

# Bond-Order Dependence of Orthobenzyl Coupling Constants Involving a Methyl Group [ $^4J(\text{MeC}-\text{CH})$ ]

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**Abstract:** A relationship between experimentally measured orthobenzyl coupling constants [ $J_{\text{ob}} = ^4J(\text{CH}_3-\text{C}1-\text{C}2-\text{H})$ ] in a series of methyl-substituted aromatic hydrocarbons has been investigated by using extensive, accurate data and a variety of criteria for the  $\pi$ -bond orders of the C1-C2 bonds. The best linear correlations of  $J_{\text{ob}}$  were found with squares of the self-consistent field molecular orbital bond orders and with the Pauling (VB) bond orders as would be expected from the theoretical expressions for coupling constants within the average energy approximation. In fact, the standard deviation in the correlation of the  $J_{\text{ob}}$  with the Pauling bond order is almost within the experimental error of the measurements (0.06 Hz). Thus,  $J_{\text{ob}}$  emerges as an experimental criterion for investigating  $\pi$ -bond orders in conjugated systems.

A previous study from these laboratories<sup>1</sup> considered the conformational, bond-order, and substituent dependencies of the long-range H-H coupling over four bonds (orthobenzyl coupling,  $J_{\text{ob}}$ ) between protons on an  $\text{sp}^3$ -hybridized  $\alpha$ -carbon and the ortho protons of aromatic systems [ $^4J(\text{Me}-\text{C}1-\text{C}2-\text{H})$ ]. Because of the generality of these relationships, the  $J_{\text{ob}}$  are a source of useful structural information. The experimental data showed reasonable and comparable correlations with the Hückel molecular orbital (HMO) bond orders, with the square of the bond orders, and with the mutual atom-atom polarizabilities associated with the C1-C2 partial  $\pi$ -bond.<sup>2</sup> In the case of the MO  $\pi$ -bond order the direct correlations, which have no basis in theoretical formulation, led to values at zero  $\pi$ -bond order that were greatly at variance with the experimental data. The theoretical basis for the interdependence of coupling constants, bond orders, and the importance of electron correlation on these parameters is discussed.

A more accurate set of experimental data for  $J_{\text{ob}}$  is given in Table I. The data base has been improved in the following ways: (i) All approximate data from the literature have been eliminated. (ii) The value for propene (-1.75 Hz),<sup>3</sup> which was used previously,<sup>1</sup> involves a significant change of substituent (hydrogen for carbon directly on the coupling path in contrast to all of the other compounds in Table I). Therefore, the  $J_{\text{ob}}$  value for a "full" double bond (-1.53 Hz) in Table I is the average of the values for 1-methylcyclobutene, 1-methylcyclopentene, 1-methylcyclohexene, and 1-methylcycloheptene.<sup>4</sup> (iii) All of the results correspond to the average for the case in which C1-C2 is a single bond,<sup>5</sup> accurate data for polynuclear aromatic hydrocarbons containing only six-membered rings, and the result ii for a "full" double bond. Since it was of interest to see how the experimental value for a full "triple" bond would fit into the correlation, the experimental value of  $^4J(\text{CH}_3-\text{H})$  for propyne was also included in Table I. The choice of data that are included in Table I was made on the assumption that whatever limitations are involved in the various bond-order criteria, they are unlikely to vary across a series thus constituted. (iv) Some of the previously reported compounds<sup>1</sup> were reexamined at 400 MHz to improve the precision of the data. However, only small corrections resulted: the largest difference in the  $J_{\text{ob}}$  values from the 100- and 400-MHz spectra was only 0.06 Hz, which is of little importance for the correlations discussed herein.

## Theoretical Section

**Importance of Electron Correlation in Nuclear Spin-Spin Coupling.** In any molecular quantum mechanical formulation of the Fermi contact contribution to nuclear spin-spin coupling,

electron correlation effects are known to be of very great importance. Many of the theoretical studies of long-range spin-spin coupling from these and other laboratories have made use of sum-over-states (SOS) methods or approximations to this based on the assumption of an average excitation energy. Both expressions follow from the original Ramsey formulation<sup>6</sup> for the Fermi contact (FC) expression for nuclear spin-spin coupling. A general sum-over-states expression for the FC coupling between nuclei N and N' is most conveniently cast into (a slightly modified) density matrix notation:<sup>7-11</sup>

$$J_{\text{NN}'} = -(2\hbar)^{-1}(16\pi\beta\hbar/3)^2\gamma_N\gamma_{\text{N}'}\sum_k\{Q_1(0\kappa_0|\text{r}_N)Q_1(0\kappa_0|\text{r}_{\text{N}'})/(E_k - E_0)\} \quad (1)$$

