I^{\text{unocc}} \lambda_{iI}^k(10) | I^0 \rangle + \sum_I^{\text{unocc}} \lambda_{iI}^k(10) | I'^0 \rangle$$

$$\lambda_{iI}^k(10) = \bar{\lambda}_{iI}^k(10) + (\epsilon_i^0 - \epsilon_I^0)^{-1} \sum_j^{\text{occ}} \sum_m^{\text{unocc}} \lambda_{jm}^k(10) G_{ijm}^0$$

$$\bar{\lambda}_{iI}^k(10) = (\epsilon_i^0 - \epsilon_I^0)^{-1} \langle i^0 | H^k(10) | I^0 \rangle$$

$$G_{ijm}^0 = \int \int i^0(1) | I^0(2) \rangle (j^0(1) m^0(2) - j^0(2) m^0(1)) r_{12}^{-1} d\tau_1 d\tau_2$$

and analogous ones for $i'^k(10)$, $\bar{\lambda}_{iI}^k(10)$, and $\lambda_{iI}^k(10)$ as well can be divided in $\bar{\lambda}_{iI}^k(10) = \bar{\lambda}_{iI}^{k,l}(10) + \bar{\lambda}_{iI}^{k,n}(10) + \bar{\lambda}_{iI}^{k,n'}(10)$, with the local term ($\sum_A^{\text{sp}} \bar{\lambda}_{iI}^k \equiv \sum_A \delta_{A,sp} \bar{\lambda}_{iI}^{k,l}(10) = (\epsilon_i^0 - \epsilon_I^0)^{-1} \sum_A^{\text{sp}} (c_{iSA}^0 c_{ISA}^0 - c_{iSA}^0 c_{ISA}^0) H_{SASA'}^k(10)$) and the nonlocal term for the π -electron system $\bar{\lambda}_{iI}^{k,n}(10) = (\epsilon_i^0 - \epsilon_I^0)^{-1} \sum_{A < B} (c_{iSA}^0 c_{iIB}^0 - c_{iIB}^0 c_{iSA}^0) H_{SA'IB}^k(10)$ and the corresponding one for the π' -electron system. Applying the ZDO approximation in the G_{ijm}^0 integral one can show that only the following λ coefficients are not zero:

$$\lambda_{iI}^{k,l}(10) = \bar{\lambda}_{iI}^{k,l}(10) + (\epsilon_i^0 - \epsilon_I^0)^{-1} \sum_j^{\text{occ}} \sum_{m'}^{\text{unocc}} \lambda_{jm'}^{k,l}(10) G_{ijm'}^0 \\ + \sum_j^{\text{occ}} \sum_m^{\text{unocc}} \lambda_{jm}^{k,l}(10) G_{ijm}^0$$

$$\lambda_{iI}^{k,n}(10) = \bar{\lambda}_{iI}^{k,n}(10) + (\epsilon_i^0 - \epsilon_I^0)^{-1} \sum_j^{\text{occ}} \sum_m^{\text{unocc}} \lambda_{jm}^{k,n}(10) G_{ijm}^0$$

$$(\lambda_{iI}^{k,l}(10) \text{ and } \lambda_{iI}^{k,n'}(10) \text{ are analogous})$$

We arrive at the following second-order energies $E_{011}^{k,l} = E_{011}^{k,l} + E_{011}^{k,n} + E_{011}^{k,\pi}$ with the local contribution $E_{011}^{k,l} = 4\sum_A \delta_{A,sp} f_A^{k,l}(10) H_{sASA}^k(01)$ and the nonlocal contribution of the π -electron system $E_{011}^{k,n} = 4\sum_{A<B} f_{AB}^{k,n}(10) H_{sAB}^k(01)$ and the similar one of the π' -electron system. The coefficients f are calculated as follows:

$$f_A^{k,l}(10) = \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \lambda_{ij}^{k,l}(10) c_{iSA}^0 c_{jSA}^0 - \sum_j^{\text{occ}} \sum_i^{\text{unocc}} \lambda_{ij}^{k,l}(10) c_{iSA}^0 c_{jSA}^0$$

$$f_{AB}^{k,n}(10) = \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \lambda_{ij}^{k,n}(10) (c_{iSA}^0 c_{jTB}^0 - c_{iTB}^0 c_{jSA}^0)$$

($f_{AB}^{k,\pi}(10)$ is analogous)

It is interesting to note that all nonlocal terms which couple the π - and π' -electron systems are zero. Since we have used the tight-binding approximation for the H^0 operator, the π' -electron system can never be cyclic conjugated. That means that all nonlocal contributions of the π' -electrons are also zero;¹⁸ i.e., $E_{11}^{k,\pi'} + E_{011}^{k,\pi'} = 0$.

C. σ -Core Contributions to the Chemical Shift. In the framework of the π theory we consider the σ core to be composed of totally localized two-center σ bonds and 1s atomic orbitals on all carbon atoms. The σ bonds are built up from sp^2 , sp -hybrid, and 1s orbitals of all hydrogen atoms. The three sp^2 hybrids and the two sp hybrids are given as¹⁹

$$(sp^2)_{iA} = 3^{1/2} 2s_A - (-)^{\delta_{i1}} (1 + \delta_{i1}) 6^{1/2} 2p_{xA'} - (-)^{\delta_{i2}} 2^{1/2} 2p_{yA'}$$

$$(sp)_{iA} = 2^{1/2} (2s_A - (-)^i 2p_{xA'})$$

The $2p_{xA'}$ and the $2p_{yA'}$ atomic orbitals on the sp^2 -hybridized atom A are defined as $2p_{xA'} = c_A 2p_{xA} - d_A 2p_{yA}$ and $2p_{yA'} = d_A 2p_{xA} + c_A 2p_{yA}$ with $c_A = (x_B - x_A) r_{AB}^{-1}$ and $d_A = (y_A - y_B) r_{AB}^{-1}$. B is an arbitrarily chosen atom which is the next neighbor of atom A.²⁰ On an sp -hybridized atom A we have the $2p_{yA'}$ orbital as defined in section A and the orbital $2p_{xA'} = b_A 2p_{xA} - a_A 2p_{yA}$. We assume that all charge densities of all atomic orbitals in the σ core are 1. Since all σ bonds are treated as localized, we will not have any nonlocal contributions from the σ core.

