

carbon, and nitrogen constants in all the compounds considered. We are not able to report the results for some other nitrile anions studied experimentally (such as tetracyanoethylene) because of convergence difficulties with the calculations. The experimental data on nitrobenzene and dinitrobenzene anions are also fairly well reproduced. It is particularly interesting that the sharp drop in the nitrogen hyperfine constant from nitrobenzene to *p*-dinitrobenzene is accounted for. The standard model for all these compounds is planar, so this effect can be interpreted without appealing to nonplanarity at the nitrogen atoms as proposed by Symons.²⁰ The calculations on *m*-dinitrobenzene suggest that the assignment of the two- and five-proton hyperfine constants by Maki and Geske²¹ may be incorrect.

The results for quinones are less satisfactory. Calculated proton hyperfine constants for hydrogens in *p*-benzosemiquinone ion are less than experimental values as are those of the corresponding protons (2, 3) in 1,4-naphthoquinone.²² Fairly large negative carbon constants are predicted for the carbon atoms in the carbonyl groups, but only a small value is found experimentally in *p*-benzosemiquinone.²³

The fluorine isotropic hyperfine coupling constants are generally well reproduced with the notable exception of the two fluoroacetamide radicals, which are calculated to be much lower than the observed values.^{24,25}

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Although these radicals are thought to be planar in the crystal, the fluorine coupling constants observed for the monofluoro and difluoro species are quite comparable to those observed for fluoromethyl and difluoromethyl radicals, respectively, and the latter are almost certainly nonplanar.¹¹ Thus the planar model B geometry may be an inappropriate choice for these molecules. Further study of these molecules is being undertaken and the results will be reported in a subsequent publication.

Conclusions

On the basis of the agreement between calculated and observed hyperfine coupling constants listed in Tables III–VI, we conclude that spin-unrestricted molecular orbital calculations carried out with the INDO approximations for atomic and molecular integrals are quite capable of accommodating isotropic hyperfine coupling phenomena in polyatomic molecules. Calculations on this level of approximation should be useful in providing a basis for the assignment of positions and signs of hyperfine coupling constants when used in close conjunction with the available experimental data. To facilitate applications of this sort, the authors are making copies of the FORTRAN-63 computer program used in these calculations available through the Quantum Chemistry Program Exchange.²⁶ It also seems likely that wave functions of this type could be used to calculate and interpret anisotropic hyperfine coupling constants, *g* tensors, and other features of the electronic structure of free radicals.

(26) Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

Calculation of the Chemical Shift of a Series of Polyenylic Ions by the "Free-Electron Model"

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Abstract: The correlation of the chemical shift with the "free-electron model" is demonstrated for a series of polyenylic ions.

The applicability of the free-electron, or particle in a box, model to the discussion of the electronic spectra of a series of polyene ions has been amply demonstrated in the literature.¹ Recently Sorensen² reported both the electronic and the nmr spectra of a series of polyenylic ions and discussed the results in terms of phenomenological equations. The linear relation given by Sorensen for the electronic spectra can be readily obtained using free-electron theory and a single empirical parameter. The results of the calculations for the electronic spectra can then be used to

predict the chemical shift of the nmr spectra. Although the correlation of electronic spectra is not surprising, the correlation of the chemical shift by free-electron theory has not been reported.

The Electronic Spectra

The polyenylic-ion series discussed may be represented by



The energy levels are given by the particle in a box treatment as $E_m = m^2h^2/8m_e a^2$, where a , the length of the box, depends on n_c , the number of carbons in the π -electron system, and on the semiempirical pa-

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(2) T. S. Sorensen, *J. Am. Chem. Soc.*, **87**, 5080 (1965).