where  $Q_1(0\kappa_0|\text{r}_N)$  denotes a transition spin density matrix evaluated at nucleus N, between the singlet 0 and triplet  $\kappa_0$  state having energies  $E_0$  and  $E_k$ , respectively. The summation in eq 1 is over all of the triplets. In simple MO treatments<sup>12,13</sup> that make use of eq 1, it is easy to show<sup>8</sup> that the summation in eq 1 is proportional to the mutual atom-atom polarizability  $\pi_{\mu\nu}$ , where  $\mu$  and  $\nu$  denote atomic orbitals at the coupled nuclei N and N'. Moreover, it has been shown<sup>14</sup> that for  $\pi$ -electron coupling between, e.g., protons, the Fermi contact contribution can be related to the product of the mutual atom-atom polarizability  $\pi_{pp'}$  for the  $\pi$ -electron path, and the two  $\sigma$ - $\pi$  exchange parameters or hyperfine coupling constants,  $a_{\sigma\pi}$  and  $a_{\sigma\pi'}$ .<sup>14,15</sup> In the case of orthobenzyl coupling, for example, the  $\sigma$ - and  $\pi$ -orbitals are

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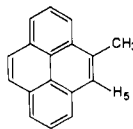
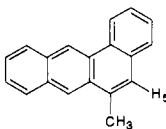
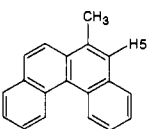
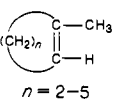
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**Table I.** Orthobenzyl Coupling Constants  $^4J(\text{Me}-\text{C}1-\text{C}2-\text{H})$  for a Series of Aromatic and Unsaturated Compounds, Hückel MO Bond Orders, Mutual Atom-Atom Polarizabilities, Self-Consistent Field MO Bond Orders, Pauling VB Bond Orders, and Bond Lengths  $r(\text{C}-\text{C}')$  in Angstroms for the C1-C2  $\pi$ -Bonds

compd no.	structure	$J_{\text{obs}}^a$ , Hz	$\eta_{\text{HMO}}^b$	$\pi_{pp'}(\text{HMO})^b, (-\beta)$	$\eta_{\text{SCF}}$	$p_{\text{LP}}^c$	$r(\text{C}-\text{C}')$ , Å
1		0.02 <sup>d</sup>	0.000	0.000	-0.009 <sup>e</sup>	0.000	1.53 <sup>f</sup>
2		-0.75 ± 0.3 <sup>g</sup>	0.667	0.1574	0.507 <sup>e</sup>	0.500	1.397 <sup>h</sup>
3		$J_{\text{CH}_3, \text{H}1} = -0.99^i$ $J_{\text{CH}_3, \text{H}3} = -0.46^i$	0.725 0.603	0.2134 0.1096	0.609 0.385	0.667 0.333	1.364 <sup>h</sup> 1.415 <sup>h</sup>
4		$J_{\text{CH}_3, \text{H}1} = -0.98 \pm 0.03$ $J_{\text{CH}_3, \text{H}2} = -0.23$	0.737 0.586	0.2307 0.0989	0.650 0.327	0.750 0.250	1.375 <sup>h</sup> 1.418 <sup>h</sup>
5		$J_{\text{CH}_3, \text{H}1} = -0.98 \pm 0.03$ $J_{\text{CH}_3, \text{H}3} = -0.2 \pm 0.01$	0.737 0.586	0.2307 0.0989	0.650 0.327	0.750 0.250	1.375 <sup>h</sup> 1.418 <sup>h</sup>
6		$J_{\text{CH}_3, \text{H}2} = -0.57$ $J_{\text{CH}_3, \text{H}4} = -0.87$	0.623 0.702	0.1235 0.1893	0.445 0.557	0.400 0.600	1.393 <sup>h</sup> 1.401 <sup>h</sup>
7		$J_{\text{CH}_3, \text{H}1} = -0.89$ $J_{\text{CH}_3, \text{H}3} = -0.56$	0.707 0.623	0.1935 0.1235	0.557 0.445	0.600 0.400	1.362 <sup>h</sup> 1.393 <sup>h</sup>
8		-0.91	0.707	0.1935	0.557	0.600	1.362 <sup>h</sup>
9		-1.16	0.76	0.2699	0.685	0.800	1.345 <sup>h</sup>
10		$J_{\text{CH}_3, \text{H}1} = -0.82$ $J_{\text{CH}_3, \text{H}3} = -0.61$	0.690 0.637	0.1775 0.1342	0.562 0.438	0.556 0.444	1.377 <sup>h</sup> 1.402 <sup>h</sup>
11		$J_{\text{CH}_3, \text{H}2} = -0.52$ $J_{\text{CH}_3, \text{H}4} = -0.92$	0.617 0.707	0.1192 0.1995	0.406 0.584	0.375 0.625	1.392 <sup>h</sup> 1.379 <sup>h</sup>
12		-1.04	0.754	0.2452	0.615	0.750	1.369 <sup>h</sup>
13		-0.73	0.669	0.1587	0.505	0.500	1.38 <sup>h</sup>
14		-0.73	0.669	0.1587	0.505	0.500	1.38 <sup>h</sup>