The second-order energies for the σ core are given in an analogous manner as for the local π - and π' -electron terms.

$$E^{k,\sigma}(11) = E_{11}^{k,\sigma} + E_{011}^{k,\sigma}$$

$$E_{11}^{k,\sigma} = \sum_A \left[\sum_{s=1s,2s,2p_x'}^A \langle s | H^k(11) | s \rangle + \delta_{A,sp^2} \langle 2p_{yA'} | H^k(11) | 2p_{yA'} \rangle \right] + \sum_H \langle 1s_H | H^k(11) | 1s_H \rangle$$

$$E_{011}^{k,\sigma} = (\Delta E)^{-1} \sum_A \sum_{s<t}^A \sum_B \sum_{u<v}^B H_{st}^k(10) H_{uv}^k(01) Q_{stuv}^0$$

$$Q_{stuv}^0 = P_{su}^0 (2\delta_{tv} - P_{tv}^0) + P_{tv}^0 (2\delta_{su} - P_{su}^0) - P_{sv}^0 (2\delta_{tu} - P_{tu}^0) - P_{tu}^0 (2\delta_{sv} - P_{sv}^0)$$

The last summation in $E_{11}^{k,\sigma}$ runs over all hydrogen atoms. $E_{011}^{k,\sigma}$ has been derived by Pople¹⁸ using uncoupled Hartree-Fock perturbation theory and approximating all energy denominators by a mean excitation energy ΔE . The summations extend over all atomic orbitals 1s, 2s, $2p_x'$, $2p_y'$, and $2p_z'$, except on sp -hybridized atoms where $s,u = 2p_{y'}$ and $t,v = 2p_z'$ is omitted, because this term is already calculated exactly in the π theory. In contrast to Pople,¹⁸ we shall not introduce further approximations in $E_{011}^{k,\sigma}$.

Evaluating all necessary integrals, we arrive at the following local contributions to the second-order energies:

$$E_{11}^l = \sum_k (E_{11}^{k,l} + E_{11}^{k,\sigma}) = e^2 (2mc^2)^{-1} \times \left\{ \sum_A \left[(1 + P_{sASA}^0) \left\langle 2p_{xA} \left| \left(\frac{4}{3} \bar{x}_A^2 + R_A \bar{z}_A \right) R^{-3} \right| 2p_{xA} \right\rangle + (3 + P_{sASA}^0) \langle 2p_{xA} | \bar{z}_A^2 R^{-3} | 2p_{xA} \rangle + (2p_{xA} | (\bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 2p_{xA} \rangle + (2s_A | (2\bar{x}_A^2 + \bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 2s_A \rangle + \langle 1s_A | (2\bar{x}_A^2 + \bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 1s_A \rangle \right] + \sum_A^{sp} (P_{sA'sA'}^0 - 1) \left[(a_A b_A - b_A a_A) A^2 \times \left\langle 2p_{xA} \left| \left(\frac{4}{3} \bar{x}_A^2 + R_A \bar{z}_A \right) R^{-3} \right| 2p_{xA} \right\rangle + (1 + (a_A a_A + b_A b_A) A^2) \langle 2p_{xA} | \bar{z}_A^2 R^{-3} | 2p_{xA} \rangle + (a_A a_A + b_A b_A) A^2 \langle 2p_{xA} | (\bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 2p_{xA} \rangle \right] + \sum_H \langle 1s_H | (2\bar{x}_H^2 + \bar{z}_H^2 + R_H \bar{z}_H) R^{-3} | 1s_H \rangle \right\}$$

$$E_{011}^{l,\sigma} = \sum_k E_{011}^{k,\sigma} = -(e\hbar/mc)^2 (2\Delta E)^{-1} \times \sum_A [f_A^l \langle 2p_{xA} | R^{-3} | 2p_{xA} \rangle + f_A^2 \langle 2p_{xA} | R^{-3} | 2p_{xA} + R_A 1s_A' \rangle + f_A^3 \langle 2s_A | R^{-3} | 2p_{xA} + R_A 1s_A' \rangle]$$

The integrals appearing in these expressions are defined in local-coordinate systems on each atom; cf. Figure 1. They are given in the Appendix together with the coefficients f_A^k . The integrals are functions of the internuclear distance R_A of atom A and the proton in question. They are shown in Figure 2. Consider the 1s orbital contributions to E_{11}^l (cf. Figure 2a). As we can see, these contributions of the carbon atom (orbital exponent $\zeta = 5.7$) can be neglected. Also we shall neglect the 1s contribution of the proton whose shielding has to be calculated since it can be included in a parameter. The contributions of all other hydrogen atoms are negligible for distances $R_A > 2.5 \text{ \AA}$, whereas for smaller ones we can expect that other effects of opposite sign, e.g., van der Waals shifts,²¹ become more important. These are, however, not included in our theory. Therefore, we can omit all terms with 1s orbitals in E_{11}^l . All other integrals in E_{11}^l can be approximated by $\text{const} \cdot R_A^{-3}$ for sufficiently large R_A . The contribution of a sp^2 -hybridized atom is isotropic around this atom. The same is true for sp -hybridized atoms only if all $P_{sA'sA'}^0 = 1$. For a uniform charge distribution, i.e., all $P_{sASA}^0 = P_{sA'sA'}^0 = 1$, the atomic contribution to E_{11}^l reduces to $e^2 (2mc^2)^{-1} \zeta (1 + 2\beta + 2\beta^2 + 4\beta^3/3) \exp(-2\beta)$ with $\beta = \zeta R_A$. Then all R_A^{-3} terms have disappeared and we will not obtain any appreciable shift for $R_A > 2 \text{ \AA}$. Therefore, for alternant hydrocarbons the neglect of E_{11}^l will be a good approximation. $E_{011}^{l,\sigma}$ depends strongly on the topology of the molecule. It should be mentioned that the third integral in $E_{011}^{l,\sigma}$ has a R_A^{-2} dependence for large R_A rather than the R_A^{-3} one as in the first two integrals.²²

