method establishes a point of contact between ab initio quantum mechanics and these classical concepts. Through an interpretation of nonempirical (although crude) FSGO wave functions, it is possible to quantify these concepts without reference to experiment, and to explore their variation with respect to chemical environment. The numerical predictions for observables presented in section III indicate a reasonable level of accuracy and sensitivity to environment and therefore reinforce the overall analysis of bonding in acyclic hydrocarbons.

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Substituent Effects on Spin Delocalization in Triplet Phenylnitrenes. 1. Para-Substituted Phenylnitrenes

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Abstract: The ESR spectra of 14 triplet 4-substituted phenylnitrenes in methylcyclohexane glasses at 77 K are reported. The zero field parameters have been calculated. E is <0.002 cm^{-1} in all cases and D varies from 0.871 to 1.008 cm^{-1}. All of the para substituents decreased D, i.e., delocalized spin density, except fluorine, where a small increase in D was noted. The results are compared to similar studies on 4-substituted diphenylmethylenes. In five cases, hyperfine splitting was noted; $a_N = 18 \pm 1$ G, indicating that the spin density on nitrogen does not change much. INDO calculations were carried out on eight of the compounds. The dipole–dipole distance, r_{12}, was calculated from D and from INDO spin densities; both gave values in the range 1.08–1.18 Å. The INDO calculations indicate that the total spin density on nitrogen remains essentially constant and that the variation of D is being determined primarily by the spatial extent of that portion of spin that is delocalized. Details of how individual substituents affect the spin density distribution are discussed and some generalizations are given for predicting spin delocalization in para-substituted phenylnitrenes.

Smolinsky and Wasserman were the first to mention the observation of the ESR spectrum of triplet phenylnitrene.[1] The details of their observation were reported in a communication by Smolinsky, Wasserman, and Yager.[2] The nitrene was generated by photolysis of phenyl azide in a Fluorolube glass at 77 K. This was the same procedure that was used previously to generate diphenylmethylene.[3] They reported two broad lines in the spectrum, at 6701 and 1620 G, which were assigned to the $\Delta m = 1$ and $\Delta m = 2$ transitions, respectively.[2] The zero field parameters, D and E, were calculated to be 0.99 and <0.002 cm^{-1}.[4,5] The broad band at 6701 G was assigned to an x,y transition.[4-7]

The ESR spectra of 4-methoxyphenylnitrene and 4-nitrophenylnitrene were reported to exhibit broad peaks at 6618 and 6671 G, respectively.[4] The low-field line was observed only in the 4-methoxy case. Coope, Farmer, Gardner, and McDowell[6] calculated the zero field parameters for all of the nitrenes reported by Smolinsky, Snyder, and Wasserman.[4] They reported D values of 1.00, 0.98, and 0.96 cm^{-1} for phenylnitrene, 4-nitrophenylnitrene, and 4-methoxyphenylnitrene. They suggested that impurities may account for the weak half-field line that was occasionally observed.[6] Moriarty and Rahman reported a D of 0.999 cm^{-1} for phenylnitrene in a phenyl azide glass.[7] Wasserman reviewed the ESR work on nitrenes and included in the review data on the D and E parameters of several nitrenes which had not been reported previously.[8] Also, the D and E values for several nitrenes were recalculated. D values of 1.009, 0.9287, 0.7961, 1.065, and 0.9978 cm^{-1} for 4-chloro-, 4-bromo-, 4-methyl-, 4-nitro-, and 4-methoxyphenylnitrenes and 0.9978 cm^{-1} for phenylnitrene were reported. The value of E in each case was reported to be <0.003, except for 4-methoxyphenylnitrene, where E was given as 0.0039 cm^{-1}.

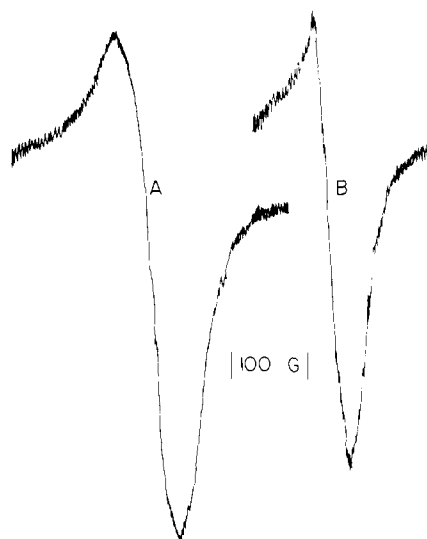In studies dealing with the effect of substituents on the re-

Figure 1. ESR spectra of (A) 4-bromophenylnitrene and (B) phenylnitrene.

