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A Theoretical Correlation of Substituent Effects in Ground-State Triplet Nitrene EPR Spectra

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WE would like to report a correlation of the EPR spectra of ground-state triplet nitrenes with computed SCF π-electron spin densities for the nitrogen atom. The EPR spectra of four nitrenes were previously reported.[1] In all observed nitrene spectra, a high field line (5000 to 8000 G) corresponding to a $\Delta m = 1$ transition was found and in some cases a $\Delta m = 2$ (half-field) transition was also detected, near 1620 G. The position of the $\Delta m = 1$ transition is determined by the values of D and E in the Hamiltonian $H = g\beta H \cdot S + DS_z^2 + E(S_x^2 - S_y^2)$.[2] Both D and E are proportional to the magnetic-dipole interaction of the unpaired electrons. The largest contribution to D should come from the unpaired electrons on the nitrogen atom, as the interaction falls off as $1/r^3$, where r is the interelectronic distance.[3] When the nitrogen atom is in conjugation with an aromatic π-electron system, we expect that one of the unpaired electrons occupies a π-molecular orbital delocalized from the nitrogen atom to the aromatic π system. The other electron is expected to be localized in a nitrogen atom p orbital which is orthogonal to the π-electron orbitals. Greater opportunity for π delocalization should reduce the density of the unpaired π-electron on the nitrogen atom and, thus, reduce the value of D. We have put this qualitative idea on a more quantitative basis by computing SCF π-electron spin densities for a large number of nitrenes.[4] We find that the position of the $\Delta m = 1$ transition is in the same order as the computed SCF π-electron spin density on the nitrogen atoms.

The azides corresponding to the nitrenes given in Table I were prepared by standard methods.[5] They were photolyzed in a rigid glass at 77°K and the spectra were obtained and analyzed as described previously.[1,6] An unambiguous assignment of D and E is not possible until additional lines are observed,[7] but assuming that changes of D are large compared to those of E within the series of compounds, either of the likely assignments[7] would be expected to give a correlation of the line positions with the unpaired spin densities on the nitrogens.

The calculations consider the distribution of spin in the corresponding neutral aniline radical (aniline minus a hydrogen atom).[8] The other electron on the nitrene nitrogen acts as a probe giving a dipole interaction. The spin densities, ρ^N_{asa}, were computed with a spin-polarized open-shell self-consistent field single determinant π-electron wave function[9] after a single annihilation.[10] The basic method of Pariser and Parr was adopted, including the assumption of zero differential overlap.[11] Spin densities, ρ^N_h, were obtained from a Hückel molecular orbital calculation derived from the final SCF matrix elements. Details of the calculations will be published elsewhere.[4] The com-

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[1] G. Smolinsky, E. Wasserman, and W. A. Yager, J. Am. Chem. Soc. **84**, 3213 (1962).

[2] K. W. H. Stevens, Proc. Roy. Soc. (London) **A214**, 237 (1952).

[3] M. Gouterman and W. Moffitt, J. Chem. Phys. **30**, 1107 (1959).

[4] L. C. Snyder (to be published).

[5] The azides were prepared by reaction of an aqueous, acidic solution of the diazonium salts with aqueous sodium azide. The characterization of the previously unreported azides will be given in a forthcoming, longer paper. All new compounds had elemental analyses consistent with theory. (E. Wasserman and G. Smolinsky.)

[6] (a) W. A. Yager, E. Wasserman, and R. M. R. Cramer, J. Chem. Phys. **37**, 1148 (1962); (b) R. W. Murray, M. Trozzolo, E. Wasserman, and W. A. Yager, J. Am. Chem. Soc. **84**, 3213 (1962).

[7] If we assume that the weak half-field lines are associated with the nitrene, then E is small, less than 0.01 cm^{-1}. The two possible assignments for the observed $\Delta m = 1$ transition are that it is a z-axis transition, or that it is composed of a pair of x and y transitions. The z-axis assignment permits a good correlation of D and the SCF electron spin density, but the line widths of the observed resonances would have to be added to H in the table. For phenylnitrene, D would then be 0.94 cm^{-1}. However, for some meta derivatives, a pair of lines is observed about 100 G apart. This is consistent with a pair of x,y transitions split by a small E (0.002 cm^{-1}). D is then about 1.0 cm^{-1}. Both assignments imply that there are other transitions possible in the range of our magnetic field variations which are not observed.

[8] The calculations were actually made for the π-electron spin density of the corresponding aryl methyl radical. However, extended computations have shown the π-electron spin density on the exterior atom to be relatively insensitive to parameter changes corresponding to a change of electronegativity of the exterior atom (reference 4).

[9] J. A. Pople and R. K. Nesbet, J. Chem. Phys. 22, 571 (1954).

[10] A. T. Amos and G. G. Hall, Proc. Roy. Soc. (London) **A263**, 483 (1961).

[11] R. G. Parr and R. Pariser, J. Chem. Phys. **23**, 711 (1955).

puted spin densities are given in Table I.

Since the lower value of D to be associated with increased π delocalization would be expected to move the line to lower magnetic field, parallel changes of H and ρ^N are expected. For the phenyl, biphenylyl, naphthyl, and anthryl nitrenes, H is almost linearly related to both the SCF and Hückel spin densities. Benzenesulfonyl nitrene fits well if one assumes $\rho^N = 1$. For nitro and methoxyphenyl nitrenes, H has the same order as ρ^N_{asa}. Only the SCF spin densities agree with the slight shifts to higher fields observed with the meta derivatives.