The quality of the approximations adopted for the evaluation of the σ -core contributions can be tested with compounds containing sp -hybridized atoms. Let us define $E_{011}^{y,l} = E_{011}^{l,y} + E_{011}^{y,l}$ ($E_{011}^{l,y} = 0$), where $E_{011}^{l,y}$ is calculated exactly within the π theory. Employing all approximations as for the σ core, we get the equivalent expression

$$\bar{E}_{011}^{y,l} = -(e\hbar/mc)^2 (2\Delta E)^{-1} \sum_A^{sp} f_A^y \langle 2p_{xA} | R^{-3} | 2p_{xA} \rangle + f_A^6 \langle 2p_{xA} | R^{-3} | 2p_{xA} + R_A 1s_A' \rangle]$$

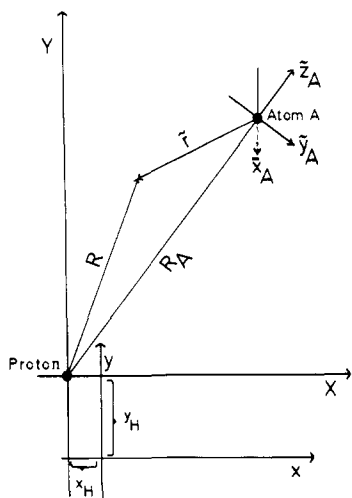


Figure 1. Local-coordinate system (x_A, y_A, z_A) for the evaluation of integrals defined as $X - X_A = x - x_A = A_A z_A - B_A y_A$, $Y - Y_A = y - y_A = B_A z_A + A_A y_A$, and $Z = z = -z_A$ with $A_A = X_A/R_A$ and $B_A = Y_A/R_A$.

D. Parametrization. The chemical shift (δ values in ppm: $\delta = 0$ for Me_4Si ; $\delta > 0$ for lower field) is calculated as follows:

$$\begin{aligned} \delta &= \delta^{\text{RC}} + \delta^{\text{LA}} + \delta_\mu^0 + \delta_\nu^q & \delta_\nu^q &= a_\nu \Delta q_\nu \\ \delta^{\text{RC}} &= -f^{\delta\pi} (E_{11}^{\pi} + E_{011}^{\pi})/3 & \delta^{\text{LA}} &= \delta_{11}^{\text{LA}} + \delta_{011}^{\text{LA}} \\ \delta_{11}^{\text{LA}} &= -E_{11}^{\text{LA}}/3 & \delta_{011}^{\text{LA}} &= -(f^{\delta\sigma} E_{011}^{\text{LA}} + E_{011}^{\text{LA}})/3 \end{aligned}$$

δ^{RC} is the RC and δ^{LA} the LA contribution to the shift. δ_μ^0 defines the zero of the δ scale for different types of protons. $f^{\delta\pi}$ is a scaling factor which corrects the errors introduced by the London approximations. In E_{011}^{π} the average excitation energy ΔE is not yet known. Therefore, we fix $\Delta E = 10$ eV arbitrarily and introduce the parameter $f^{\delta\sigma}$ instead. The last term is the contribution of the excess π -electron density Δq_ν on the bonded carbon atom ν .²³

Results and Discussion

A. Alternant Hydrocarbons. The parameters $f^{\delta\pi}$, $f^{\delta\sigma}$, and δ_μ^0 have been determined by fitting the calculated δ values to 125 experimental ones of alternant hydrocarbons built up of benzene rings and double and triple bonds.^{24,25} The δ_ν^q contribution was not taken into consideration since all excess charge densities Δq_ν are zero (benzenoid hydrocarbons) or very small. For all compounds standard geometries were used.²⁶ Self-consistent bond lengths gave nearly the same results and are not re-

Table II. Parameters for the Calculation of Chemical Shifts and Regression Lines $\delta_{\text{exptl}} = (a \pm \Delta a)\delta + (b \pm \Delta b)$ with Standard Errors Δa and Δb and the Linear Correlation Coefficients \bar{r} (δ Values in ppm)

	$\delta = \delta^{\text{RC}} + \delta_\mu^0$	$\delta = \delta^{\text{RC}} + \delta^{\text{LA}} + \delta_\mu^0$
$\delta_1^0 a$	6.06	5.06
$\delta_2^0 b$	6.49	5.46
$\delta_2^0 - \delta_1^0$	0.44	0.40
$\delta_3^0 c$	5.34	5.02
$\delta_4^0 d$	6.25	5.20
$\delta_5^0 e$	2.75	5.54
$f^{\delta\pi}$	0.8176	0.5569
$f^{\delta\sigma}$		0.6423
$a \pm \Delta a$	1.0000 ± 0.0131	1.0008 ± 0.0104
$b \pm \Delta b$	-0.0000 ± 0.0935	0.0054 ± 0.0742
\bar{r}	0.990	0.993

^a Benzenoid nonovercrowded protons. ^b Benzenoid overcrowded protons. ^c Olefinic α protons. ^d Olefinic β protons. ^e Acetylenic protons.