Table I. Resonance Fields and Zero Field Parameters for Triplet 4-Substituted Phenylnitrenes[a]

4-Substituted phenylnitrene	Field, G	Rel field,[b] G	$D \times 10,^j$ cm^{-1}	Half-line width at half height, G
F	6724.6	+23.6	10.08	23
H	6701.0	0	9.99[d]	23
CH$_3$	6646.0	−55.0	9.78[e]	45
C$_2$H$_5$	6643.3	−57.6	9.77	43
OH	6636.5	−64.5	9.74	67
CO$_2$H	6636.1	−64.9	9.74	26
NO$_2$	6609.9	−91.1	9.64[f]	40
CN	6581.4	−119.6	9.53	33
Cl	6575.4	−125.6	9.51[g]	24
CO$_2$C$_2$H$_5$	6551.9	−149.1	9.42	45
CH$_3$O	6538.0	−162.9	9.36[h]	33
Br	6471.1	−229.8	9.11[i]	42
COCH$_3$	6469.7	−231.3	9.11	38
N(CH$_3$)$_2$	6429.8	−271.2	8.96	21
I	6364.1	−336.9	8.71	122

[a] In a methylcyclohexane glass at 77 K. $H_0 = 0.301\ 82$ cm^{-1}. [b] Relative to phenylnitrene. [c] Reference deleted in revision. [d] Reported: 1.00, ref 5 and 6; 0.999, ref 7; 0.9978, ref 8. [e] Reported: 0.9761, ref 8. [f] Reported: 0.98, ref 6; 1.065, ref 8. [g] Reported: 1.009, ref 8. [h] Reported: 0.9978, ref 8; 0.96, ref 6. [i] Reported: 0.9287, ref 8. [j] Estimated error, ±0.001 cm^{-1}.

actions of 4-substituted phenylnitrenes, it became necessary to know accurately and in some detail just how a para substituent affects a triplet phenylnitrene. With this goal in mind, the ESR spectra of 14 4-substituted phenylnitrenes were determined, including reexamination of some of those reported previously. In the early work, it was assumed that the values of D and E were unaffected by the nature of the glassy matrix. The effect is small, but Wasserman reports variations up to as much as 2%.[8] Since para substitution causes variations in D of only about 10%, it is important to determine the spectra in the same glassy matrix.[9] In this work, the triplets were generated by photolysis of the corresponding azides in methylcyclohexane glasses at 77 K. The solutions were carefully degassed on a high vacuum line by the freeze–thaw technique to avoid oxygen. They were then rapidly chilled in an ESR Dewar. The samples were photolyzed for 15 min, 5 cm away from a 250-W low-pressure mercury lamp.

In order to obtain relative field positions accurately, all of the work was done using a dual cavity, with phenylnitrene in one side and the 4-substituted phenylnitrene in the other side. In this way, the effects of small variations in the magnetic field or microwave frequency could be minimized. The line positions were determined as described by Wasserman, Snyder, and Yager.[10] The line positions are listed in Table I. The experimental positions have all been adjusted relative to phenylnitrene at 6701.0 and a microwave frequency of 0.301 82 cm^{-1}.

The rather large variation of D and E values reported in the literature arises from several sources of error. Some of these arise from the method of calculation. In this work, two methods were used to calculate the zero field parameters. In one of these, the program developed by Kornegay and Snyder was used.[11] In this program, the input parameters are D, E, the microwave frequency, and one-half the line width at half height (the line position is not part of the input). The input parameters are adjusted to fit both line position and line shape. The second method used is based on the fact that for the 4-substituted phenylnitrenes, E is small (<0.002 cm^{-1}) and can be neglected. Since the observed resonance is an x,y transition,[6,8,10] the resonance field is given by

$$H_{xy}^2 = (g_e/g_{xy})^2 H_0^2 \pm D/g_e\beta$$

If it is assumed that $g_e = g_{xy}$ within the accuracy of the calculation, D can be calculated directly from the line position. The results are given in Table I. The values obtained by the two procedures in some of the cases differ by as much as 1%. The

difference arises because the line shape program does not reproduce the phenylnitrene spectrum very well at the low-field end. The lines are narrow enough that the hyperfine splitting due to the nitrogen affects the shape of the envelope at low fields, making the low-field maximum of the derivative spectrum much sharper than predicted by the program (a typical spectrum is shown in Figure 1).

