windows and a path length of 0.06 mm. was filled with mixtures of olefins of known ratios. The relative intensities of peaks were used to make a graph against which the unknown was compared.

Ultraviolet Analysis.—Quantitative analysis by ultraviolet spectroscopy utilized a Cary double beam recording spectrophotometer. At least four samples were used for each recorded value. The following equation was used to obtain the composition of the unknown mixture

$$\epsilon_{exp} = \epsilon_1 X_1 + \epsilon_2 (1 - X_1)$$

in which ϵ_{exp} is the observed extinction coefficient, ϵ_1 and ϵ_2 are the extinction coefficients of the pure compounds at the wave length used, and X_1 the mole fraction of component 1. The ϵ used for VIII at 245 mμ was 200.

Precision of Results.—Limits of error are somewhat difficult to assess, as several analytical methods enter in. Analyses by gas chromatography were done on eight acetolysis products. There was considerable variation in percentages of individual components, presumably due to differing amounts of double-bond-position isomerization for different reaction times. Five of these (including the quoted run) done for reaction times of 57–76 hours averaged 87.56% of methyl-migrated product with an average deviation of 0.24%. The percentages from Tables III and V (determined for the quoted run) were used to find the contributions of each component in the two two-component peaks. Inclusion of the other three runs (36, 44 and 97 hours) raised the average to 88.46 and the average deviation to 1.12%. Application of the percentages in Tables II and IV to these data obtained under different conditions is questionable, however. Unless undetected systematic errors enter in, our percentage of methyl-migrated material in acetolysis seems easily good within 1%. The formolysis and deamination reactions were not studied so extensively, but there seems no reason for suspecting them to be of notably poorer precision.

# Unpaired Electron Distribution in π-Systems

By D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips and T. L. Cairns

Electron spin densities have been mapped by n.m.r. contact shifts in a series of aryl groups attached by the azo linkage to the γ-position of nickel aminotroponeimineates, and the results compared with those obtained previously for the analogous substituents attached to the nitrogen atoms of aminotroponeimines. Although observed spin density distributions for a given substituent attached at the two points are similar, the differences suggest that the conjugated system of the γ-arylazo group is extended into the region of the seven-membered ring, whereas the substituent at the nitrogen atom is essentially isolated from the seven-membered ring. In addition, methyl contact shifts in paramagnetic aromatic systems, which arise primarily from effects of hyperconjugation, were found to depend markedly on position of methyl substitution. Similarly, direct evidence in the form of F^{19} contact shifts is presented for participation by fluorine in conjugation in fluoroaromatics.

We have reported previously that the proton resonances in the n.m.r. spectra of the paramagnetic nickel(II) chelates of aminotroponeimines (I) are shifted from the positions observed for the corre

I   II
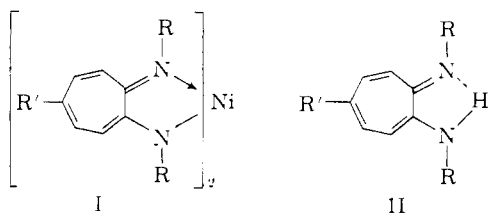
sponding protons in the free ligands (II) by as much as 7000–10,000 c.p.s. at 60 Mc./sec.[1–4] These shifts (arising from isotropic hyperfine contact interactions[5]) are due to the enhanced or diminished magnetic field at the proton resulting from the presence of a fractional unpaired electron on carbon. This unpaired electron arises from delocalization of an unpaired electron which is produced at the nitrogen atom through $d\pi$–$p\pi$ bonding with nickel. This finding provides an approach utilizing n.m.r. for (1) measurement of the unpaired electron distributions in π-electron systems,[1–4] (2) establishing the relative ability of different functional groups to

(1) W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960).

(2) R. E. Benson, D. R. Eaton, A. D. Josey and W. D. Phillips, *J. Am. Chem. Soc.*, **83**, 3714 (1961).

(3) D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962).

(4) D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

(5) E. Fermi, *Z. Physik*, **60**, 320 (1930).

delocalize an odd electron (conjugating ability)[2,6] and (3) obtaining information on both C–H and C–F bonding on sp²- and sp³-carbon atoms.[4,6]

The present paper reports unpaired electron distributions in a number of aromatic substituents joined by the azo function to the γ-position of a nickel(II) aminotroponeimineate. This study provides further information on C–H and C–F bonding in sp² and C–H bonding in sp³ situations and permits correlation of these new results with those of our prior findings obtained for the same substituents attached to the nitrogen atoms of the aminotroponeimines.