Table I (Continued)

compd no.	structure	$J_{\text{obs}},^a$ Hz	$\eta_{\text{HMO}}^b$	$\pi_{pp}(\text{HMO})^b, (-\beta)$	$\eta_{\text{SCF}}$	$\rho_{\text{LP}}^c$	$r(\text{C}-\text{C}'), \text{\AA}$
15		-1.16	0.777	0.2738	0.684	0.833	1.346 <sup>i</sup>
16		-1.18	0.783	0.2835		0.857	1.34 <sup>k</sup>
17		-1.08	0.765	0.2521	0.655	0.750	1.342 <sup>i</sup>
18		-1.53	1.000	0.5000	0.799 <sup>e</sup>	1.000	1.34 <sup>m</sup>
19	H-C≡C-CH <sub>3</sub>	-2.93 <sup>n</sup>	2.000	1.0000	1.516 <sup>e</sup>	2.000	1.20 <sup>o</sup>

<sup>a</sup>Coupling constants are either from ref 1 or from this work and are assumed to be accurate to  $\pm 0.05$  Hz unless otherwise specified. <sup>b</sup>Reference 2. <sup>c</sup>Reference 28. <sup>d</sup>Average for a number of compounds of similar geometry, viz., compounds 5, 6, 8, 9, and 11 in ref 5. <sup>e</sup>Reference 30. <sup>f</sup>Iijima, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1291. <sup>g</sup>Williamson, M. P.; Kostelnik, R. J.; Castellano, S. M. *J. Chem. Phys.* **1960**, *49*, 2218. <sup>h</sup>Reference 31. <sup>i</sup>Average for a number of methylnaphthalenes, viz., compounds 3-7 in ref 1. <sup>j</sup>Hazell, A. C.; Larsen, F. K.; Lehmann, M. D. *Acta. Crystallogr.* **1972**, *B28*, 2977. <sup>k</sup>Friedlander, P. H.; Sayre, D. *Nature* **1956**, *178*, 999. <sup>l</sup>Hirshfield, F. L.; Sandler, S.; Schmidt, G. M. *J. Chem. Soc.* **1963**, 2108. <sup>m</sup>Costain, C. C.; Stoicheff, B. P. *J. Chem. Phys.* **1959**, *30*, 777. <sup>n</sup>Shoolery, J. N.; Johnson, L. F.; Anderson, W. A. *J. Mol. Spectrosc.* **1960**, *5*, 110. <sup>o</sup>Simonetta, M.; Gavezotti, A. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; pp 1-56.

centered on C<sub>2</sub> of the C2-H fragment,  $\pi'$  is on C1, and  $\sigma'$  is associated with the CH<sub>3</sub> of the C1-CH<sub>3</sub> fragment.

Major inadequacies of simple MO treatments are due to the failure to distinguish between excited singlets and triplets and the neglect of configuration interaction in the ground state and in the triplet manifold.<sup>16</sup> The latter is particularly important for those cases in which  $p$  and  $p'$  are in the same subset of the alternant system, e.g., metabenzyllic coupling. Correlation effects are implicit in the valence bond (VB) formulation,<sup>10,11</sup> which includes an explicit sum over triplets as this also gives a satisfactory description of most types of long-range H-H coupling. The VB method with a sum over triplets has not been extensively applied because even in its semiempirical form, a molecule with  $2n$  electrons requires the calculation of a ground-state wave function having  $[(2n)!/n!(n+1)!]$  nonpolar singlet structures and  $3[(2n)!/(n+2)!(n-1)!]$  nonpolar triplets.

Within the SOS framework of eq 1 (or any other more sophisticated formulation, for that matter<sup>17</sup>) there is not yet any conceptual basis for relating nuclear spin-spin coupling to the effects of electron correlation. Within the average energy approximation framework, however, the relationship assumes a very attractive form,<sup>18-20</sup> e.g., the coupling constant between nuclei N and N' is given by the expression

$$J_{\text{NN}'} = -(3h\Delta E)^{-1}(16\pi\hbar/3)^2\gamma_{\text{N}}\gamma_{\text{N}'}Q_{\text{c}}(r_{\text{N}},r_{\text{N}'}) \quad (2)$$

where  $\Delta E$  is the average excitation energy and  $Q_{\text{c}}(r_{\text{N}},r_{\text{N}'})$  denotes the density of spin-spin coupling<sup>7,9</sup> evaluated at the positions of the coupled nuclei N and N'. More generally, the spin coupling function  $Q_{\text{c}}(r_1,r_2)$  is related to the spinless components of the two-particle density matrix:<sup>7,21</sup>

$$Q_{\text{c}}(r_1,r_2) = 3[P_2^{\alpha\alpha}(r_1,r_2) - P_2^{\alpha\beta}(r_1,r_2)] \quad (3)$$

