compounds. Uncertainties in substituent conformations connot account for the discrepancies noted in comparing calculated with experimental couplings directly. A simple adjustment of the $s^2(0)$ values based upon Slater's rules does not give substantial improvement. The present method predicts a rather precise additivity relationship for substituent effects on the couplings, in general agreement with relevant experimental results

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Oxygen-17 and Carbon-13 σ–π Parameters of the Carbonyl Group Calculated Using Localized σ Bonds

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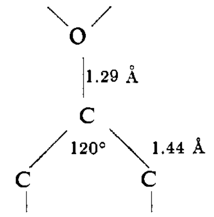
Abstract: σ–π polarization parameters for ^{17}O and ^{13}C were calculated semiempirically for the carbonyl group in the π fragment $(>C)_2C{=}O$. Three models were treated: model I with sp hybridization on oxygen, model II with sp^2 hybridization on oxygen, and model III with sp^2 hybridization on oxygen and a polarity parameter for the C–O bond. The method used was that of Melchior, in which localized σ bonds are constructed between each pair of atoms, each such bond being orthogonal to all others in the set. The excitation energies needed to evaluate the elements of the Q matrix were treated as parameters. However, the values of the intrabond excitation energies giving the best fit of calculated and "experimental" Q values were close to energies calculated for the corresponding bonds in small molecules. Experimental Q values were derived from the observed proton, ^{17}O, and ^{13}C hyperfine splittings in the p-benzosemiquinone radical. The following ranges of values were found for the elements of the $Q(^{17}O)$ and $Q(^{13}C)$ matrices: $Q_{OO}^{O} = 59 \pm 5$, $Q_{cross}^{O} = -7 \pm 1.9$, $Q_{CC}^{O} = -21 \pm 3.4$, $Q_{CC}^{C} = 44 \pm 5$, $Q_{cross}^{C} = 6.2 \pm 0.5$, and $Q_{OO}^{C} = -17.8 \pm 2$ G. It was found that, as Melchior predicts in general, the above values are relatively insensitive to the details of the σ-bonding scheme. The σ–π polarization parameters obtained for ^{17}O and ^{13}C compare well with those derived by other methods.

In π radicals the interaction between σ and π electrons is the physical basis for the interpretation of experimental hyperfine splitting constants in terms of the distribution of the unpaired electron in the π system. σ–π interaction constants for organic radicals have been estimated theoretically by a number of methods of varying sophistication and with varying success. A general theory for any atom in a π system has been presented by McLachlan, Dearman, and Lefevre,[2a] and rederived in a simpler fashion by Henning.[2b] The application of the theory to a particular molecular fragment requires some choice to be made for the molecular orbitals involved. In a few cases it has been possible to use the results of theoretical calculations on small molecules related to the fragment under consideration. More often a reasonable model system is used consisting of the usual LCAO π system and some choice of interatomic hybrids for the σ system. Recently in an important paper, Melchior[3] has shown that the neglect of overlap between the localized molecular orbitals of the basic σ set "leads to an artificial sensitivity of Q_{AA}^{A} to σ-bonding details." This significant finding has encouraged us to reexamine the σ–π parameters for the carbonyl group, for which ^{13}C and ^{17}O hyperfine splittings have recently been observed in a large number of radicals.[4,5] In the present paper we derive values for the σ–π parameters of ^{13}C and ^{17}O in the fragment



which occurs in quinones. We use Melchior's method to construct the σ bonding and antibonding orbitals. All overlap integrals are included and all one-, two-, three-, and four-center exchange integrals are taken into account. Calculations were carried out for sp and sp^2 hybridization on oxygen, and also with a polarity parameter for the C–O bond.

The results compare favorably with those obtained by other methods,[5,6] and have the advantage that the various contributions to each σ–π parameter can be related to localized bonds, which are chemically easier to visualize than the molecular orbitals derived from SCF or CI calculations. Perhaps the most significant result is that, as Melchior predicts, the values found for the parameters are relatively insensitive to the details

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[1] (a) Technion—Israel Institute of Technology; (b) Weizmann Institute of Science.

[2] (a) A. D. McLachlan, H. H. Dearman, and R. Lefevre, *J. Chem. Phys.*, 33, 65 (1960); (b) J. C. M. Henning, *ibid.*, **44**, 2139 (1966).

[3] M. T. Melchior, *ibid.*, **50**, 511 (1969).

[4] K. D. Sales, *Advan. Free Radical Chem.*, 3, 139 (1969).

[5] (a) M. Broze and Z. Luz, *J. Chem. Phys.*, **51**, 738 (1969); (b) M. Broze, Z. Luz, and B. L. Silver, *ibid.*, **46**, 4891 (1967).

[6] M. R. Das and G. K. Fraenkel, *ibid.*, **42**, 1350 (1965).

of the σ bonding. Thus the σ–π parameters calculated in the present work can be confidently expected to be transferable, to a good approximation, from one molecule to another.

It should be noted that we use a basis set constructed from Slater nodeless orbitals while Melchior uses SCF atomic orbitals. The final results should not, however, depend significantly on which basis set is chosen.

Method of Calculation

σ–π parameters were calculated for the carbon (^{13}C) and the oxygen (^{17}O) nuclei of the carbonyl group in the molecular fragment shown above.

All the atoms lie in the xy plane, which contains the interatomic σ bonds and the lone-pair orbitals of oxygen.