Introduction

The use of aminotroponeimines as probes for providing information regarding electronic structure of π-systems is markedly facilitated by the chemical and physical properties of these compounds. A broad spectrum of N-substituted derivatives can be obtained by reaction of the tetrafluorocycloheptadienes with appropriately substituted primary amines.[7] In addition, the aminoimines as a class show aromatic character and undergo attack by certain electrophilic reagents at the γ-position. The γ-arylazo derivatives reported in this paper were prepared by action of the appropriate diazonium fluoroborates on the aminoimine. These compounds and their zinc and nickel chelates have sufficient solubility in deuteriochloroform or

(6) D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *Disc. Faraday Soc.*, in press (1962).

(7) W. R. Brasen, H. E. Holmquist and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).

carbon disulfide to allow determination of their n.m.r. spectra.

Although the tetrahedral forms of the nickel(II) chelates are paramagnetic with a magnetic moment approaching 3.2 Bohr magnetons corresponding to two unpaired electrons on nickel, the separate resonances comprising the n.m.r. spectra are much narrower than those usually observed for paramagnetic species.[8] Furthermore, first-order nuclear spin–spin coupling is observed for protons of the γ-arylazo substituent and this, together with the now predictable contact shifts to high and low field, allow ready identification of the individual protons. The extent to which a proton resonance is shifted in the paramagnetic nickel chelate from its position in the diamagnetic ligand or zinc chelate provides a direct measure of the spin density at that carbon atom.

In the nickel(II) chelates of the aminotroponeimines, a fractional unpaired electron whose sense is positive (parallel to that of the spin on nickel) is placed on nitrogen by virtue of $d\pi$–$p\pi$ bonding with nickel. This fractional unpaired electron is delocalized onto the 7-membered ring placing positive spin at $C\alpha$ and $C\gamma$. At the γ-position, the unpaired electron is further delocalized through the azo group onto the aryl substituent. The contributing valence bond structures are shown in Fig. 1. The presence of an unpaired electron on this non-alternant system results in spin polarization of the paired electrons present in the π-system. As a consequence of this spin correlation effect, negative spin density arises at carbon atoms adjacent to those having positive spin density.

Spin is placed on hydrogen attached to these sp^2-carbons by the indirect π–σ spin polarization mechanism[9] and, consequently, the protons sense a spin density opposite in sign to that of the carbon atoms to which they are attached. The contact field at the proton is reflected in an n.m.r. shift, with protons attached to sp^2-carbon atoms possessing positive spin density moving to high field and those attached to sp^2-carbon atoms bearing a negative spin density moving to low field. From consideration of contributing valence bond structures, the signs of the spin densities on carbon can be predicted for conjugated substituents which are attached to nitrogen or to the γ-position through a conjugating group. A positive spin density is assigned to nitrogen, and the signs of the spin densities are considered to alternate throughout these non-alternant systems.

Results and Discussion

Contact Shifts and Spin Densities.—Contact shifts in the nickel(II) aminotroponeimineates have been discussed previously[1–4,6] and are given by eq. 1.

$$\frac{\Delta f}{f_i} = -a_i \frac{\gamma_e}{\gamma_N} \frac{g\beta S\,(S+1)}{2SkT(e^{\Delta G/kT}+3)} \qquad (1)$$

Here f is the frequency at which resonance is observed (60 Mc./sec. for H^1 and 56.4 Mc./sec. for F^{19}), Δf_i is the contact shift for ith nucleus in the paramagnetic nickel(II) aminotroponeimineate,[10] a_i

(8) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961).

(9) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

is the corresponding contact interaction constant, γ_e and γ_N are the magnetogyric ratios of the electron and nucleus, respectively, g is the g-value of the paramagnetic species, β is the Bohr magneton, ΔG is the free energy difference between the square planar (diamagnetic) and tetrahedral (paramagnetic) forms[11] of the chelate, and the other symbols have their usual significance. For aromatic C–H fragments, contact constants and spin densities centered on $p\pi$-orbitals of carbon are related by eq. 2.[12,13]

$$a_i \cong -22.5\rho_{C_i} \qquad (2)$$

Relative carbon $p\pi$-spin densities for a nickel(II) aminotroponeimineate are obtained from the proton spectrum at a single temperature using eq. 1 and 2, but to obtain absolute values of ρ, Δf values over a broad temperature range are required to permit evaluation of ΔG. We have previously found that for a large number of these aminotroponeimineates (in the fully paramagnetic form) $\rho_{C\beta}$ is relatively constant and has a value of -0.0210.[4] Equation 3 has been used to calculate the absolute spin

$$\rho_{C_i} = \rho_{C\beta} \times (\Delta f)_i / \Delta f_{H\beta} \qquad (3)$$

densities from room temperature data. In order to check this simplified procedure for the present series of compounds, the proton spectra of the nickel chelates of the o-tolylazo and o-fluorophenylazo compounds were obtained over the temperature range $-60°$ to $50°$. From these temperature studies, values of -0.0212 and -0.0208 for $\rho_{C\beta}$ were determined for the o-tolylazo and o-fluorophenylazo derivatives, respectively, justifying the use of eq. 3 for calculation of spin densities for the remaining compounds.