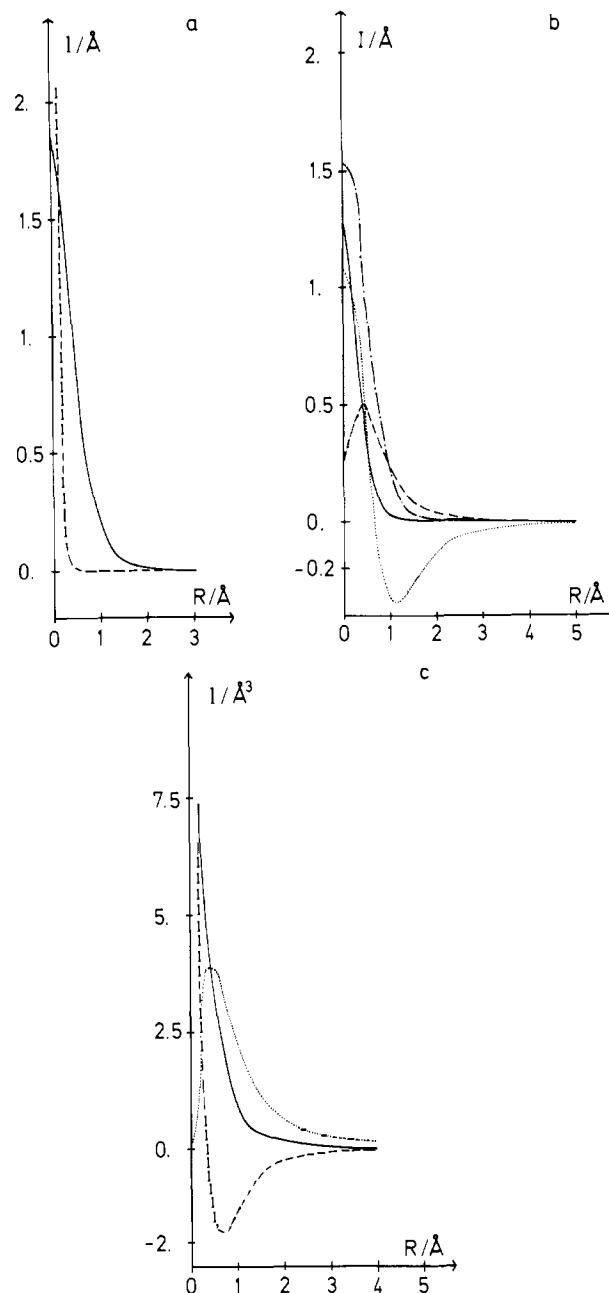


Figure 2. Integrals as a function of the proton atom A distance R_A : (a) integral $\langle 1s_A | (2\bar{x}_A^2 + \bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 1s_A \rangle$ with orbital exponent $\zeta = 1$ (—) and $\zeta = 5.7$ (---); (b) integrals $\langle 2p_{xA} | (\frac{4}{3}\bar{x}_A^2 + R_A \bar{z}_A) R^{-3} | 2p_{xA} \rangle$ (—), $\langle 2p_{xA} | \bar{z}_A^2 R^{-3} | 2p_{xA} \rangle$ (---), $\langle 2p_{xA} | (\bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 2p_{xA} \rangle$ (···), and $\langle 2s_A | (2\bar{x}_A^2 + \bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 2s_A \rangle$ (-·-·) with orbital exponent $\zeta = 1.625$; (c) integrals $\langle 2p_{xA} | R^{-3} | 2p_{xA} \rangle$ (—), $\langle 2p_{xA} | R^{-3} | 2p_{xA} + R_A 1s_A \rangle$ (---), and $\langle 2s_A | R^{-3} | 2p_{xA} + R_A 1s_A \rangle$ (···) with orbital exponent $\zeta = 1.625$.

ported here. All parameters are given in Table II together with the results of a linear regression analysis of experimental and calculated chemical shifts. The inclusion of the LA contributions gives a slightly greater correlation coefficient. The maximal absolute difference between experimental and calculated shifts is reduced from 1 to 0.6 ppm. The calculated shifts of olefinic β protons and of acetylenic protons are considerably improved by LA effects, whereas benzenoid protons are reproduced slightly better if only RC contributions are considered. Since RC effects are fairly unimportant for the olefinic and acetylenic protons in contrast to benzenoid protons, we can conclude that obviously the local contributions of the σ core are calculated with less accuracy than the RC contributions. This is not surprising since we neglect charge-density

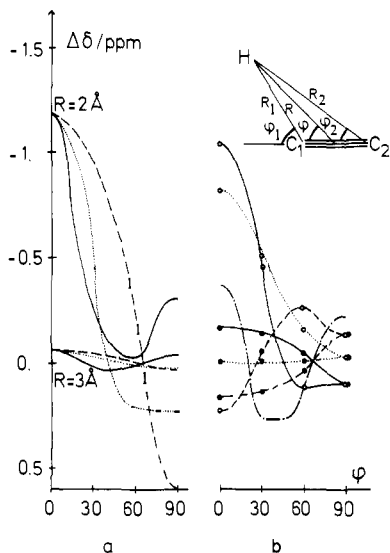


Figure 3. (a) Anisotropic shift $\Delta\delta$ ($\Delta\delta > 0$: shifts to lower field) of a triple bond as a function of φ for $R = 2$ and $R = 3$ Å: (—) calculated as $\Delta\delta = \delta - \delta_0^0$; (---) McConnell equation³⁰ $\Delta\delta = -(\Delta\chi/3)R^{-3}(1 - 3\cos^2\varphi)$ with $\Delta\chi$ [$\text{cm}^3 \text{mol}^{-1}$] = -14.2 ($R = 2$ Å), -2.4 ($R = 3$ Å); (⋯) McConnell equation modified by Pople³¹ $\Delta\delta = (-\Delta\chi/3) \sum_{i=1,2} R_i^{-3} (1 - 3\cos^2\varphi_i)$ with $\Delta\chi = -4.2$ ($R = 2$ Å), -1.0 ($R = 3$ Å). (b) Individual contributions to the anisotropic shift $\Delta\delta = \delta - \delta_0^0$ for $R = 2$ Å as a function of φ : δ_{01}^0 (---), δ_{11}^0 , $\pi = -\sum_k E_{11}^k/3$ (—), $\delta_{11}^0 = -\sum_k E_{11}^k/3$ (---), $\delta_{11}^0 = \delta_{11}^0 + \delta_{11}^0$ (---), δ_{11} terms are divided into atomic contributions (atom 1, ○; atom 2, ●).

changes in the σ core. In olefinic compounds these charge-density changes might yield additional shifts up to 0.5 ppm.²⁷ Therefore, it is not surprising that the maximal error in our calculated shifts is about the same magnitude. For acetylenic protons $|E_{01}^{\sigma}|$ yields shifts up to 0.5 ppm with the studied compounds, whereas for all other proton types, this term is negligible. In most of the molecules with sp-hybridized atoms, E_{01}^{σ} approximates E_{01}^{π} very well. If we calculate δ considering only the RC effect, we should expect that $\delta_1^0 \approx \delta_3^0 \approx \delta_4^0$. Actually we find $\delta_{1,3,4}^0 = 5.80 \pm 0.46$ ppm. Including also the LA contributions we should have a common values for all δ_μ^0 except δ_2^0 . We see in Table II that $\delta_{1,3,4,5}^0 = 5.28 \pm 0.26$ ppm, the deviation now being reduced by 44%. This reflects the importance of LA effects. The difference of δ_2^0 and δ_1^0 can be ascribed to the van der Waals low-field shift²¹ of overcrowded protons.