The unpaired electron moves in a pπ system consisting of a linear combination of $2p_z$ orbitals on the four atoms. The nodal plane of the π system contains the four nuclei. Interatomic distances were taken as C–C, 1.44; C–O, 1.29 Å. These values were taken from the results of a calculation on benzosemiquinone using the method of Nishimoto and Forster.[7] They lie between the experimentally determined values for p-benzoquinone and hydroquinone.[8]

The atomic basis orbitals used in describing the σ system were the 1s, 2s, $2p_x$, and $2p_y$ orbitals on each atom, comprising 16 orbitals. Slater orbitals were used, the exponents for oxygen and carbon being taken from Clementi, *et al.*[9]

In order to calculate σ–π parameters for the atoms N in the above fragment, it is necessary to evaluate the elements of the σ–π polarization matrix

$$Q_{rs}^{N} = \frac{16}{3}\pi g_N \beta_N \sum_i \sum_p \frac{\langle \sigma_i (p_z)_r | e^2/r_{12} | (p_z)_s \sigma_p^* \rangle}{[E(0) - E(i \rightarrow p)]} \times \sigma_i(r_N)\sigma_p^*(r_N) \quad (1)$$

Equation 1 is identical with eq 26 in Henning's paper,[2b] g_N is the nuclear g value, β_N the nuclear Bohr magneton, σ_i and σ_p^* are occupied and unoccupied σ MO's, $\sigma_i(r_N)$ is the value of the orbital σ_i at nucleus N, $(p_z)_r$ is $2p\pi$ orbital on atom r, and $[E(0) - E(i \rightarrow p)]$ is the singlet–triplet excitation energy from the MO i to the MO p.

To proceed, the form of the σ molecular orbitals must be chosen, and this is done by Melchior's method. Very briefly this consists of the following steps. (1) Between each pair of atoms a σ-bonding "equivalent" MO is formed from a linear combination of hybrids centered on each atom. A σ-antibonding MO, orthogonal to each bonding MO, is constructed from the same hybrids. The hybrids are based on 2s, $2p_x$, and $2p_y$ orbitals. The set of antibonding σ orbitals is labeled $\{\phi_A\}$. (2) To the set of σ-bonding orbitals are added any lone-pair orbitals and "inner shell" 1s orbitals, to form an augmented set $\{\phi_G\}$. (3) The two sets, $\{\phi_A\}$ and $\{\phi_G\}$, are separately orthonormalized by a Lowdin-type transformation to give the sets $\{\phi_A'\}$, $\{\phi_G'\}$. The set $\{\phi_G'\}$ is taken as the ground-state (bonding) σ system. This transformation causes relatively little mixing of the original set of equivalent orbitals. (4) The set $\{\phi_A'\}$ is orthogonalized to the set $\{\phi_G'\}$ to give a set $\{\phi_A''\}$, which we take as the σ-antibonding system. This step involves a Schmidt-type orthogonalization, which, unlike the Lowden transformation, causes considerable mixing of the original set $\{\phi_A\}$.

Using the above sets of bonding and antibonding orbitals, $\{\phi_G'\}$ and $\{\phi_A''\}$, we now evaluate the elements of the matrix Q^A (eq 1).

In practice it is necessary to evaluate the relevant exchange integrals and the singlet–triplet (σ bonding → σ antibonding) excitation energies in eq 1. The other parameters, $\sigma(r_A)$, follow simply from the form of the σ MO and the exponents used in the Slater orbitals. In addition, the successive transformations of the equivalent orbitals to give the sets $\{\phi_G'\}$ and $\{\phi_A''\}$ involve the use of various overlap matrices defined in eq 2-20–2-22 of Melchior's paper.

Overlap Integrals. A computer program was written to evaluate overlap integrals from the general expression given by Roothaan.[10] For those cases where the relevant orbital exponents differed only slightly in value ($\tau < 0.05$ in Roothaan's nomenclature) the integrals were calculated from the expression for $\tau = 0$.

Exchange Integrals. One-, two, three-, and four-center integrals over Slater atomic orbitals were computed using a program written in Autocode by N. Epstein of this department.

The elements of the Q matrix for ^{13}C and ^{17}O in the carbonyl group were calculated for three different models: model I, with sp hybridization on oxygen; model II, with sp^2 hybridization on oxygen; and model III, with sp^2 hybridization on oxygen and a polarity parameter of 0.7 for the carbonyl σ bond.

Results

The σ bonding and antibonding molecular orbitals of the C_2—C=O fragment were determined for models I, II, and III using the above method. The resulting orbitals were used in eq 1 to obtain the different contributions to the Q matrix for ^{17}O and ^{13}C. The excitation energies required in the denominator of eq 1 are at this stage left as parameters, symbolized by the letters A to F: A = oxygen nonbonding → C–O σ antibonding; B = C–O σ bonding → C–N σ antibonding; C = C–C σ bonding → C–C σ antibonding; D = C–C σ bonding → C–C′ σ antibonding; E = C–C σ bonding → C–O σ antibonding; and F = C–O σ bonding → C–C σ antibonding. In terms of these energies we obtain, for model I

$$Q_{OO}^{O} = -6.4 + 32.1/A + 38.2/B$$

$$Q_{cross}^{O} = -0.5 - 2.1/A - 2.8/B$$

$$Q_{CC}^{O} = -1.2 + 2.1/A - 25.8/B + 1.1/E$$

$$Q_{CC}^{C} = -16.2 + 12.5/B + 22.8/C + 13.2/D + 21.4/E + 9.6/F$$

$$Q_{cross}^{C} = -0.4 + 1.4/B + 2.1/C + 0.9/E + 4.3/F$$

$$Q_{OO}^{C} = -1.9 + 1/A - 18.5/B + 0.3/C + 0.8/E - 2/F$$

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(7) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

(8) "Interatomic Distances," Special Publications No. 11 and 18, The Chemical Society, London, 1958, 1965.