Therefore, the nuclear spin coupling is proportional to the difference between the probability  $P_2^{\alpha\alpha}(r_{\text{N}},r_{\text{N}'})$  of their simultaneously being electrons of the same ( $\alpha$ ) spin in volume element at  $r_{\text{N}}$  (at nucleus N) and in volume element at  $r_{\text{N}'}$  (at nucleus N') and the corresponding probability  $P_2^{\alpha\beta}(r_{\text{N}},r_{\text{N}'})$  per unit volume of their simultaneously being electrons of opposite spins at these positions. Moreover, these spinless components of the two-particle density matrices can be written in terms of one-particle density matrices<sup>18</sup>  $P_1(r_1)$ ,  $P_1(r_2)$  and the correlation functions for electrons with the same  $f^{\alpha\alpha}(r_1,r_2)$  and opposite  $f^{\alpha\beta}(r_1,r_2)$  spin:

$$P_2^{\alpha\alpha}(r_1,r_2) = P_1^{\alpha}(r_1)P_1^{\alpha}(r_2)[1 + f^{\alpha\alpha}(r_1,r_2)] \quad (4a)$$

$$P_2^{\alpha\beta}(r_1,r_2) = P_1^{\alpha}(r_1)P_1^{\beta}(r_2)[1 + f^{\alpha\beta}(r_1,r_2)] \quad (4b)$$

Since all of the molecules of interest are in singlet ground states  $P_1^{\alpha}(r_1) = P_1^{\beta}(r_1) = 1/2P_1(r_1)$ , so that the spin-spin coupling function is proportional to the differences in the correlation functions for electrons of the same and opposite spins:<sup>8</sup>

$$Q_{\text{c}}(r_1,r_2) = 3/4P_1(r_1)P_1(r_2)[f^{\alpha\alpha}(r_1,r_2) - f^{\alpha\beta}(r_1,r_2)] \quad (5)$$

For the cases of long-range coupling in simple, unsaturated systems such as propene or cyclohexene, the extraction of the (hypothetically isolated)  $\pi$ -system ( $p1-p2$ ) leads to a situation in which all of the elements of the one particle density matrix are equal, so that  $f^{\alpha\alpha}(r_1,r_2) \rightarrow -1$ ; this just corresponds to 100% negative correlation since given an electron spin in volume element at  $p1$  there is zero probability of finding an electron of the same spin in volume element at  $p2$ . In delocalized  $\pi$ -systems, however, the correlation function  $f^{\alpha\alpha}(r_1,r_2)$  is smaller in magnitude because there are more than two electrons with the same spin. In fact, the various bond orders provide measures for the differences in the correlation functions in eq 5.

In the single-determinant approximation of SCF MO theory,  $f^{\alpha\beta}(r_1,r_2)$  vanishes identically, and the correlation function for electrons of the same spin is given by

$$f^{\alpha\alpha}(r_1,r_2) = -P_1^{\alpha}(r_1,r_2)P_1^{\alpha}(r_2,r_1)/P_1^{\alpha}(r_1)P_1^{\alpha}(r_2) \quad (6)$$

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(21) Integrals over the Dirac  $\delta$  function terms in the spin-coupling Hamiltonian take  $r_1$  and  $r_2$  to  $r_{\text{N}}$  and  $r_{\text{N}'}$ , respectively.

where the terms in the numerator are off-diagonal elements of the one-particle density matrix, e.g., these correspond to the bond orders in the independent particle model description. As a consequence, all  $Q_c(r_1, r_1)$  in eq 5 have only negative signs, in disagreement with the experimental patterns wherein coupling constants between hydrogens separated by an even numbers and odd numbers of bonds tend to be negative and positive, respectively. This sign difficulty can be overcome by techniques such as the alternant molecular orbital method, which also includes correlation between electrons of opposite spin.<sup>8</sup>