In Table III the individual contributions to the proton shielding in acetylene, ethylene, benzene, and a hypothetical cyclohexatriene are given. The high-field shift of the acetylene proton in comparison to the ethylene proton is mainly due to the different δ_{01}^{π} values. In benzene, δ^{RC} and δ_{01}^{π} contribute to the low-field shift. The calculated δ^{RC} value agrees with that obtained without the London approximations²⁸ and with Pople's experimental estimate.⁸ The calculated difference between the shifts of benzene and cyclohexatriene is 1.48 ppm in good agreement with the value estimated by Spiess and Schneider.²⁹ RC and LA effects contribute almost equally to this value.

B. Anisotropy of the Triple Bond. The magnitude of the shielding $\Delta\delta$ caused by the local anisotropy of a triple bond is usually calculated with the McConnell equation³⁰ or its modification by Pople³¹ (the formulas are given in the caption to Figure 3). In Figure 3a $\Delta\delta$ is shown as a function of the distance R between the hydrogen and the middle of the triple bond and of the angle φ between R and the triple-bond axis. Consider first the values obtained in our theory. For $R = 2$ Å we get for $\varphi < 60^\circ$, the expected decrease of the high-field shift with increasing φ . If $\varphi > 60^\circ$, the high-field shift increases again. The difference between maximal and minimal high-field

Table III. RC and LA Contributions to the Shielding in Acetylene, Ethylene, Benzene, and a Hypothetical Cyclohexatriene (δ Values in ppm)

compd	δ^{RC}	δ_{11}^{π}	δ_{01}^{π}	δ^{LA}	δ	δ_{exptl}
acetylene	0	-3.22	0.03	-3.19	2.35	1.80 ^b
ethylene	0	-3.01	3.30	0.29	5.31	5.29 ^b
benzene	0.72	-3.02	4.39	1.37	7.14	7.27 ^c
cyclohexatriene ^a	0	-3.02	3.63	0.61	5.66	

^a Calculated as the sum of three double bonds in a geometrical arrangement as in benzene. ^b F. A. Bovey, "NMR Data Tables for Organic Compounds", Vol. I, Interscience, New York, N.Y., 1967. ^c C. W. Haigh and R. B. Mallion, *Mol. Phys.*, **18**, 737-750 (1970).

Table IV. Calculated and Experimental Chemical Shifts of Protons with Distances $R \leq 3$ Å from the Middle of a Triple Bond

compd ^a	proton	δ	δ_{exptl}	$\delta - \delta_{\text{exptl}}$
1	1	5.85	5.73 ^b	0.12
	2	6.60	6.31 ^c	0.29
3	1	6.45	6.09 ^d	0.36
	2	7.11	7.23	-0.12
5	1	7.04	7.42 ^e	-0.38
	2	7.12	7.24	-0.12
	3	7.17	7.45 ^e	-0.28
2	1	7.17	7.28	-0.11
	3	7.16	7.26	-0.10

^a See Diagram 1. ^b F. A. Bovey, "NMR Data Tables for Organic Compounds", Vol. I, Interscience, New York, N.Y., 1967. ^c K. Endo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 2557-2560 (1970). ^d A. Hiller, E. Kleinpeter, and K. Schulze, *Org. Magn. Reson.*, **8**, 246-251 (1976). In this paper the experimental values are given with $\delta(\text{hexamethylidisiloxane}) = 0$. They have been converted to $\delta(\text{Me}_4\text{Si}) = 0$ with $\delta(\text{Me}_4\text{Si}) = 0.05$ ppm for hexamethylidisiloxane; H. Schmidbauer, *Chem. Ber.*, **97**, 270-281 (1964). ^e Reference 34.

shift is about 1.2 ppm. For $R = 3$ Å we have a similar course of $\Delta\delta$; the minimum is, however, shifted to lower φ and the difference between maximal and minimal $\Delta\delta$ is only about 0.1 ppm. The anisotropies $\Delta\chi$ in the McConnell equations have been chosen to get the same $\Delta\delta$ as with our theory for $\varphi = 0$. Then, for each R another $\Delta\chi$ has to be determined. Possibly this explains the numerous different $\Delta\chi$ proposed in the literature; cf. ref 31. In the Pople-McConnell equation $\Delta\delta$ is calculated as in our theory as a sum of atomic contributions. Therefore, it is not surprising that $\Delta\delta$ calculated with this equation resembles much more the $\Delta\delta$ calculated by our method than with the values of the original McConnell equation. We can conclude that for $R > 3$ Å we will not have significant anisotropic shifts $\Delta\delta$ of the triple bond. For $R < 3$ Å any prediction of $\Delta\delta$ is extremely difficult since small changes in the geometry yield great changes in $\Delta\delta$. Therefore, the use of the McConnell equations is senseless. In Figure 3b all individual contributions to $\Delta\delta$ calculated in our theory are given for $R = 2$ Å. The behavior for $\varphi > 60^\circ$ is mainly governed by the δ_{01}^{π} term. The total contribution of the atom which is further away (atom 2) to δ_{11}^{π} is nearly negligible. But this is only true if σ and π charge densities are 1. For example, increasing the σ or decreasing the π charge of atom 2 results in a low field shift contribution of this atom for $\varphi < 60^\circ$. The error made by the neglect of charge-density changes in the σ core might amount up to 0.3 ppm. Also the neglect of changes in the bond orders of the σ bonds may cause errors in the calculated δ_{01}^{π} values. Furthermore, it seems possible that for low R values additional low-field shifts might arise for similar reasons as the van der Waals shifts of overcrowded protons. Therefore,

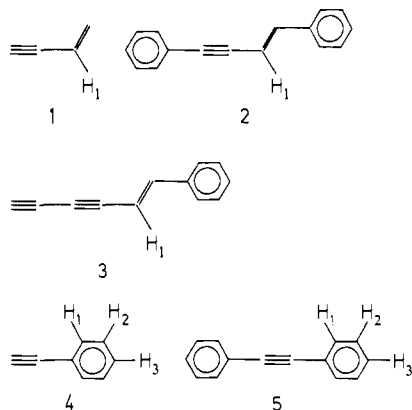
Table V. Individual Contributions to the Chemical Shifts in *trans*-Buta-1,3-diene Divided in Short-Range Contributions, i.e., Contributions from the Bonded Carbon Atom, and Long-Range Contributions

proton ^a	short-range contributions			long-range contributions			δ_{exptl}^b
	δ_{11}^{LA}	δ_{011}^{LA}	δ^{LA}	δ_{11}^{LA}	δ_{011}^{LA}	δ^{LA}	
1	-2.97	3.79	0.82	-0.03	-0.45	-0.48	5.06
2	-2.97	3.79	0.82	-0.04	-0.42	-0.46	5.16
3	-2.97	4.68	1.71	-0.05	-0.64	-0.69	6.26

^a See Diagram 2. ^b Reference 32.

we do not expect that our theory correctly reproduces the "long-range" effect of a triple bond if $R < 3 \text{ \AA}$.