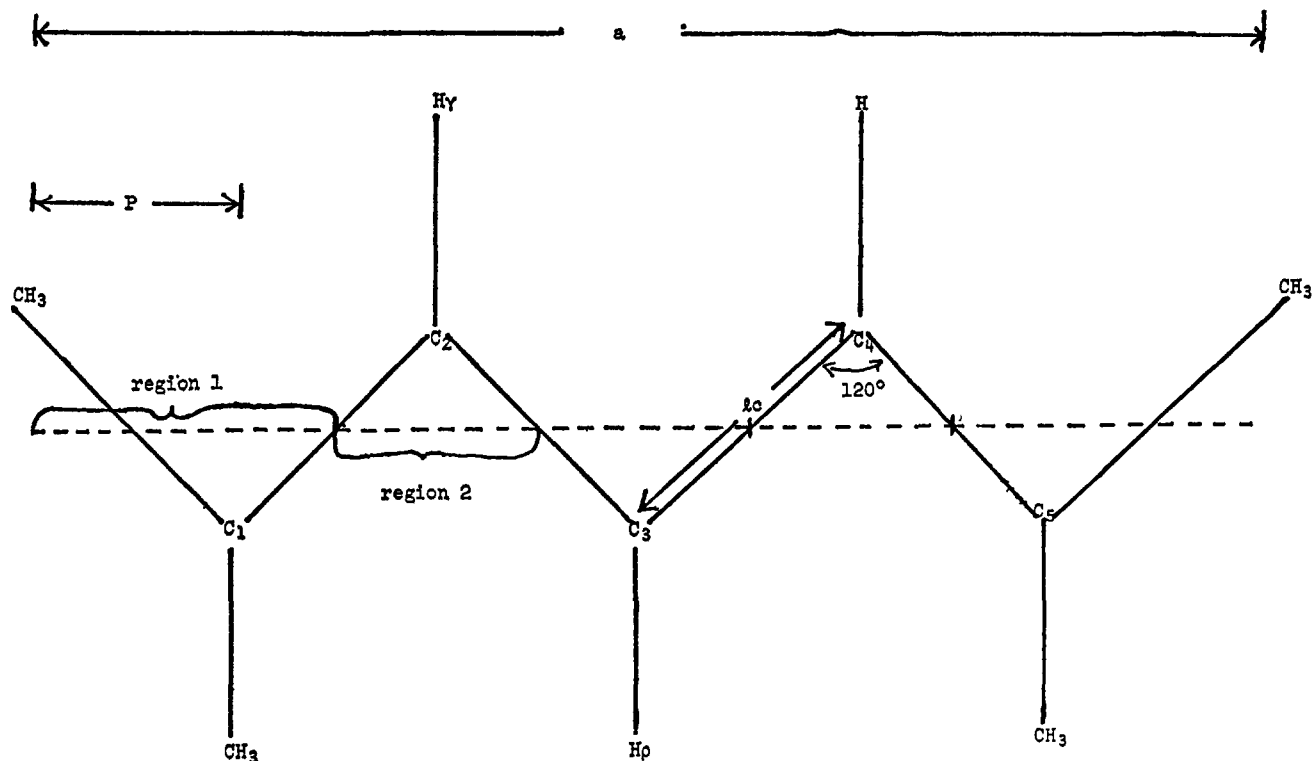


Figure 1. Free-electron model of polyene.

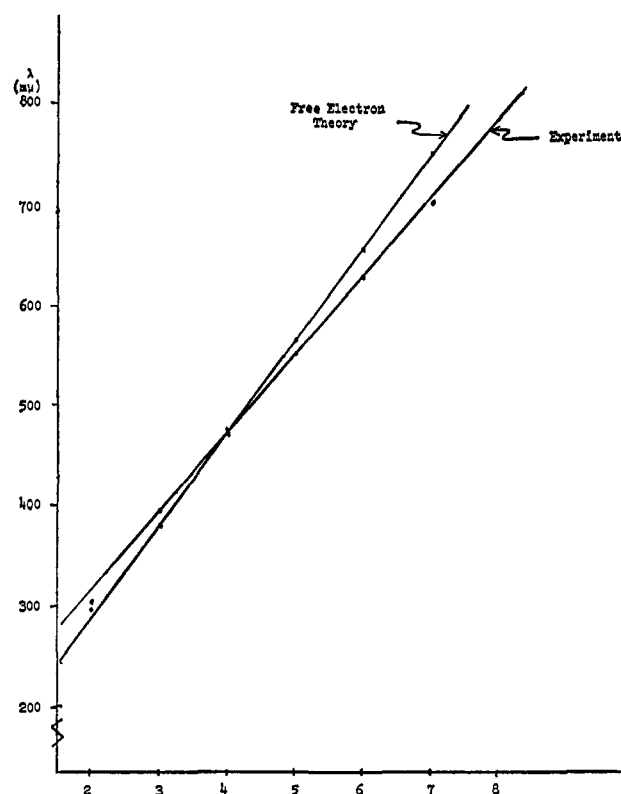


Figure 2. λ_{\max} vs. length of polyene chain.

parameter p , the penetration beyond the terminal carbons of the conjugated system.

Sorensen reports that application of free-electron theory to the electronic spectra requires a to be "too small to be realistic" when it is written as $a = l_c(n_c -$

$1) + 2p$, where l_c is the average bond length, about 1.4 Å, and p is taken constant for the series. Hence, in this work the polyenylic ion is taken (Figure 1) as a bent chain in the all-*trans* conformation³ with all C-C bond lengths the same and the extent of the box, a , as

$$a = [l_c(\cos 30^\circ)(n_c - 1)] + 2p$$

The value of l_c is taken as 1.4 Å and the penetration, p , is obtained from λ_{\max} observed for one of the polyenylic ions in the series. This value of p can then be used to predict λ_{\max} for the remaining members of the series. The values calculated for $p = 1.4$ Å (obtained from λ_{\max} for $n = 4$) are plotted along with the experimental values in Figure 2. As Figure 2 indicates, this free-electron model can correlate λ_{\max} with n .