(9) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(10) C. C. J. Roothan, *ibid*, **19**, 1445 (1951).

for model II

$$\begin{aligned}
Q_{\mathrm{OO}}{}^{\mathrm{O}} &= -5.4 + 37.8/A + 24.6/B \\
Q_{\mathrm{cross}}{}^{\mathrm{O}} &= -0.4 - 3/A - 2.4/B \\
Q_{\mathrm{CC}}{}^{\mathrm{O}} &= -1 + 0.2/A - 19.4/B + 1.2/E \\
Q_{\mathrm{CC}}{}^{\mathrm{C}} &= -16.1 + 13.1/B + 22.2/C + 12.8/D + \\
&\qquad 21.4/E + 9.2/F \\
Q_{\mathrm{cross}}{}^{\mathrm{C}} &= -0.4 \times 1.6/B + 2/C + 1.2/E + 3.9/F \\
Q_{\mathrm{OO}}{}^{\mathrm{C}} &= -1.7 + 1/A - 16.7/B + 0.3/C + 0.9/E - \\
&\qquad 2.1/F
\end{aligned}$$

and for model III

$$\begin{aligned}
Q_{\mathrm{OO}}{}^{\mathrm{O}} &= -4.9 + 34/A + 26.9/B \\
Q_{\mathrm{cross}}{}^{\mathrm{O}} &= -0.4 - 4.1/A - 4.2/B \\
Q_{\mathrm{CC}}{}^{\mathrm{O}} &= -1 - 0.3/A - 20.6/B + 1.4/E \\
Q_{\mathrm{CC}}{}^{\mathrm{C}} &= -16.8 + 12/B + 22.3/C + 12.8/D + \\
&\qquad 22.9/E + 7.6/F \\
Q_{\mathrm{cross}}{}^{\mathrm{C}} &= -0.6 + 2.5/B + 1.9/C + 1.6/E + 3.1/F \\
Q_{\mathrm{OO}}{}^{\mathrm{C}} &= -1.6 + 0.7/A - 15.6/B + 0.3/C + \\
&\qquad 1.1/E - 2.4/F
\end{aligned}$$

Energies. To obtain numerical values of the elements of the Q matrices it is necessary to make some choice for the excitation energies. There is almost no direct experimental data from which these energies can be obtained. Ideally an *ab initio* calculation should be performed on each molecule, but this is not in the spirit of the present semiempirical approach. Very good calculations have been carried out on the molecules formaldehyde, CO, and C_2. Of course these calculated energies are for different molecular orbitals from those constructed in the present work, but they provide a guide to the choice of excitation energies in larger molecular fragments. In the following sections the different types of excitation relevant to the $C_2{=}C{=}O$ fragment are discussed separately. On the basis of this discussion we will subsequently make a set of choices for the excitation energies needed to evaluate the elements of the Q matrix. A point that will emerge is that the range of semiempirical energies finally chosen not only gives reasonable values for the σ–π parameters, but, when comparison is possible, they are close to the analogous excitation energies calculated theoretically for the small molecules listed above.

Inner Shell to σ-Antibonding Excitation Energies. The 1s → σ^* excitation energy has sometimes been taken as the 1s → 2s excitation energy for the relevant atom as found from the X-ray term values. This is probably a very good approximation as can be seen by a comparison of the values for the carbon and oxygen atoms with those derived for the results of Ransil and Nesbet, *et al.*, for the CO molecules.[11,12] We have derived 1s → σ^* excitation energies from their results using the expression[5]

$$E_{ki}(\text{triplet} \rightarrow \text{singlet}) = E_k - E_i - \langle \sigma_k \sigma_i^* | \sigma_k \sigma_i^* \rangle$$

in which the exchange integrals were evaluated for Slater orbitals using Clementi's exponents.[9] The results are included in Table I together with the excitation energies used by Broze and Luz[5a] for their σ–π calculations on the carbonyl group, using SCF wave functions for formaldehyde.

Table I. Calculated Excitation Energies (au) for the C–O Bond

Excitation energy	C–O[12]	C–O[11]	H_2CO[5a]
$1s_O \rightarrow$ C–O*	20.55	20.5	20.9
$2s_O \rightarrow$ C–O*	1.21	1.12	1.52
C–O → C–O*	1.2 0.93	1.37 1.22	0.81
$1s_C \rightarrow$ C–O*	11.35	11.2	11.35

Nonbonding to σ-Antibonding Excitation Energies. Using the results of Ransil and Nesbet on the C–O molecule we arrive at values of 1.12 and 1.21 au, respectively for the n → σ^* excitation energy from the oxygen nonbonding (lone-pair) orbitals. For the corresponding transition in the formaldehyde molecule, Newton and Palke's[13] results give[5a] 1.52 au. On the experimental side it is generally accepted that the n → π^* absorption band in the carbonyl group is at longer wavelengths than the $\pi \rightarrow \pi^*$ band, and it can therefore be expected that the n → σ^* excitation energy will be comparable to or less than that for the $\sigma \rightarrow \sigma^*$ transition. In estimating the values of the elements of the Q matrices we have taken the n → σ^* excitation energy as a fixed proportion of the intrabond excitation energy. It will subsequently appear that the final results for the Q matrices are not very sensitive to the ratio of n → σ^* to intrabond energies.