The magnitude of the error can be seen in Table IV. The olefinic protons of **1**, **2**, and **3** ($R \approx 2.7\text{--}2.8 \text{ \AA}$, $\varphi \approx 20^\circ$) are calculated at too low a field, whereas the benzenoid ortho protons of **4** and **5** ($R \approx 3 \text{ \AA}$, $\varphi \approx 45^\circ$) are obtained at too high a field. CNDO/2²⁶ calculations show that the charge densities in the benzene rings of **4** and **5** do not differ significantly from



the assumed values in our theory, quite in contrast to those of the atoms of the triple bond. Therefore, we can attribute the additional downfield shift of about 0.2 ppm to the long-range effect of the triple bond. Let us define Δq_H and Δq_C as the increment in the electron density on an olefinic hydrogen and its bonded carbon atom relative to the corresponding densities in ethylene. The change of the chemical shift due to this charge increment is given approximately by²⁷ $\Delta\delta = -16.0\Delta q_H - 8.29\Delta q_C$. In **1**, **2**, and **3** the CNDO/2 method yields $\Delta q_H \approx 0$ and $\Delta q_C \approx 0.06$ thus giving an upfield shift of ~ 0.5 ppm. If it is supposed that in **1**, **2**, and **3** the long-range effect of the triple bond gives a low-field shift of ~ 0.2 ppm as in **4** and **5**, we get a total shift of ~ 0.3 ppm to higher field. Thus it is well explained that we calculate the protons of **1**, **2**, and **3** at too low a field.

C. Anisotropy of the Double Bond. It is generally assumed today that the shielding of a double bond can be described by a shielding cone giving deshielding in the plane of the double bond and its substituents and shielding above and below this plane.³² This assumption seems to be supported by the fact that the β protons in *trans*-buta-1,3-diene are deshielded compared to the α protons.³² It should be noted, however, that this shielding cone is obtained by applying the McConnell equation³⁰ which is applicable only to bonds with axial symmetry. A modification of the McConnell equation which is appropriate for the double bond has been given by ApSimon et al.³³ In Figure 4 the anisotropic shift $\Delta\delta$ of the isolated double bond is shown as a function of R and φ , both being defined in section B. The ApSimon equation yields shielding as well as deshielding, whereas our theory predicts shielding only for small R and φ . If $R = 3 \text{ \AA}$, we calculate only deshielding. The difference between maximal and minimal anisotropic effects is, however, much smaller with our theory than with the ApSimon equation. For $R = 2 \text{ \AA}$ the difference is ~ 0.5 ppm, thus being

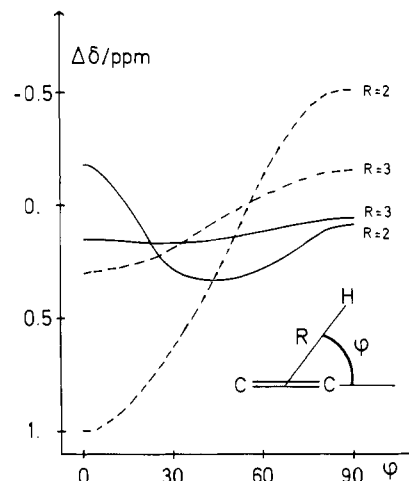
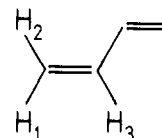


Figure 4. Anisotropic shift $\Delta\delta$ ($\Delta\delta > 0$: shifts to lower field) of a double bond as a function of φ for $R = 2$ and $R = 3 \text{ \AA}$: (—) calculated as $\Delta\delta = \delta - \delta_{30}$; (---) modified McConnell equation of ApSimon et al.³³

much smaller than with the triple bond. Let us now consider the individual contributions to the chemical shifts in *trans*-buta-1,3-diene (Table V). The δ_{11}^{LA} terms are nearly the same for all protons. The β proton is calculated to be ~ 0.7 ppm at lower field than the α protons due to the greater short range δ_{011}^{LA} contribution for the β proton. An additional deshielding of ~ 0.3 ppm for the β proton has to be attributed to charge-density changes.²⁷ The calculated total deshielding of the β proton compared with the α protons is therefore ~ 1 ppm which is in good agreement with the experimental values. We can conclude that the deshielding of the β proton with respect to the α protons in butadiene cannot serve as a proof for the widely accepted anisotropy cone of the double bond. Furthermore, we can state that for $R < 3 \text{ \AA}$ the errors in the long-range anisotropic shift of a double bond made by the neglect of σ core charge-density changes are not so severe as with the triple bond. The comparison of Table V with Figure 4 shows that long-range effects of conjugated double bonds differ markedly from those of an isolated double bond.



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Appendix

The integrals shown in Chart A1 are needed for the evaluation of E_{11}^1 and E_{011}^1 . $1s_A$, $2s_A$, $2p_{x_A}$, $2p_{y_A}$, and $2p_{z_A}$ are Slater orbitals with orbital exponent ζ_A defined in the local axes on atom A as shown in Figure 1. The function $1s_A'$ has a radial and angular part as the $1s_A$ function; however, the normalization constant is the same as with the $2p$ functions. All inte-

grals can be obtained using prolate spheroidal coordinates ($\beta = \zeta_A R_A$).