TABLE I. Nitrogen π-electron spin density and the $\Delta m = 1$ line position for nitrenes.

Nitrene	H obs.	ρ^N_{asa}	ρ^N_h
benzenesulfonyl	7795	[1.0][c]	[1.0][c]
3-nitrophenyl	6857	0.760	0.571
3-methoxyphenyl[a,b]	6713	0.754	0.571
phenyl[a]	6701	0.752	0.571
4-nitrophenyl	6671	0.747	0.540
4-methoxyphenyl[a]	6618	0.729	0.513
4-biphenylyl	6526	0.739	0.516
2-naphthyl	6435	0.729	0.529
1-naphthyl[a]	6130	0.660	0.450
2-anthryl	6077	0.690	0.471
1-anthryl[a]	5754	0.610	0.381

[a] A $\Delta m = 2$ line is observed near 1620 G.
[b] Two lines are observed.
[c] An assumed spin density.

More fruitful comparisons will be possible when D and E are accurately known. However, the main features of the correlation are unlikely to be altered. The isoelectronic aromatic methylenes, appear to be more suited for abstraction of these parameters and substituent effects in these are being investigated.[12]

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[12] R. W. Murray, L. C. Snyder, A. M. Trozzolo, and E. Wasserman (to be published).

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Optical Rotation

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THROUGHOUT the brief history of quantum-mechanical optical rotation theory there have developed two trends: exact, but lengthy, perturbation theory calculations applied to individual molecules, and less precise, but more general, calculations based on approximate expressions for the interaction between charges. Although the second method has led to the derivation of relatively simple formulas with wide generality, it has had only limited success in predicting signs and magnitudes of the optical rotation. The more exact calculations, on the other hand, have enjoyed a marked degree of success in predicting these quantities. In the following section we outline a method, which it is hoped, will embody the simplicity of the one and the precision of the other.

If one assumes isolated groups interacting through space and applies first-order perturbation theory to the appropriate zeroth-order wave functions in conjunction with the Rosenfeld[1] equation:

$$\beta = \frac{2}{3\pi}\sum_A \frac{R_A}{\nu_{OA}^2 - \nu^2} = \frac{2}{3\pi}\sum_A \mathrm{Im}\,\frac{\mathbf{p}_{OA}\cdot\mathbf{m}_{AO}}{\nu_{OA}^2-\nu^2}\,, \tag{1}$$

one obtains[2]

$$\begin{aligned} R_A = \mathrm{Im}\,\mathbf{p}_{ioa}\cdot\mathbf{m}_{ioa} \quad 2\sum_{j\neq i}\sum_{b\neq a} &\\ \times \frac{\mathrm{Im}\,V_{ioa;job}(\mathbf{p}_{ioa}\cdot\mathbf{m}_{jbo}\nu_a + \mathbf{p}_{job}\cdot\mathbf{m}_{iao}\nu_b)}{h(\nu_b^2-\nu_a^2)} &\\ - \sum_{j\neq i}\sum_{b\neq a}\frac{\mathrm{Im}\,V_{iab;joo}(\mathbf{p}_{ioa}\cdot\mathbf{m}_{ibo} + \mathbf{p}_{iob}\cdot\mathbf{m}_{iao})}{h(\nu_b-\nu_a)} &\\ - \sum_{j\neq i}\sum_{b\neq a}\frac{\mathrm{Im}\,V_{iob;joo}(\mathbf{p}_{ioa}\cdot\mathbf{m}_{iab} + \mathbf{p}_{iab}\cdot\mathbf{m}_{iao})}{h\nu_b} &\\ - \sum_{j\neq i}\frac{\mathrm{Im}\,V_{ioa;joo}(\mathbf{p}_{iaa} - \mathbf{p}_{ioo})\cdot\mathbf{m}_{iao}}{h\nu_a} &\\ - \frac{2\pi}{c}\sum_{j\neq i}\sum_{b\neq a}\frac{V_{ioa;job}\nu_a\nu_b(\mathbf{R}_j-\mathbf{R}_i)\cdot(\mathbf{p}_{job}\times\mathbf{p}_{ioa})}{h(\nu_b^2-\nu_a^2)}, & \end{aligned} \tag{2}$$

where R_A is the rotational strength of the Ath transition in the molecule; $\mathbf{p}_{OA}$, $\mathbf{m}_{AO}$ are the electric and magnetic dipole moments of transitions in the molecule as a whole; $\mathbf{p}_{oa}$, $\mathbf{p}_{ob}$, $\mathbf{m}_{ao}$, $\mathbf{m}_{bo}$ are the electric and magnetic dipole moments of transitions in individual groups; ν_a, ν_b are group transition frequencies; $V_{ioa,job}$,etc. $= \int \psi_{io}\psi_{ia}^*\psi_{jo}\psi_{jb}V_{ij}d\psi_i d\psi_j$; and V_{ij} is the interaction between groups i and j.

The above equation gives the contribution of a single transition in a particular group of the molecule

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[1] L. Rosenfeld, Z. Physik **52**, 161 (1928).

[2] I. Tinoco, Advan. Chem. Phys. **4**, 113 (1962).