In the molecular orbital description of McConnell,<sup>22</sup> the  $\pi$ -electron coupling is given by

$$J_{HH'} = (4h)^{-1} a_H a_{H'} \eta_{pp}^2 / \Delta E \quad (7)$$

where the  $a_H$  and  $a_{H'}$  denote proton hyperfine coupling constants for related free radical fragments,  $\eta_{pp}$  is the mobile  $\pi$ -bond order, and  $\Delta E$  is an average excitation energy. If there is more than one coupling path, e.g., the orthogonal set of  $\pi$ -bonds in acetylene or propyne, then it is necessary to introduce a summation over the bond pairs in eq 7 and related equations. For the case of allylic and orthobenzylic H-H coupling, one of the hyperfine constants is appropriate to the C1-CH<sub>3</sub> moiety and has a dependence on dihedral angle of the form<sup>23</sup>

$$a_H = A' \sin^2 \phi + B' \quad (8)$$

where  $\phi$  is the dihedral angle measured from the nodal plane of the  $\pi$ -orbital (typically,  $A' \sim 150$  MHz and  $B' \sim 0$ ). The C2-H hyperfine coupling constant has a negative sign and is independent of the dihedral angle so that the allylic/orthobenzylic coupling constants are of the form<sup>1</sup>

$$J_{HH'} = (A \sin^2 \phi + B) Q_c(r_1, r_2) \quad (9)$$

By way of contrast, in VB descriptions, which invoke the average energy approximation, the spin-spin coupling function is given by the expression<sup>24,25</sup>

$$Q_c(r_1, r_2) = -\frac{1}{2} \sum_{j,l} c_j c_l (1/2)^{n-l} \sum_{\mu,\nu} \{ [1 + 2f_{j\mu\nu}] \phi_\mu(r_1) \phi_\nu(r_2) \times \phi_\mu(r_1) \phi_\nu(r_2) + [2 + f_{j\mu\nu}] \phi_\mu(r_1) \phi_\nu(r_2) \phi_\nu(r_1) \phi_\mu(r_2) \} \quad (10)$$

where the  $c_j$  are the coefficients of the linearly independent VB singlet canonical structures<sup>10,24-26</sup> for a system of  $2n$  electrons, and in the superposition diagram of structures  $j$  and  $l$ ,  $i_{jl}$  is the number of islands and  $f_{j\mu\nu}$  assumes the values 1, -2, and  $-1/2$  depending on whether orbitals  $\mu$  and  $\nu$  are in the same island separated by an odd or even number of bonds or are in different islands, respectively. Equation 10 can be rewritten in terms of the Penney-Dirac bond orders:

$$Q_c(r_1, r_2) = -\frac{1}{2} \sum_{\mu,\nu} \{ p_{PD}(\mu, \nu) \phi_\mu(r_1) \phi_\nu(r_2) \phi_\mu(r_1) \phi_\nu(r_2) + \frac{1}{2} [1 + p_{PD}(\mu, \nu)] \phi_\mu(r_1) \phi_\nu(r_2) \phi_\nu(r_1) \phi_\mu(r_2) \} \quad (11)$$

where the Penney-Dirac bond order is defined by the expression

$$p_{PD}(\mu, \nu) = \frac{1}{3} \sum_{j,l} c_j c_l (1/2)^{n-l} [1 + 2f_{j\mu\nu}] \quad (12)$$

Thus, through eq 2 and 12 and with neglect two-center terms of the type  $\phi_\mu(r_N) \phi_\mu(r_{N'})$ , it is interesting to note that the nuclear spin-spin coupling is linearly related to the Penney-Dirac bond order  $p_{PD}(\mu, \nu)$  rather than the quadratic dependence on the MO bond order in eq 7, for example. Because of the rapid increase in the number of VB structures (for example, many of the entries in Table I have 18  $\pi$ -electrons; the size of the matrices, to be diagonalized to calculate the coefficients that enter these bond orders, would be 4862 by 4862), the Penney-Dirac bond orders

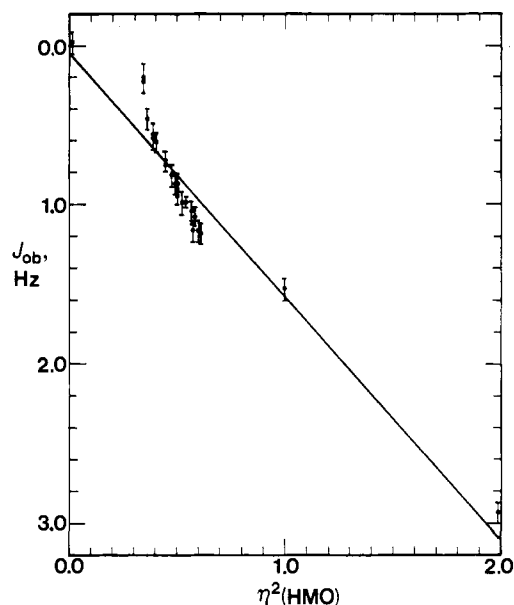


Figure 1. Experimental data for  $J_{\text{obs}}$  plotted as a function of the square  $\eta^2$  of the HMO  $\pi$ -bond order. The straight line conforms to the linear least-squares fit specified in eq 15.