In comparing the calculated D values in Table I with those in the literature there are several discrepancies. (See footnotes to Table I.) In the case of 4-methoxyphenylnitrene, we were unable to detect an E value as reported;[8] also our D value is much lower. In the case of 4-nitrophenylnitrene, our D is considerably less than that for phenylnitrene, consistent with the report by Coope et al.,[6] but inconsistent with the value of 1.065 cm^{-1} reported by Wasserman.[8] Also the value of D for 4-chlorophenylnitrene was reported[8] to be larger than that for phenylnitrene, whereas the value reported here is much smaller.

In several cases, hyperfine splitting could be observed. In the spectra of 4-chloro-, 4-carboxy-, and 4-dimethylaminophenylnitrenes, the high-field side of the envelope appeared to be weakly split into a triplet. For 4-fluorophenylnitrene, the spectrum was much better resolved as shown in Figure 2. The four lines apparently arise from equal coupling to fluorine and nitrogen. The ESR spectrum of 4-iodophenylnitrene was very broad apparently owing to coupling with iodine. The broad envelope showed weak splittings of about 85 G with some smaller splittings of about 17 G. The estimated coupling constants for all of those compound are listed in Table II.

In the case of 4-acetylphenylnitrene, a shoulder at 6810 G on the high-field side of the main peak was noted. It was felt initially that this was due to the yet to be observed z transition. However, the position is at a little too low a field for a D value of 0.911 cm^{-1}. Also, no such peak could be found in the 4-dimethylaminophenylnitrene spectrum, where the x,y transition is at even lower field and separation of the peaks should be even better. As a result, the shoulder at 5810 G is being tentatively assigned to an impurity, possibly the 2-acetylphenylnitrene.

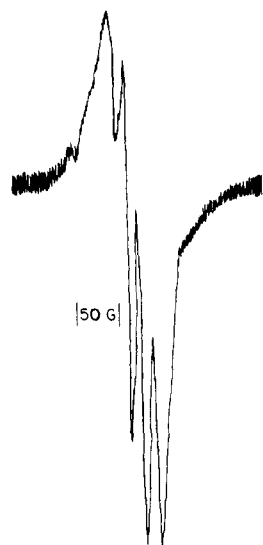As can be seen in Table I, all para substituents shifted the

Figure 2. ESR spectrum of *p*-fluorophenylnitrene.

Figure 3. Model for triplet phenylnitrene.

Figure 4. *D* of 4-substituted phenylnitrenes vs. *D* of 4-substituted diphenylmethylenes.

Table II. Hyperfine Coupling Constants in 4-Substituted Phenylnitrenes

4-Substituted phenylnitrene	a_N, G	a_X, G
Cl	18.0	
F	17.5	17.5 (F)
CO₂H	18.6	
N(CH₃)₂	19.2	
I	~17	~85 (I)

Figure 5. Triplet phenylnitrene resonance structures.

line position to lower fields except fluorine, which shifted the line to slightly higher fields. These shifts are reflected in lower values of D for all para-substituted phenylnitrenes except 4-fluorophenylnitrene, where the D is larger than that for phenylnitrene. These observations are similar to those effects noted in 4-substituted diphenylmethylenes.[12] The effect of the substituents on D does not show any type of Hammett equation dependence; both electron-donating groups and electron-withdrawing groups are equally effective in lowering D.

In discussing the data, the model proposed by Smolinsky, Snyder, and Wasserman[4] will be used, in which it is assumed that the nitrogen is sp hybridized with the lone pair in the sp orbital and the spins in orthogonal p orbitals. One of the p orbitals is in the plane of the ring and hence its spin is localized, while the other is free to overlap with the π cloud of the aromatic ring and hence the spin can be partially delocalized. The model is illustrated in Figure 3. In this model, $D \propto 1/r_{12}^3$, where r_{12} is the average distance between centers of spin density. Hence a decrease in D is the result of an increase in r_{12}, i.e., greater spin delocalization.