Charge Densities

The number of π electrons in the polyenylic ion above is $2(n - 1)$. Hence, the first $(n - 1)$ orbitals will each be doubly occupied. Using the particle in a box eigenfunctions

$$\psi_m = \left(\frac{2}{a}\right)^{1/2} \sin \frac{m\pi x}{a}$$

the electron density in any region of the chain between points b and c is

$$\rho_{b,c} = 2 \sum_{m=1}^{n-1} \int_b^c \psi_m^2 dx = 2 \sum_{m=1}^{n-1} \left(\frac{2}{a}\right) \int_b^c \sin^2 \frac{m\pi x}{a} dx$$

The π -electron density, ρ_r , to be associated with carbon C_r will then be $\rho_{b,c}$ where b and c are the points on either side of the carbon C_r .

(3) There is some evidence, but no conclusive proof, for this assumption: T. S. Sorensen, private communication.

Two such regions are noted in Figure 1. Region 2 extends from the midpoint of the C₁-C₂ bond to the midpoint of the C₂-C₃ bond. However, the end regions, as exemplified by region 1, extend from the midpoint of the C₁-C₂ bond to the end of the "box." This difference between the end regions and the others must be kept in mind when considering relative electron densities. The values of the positive charge, $\rho_r^+ = 1 - \rho_r$, for each carbon r of the first five members of the series are given in Table I.

Table I. Excess Positive Charge Associated with the Carbon Centers

Carbon ion n	Carbon r					
	1	2	3	4	5	6
2	0.4422	0.116				
3	0.238	0.096	0.332			
4	0.134	0.085	0.245	0.072		
5	0.071	0.078	0.191	0.061	0.199	
6	0.028	0.073	0.154	0.056	0.164	0.051

In Figure 3 the positive charge on carbons 1, 2, and 3 are plotted against $1/n$. In the case of the first and third carbons, the plots are well represented as the straight lines

$$\rho_1^+ = +1.25\left(\frac{1}{n}\right) + k_1 \quad (1)$$

$$\rho_3^+ = +1.10\left(\frac{1}{n}\right) + k_3 \quad (2)$$

The charge on the second carbon exhibits marked curvature if the lower values of n are included but for larger values of n is approximated by the straight line

$$\rho_2 = +0.117\left(\frac{1}{n}\right) + k_2 \quad (3)$$

Applications to Nmr

The position of the nmr signal depends upon the electron density on the carbon to which the proton is bonded and is found to change as the length of the polyenylic ion changes. Sorensen reports a set of τ values for the protons on each of three carbons in the series. The values may be described by the following equations

$$\tau_{\text{methyl proton}} = -3.53\left(\frac{1}{n}\right) + c_1 \quad (4)$$

$$\tau_2 = -2.02\left(\frac{1}{n}\right) + c_2 \quad (5)$$

$$\tau_3 = -12.8\left(\frac{1}{n}\right) + c_3 \quad (6)$$

Combining the appropriate empirical relation for τ , e.g., eq 6, and the pertinent theoretical relation for ρ^+ , e.g., eq 2, yields the equation giving the relation between τ and ρ^+ directly as

$$\tau_3 = -11.6\rho_3^+ + K_3 \text{ for carbon 3} \quad (7)$$

Similarly

$$\tau_2 = -11.4\rho_2^+ + K_2 \text{ for carbon 2} \quad (8)$$

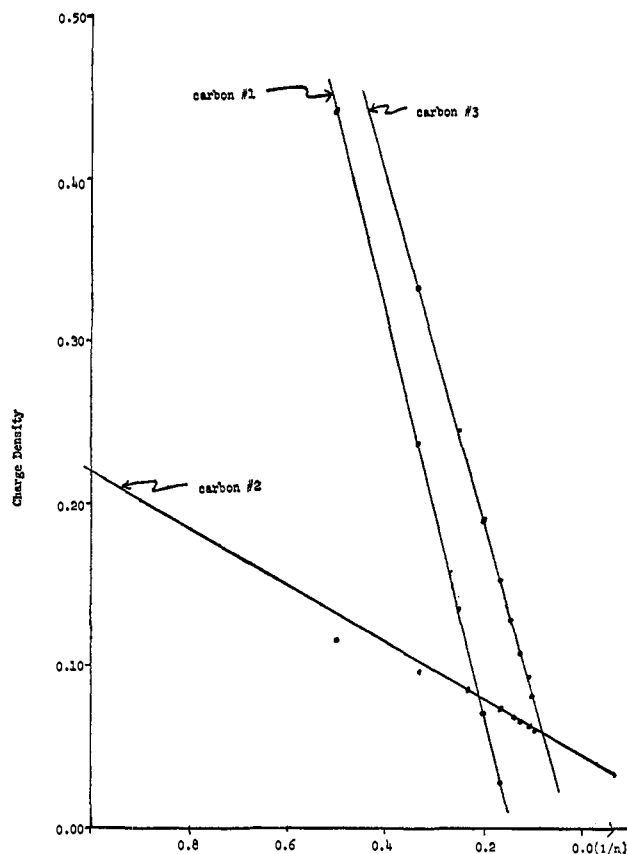


Figure 3. Charge density as a function of ion length.