σ-Bonding to σ-Antibonding Excitation Energies. (a) Intrabond. Values for the $\sigma \rightarrow \sigma^*$ excitation energies for the C–O and C–C molecules derived from Ransil's and Nesbet's calculations on CO and from Newton and Palke's calculation on formaldehyde are shown in Table I. The similarity of the values for CO and formaldehyde is shown in Table I. The similarity of the values for CO and formaldehyde encourages us to suppose that the intrabond $\sigma \rightarrow \sigma^*$ energy lies at about 1 ± 0.2 au for the carbonyl group in molecules. In the present work this energy is taken as a variable parameter, and it will be seen that to fit the experimental and calculated hyperfine splittings of ^{13}C and ^{17}O in the carbonyl group of semiquinones it is necessary to take a value of about 1.05 ± 0.05 au.

(b) Interbond. Excitations of the type $\sigma(\text{C–O}) \rightarrow \sigma^*(\text{C–C})$ and $\sigma(C_i\text{–}C_j) \rightarrow \sigma^*(C_i\text{–}C_k)$, etc., are probably the most difficult to estimate. Melchior, in treating the $CH_2CH_2^+$ ion, has calculated the elements of the Q matrix as functions of the ratio R of the intrabond (E_r) to the interbond (E_q) excitation energies. He considers values of R ranging from 0.5 to 1.0, since he presents arguments for supposing that in general E_r is larger than E_q. As a first approximation no distinction was made between CC′ and CH bonds.

In this work the ratios R of intrabond to interbond $\sigma \rightarrow \sigma^*$ excitation energies are taken as a variable parameter. Values for R of 0.55 and 0.75 were used. Melchior found that for $CH_2CH_2^+$ and for CH_3 a value

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(11) B. J. Ransil, *Rev. Mod. Phys.*, 32, 245 (1960).

(12) H. Lefebvre-Brion, C. M. Moser, and R. K. Nesbet, *J. Chem. Phys.*, 34, 1950 (1961).

(13) M. D. Newton and W. E. Palke, *ibid.*, 45, 2329 (1966).

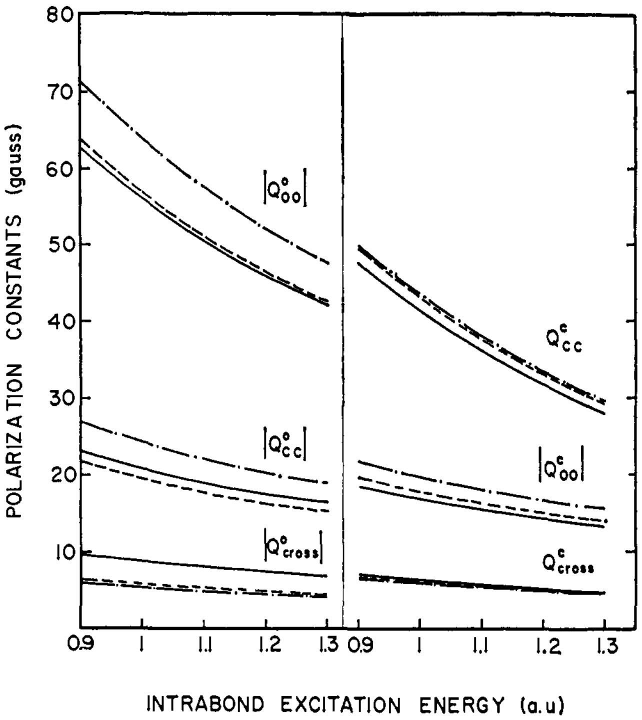

Figure 1. Polarization constants as a function of the intrabond excitation energy for three different models: -·-·, model I; ----, model II; ——, model III (see text). The n → σ^* excitation energy is equal to the intrabond excitation energy and the intrabond-to-interbond excitation energy ratio is taken as 0.55.

of 0.55 gave good results. However, as will be seen below, the final results for the Q matrix are not very sensitive to the value taken for R.

Guided by the above facts, values of the elements of the Q matrix were determined for models I, II, and III as functions of the intrabond $\sigma \rightarrow \sigma^*$ excitation energy P, for the following four sets of conditions.

$$A = B = C = P \qquad D = E = F = P/0.55 \qquad \text{(i)}$$

$$A = B = C = P \qquad D = E = F = P/0.75 \qquad \text{(ii)}$$

$$A = 0.9P \qquad B = C = P \qquad D = E = F = P/0.55 \qquad \text{(iii)}$$

$$A = 0.9P \qquad B = C = P \qquad D = E = F = P/0.75 \qquad \text{(iv)}$$

The results are presented graphically in Figures 1-4 as functions of P.