The use of this model, in which electron pair delocalization is neglected, is justified by the following considerations. In Figure 4 is a plot of the D values for 4-substituted diphenylmethylenes[12] vs. the D values for 4-substituted phenylnitrenes. This plot would not be expected to show good correlation, since there are geometrical considerations in the diphenylmethylenes that have to be taken into account.[12] Nevertheless, the plot is instructive. The groups that do not correlate at all are the carboalkoxy, cyano, and nitro groups. These are just the groups that would be expected to conjugate with and delocalize the electron pair on the nitrene nitrogen. However, it should be noted that electron pair delocalization, i.e., as shown in II, Figure 5, would lead to electron spin localization and D should increase, not decrease as observed. Clearly the effect being observed is electron spin delocalization, not electron pair de-

localization. One is tempted to ascribe the differences in the effect of these substituents in the two systems to contributions from structures such as III; however, evidence will be presented that these groups do not remove spin density from the nitrogen.
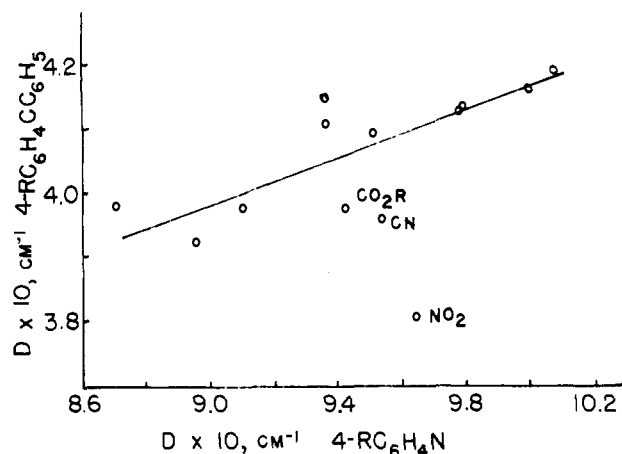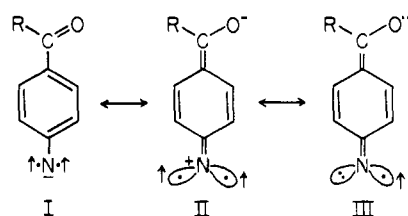
Several workers have undertaken molecular orbital calculations on arylnitrenes. Smolinsky, Snyder, and Wasserman[4] carried out both Hückel calculations and SCF calculations using the Pariser-Parr approach. In each case they calculated the spin density on the nitrogen atom and compared it with the observed field positions of the *x,y* transition of the nitrene. Both methods correctly predicted the right order in the field positions of phenylnitrene, 4-nitrophenylnitrene, and 4-methoxyphenylnitrene. Coope, Farmer, Gardner, and McDowell[6] also did Hückel calculations, and their results agree with those of the earlier workers. However, they pointed out that the spin densities calculated by the Pariser-Parr approach were too high and would lead to a prediction of a D parameter for phenylnitrene of ~1.5 cm⁻¹. Wasserman in a footnote[8] indicated that the better fit of the Hückel spin densities over the SCF spin densities was due to the fact that there is some delocalization of spin density from the in-plane orbital through the σ bonds, and that when this is taken into account, a better fit is obtained with SCF densities. More recently, Alvarado, Grivet, and Mijoule[13] carried out CNDO calculations on phenylnitrene and concluded that spin-orbit coupling was dominant over dipole-dipole interactions. They calculate D as −1.56 with spin-orbit coupling included and +0.960 without it. This work cannot really be assessed properly until the sign of D can be determined. (Their calculations also predict that phenylnitrene should be a ground state singlet.)

In order to get a better feeling for the details of how a substituent affects D and to help resolve some of the above prob-

Table III. Spin Densities Calculated with INDO Program

4-Substituted phenylnitrene	Spin density							
	C_1	C_2	C_3	C_4	H_2	H_3	R total	N
H	−0.2632	0.2611	−0.1398	0.1954	−0.0110	0.0088	−0.0079	1.8376
CH$_3$	−0.2668	0.2615	−0.1433	0.1962	−0.0110	0.0089	0.0084	1.8336
NO$_2$	−0.2704	0.2598	−0.1443	0.1882	−0.0110	0.0090	0.0214	1.8357
CN	−0.2724	0.2649	−0.1497	0.1916	−0.0113	0.0093	0.0206	1.8335
F	−0.2670	0.2613	−0.1428	0.1876	−0.0110	0.0087	0.0224	1.8340
OH	−0.2671	0.2590	−0.1409	0.1746	−0.0109	0.0086	0.0342	1.8281
OCH$_3$	−0.2682	0.2596	−0.1421	0.1721	−0.0110	0.0087	0.0362	1.8279
N(CH$_3$)$_2$	−0.2693	0.2589	−0.1715	0.1715	−0.0110	0.0089	0.0480	1.8248