These last two equations suggest a proportionality for the chemical shift of approximately 11.5 ppm per unit charge.

The change in the chemical shift of the methyl protons is taken as depending upon the charge density on carbon 1, to which the methyl group is attached. Combining eq 1 and 4 yields

$$\tau_{\text{methyl proton}} = -2.8\rho_1^+ + K_1 \quad (9)$$

Equation 9 suggests a 2.8-ppm shift per unit of charge density. This compares with the literature values of 3.27 or 4.25.^{4,5}

Discussion

The preceding section and that on Electronic Spectra would indicate that this rather simple particle in a box model for a series of polyenylic ions allows correlation not only of the uv spectra but also the nmr results. The proportionality constants of the nmr chemical shift per unit charge support those given in the literature. Further the approximate alternation of charge density on the carbon center assumed by Sorensen is indeed exhibited by the data of Table I.

In Sorensen's phenomenological treatment a parameter ϵ to be associated with excess positive charge on the methyl groups was introduced. His experimental evidence indicated that ϵ decreased with increasing n . The present model predicts an excess negative charge due to the π electrons in the region of the molecule from one-half bond length beyond C₁ to the end of the box, which is in the same region as ϵ . Calling the excess

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Table II. Negative Charge Associated with Methyl Groups

<i>N</i>	2	3	4	5	6
ϵ'	0.046	0.072	0.086	0.096	0.104

electron density ϵ' , Table II gives the values of ϵ' for several ions in the series. The trend of the negative charge, ϵ' , increasing with *n* would result in the positive

charge in this region decreasing with *n*, supporting Sorensen's observation.

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Electron Spin Resonance of Radical Intermediates in the Thermal Decomposition of Diazo Compounds¹

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Abstract: Electron spin resonance (esr) spectra have been obtained for the stable free-radical intermediates formed during the thermal decomposition of a number of aliphatic diazo compounds. Analyses of the esr hyperfine spectra determined for pyrolyzed diphenyldiazomethanes, diazofluorene, azibenzil, diazoacenaphthenone, and diazophenanthrone show that these intermediates are biradicals or biradical polymers resulting from the secondary reaction of an initially formed carbene. The formation of stable biradicals from these diazo compounds is evidence for the triplet-state nature of their carbene intermediates.

Electron spin resonance (esr) is proving to be an extremely useful technique for detecting and identifying free-radical intermediates in chemical reactions. From a knowledge of the starting materials, reaction products, and analyses of hyperfine spectra, one can infer chemical structures for the radical intermediates. This approach has been successfully applied to mechanism studies of a number of chemical reactions including olefin additions,^{2a} the pyrolysis of diazonium salts,^{2b} and the photolysis of alcohols and ketones.³ In this paper we describe the application of esr to the study of the radical intermediates formed during the thermal decomposition of aliphatic diazo compounds.

The pyrolysis of diazo compounds is known to produce divalent carbon (carbene) intermediates, the nature and reactivity of which have been the subject of a large number of investigations.⁴⁻¹⁰ Much of the interest has centered on the distinction between the two possible electronic ground-state configurations of divalent carbon species, the singlet and the triplet state. ESR experiments on several diazo compounds photolyzed at low temperatures have proven the

existence of stable triplet-state carbenes,^{11,12} which would be expected to undergo radical or biradical reactions.^{13,14} The radical-like behavior of carbenes has been proposed for addition,^{5,15,16} insertion,¹⁷ and rearrangement¹⁸ reactions.

We have studied the esr of the doublet-state radical intermediates formed during the thermal decomposition of a number of diazo compounds in inert liquid solvents. The compounds selected were those for which aromatic substituents would tend to stabilize any radical intermediates. The results of our studies for diphenyldiazomethanes, diazofluorene, azibenzil, diazoacenaphthenone, and diazophenanthrone show that in all cases, stable free-radical intermediates are produced in the decomposition process. The structures of these radical intermediates have been inferred by analysis of the esr spectra and related, where possible, to the final products of decomposition.

Experimental Procedure

Preparation of Diazo Compounds. Diphenyldiazomethane, diazofluorene, azibenzil, and substituted diphenyldiazomethanes were prepared by oxidation of the corresponding hydrazones with HgO.¹⁹ The hydrazones were prepared from the respective ketones

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