Discussion

To judge the validity of the above results it is necessary to compare them with experimental data. For this purpose we have chosen the observed ^{13}C and ^{17}O hyperfine constants in *p*-benzosemiquinone. In this radical the proton hyperfine splitting constant is insensitive to solvent effects, and if we use McConnell's equation, $a_H = Q\rho_C{}^{\pi}$, with a value of -23 G for Q, we derive a spin density on the neighboring carbon of 0.105. Some authors have taken $Q_{CC}{}^{H}$ as high as -27 G but have neglected the positive contribution of the off-diagonal elements of the Q matrix for a_H. The value of -23 G can be looked upon as an effective Q for use in McConnell's equation, including the effect of the off-diagonal elements in the Q^H matrix. It follows that the sum $\rho_O + \rho_C$ of the spin densities on the carbonyl oxygen and carbon atoms of one carbonyl group is 0.29. We now proceed to derive the Q^O and Q^C matrices as follows. The experimental values of a^O and a^C are written as functions of P, ρ_C, and ρ_O. Using the fact that $\rho_O + \rho_C = 0.29$ we can eliminate ρ_O from the equations. The equations for a^O and a^C are then solved simultaneously to give values for P and

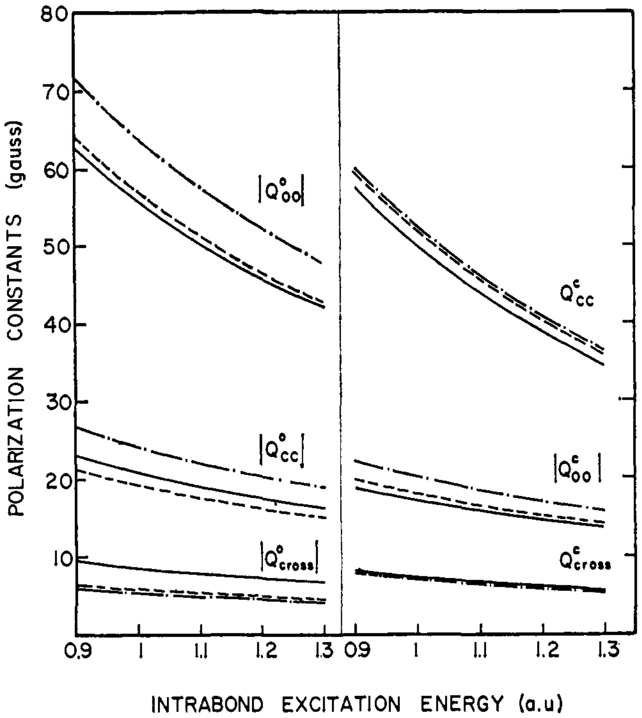

Figure 2. Same as in Figure 1. The intrabond-to-interbond excitation energy ratio is taken as 0.75.

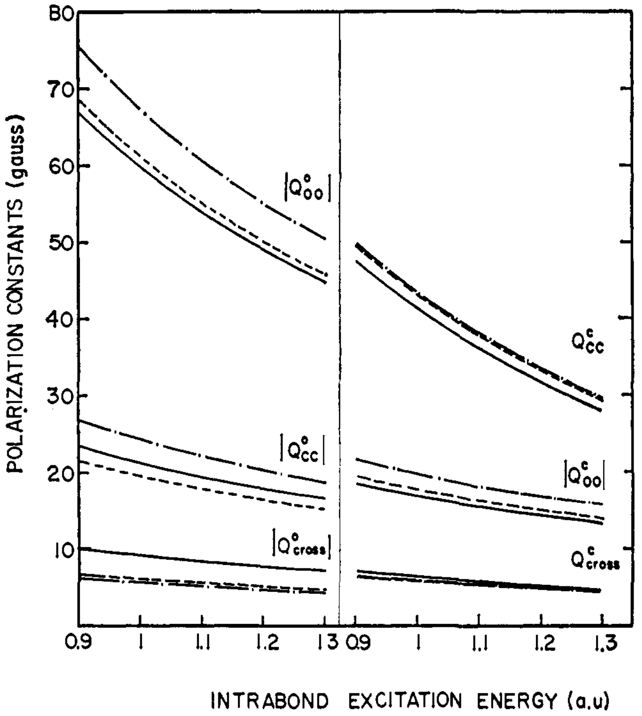

Figure 3. Same as in Figure 1. The n → σ^* excitation energy is equal to 0.9 of the intrabond excitation energy and the intrabond-to-interbond excitation energy ratio is taken as 0.55.

Table II. Polarization Constants and Hyperfine Splittings in 1,4-Benzosemiquinone

A	C	Model	P	Q_{OO}^{O}	Q_{cross}^{O}	Q_{CC}^{O}	Q_{CC}^{C}	Q_{cross}^{C}	Q_{OO}^{C}	ρ_1	ρ_7
P	$P/0.75$	I	1.07	59.2	−5.1	−22.6	47.7	6.5	−18.8	0.103	0.186
P	$P/0.75$	II	1.05	54.0	−5.5	−18.4	48.5	6.7	−17.2	0.097	0.193
P	$P/0.75$	III	1.05	53.1	−8.3	−19.9	46.8	6.9	−16.4	0.098	0.192
P	$P/0.55$	I	1.0	63.9	−5.4	−24.3	43.4	6.0	−19.8	0.110	0.180
P	$P/0.55$	II	0.98	58.0	−5.9	−19.8	44.1	6.2	−18.0	0.104	0.185
P	$P/0.55$	III	0.97	57.6	−8.9	−20.6	42.8	6.6	−17.3	0.106	0.183
$0.9P$	$P/0.75$	I	1.13	58.9	−5.1	−21.2	44.3	6.1	−17.8	0.105	0.185
$0.9P$	$P/0.75$	II	1.11	54.4	−5.5	−17.4	44.8	6.3	−16.2	0.099	0.191
$0.9P$	$P/0.75$	III	1.11	56.3	−8.7	−19.8	46.4	6.9	−16.3	0.100	0.190
$0.9P$	$P/0.55$	I	1.05	63.9	−5.4	−22.9	40.6	5.7	−18.8	0.113	0.177
$0.9P$	$P/0.55$	II	1.05	58.3	−5.9	−18.7	40.5	5.8	−17.0	0.108	0.182
$0.9P$	$P/0.55$	III	1.04	57.6	−8.9	−20.5	39.4	6.2	−16.3	0.109	0.181