Table IV. center of Delocalized Spin and Dipole–Dipole Distance

4-Substituted phenylnitrene	r, Å	r_{12}, Å	
		Calcd from r	Calcd from D
H	0.562	1.08	1.094
CH$_3$	0.624	1.11	1.102
NO$_2$	0.683	1.14	1.107
CN	0.731	1.17	1.112
F	0.662	1.13	1.091
OH	0.679	1.14	1.103
OCH$_3$	0.687	1.15	1.118
N(CH$_3$)$_2$	0.735	1.18	1.135

lems, the more sophisticated INDO calculations were undertaken. The program used was that written by Dobosh.[14] The spin densities on all of the atoms in phenylnitrene and seven 4-substituted phenylnitrenes were calculated. The data are given in Table III. The spin density on the nitrene nitrogen is amazingly constant, varying less than ±0.35%. That the spin density of nitrogen is essentially constant is varified by the coupling constants in Table II, which are all in the range 18 ± 1 G. (The INDO program predicts 14 G.) If this is the case, the variation of D is being determined primarily by the spatial extent to which that portion of the spin that is being delocalized is spread over the ring and the substituent, not primarily by changes in spin density on the nitrene nitrogen. Apparently this possibility was not given serious consideration by previous workers. Using the spin densities in Table III, it is simple to calculate the mathematical center of delocalized spin density; this is expressed as r, the distance along the symmetry axis from the nitrogen. The calculated r is listed in Table IV. The values qualitatively increase as the value of D decreases with two exceptions: methoxy and cyano are inverted and the r for fluoro is too large.

The value of D can be used to quantitatively estimate spin delocalization:

$$D = \frac{3\mu e/2(1 - 3\cos^2\theta)}{r_{12}^3} \qquad (1)$$

where r_{12} is the distance between the parallel dipoles, θ is the angle between the dipole and the vector r_{12}, and μ_e is the electron magnetic moment. If D is in gauss and r_{12} is in ångstroms, the equation reduces to

$$D = \frac{1.393 \times 10^4 (1 - \cos^2\theta)}{r_{12}^3} \qquad (2)$$

The distance r_{12} should not be confused with r; r is the distance along the C–N bond between mathematically calculated centers of spin (actually there is very little spin density at these centers of spin except for the portion in s orbitals), whereas r_{12} is the real distance between the spin density in the p orbital of nitrogen of the x axis to some point in the π system located at r ångstroms from the nitrogen along the direction of the y axis. This is illustrated schematically in Figure 6. Since the angle

between the dipole on nitrogen and the delocalized dipole averages out to 90° (because of the symmetry), eq 2 reduces to $D = 1.393 \times 10^4/r_{12}^3$. The value of r_{12} calculated from this equation is listed in Table IV. If one can estimate the distance, a, shown in Figure 6, one can also estimate r_{12} from the magnitude of r $[r_{12} = (2a^2 + r^2)^{1/2}]$. If a is chosen as 0.65 Å[8] (the covalent radius of nitrogen) the calculated r_{12} agrees very well with that obtained from D as can be seen in Table IV.

In attempting to account for the magnitude of D, Wasserman[8] postulated that the spin density localized on nitrogen in the in-plane orbital was delocalized to the extent of 15% through the σ system. There are three arguments against this point of view. If you examine the spin Hamiltonian in detail, and add up the spin densities in the s, p$_x$, and p$_y$ orbitals, the total is 0.99+, indicating no such delocalization. The second argument is that if such delocalization occurs one would not expect good agreement between the experimental r_{12} and the theoretical r_{12}. Finally, the original concept of 15% delocalization came from a consideration of the D of p-phenylenedinitrene,[8,15] and this value has been shown to be incorrect.[16]

One other test of the INDO calculations can be made. According to eq 2, a plot of $1/r_{12}^3$ (calculated from r) vs. the experimental D parameters should be linear. The result is shown in Figure 7. The substituents seem to fall on two lines; one with all those substituents bearing a lone pair and the rest on the other line. (The theoretical slope is given by the dashed line.) This is possibly due to small changes in the C–N bond length (1.38 Å was used in the calculations). This view is supported by the fact that a plot of the spin densities at C_1 vs. D shows a similar segregation. Figure 7 can be used to predict D parameters.[17]