Chart A1

$$\langle 1s_A | \bar{x}_A^2 R^{-3} | 1s_A \rangle = \zeta_A [\beta^{-3} - \exp(-2\beta)(1 + 2\beta^{-1} + 2\beta^{-2} + \beta^{-3})]$$

$$\langle 1s_A | (\bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 1s_A \rangle = \zeta_A [-2\beta^{-3} + \exp(-2\beta)(2\beta + 3 + 4\beta^{-1} + 4\beta^{-2} + 2\beta^{-3})]$$

$$\langle 2s_A | \bar{x}_A^2 R^{-3} | 2s_A \rangle = \zeta_A [5\beta^{-3}/2 - \exp(-2\beta)(\beta^2/3 + 4\beta/3 + 19/6 + 5\beta^{-1} + 5\beta^{-2} + 5\beta^{-3}/2)]$$

$$\langle 2s_A | (\bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 2s_A \rangle = \zeta_A [-5\beta^{-3} + \exp(-2\beta)(2\beta^3/3 + 5\beta^2/3 + 11\beta/3 + 41/6 + 10\beta^{-1} + 10\beta^{-2} + 5\beta^{-3})]$$

$$\langle 2p_{\bar{x}_A} | \bar{x}_A^2 R^{-3} | 2p_{\bar{x}_A} \rangle = \zeta_A [9\beta^{-3}/2 - 27\beta^{-5} + \exp(-2\beta)(3/2 + 9\beta^{-1} + 27\beta^{-2} + 99\beta^{-3} + 54\beta^{-4} + 27\beta^{-5})]$$

$$\langle 2p_{\bar{x}_A} | R_A \bar{z}_A R^{-3} | 2p_{\bar{x}_A} \rangle = \zeta_A [-9\beta^{-3}/2 + \exp(-2\beta)(\beta^2 + 3\beta + 6 + 9\beta^{-1} + 9\beta^{-2} + 9\beta^{-3}/2)]$$

$$\langle 2p_{\bar{x}_A} | \bar{z}_A^2 R^{-3} | 2p_{\bar{x}_A} \rangle = \zeta_A [3\beta^{-3}/2 + 36\beta^{-5} - \exp(-2\beta)(\beta^2 + 4\beta + 23/2 + 27\beta^{-1} + 51\beta^{-2} + 147\beta^{-3}/2 + 72\beta^{-4} + 36\beta^{-5})]$$

$$\langle 2p_{\bar{x}_A} | (\bar{z}_A^2 + R_A \bar{z}_A) R^{-3} | 2p_{\bar{x}_A} \rangle = \zeta_A [-9\beta^{-3} - 72\beta^{-5} + \exp(-2\beta)(2\beta^3 + 5\beta^2 + 13\beta + 63/2 + 66\beta^{-1} + 114\beta^{-2} + 153\beta^{-3} + 144\beta^{-4} + 72\beta^{-5})]$$

$$\langle 2s_A | R^{-3} | 2p_{\bar{z}_A} + R_A 1s_A' \rangle = \zeta_A [3^{1/2} \beta^{-2}/2 - (2)(3^{1/2})^{-1} \exp(-2\beta)(4\beta + 6 + 6\beta^{-1} + 3\beta^{-2})]$$

$$\langle 2p_{\bar{x}_A} | R^{-3} | 2p_{\bar{x}_A} \rangle = \zeta_A [\beta^{-3} - \exp(-2\beta)(1 + 2\beta^{-1} + 2\beta^{-2} + \beta^{-3})]$$

$$\langle 2p_{\bar{z}_A} | R^{-3} | 2p_{\bar{z}_A} + R_A 1s_A' \rangle = \zeta_A [-2\beta^{-3} + \exp(-2\beta)(2\beta + 3 + 4\beta^{-1} + 4\beta^{-2} + 2\beta^{-3})]$$

If atom A is sp² hybridized, the coefficients f_A^i are given as in eq A1-A3. If atom A is sp hybridized, we have the formulas A4-A9.

$$f_A^1 = 4 + \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp^2} P_{SA'IB}^0 [(c_A d_B + c_B d_A) A_A B_A (W_{BA}^{111} - W_{BA}^{122}) + (d_A d_B - c_A c_B) (W_{BA}^{112} + W_{BA}^{121}) + (c_B d_A - c_A d_B) \times (W_{BA}^{112} - W_{BA}^{121}) + (d_A d_B + c_A c_B) (W_{BA}^{111} + W_{BA}^{122}) + c_B (A_A^2 (c_A W_{BA}^{122} - d_A W_{BA}^{121}) + B_A^2 (c_A W_{BA}^{111} + d_A W_{BA}^{112})) + d_B (A_A^2 (d_A W_{BA}^{111} - c_A W_{BA}^{112}) + B_A^2 (d_A W_{BA}^{122} + c_A W_{BA}^{121}))] + \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp} P_{SA'IB}^0 [(a_B A_A^2 + b_B A_A B_A) (d_A W_{BA}^{31} - c_A W_{BA}^{32}) + (b_B B_A^2 + a_B A_A B_A) (c_A W_{BA}^{31} + d_A W_{BA}^{32}) + (c_A b_B + d_A a_B) W_{BA}^{31} + (d_A b_B - c_A a_B) W_{BA}^{32}] \quad (A1)$$

$$f_A^2 = 2 + \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp^2} P_{SA'IB}^0 [(c_A A_A - d_A B_A) (c_B W_{BA}^{111} A_A + W_{BA}^{121} B_A) - d_B (W_{BA}^{111} B_A - W_{BA}^{121} A_A) + (d_A A_A + c_A B_A) (c_B (W_{BA}^{112} A_A + W_{BA}^{122} B_A) - d_B (W_{BA}^{112} B_A - W_{BA}^{122} A_A))] + \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp} P_{SA'IB}^0 (a_B B_A - b_B A_A) [W_{BA}^{31} (d_A B_A - c_A A_A) - W_{BA}^{32} (c_A B_A + d_A A_A)] \quad (A2)$$

$$f_A^3 = \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp^2} P_{SA'IB}^0 [W_{BA}^{23} (d_B A_A + c_B B_A) + W_{BA}^{13} (c_B A_A - d_B B_A)] + \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp} P_{SA'IB}^0 W_{BA}^{33} (b_B A_A - a_B B_A) \quad (A3)$$

$$f_A^4 = 2 + f_A^6 + \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp} [P_{SA'IB}^0 + P_{SA'IB}^0 (1 + f_A^6)] + \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp^2} P_{SA'IB}^0 [A_A B_A (c_B (a_A W_{BA}^{211} - b_A W_{BA}^{221}) + d_B (b_A W_{BA}^{211} + a_A W_{BA}^{221})) + a_A (A_A^2 + 1) (d_B W_{BA}^{211} - c_B W_{BA}^{221}) + b_A (B_A^2 + 1) (d_B W_{BA}^{221} + c_B W_{BA}^{211})] \quad (A4)$$