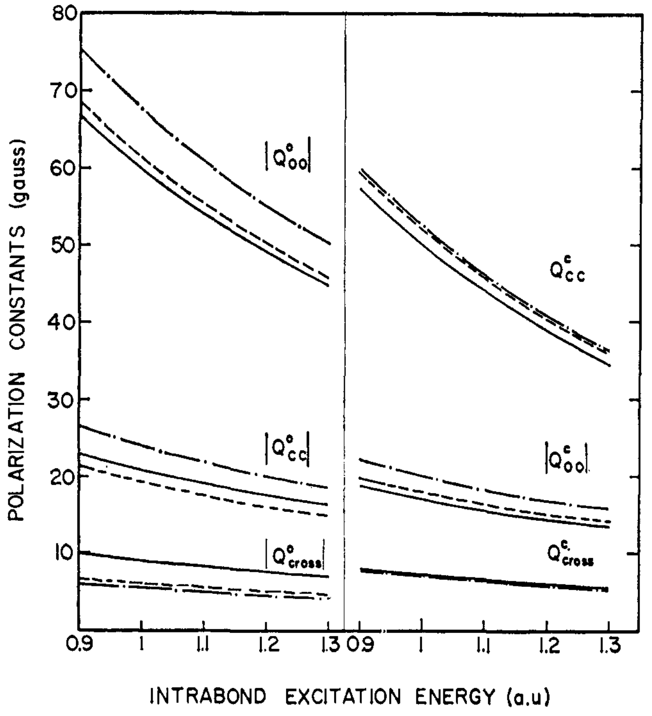

Figure 4. Same as in Figure 1. The n → σ^* excitation energy is equal to 0.9 of the intrabond excitation energy and the intrabond-to-interbond excitation energy ratio is taken as 0.75.

ρ_C for each of the 12 possible permutations of the three models and the four assumptions about A and C. The values of P are then used to give numerical values for the Q^O and Q^C matrices. Regarding the experimental values of a^O and a^C, hyperfine splittings due to ^{17}O and ^{13}C have been observed in a large number of solvents and we have taken results for an aprotic solvent, dimethyl sulfoxide, in which the interaction between the oxygen atom and the solvent is minimal. The observed splitting constants can then be written

$$a^O = 9.42 = Q_{OO}^{O}(P)\rho_O + Q_{cross}^{O}(P)\sqrt{(\rho_O\rho_C)} + Q_{CC}^{O}(P)\rho_C$$

$$a^C = -2.13 = Q_{CC}^{C}(P)\rho_C + Q^{C}_{cross}(P)\sqrt{(\rho_O\rho_C)} + Q_{OO}^{C}(P)\rho_O + 2Q_{cross}^{C}(CC')\sqrt{\rho_C}(0.105) + 2Q_{C'C}^{C}(0.105)$$

The unknowns in these equations are Q_{OO}^{O}, $(Q_{CO}^{O} + Q_{OC}^{O}) = Q_{cross}^{O}$, Q_{CC}^{O}, Q_{CC}^{C}, Q_{cross}^{C}, Q_{OO}^{C} (which are all functions of the one parameter P), and ρ_C and ρ_O. The values of $Q_{cross}^{C}(CC')$ $(Q_{CC'}^{C} + Q_{C'C}^{C})$ and of $Q_{C'C'}^{C}$ are taken as +3.6 and −9.0 G from Melchior's analysis of $CH_2CH_2^+$. It is then possible to estimate the term involving $\rho_C\rho_{C'}$ by taking ρ_C as 0.1. The solutions of the above equations are in fact insensitive to small variations in the unknown ρ_C. Solving the equations we obtain the results listed in Table II.

It can be seen that the calculated values for the Q's and the ρ's are not very sensitive to the particular choice of σ-bonding model, the ratio of nonbonding to intrabond excitation energy, or the ratio of intra- to interbond excitation energies. It is particularly significant, and encouraging for the further application of Melchior's method, that the results for models I, II, and III are so similar, a result which is not particularly dependent on the choice of excitation energies.

The orbitals for the C–O molecule calculated by Ransil and by Nesbet include two orbitals, lying close together, which are both σ bonding in character. The excitation energies to the σ antibonding orbital from these two orbitals are given in Table I. It can be seen that the average value of 1.05 au for P, given in Table II, lies within the range of theoretically calculated excitation values in Table I.

σ–π Parameters for ^{13}C. From Table II it can be seen that the values (in gauss) for the ^{13}C Q matrix elements fall within the following ranges

$$Q_{CC}^{C} = +39.5 \text{ to } +49$$

$$Q_{OO}^{C} = -15.7 \text{ to } -19.8$$

$$Q_{cross}^{C} = +5.7 \text{ to } +6.7$$

These figures are insensitive to any reasonable variation in the value used for Q_{CH}^{H} in deriving the spin density on the neighboring carbons. For comparison Das and Fraenkel[6] give values of +33.9 and −27.1 G for Q_{CC}^{C} and Q_{OO}^{C}, respectively, Broze and Luz[5] give +36 and −24.3 G, Gulick and Geske[14] +32.7 and −25.1 G. These results are, however, very sensitive to the calculated spin densities. Since calculated spin densities are very uncertain in molecules other than simple hydrocarbons, Q values obtained by this method will be correspondingly uncertain.