Since the spin density on nitrogen is essentially constant, the value of D is being determined by small changes in spin densities on the substituent and the atoms in the ring. The center of delocalized spin density r is given by

$$r = \Sigma r_i \rho_i$$

where r_i is the distance along the symmetry axis of spin density ρ_i. These $r_i\rho_i$ terms are listed in Table V for the carbons and the substituent. It can be seen from this table that the terms for C_1, C_2, and C_3 are fairly constant throughout the series, and r is given by

$$r \approx -0.24 + r_4\rho_4 + r_R\rho_R$$

Thus, the center of delocalized spin density is being determined primarily by the spin density on C_4 and on the substituent, and it is these spin densities that affect D most.

A study of results in Table V allows for some quite specific generalizations concerning the effects of three types of substituents on r and consequently on D.

1. Alkyl groups delocalize spin density and decrease D by virtue of the fact that their introduction replaces a group with a negative spin density (H) with one capable of assuming a net positive spin density. The alkyl groups remove the positive spin density from the ortho and para positions (C_3's and C_1) with the resultant increase in r, leaving these carbons with an in-
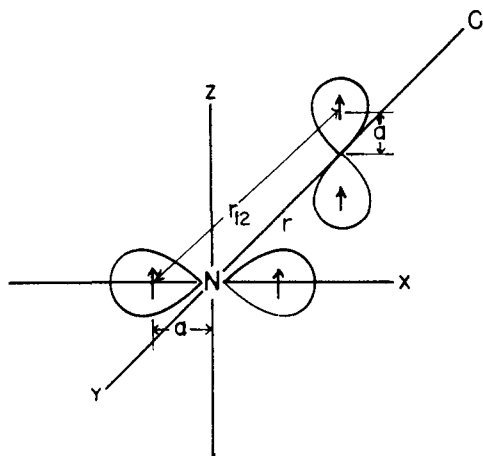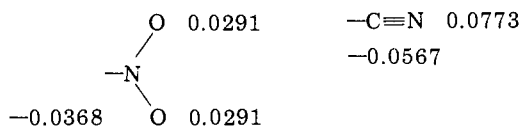
Figure 6. The relationship between r and r_{12}.

Table V. Contributions to r by Spin Densities on the Ring Carbons and the Substituent

4-Substituted phenylnitrene	$r_i \rho_i$				
	C_1	$C_2{}^a$	$C_3{}^a$	C_4	R
H	−0.363	1.086	−0.973	0.817	−0.042
CH_3	−0.368	1.088	−0.997	0.820	0.048
NO_2	−0.373	1.081	−1.004	0.787	0.121
CN	−0.376	1.102	−1.042	0.801	0.131
F	−0.368	1.087	−0.994	0.784	0.116
OH	−0.369	1.077	−0.981	0.730	0.192
OCH_3	−0.370	1.080	−0.989	0.719	0.202
$N(CH_3)_2$	−0.372	1.077	−0.990	0.717	0.271

^{a} Total for both carbons.

creased negative spin density.

2. Conjugated unsaturated groups, such as nitro and cyano, delocalize spin density and decrease D by assuming rather large positive spins. As seen below the excess positive spin density is on the second atom from the ring.

$$
\begin{array}{ll}
\text{O} \quad 0.0291 & \text{—C}\equiv\text{N} \quad 0.0773 \\
\diagup & \qquad\qquad -0.0567 \\
\text{—N} & \\
\diagdown & \\
-0.0368 \quad \text{O} \quad 0.0291 &
\end{array}
$$

Because of the alternation of spin in conjugated groups, such groups will always assume the spin of the atom to which they are attached. The excess of positive spin density comes from the positions ortho and para to the group (C_3's and C_1), leaving these positions with a more negative spin density.

3. Saturated groups with electron pairs such as hydroxy, methoxy, and dimethylamino delocalize spin density and decrease D by assuming rather large positive spins. The largest part of the spin density comes from the ortho and para positions (C_3's and C_1), making them more negative, but in addition, a large amount of spin density moves off of C_4 to the substituent. A secondary effect is the well-known fact that nitrogen can assume a larger spin density than oxygen and this is the primary reason why the D value is so low in the dimethylamino case. Chlorine, bromine, and iodine also fall in this group, but fluorine is not accommodated.