Values of ΔG obtained by substituting a_H in eq. 1 varied linearly with temperature as demanded by eq. 4.

$$\Delta G = \Delta E - T\Delta S \qquad (4)$$

From such plots, the values $\Delta E = 1.57$ kcal. and $\Delta S = 8.7$ e.u. were obtained for the o-tolylazo compound. Data for the o-fluorophenylazo compound yielded the values $\Delta E = 1.77$ kcal. and $\Delta S = 9.0$ e.u. for the square planar $\rightleftarrows$ tetrahedral equilibrium. These values are closely similar to those previously reported for other nickel(II) N,N'-diethylaminotroponeimineates.[11] It appears, therefore, that substituting arylazo groups at the γ-position has relatively little influence on the magnetic properties of these chelates.

Contact shifts and spin density distributions for ten γ-(arylazo)-aminotroponeimineates are presented in Table I. Analyses of the spectra are

(10) The origin of the contact shift for a given proton is taken as the position of resonance for the proton in the ligand or zinc chelate.

(11) It appears that the interconversion between the tetrahedral and the square planar forms, estimated from n.m.r. line widths to be at a frequency of 10^9–10^{10} sec.$^{-1}$, provides an electronic relaxation time sufficiently short to give resonance lines that are relatively narrow (2–20 c.p.s.) for a paramagnetic species. An "averaged" resonance is observed since the frequency of interconversion is greater than the resonance shift of analogous protons in the two forms, expressed in frequency units. However, evidence for the separate existence of both forms has been found in the electronic spectra of the aminotroponeimineates. See D. R. Eaton, W. D. Phillips and D. J. Caldwell (to be published).

(12) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

(13) S. I. Weissman, T. R. Tuttle and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).

TABLE I

CONTACT SHIFTS^a AND SPIN DENSITIES

$$X\text{--}N=N-\!\!\!\!\begin{array}{c}\text{[benzene-diazaannulene]}\end{array}\!\!\!\!Ni$$