are not generally available. Pauling<sup>26</sup> proposed a very simple, alternative scheme for VB-related  $\pi$ -bond orders [here designated  $p_{LP}(p, p')$  in aromatic compounds] and the relationship of these to C-C bond distances in aromatic compounds has been a subject of considerable interest.<sup>26-29</sup> Their computation does not even require a knowledge of the wave function; they are obtained simply as the fraction of Kekulé ("unexcited" in the terminology of Pauling) structures that have a formal  $\pi$ -bond between  $p$  and  $p'$ . Alternatively, it has been noted<sup>28</sup> that these bond orders may also be computed from tabulated HMO data,<sup>2</sup> but the relationship is not a linear one. For the purposes of this study it was of interest to see how the Pauling bond orders are related to the more complicated Penney-Dirac bond orders. If only Kekulé-type structures are included and are assumed to make equal contributions to the ground-state wave function, then the VB ground-state wave function is given by

$$\Psi_0 = (N_K)^{-1/2} \sum_j \Phi_j \quad (13)$$

where  $N_K$  is the number of Kekulé-type (unexcited) structures with wave functions  $\Phi_j$ . With the additional assumption that the only superposition diagrams are those for which  $j = l$ , the Pauling bond order is given by the expression

$$p_{LP}(p, p') = (N_K)^{-1} \sum_j [1 + 2f_{jpp'}] / 3 \quad (14)$$

where the terms in the summation are 1 or 0 depending on whether  $p$  and  $p'$  are bonded or nonbonded, respectively, in the superposition diagram of Kekulé-type structures only.

**Computation Methods.** The SCF MO  $\pi$ -bond orders were obtained from STO-3G calculations using the GAUSSIAN-76 and GAUSSIAN-82 computer programs. Geometries optimized at the STO-3G level were used for the noncyclic molecules and benzene,<sup>30</sup> while experimental geometries were used for the polycyclic compounds. Self-consistency errors introduced by the use of experimental geometries are expected to be minimal: a test calculation for phenanthrene with an STO-3G-optimized geometry gave  $\pi$ -bond orders for 6, 7, and 9 as (0.414, 0.582), (0.581, 0.414), and 0.687. These differ by up to 7% compared with the values reported in Table I.

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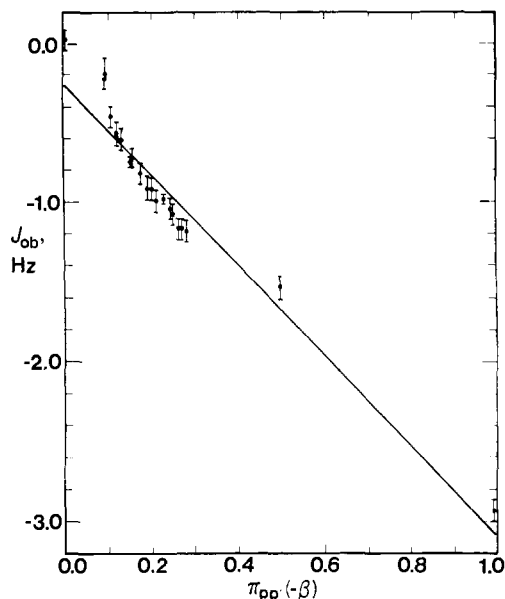


Figure 2. Experimental data for  $J_{ob}$  plotted as a function of the HMO mutual atom-atom polarizability  $\pi_{pp'}$  in units of  $-\beta$ . The straight line conforms to the linear least-squares fit specified in eq 17.

**Comparisons of Various Correlations.** The data from Table I are plotted in Figure 1 as a function of the square of the HMO bond orders. The straight line through the points was based on a linear least-squares analysis of the data and leads to the equation

$$J_{ob} = -1.528\eta_{HMO}^2 - 0.054 \text{ Hz} \quad (15)$$

with correlation coefficient  $r^2 = 0.9212$ . Since some authors have attempted to correlate these coupling constants linearly with the HMO  $\pi$ -bond orders even though there is no theoretical basis for such a correlation, it is interesting to note that the expression obtained on least-squares analysis is

$$J_{ob} = -1.660\eta_{HMO} - 0.326 \text{ Hz} \quad (16)$$

with correlation coefficient  $r^2 = 0.8835$ . Not only does this give the poorest correspondence with the experimental data for the aromatic compounds, there is a substantial magnitude for zero  $\pi$ -bond order.