The above generalizations can be used to predict the effect of meta substituents on D. A methyl group should delocalize positive spin density in the meta position in the same way as in the para position resulting in a smaller D. When conjugated unsaturated groups, such as a nitro group, are placed on the meta carbon, which has a negative spin density, the substituent will assume the negative spin density and the result will be localization of positive spin density and an increased D. Finally,
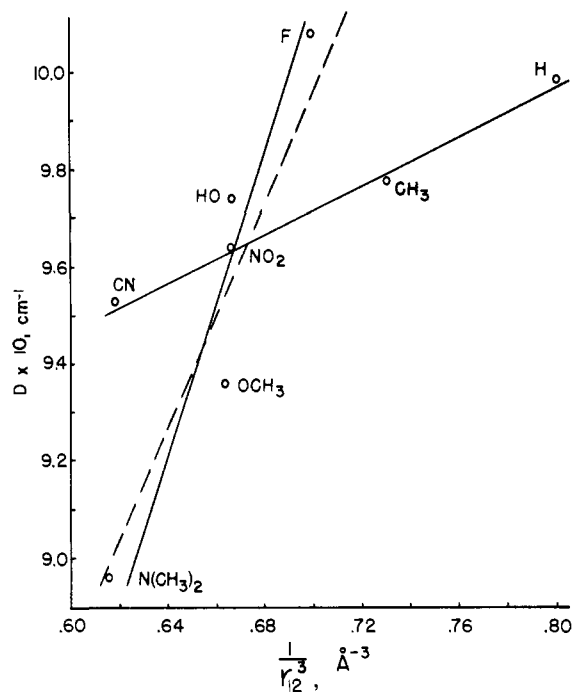
Figure 7. D of 4-substituted phenylnitrenes vs. INDO calculated $1/r_{12}$.

the saturated groups with electron pairs such as methoxy would delocalize positive spin onto the group, but this effect would be offset to a considerable degree by removing negative spin density from C_3. Judging from the numbers in Table V, the former effect would be larger than the latter and the net result would be spin delocalization and a decrease in D.

Experimental Section

The ESR spectra were all run on a Varian 4500 equipped with Field Dial II. The microwave frequency was perpendicular to the external field. A dual cavity was used. The phenyl azide standard was modulated with 200 Hz and the substituted phenyl azide with 100 kHz. All spectra were recorded in the direction of increasing field.

All of the azides were prepared by reaction of the diazonium salt with sodium azide, except 4-azidophenol.

4-Azidophenol. To a stirred cold solution of 50 g (0.46 mol) of 4-aminophenol in 150 mL of concentrated hydrochloric acid and 400 mL of water was added dropwise 35 g (0.47 mol) of sodium nitrite in 150 mL of water. The temperature was maintained below 4 °C. After 15 min, 41.5 g (0.60 mol) of hydroxylamine hydrochloride in 75 mL of water was added. The solution was poured quickly into 2 L of ice water containing 750 g of sodium carbonate. This mixture was stirred at 4 °C overnight. The basic solution was extracted with ether to remove the base-insoluble materials. The aqueous solution was acidified and extracted with ether. The ether solution was dried over magnesium sulfate, filtered, and evaporated to give 32 g (55%) of the crude product as a dark oil. Crystallization from pentane and toluene at dry ice temperatures gave the pure material as a yellow solid, mp 25 °C. (An attempt to distill the compound at 70 °C under reduced pressure resulted in a violent explosion.) IR (neat) 3333, 2105, 1227 cm⁻¹; NMR (CCl₄) 6.34 (broad s, 1 H), 6.74 ppm (s, 4 H).

4-Ethylphenyl Azide. The compound was prepared from the diazonium salt and sodium azide in 90% yield: bp 52 °C (0.15 mm); IR (neat) 2121 cm⁻¹; NMR (CCl₄) 1.17 (t, 3 H), 2.55 (q, 2 H), 6.94 ppm (m, 4 H).

Anal. Calcd for $C_8H_9N_3$: C, 65.30; H, 6.14; N, 28.56. Found: C, 65.38; H, 6.40; N, 28.73.