$$f_A^5 = f_A^5 + \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp} [P_{SA'IB}^0 + P_{SA'IB}^0 (f_A^5 - 1)] + \frac{1}{2} (a_A B_A - b_A A_A) \sum_{\substack{B \neq A \\ (A-B)}}^{sp^2} P_{SA'IB}^0 [W_{BA}^{211} (d_B B_A - c_B A_A) - W_{BA}^{221} (d_B A_A + c_B B_A)] \quad (A5)$$

$$f_A^6 = \frac{1}{2} (b_A A_A - a_A B_A) \sum_{\substack{B \neq A \\ (A-B)}}^{sp} W_{BA}^4 (P_{SA'IB}^0 + P_{SA'IB}^0) + \frac{1}{2} \sum_{\substack{B \neq A \\ (A-B)}}^{sp^2} P_{SA'IB}^0 [W_{BA}^{222} (c_B B_A + d_B A_A) + W_{BA}^{12} (c_B A_A - d_B B_A)] \quad (A6)$$

$$f_A^4 = P_{SA'SA'}^0 + P_{SA'SA}^0 (1 - P_{SA'SA'}^0) - \sum_{\substack{B \neq A \\ (A-B)}}^{sp} P_{SA'IB}^0 P_{SA'IB'}^0 \quad (A7)$$

$$f_A^5 = 1 + (a_A B_A - b_A A_A)^2 \quad (A8)$$

$$f_A^6 = (a_A A_A + b_A B_A)^2 \quad (A9)$$

W are matrices containing the σ bond orders for all types of orbitals. We define

$$A_1 = c_A x_{AB} - d_A y_{AB}$$

$$A_2 = (-6^{-1/2} c_A + 2^{-1/2} d_A) x_{AB} + (6^{-1/2} d_A + 2^{-1/2} c_A) y_{AB}$$

$$A_3 = (-6^{-1/2} c_A - 2^{-1/2} d_A) x_{AB} + (6^{-1/2} d_A - 2^{-1/2} c_A) y_{AB}$$

$$A_1' = b_A x_{AB} - a_A y_{AB} \quad A_2' = -A_1'$$

$$B_1 = -c_B x_{AB} + d_B y_{AB}$$

$$B_2 = (6^{-1/2} c_B - 2^{-1/2} d_B) x_{AB} - (6^{-1/2} d_B + 2^{-1/2} c_B) y_{AB}$$

$$B_3 = (6^{-1/2} c_B + 2^{-1/2} d_B) x_{AB} - (6^{-1/2} d_B - 2^{-1/2} c_B) y_{AB}$$

$$B_1' = -b_B x_{AB} + a_B y_{AB} \quad B_2' = -B_1'$$

with $x_{AB} = x_B - x_A$ and $y_{AB} = y_B - y_A$. We get $m^{(k)} = 3(j - 1) + i$ if $A_i > 0$ and $B_j > 0$ ($k = 1$), $A_i > 0$ and $B_j' > 0$ ($k = 2$), or $A_i' > 0$ and $B_j > 0$ ($k = 3$) and we get $m^{(4)} = i$ if $A_i' > 0$. Now we obtain the W_{AB}^{ikl} as matrix elements according to $W_{AB}^{ikl} = W^i(k, l, m^{(i)})$ for $i = 1, 2$, $W_{AB}^{3k} = W^3(k, m^{(3)})$, and $W_{AB}^4 = W^4(m^{(4)})$ (Chart A2).

Chart A2

$W^1(k,l,m^{(1)})$		l		
$m^{(1)}$	k	1	2	3
1	1	-4/3	0	-8 ^{1/2} /3
	2	0	0	0
2	1	2/3	0	2 ^{1/2} /3
	2	-2/3 ^{1/2}	0	-(2/3) ^{1/2}
3	1	2/3	0	2 ^{1/2} /3
	2	2/3 ^{1/2}	0	(2/3) ^{1/2}
4	1	2/3	-2/3 ^{1/2}	-8 ^{1/2} /3
	2	0	0	0
5	1	1/3	3 ^{-1/2}	2 ^{1/2} /3
	2	3 ^{-1/2}	-1	-(2/3) ^{1/2}
6	1	-1/3	3 ^{-1/2}	2 ^{1/2} /3
	2	-3 ^{1/2}	1	(2/3) ^{1/2}
7	1	2/3	2/3 ^{1/2}	-8 ^{1/2} /3
	2	0	0	0
8	1	-1/3	-3 ^{-1/2}	2 ^{1/2} /3
	2	3 ^{-1/2}	1	-(2/3) ^{1/2}
9	1	-1/3	-3 ^{-1/2}	2 ^{1/2} /3
	2	-3 ^{-1/2}	-1	(2/3) ^{1/2}

$W^2(k,l,m^{(2)})$		l	
$m^{(2)}$	k	1	2
1	1	-2/3 ^{1/2}	-2/3 ^{1/2}
	2	0	0
2	1	3 ^{-1/2}	3 ^{-1/2}
	2	-1	-1
3	1	3 ^{-1/2}	3 ^{-1/2}
	2	1	1
4	1	2/3 ^{1/2}	-2/3 ^{1/2}
	2	0	0
5	1	-3 ^{-1/2}	3 ^{-1/2}
	2	1	-1
6	1	-3 ^{-1/2}	3 ^{-1/2}
	2	-1	1

$W^3(l,m^{(3)})$		l		
$m^{(3)}$		1	2	3
1	0	-2/3 ^{1/2}		-(2/3) ^{1/2}
2	2/3 ^{1/2}	0		(2/3) ^{1/2}
3	3 ^{-1/2}	-1		-(2/3) ^{1/2}
4	-3 ^{-1/2}	1		(2/3) ^{1/2}
5	3 ^{-1/2}	1		-(2/3) ^{1/2}
6	-3 ^{-1/2}	-1		(2/3) ^{1/2}

$W^4(m^{(4)})$		l
$m^{(4)}$		1
1		-1
2		1

Supplementary Material Available: A listing of experimental and calculated ¹H chemical shifts for 42 different compounds (8 pages). Ordering information is given on any current masthead page.

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