In Figure 2 the  $J_{ob}$  from Table I are plotted as a function of the HMO mutual atom-atom polarizabilities  $\pi_{pp'}$  in units of  $-\beta$ . It is clear that the improvement in the correlation is substantial and the linear least-squares analysis gives the result

$$J_{ob} = -2.849\pi_{pp'} - 0.248 \text{ Hz} \quad (17)$$

with correlation coefficient  $r^2 = 0.9333$ . It is gratifying that the best correlation among the HMO results is with the one with the best theoretical justification. However, a major limitation of the HMO method is the assumption that all off-diagonal elements (the resonance integrals  $\beta$ ) of the Hamiltonian matrix between bonded atoms are identical even though the bond lengths may be different. Moreover, in self-consistent field MO methods the  $\pi$ -bond orders tend to be reduced below the HMO values (see Table I) primarily because the  $\pi$ -overlap integral enters the denominators of the expressions for the coefficients of the atomic orbitals, e.g., the  $\pi$ -bond of ethylene.<sup>30</sup> In Figure 3 the  $J_{ob}$  are plotted as a function of the squares of the SCF bond orders. Clearly, the correlation is better than any of the HMO results, and the linear regression gives the relationship

$$J_{ob} = -2.457\eta_{SCF}^2 - 0.056 \text{ Hz} \quad (18)$$

with correlation coefficient  $r^2 = 0.9844$ . This equation is plotted (solid line) in Figure 3. It is interesting to note that even the correlation with the SCF bond order is better than any of the HMO results:

$$J_{ob} = -2.112\eta_{SCF} - 0.315 \text{ Hz} \quad (19)$$

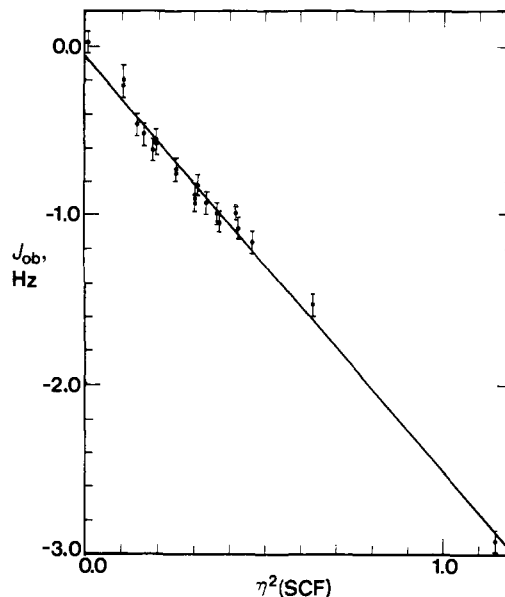


Figure 3. Experimental data for  $J_{ob}$  plotted as a function of the square  $\eta_{SCF}^2$  of the SCF  $\pi$ -bond order. The straight line conforms to the linear least-squares fit specified in eq 18.

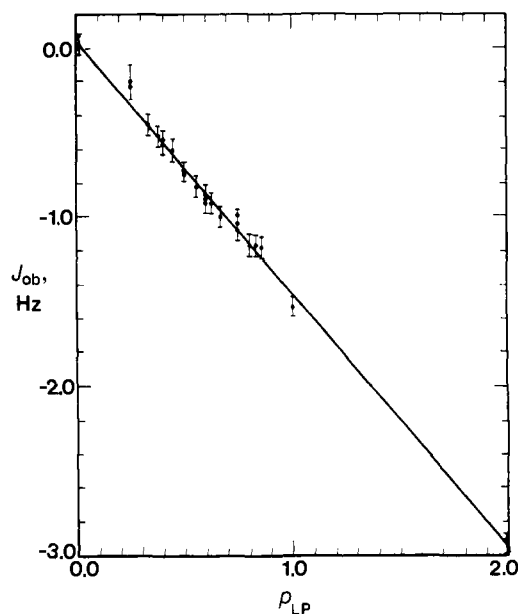


Figure 4. Experimental data for  $J_{ob}$  plotted as a function of the Pauling  $\pi$ -bond orders  $\rho_{LP}$ . The straight line conforms to the linear least-squares fit specified in eq 20.

with correlation coefficient  $r^2 = 0.9708$ . However, the intercept of  $-0.315$  Hz is not consistent with the experimental data, which suggests a smaller absolute magnitude in the limit of small  $\pi$ -bond order. It is interesting to note that the SCF method gives a small negative ( $-0.009$ ) bond order for the saturated hydrocarbon. It is unfortunate that the SCF mutual atom-atom polarizabilities were not available for this series of molecules as it would be expected in analogy to the HMO results that these would give the best correlation in the series of SCF calculations.

It was noted that the Penney-Dirac bond orders are available for only a few of the compounds in Table I. However, the Pauling bond orders can be calculated quite simply. Accordingly, the  $J_{ob}$  from Table I are plotted as a function of  $\rho_{LP}$  in Figure 4. The solid line in the figure conforms to the least-squares fit of the data

$$J_{ob} = -1.501\rho_{LP} + 0.050 \text{ Hz} \quad (20)$$

with correlation coefficient  $r^2 = 0.9906$ . Thus, the agreement with this very simple VB-related bond order is somewhat better than