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Theoretical Elucidation of Faraday *B* Terms in the Magnetic Circular Dichroism of Monosubstituted Benzenes. Use of the CNDO/S–CI Approximation

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Abstract: The transition energies, the oscillator strengths, and the Faraday *B* terms of phenol, aniline, benzaldehyde, nitrosobenzene, and nitrobenzene were calculated within the framework of the CNDO/S–CI approximation. The results were in good agreement with the experimental data obtained from the magnetic circular dichroism (MCD) and absorption spectra. The excited electronic states of these monosubstituted benzenes were characterized not only by comparing the excited states of the monosubstituted benzenes with those of benzene itself but also by considering the electron migration between the benzene ring and the substituent groups. The perturbing mechanism for the Faraday *B* terms of $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transition in monosubstituted benzenes was clarified. The signs of the magnetic mixing among four lowest $\pi^* - \pi$ states in phenol, aniline, and benzaldehyde were explained by the simplified model consisting of four frontier molecular orbitals.

The magnetic circular dichroism (MCD) spectra of substituted benzenes have provided considerable interest for many investigators, because of the sensitivity to the nature of the substituent groups.[1-6] The first and the second $\pi^* \leftarrow \pi$ transition of substituted benzenes containing an electron-donating substituent exhibit the negative and positive MCD bands, respectively, whereas the situation is reversed for the benzenes with electron-accepting groups. The signs and magnitudes of the MCD of various substituted benzenes have been correlated with the Hammett σ_{para} values of substituents[1] and with the empirical transition moment parameter.[2] The sign and the order of magnitude of the MCD of various substituted benzenes have been clearly reproduced by the numerical calculations[3-5,6a] on the basis of the Pariser–Parr–Pople (PPP) method.[7] Recently Michl[6,8] has explained the approximate mirror image relation of the MCD spectra of the benzenes having substituent groups of opposite nature, as a result of the removal of alternant pairing symmetry in the parent benzene chromophore.

On the other hand, several authors[9-16] have calculated the Faraday *B* terms of the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow \sigma$ transitions of aromatic organic compounds within the framework of the complete neglect of differential overlap (CNDO),[17,18] all valence electrons LCAOMO–SCF procedure. The CNDO method has much advantage not only in evaluating the effects of the magnetic mixing between $\pi^* - \sigma$ and $\pi^* - \pi$ states, but also in calculating the Faraday *B* terms of the $\pi^* \leftarrow n$ transitions. Sprinkel et al.[13] have calculated the *B* terms of indole and interpreted that the main contribution to the Faraday *B* terms of the lowest $\pi^* \leftarrow \pi$ transition of indole comes from the mag-netic coupling of the $\pi^* - \sigma$ states around 50 000 cm^{-1} with the lowest $\pi^* - \pi$ state. The Faraday *B* terms of the vibronically induced $\pi^* \leftarrow n$ transition in formaldehyde[11] and those for the allowed $^1A_{2u} \leftarrow {}^1A_{1g}$ ($\pi^* \leftarrow \sigma$) transition in benzene[14] have also been calculated using wave functions obtained from the CNDO method. More recently, Faraday *B* terms of two lowest $\pi^* \leftarrow \pi$ transitions of aniline, phenol, fluorobenzene, benzonitrile, and benzaldehyde have been calculated using the CNDO/S–CI method.[15] In the previous paper,[16] we have reported the CNDO treatment for the Faraday *B* terms of the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions of pyridine and azines. Although the *B* term of the $\pi^* \leftarrow \pi$ transition in these azaheterocycles is mainly induced by the magnetic mixing among $\pi^* - \pi$ states, the effect of the mixing of the $\pi^* - \sigma$ states with the $\pi^* - \pi$ state cannot be neglected in the lowest $\pi^* \leftarrow \pi$ transition of pyridazine and pyrimidine. The Faraday *B* term of the lowest $\pi^* \leftarrow n$ transition in the azaheterocycles is shown to originate from the magnetic mixing of the $\pi^* - \pi$ states with the lowest $\pi^* - n$ state and from the coupling of the $\pi^* - n$ states to the ground state.

In the present article, we apply the CNDO/S–CI method to the calculation of the Faraday *B* terms of the $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions of phenol, aniline, benzaldehyde, nitrosobenzene, and nitrobenzene, and discuss the perturbing mechanism for the Faraday *B* terms of the low-lying electronic transitions of these monosubstituted benzenes.

Experimental Section

Nitrosobenzene (Tokyo Chemical Industry Co., Ltd.) was purified by vacuum sublimation. The MCD spectra were recorded with a