Melchior's conclusion that the value of σ–π parameters calculated by his method will be insensitive to the details of σ bonding is fully confirmed by the present results. We believe that the values obtained above are transferable to any radical containing the conjugated

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(14) M. Gulick, Jr., and D. H. Geske, *J. Amer. Chem. Soc.*, 88, 4119 (1966).

Table III. Calculated Spin Densities by Various Procedures

	ρ_1[a]	ρ_2	ρ_7
Present work	0.097–0.113	0.105	0.177–0.193
Semiempirical[b]	0.113	0.100	0.187
McLachlan SCF[c]	0.098	0.103	0.195
McLachlan SCF[d]	0.094	0.098	0.211
Variable electronegativity SCF[d]	0.107	0.087	0.219
SCF + CI[e]	0.043	0.077	0.302

[a] ρ_1 refers to the carbonyl carbon, ρ_2 to the other ring carbons, and ρ_7 to oxygen. [b] G. K. Fraenkel, *Pure Appl. Chem.*, **4**, 143 (1962). [c] J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962). [d] B. L. Silver, *Theor. Chim. Acta*, **9**, 192 (1967). [e] O. Kikuchi and K. Someno, *Bull. Chem. Soc. Jap.*, **40**, 2972 (1967).

fragment C—C(—C)═O. The cross terms in Q, which are usually neglected, are seen to give a sizable contribution to a^{C}.

σ–π Parameters for ^{17}O. The range of values (in gauss) for the elements of the Q matrix for ^{17}O are

$$Q_{\mathrm{OO}}{}^{\mathrm{O}} = +53.9 \text{ to } +64$$

$$Q_{\mathrm{CC}}{}^{\mathrm{O}} = -17.6 \text{ to } -24.3$$

$$Q_{\mathrm{cross}}{}^{\mathrm{O}} = -5.1 \text{ to } -8.9$$

The gyromagnetic ratio of ^{17}O has been taken as positive in assigning the signs of the above polarization constants. By comparison Geske and Gulick obtain 40.4 G for $Q_{\mathrm{OO}}{}^{\mathrm{O}}$ and 16.7 G for $Q_{\mathrm{CC}}{}^{\mathrm{O}}$ (both with the same sign) from an analysis of solvent effects on ^{13}C and ^{17}O splittings in p-benzosemiquinone. Broze and Luz give 48.7, −0.46, and −6.03 G, respectively, for the above Q values, calculated theoretically from an SCF wave function for formaldehyde.

In general the σ–π parameters obtained here range over values similar to those derived from semiempirical correlations of calculated spin densities with observed splitting constants. In agreement with other workers we find a large negative contribution to a^{C} in the carbonyl group from spin density on the neighboring oxygen atom. A similar term for a^{O} arising from spin density on the carbon atom is also predicted by the present results. This is in contrast to the theoretical results of Broze and Luz, who find a very small contribution, and Gulick and Geske, who find a *positive* contribution from ρ_{C} to a^{O}.

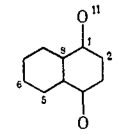
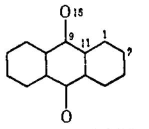
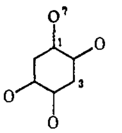
Spin Densities. It is interesting to consider the magnitudes of the spin densities obtained by the solution of the previous three simultaneous equations. The results are included in Table II, and for comparison we have collected the results of various theoretical calculations and semiempirical estimations in Table III.

The spin densities derived in this work are seen to agree well with most of the theoretical results, the discrepancies being the worst for the more sophisticated methods of calculation. It is interesting to take a set of Q values falling near the middle of the calculated range of Q's and use them to derive experimental spin densities from the observed spectrum of 9,10-anthrasemiquinone, 1,4-naphthasemiquinone, and 2,5-dioxo-1,4-benzosemiquinone. Using an effective value of −23 G for Q in McConnell's equation the spin densities on the carbon atoms attached to protons were estimated from the experimental proton splittings. The spin densities at bridge carbon atoms were taken from a calculation and the sum of the spin densities on the carbonyl group was obtained by difference. The results are shown in Table IV.

It is seen that the values for the spin densities based on the Q values derived in the present work agree well with other theoretical estimates.

After the completion of this article a paper appeared, by Yonezawa, Kawamura, and Kato,[15] containing a study of the isotropic hyperfine coupling

Table IV. Calculated and Experimental Spin Densities

	Position	Observed splitting	"Exptl" spin density	Calcd spin density MSCF[5a]	Calcd spin density VESCF[b]	Calcd spin density MSCF[c]
 (DMSO and DMF)	1		0.106	0.107	0.093	0.109
	2	$a^{\mathrm{H}} = -3.31$	0.144	0.135	0.140	0.142
	5	$a^{\mathrm{H}} = -0.30$	0.013	0.036	0.067	0.014
	6	$a^{\mathrm{H}} = -0.63$	0.027	0.015	0.016	0.028
	9		(0.04)[d]			0.039
	11	$a^{\mathrm{O}} = 8.58$	0.170	0.180	0.184	0.167
 (DMSO and DME)	1	$a^{\mathrm{H}} = -0.30$	0.013	0.012	0.009	0.011
	2	$a^{\mathrm{H}} = -0.98$	0.043	0.038	0.018	0.040
	9	$a^{\mathrm{C}} = -0.47$	0.109	0.123	0.121	0.123
	11		(0.062)[d]	0.060	0.065	0.064
	15	$a^{\mathrm{O}} = 7.53$	0.154	0.156	0.194	0.146
 H_2O (KOH)	1	$a^{\mathrm{C}} = 2.63$	0.156	0.152		
	3	$a^{\mathrm{H}} = +0.79$				
		$a^{\mathrm{C}} = -6.66$	−0.048[b]	−0.052		
	7	$a^{\mathrm{O}} = 4.57$	0.118	0.124		

[a] This value was calculated without use of hydrogen hyperfine splitting. [b] See ref *d* of Table III. [c] See ref *c* of Table III. [d] Calculated value.