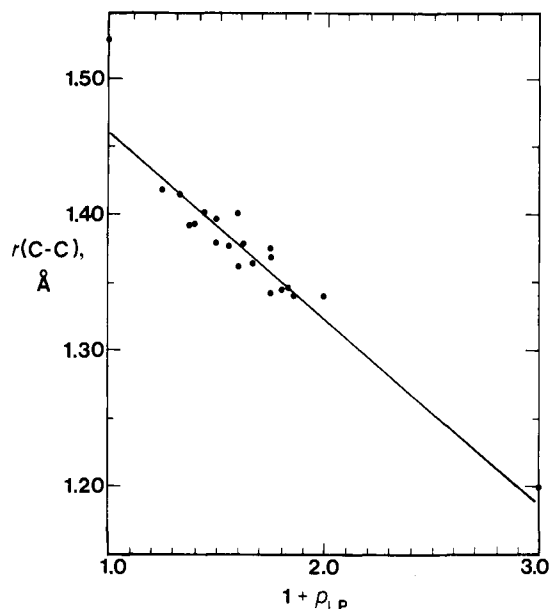


Figure 5. Experimental data for the C-C bond distances,  $r(\text{C-C})$  in angstroms plotted as a function of the  $\sigma$ -bond order plus Pauling  $\pi$ -bond order  $1 + \rho_{LP}$ . The straight line conforms to the linear least-squares fit  $r(\text{C-C}) = -0.136(1 + \rho_{LP}) + 1.597 \text{ \AA}$ . The standard deviation in  $r(\text{C-C})$  is 0.019  $\text{\AA}$ , and the correlation coefficient  $r^2 = 0.8762$ .

with any of the SCF results. In comparison, the correlation of Pauling bond order with bond length, which is plotted in Figure 5, is not as good even though this has been considered to be one of the better uses of this type of bond order.

On purely empirical grounds the orthobenzylic coupling constants emerge as a valuable experimental method for investigations of bonding in conjugated systems, particularly in view of the fact that unlike vicinal (cis) H-H coupling constants, which are a very well investigated parameter,<sup>31,32</sup>  $J_{ob}$  exhibit very little dependence<sup>4</sup> on other structural variables such as ring size and the presence of substituents on the aromatic rings.

#### Experimental Section

**Spectral Data.** All experimental NMR data in Table I were obtained on a Bruker Instruments WM-400 spectrometer using 5-mm sample tubes with approximately 5% w/v solutions in chloroform-*d* unless otherwise stated. Digital resolution was at least 0.05 Hz. All spectra were interpreted as first-order, and orthobenzylic coupling constants were assumed to be negative.<sup>4</sup> Details are given in the supplementary material.

**Syntheses.** The details of the syntheses of 2-methyltriphenylene (10), 3-methylchrysene (11), 6-methylchrysene (12), 1-methylpyrene (13), 2-methylpyrene (14), 4-methylpyrene (15), 6-methylbenzanthracene (16), and 6-methyl[3,4]benzphenanthrene (17) are given in the supplementary material.

**Supplementary Material Available:** Descriptions of experimental procedures, syntheses of compounds, and spectral analyses (16 pages). Ordering information is given on any current masthead page.

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## Amide V Overtone Assignment of a Conformation-Sensitive Band in the UV Resonance Raman Spectra of Peptides and Proteins

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**Abstract:** A band in the 1300–1500-cm<sup>-1</sup> region has been observed to be enhanced in the UV resonance Raman spectra of peptides and proteins. We show, on the basis of normal-mode analysis of experimental data from *N*-methylacetamide (NMA) and several conformations of poly(L-glutamic acid), that this band can be definitively assigned to the overtone of the amide V mode. The results of <sup>13</sup>C<sup>15</sup>N isotopic substitution on some NMA analogues support this assignment. The sensitivity of this band to polypeptide chain conformation can make it a new sensitive probe of secondary structure in proteins.

We recently presented<sup>1,2</sup> experimental evidence that a band in the ~1400-cm<sup>-1</sup> region of the UV resonance Raman spectra of aqueous solutions of peptides and polypeptides is associated with the amide  $\pi$ - $\pi^*$  electronic transition of the peptide group and that its vibrational mode, because of the disappearance of the band on deuteration, must have an NH component. Although not seen in preresonance spectra,<sup>3,4</sup> such a band has been observed in UV resonance spectra of *N*-methylacetamide<sup>5,6</sup> (NMA; although at the higher frequency of 1496 cm<sup>-1</sup>), in polypeptides,<sup>4,7</sup> and in proteins.<sup>8-10</sup> Previous to our study,<sup>1</sup> it had not been conclusively assigned, having been attributed to CH<sub>3</sub> antisymmetric bend in

NMA,<sup>3,5</sup> to CH<sub>2</sub> wag or twist in poly(L-lysine) (PLL)<sup>7</sup> and CH<sub>2</sub> bend in cytochrome c,<sup>9</sup> to COO<sup>-</sup> symmetric stretch in ionized

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