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(15) T. Yonezawa, T. Kawamura, and H. Kato, *J. Chem. Phys.*, **50**, 3482 (1969).

constants of second-row elements in π radicals. The unrestricted SCFMO method was used to calculate σ–π parameters for a number of molecular fragments. The parameters derived for ^{17}O in the C–O fragment were $Q_{OO}{}^{O} = 55.6$, $Q_{CC}{}^{O} = -16.9$, $Q_{cross}{}^{O} = -13.7$ G (where we have used the sign convention of this paper). These values are close to those derived in the present work. On the other hand a semiempirical estimation of ^{17}O σ–π parameters by Yonezawa, Kawamura, and Kato gives the completely unacceptable values $Q_{OO}{}^{O} = 22$, $Q_{CC}{}^{O} = -75$, $Q_{cross}{}^{O} = -72$ G. As the authors point, out the values calculated by fitting calculated spin densities to observed splitting constants are extremely sensitive to the calculated spin densities. In general it can be concluded that semiempirical correlations of this kind are unreliable except for the comparatively simple case of proton hyperfine splitting constants.

Acknowledgment. We wish to thank Dr. M. T. Melchior for sending us a preprint of his paper on the isotropic hyperfine interaction, and for his constructive criticism of our work. Many of his suggestions as to the content and presentation of our results have been incorporated in this paper.

A Critical Test of the Acree Hypothesis in Nucleophilic Displacement Reactions

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Abstract: In applying kinetic data for bimolecular reactions involving neutral molecules and ionizable species to the Acree equation, $k = k_i\alpha + k_m(1 - \alpha)$, where k is the observed second-order rate constant, k_i and k_m are rate constants for the reactions of ions and ion pairs, respectively, and α is the degree of dissociation, it is generally assumed that k_i and k_m are independent of the ionic strength. Second-order specific rates, k, for the exchange of ^{131}I between methyl iodide and alkali iodides (NaI, KI, RbI, and CsI, respectively) in methanol at 25°, where these salts are associated to only a few per cent, decrease with increasing ionic strength. It is shown that this change is due to kinetic salt effects (changes in activity coefficients of reactants and transition-state complex with ionic strength) as well as changes in ionic association and different reactivities of free and paired ions. For the range of concentration of ionic halide investigated, 2×10^{-4}–8×10^{-3} *M*, the reaction of free halide ions is subject to a negative salt effect of between 3 and 4%. A necessary consequence of the Acree hypothesis is that k_i should be independent of the nature of the cation. It is verified that this is so; the rate constants, k_i, for those exchanges in which NaI, KI, RbI, and CsI, respectively, are involved are in the ratios, 1.001 : 1.005 : 0.998 : 0.995. The degree of association is too insignificant to permit quantitative conclusions concerning the reactivity of paired ions, though the data do not exclude a contribution of ion pairs to the reaction rate.

The Acree hypothesis[2] that the specific rate of certain bimolecular reactions between neutral molecules and ionizable reagents varies with dilution because of different reactivities of free and paired ions has been extensively studied (see ref 3 for reviews on this subject). According to Acree, the observed second-order rate constant, k, may be expressed

$$k = k_i\alpha + k_m(1 - \alpha) \qquad (1)$$

where k_i and k_m are specific rates of reactions of free and paired ions, respectively, and α is the degree of dissociation of the ionic reactant.

Reaction rate data for several isotopic exchange reactions of the type $RY + A^+Y^{*-} \rightleftarrows RY^* + A^+Y^-$, where RY is a neutral molecule and A^+Y^- an ionic reactant, have previously[3b] been treated by means of eq 1 in order to obtain information concerning the reactivities of free and paired ions. In these studies, k_i and k_m have been regarded as independent of the ionic strength. However, it cannot be excluded that especially k_i, the second-order specific rate for exchange between RY and Y^{*-}, may be subject to a nonnegligible dependence on the ionic strength (kinetic salt effect). The main objective of the present research was to examine the possible existence of an effect of this kind. A secondary aim was to investigate whether k_i is independent of the nature of the counterion to Y^- in the ionic reactant, A^+Y^-.

The reactions studied in the present work, *viz.* the exchange of radioiodine between methyl iodide and alkali iodides in dry methanol at 25°, were selected because alkali iodides are only slightly associated in this medium, a fact which facilitates separation of the effect of ionic strength on the reaction rate from the effect of ion-pair formation.

Experimental Section

Reagents. Sodium, potassium, rubidium, and cesium iodides (Merck, Suprapur) were dried at 110° for 2 hr and allowed to cool in a vacuum desiccator.

Carrier-free $^{131}I^-$ was used to label these salts. The radioactive iodine was obtained as sodium iodide in a dilute aqueous sodium thiosulfate solution from the Atomic Energy Establishment, Kjeller, Norway. Potassium, rubidium, and cesium radioiodides were pre-

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