R	X	Position	Contact shift, Δf^a	$\Delta f/\Delta f_{H\beta}$	ρ_C
C$_6$H$_5$	C$_6$H$_5$	α	+1325^b	−1.823	+0.0383
		β	−727	+1.000	−.0210
		ortho$_R$	+245	−0.337	+.00708
		meta$_R$	−237	+.326	−.00685
		para$_R$	+363	−.499	+.0105
		ortho$_X$	+262	−.360	+.00756
		meta$_X$	−91	+.125	−.00263
		para$_X$	+302	−.415	+.00872
C$_2$H$_5$	–⟨ ⟩–NO$_2$	α	+4491	−1.754	+.0368
		β	−2560	+1.000	−.0210
		CH$_2$	−8264	+3.228	
		CH$_3$	−840	+0.329	
		ortho	+1244	−.486	+.0102
		meta	−495	+.193	−.00405
C$_2$H$_5$	[naphthyl]	α	+5138	−1.746	+.0367
		β	−2942	+1.000	−.0210
		CH$_2$	−8599	+2.923	
		CH$_3$	−787	+0.268	
		2	+1622	−.551	+.01157
		3	−455	+.1547	−.00325
		4	+1849	−.628	+.01319
		5	+312	−.1061	+.00223
		6	−190	+.0646	−.00136
		7	+242	−.0822	+.00173
		8	−277	+.0952	−.00200
C$_2$H$_5$	[naphthyl]	α	+5188	−1.740	+.0365
		β	−2982	+1.000	−.0210
		CH$_2$	−8671	+2.908	
		CH$_3$	−788	+0.264	
		1	+1836	−.616	+.01294
		3	+712	−.239	+.00502
		4	−230	+.0771	−.00162
		5	−348	+.1167	−.00245
		6	+741	−.248	+.00521
		7	−178	+.0597	−.00125
		8	+601	+.202	+.00424
C$_2$H$_5$	[fluorophenyl]	α	+5073	−1.739	+.0362
		β	−2918	+1.000	−.0208
		CH$_2$	−8591	+2.944	
		CH$_3$	−798	+0.273	
		ortho	+1258	−.431	+.00896
		meta	−363	+.124	−.00258
		meta'	−328	+.112	−.00233
		para	+1356	−.465	+.00967
C$_2$H$_5$	[fluorophenyl]	α	+5071	−1.743	+.0363
		β	−2909	+1.000	−.0208
		CH$_2$	−8598	+2.956	
		CH$_3$	−806	+0.277	
		ortho	+1262	−.434	+.00903
		ortho'	+1211	−.416	+.00865
		meta	−373	+.128	−.00266
		para	+1371	−.471	+.00980
C$_2$H$_5$	[fluorophenyl]	α	+5206	−1.739	+.0362
		β	−2994	+1.000	−.0208
		CH$_2$	−8706	+2.908	
		CH$_3$	−791	+0.264	
		ortho	+1216	−.406	+.00844
		meta	−303	+.101	−.00210
C$_2$H$_5$	[methylphenyl]	α	+5291	−1.750	+.0371
		β	−3023	+1.000	−.0212
		CH$_2$	−8750	+2.894	
		CH$_3$	−789	+0.261	
		ortho	+1218	−.403	+.00854
		meta	−356	+.118	−.00250
		meta'	−368	+.122	−.00259
		para	+1312	−.434	+.00920
		oCH$_3$	−804	+.266	
C$_2$H$_5$	[phenyl]	α	+5272	−1.753	+.0372
		β	−3007	+1.000	−.0212
		CH$_2$	−8746	+2.909	
		CH$_3$	−793	+0.264	
		ortho	+1206	−.401	+.00850
		ortho'	+1184	−.394	+.00835
		meta	−354	+.118	−.00250
		para	+1304	−.434	+.00920
		mCH$_3$	+425	−.141	
C$_2$H$_5$	–⟨ ⟩–CH$_3$	α	+5304	−1.744	+.0370
		β	−3041	+1.000	−.0212
		CH$_2$	−8778	+2.887	
		CH$_3$	−734	+0.241	
		ortho	+1214	−.399	+.00846
		meta	−344	+.113	−.00241
		pCH$_3$	−1300	+.427	

^{a} $\Delta f = f_{(Ni\ chelate)} - f_{(diamagnetic\ ligand\ or\ Zn\ chelate)}$ in cps. at 60 Mc./s. in carbon disulfide at 25°, referenced internally to tetramethylsilane to eliminate bulk susceptibility effects. ^{b} Spectrum determined in CDCl$_3$.

based on considerations of the signs of the contact shifts as determined by simple valence bond structures, the relative intensities of the resonances, and the observed spin–spin splittings. As an example of such an analysis, the spectrum of compound Ia is shown in Fig. 2.

[Structure Ia, labeled: p-N, m-N, o-N, m-γ, p-γ, o-γ, 3, α, N, Ni]
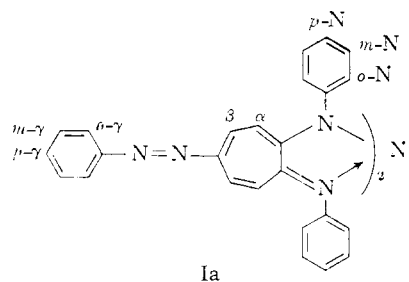
Ia

Valence bond structures of the type shown in Fig. 1 may be written placing the unpaired electron on the α-, o-γ-, p-γ-, o-N- and p-N-positions, and pπ-spin densities centered on these carbon atoms are expected to be positive. Resonances of protons attached to these carbon atoms are, therefore, shifted to high field. Spin correlation effects lead to negative spin density at the β-, m-γ- and m-N-carbon atoms, and as a result the resonances of the protons attached to these carbons move to low field. The doublets to extreme high and low field are assigned to Hα and Hβ, respectively, on the basis of our earlier studies. The resonances of the three non-equivalent sets of protons of the N-phenyl substituent appear as a triplet (two overlapping doublets) to low field (m-N), and a doublet (o-N) and a triplet (p-N) to high field. The pattern of resonances for the γ-phenyl group is similar, but the intensities of the resonances are halved. This assignment of resonances is indicated in Fig. 2.

For the γ-(fluorophenylazo) derivatives the simple multiplet structure of the protons on the phenyl ring is somewhat complicated by longer range H–F couplings, but it was possible to complete the assignment by reference to the F^{19} spectra.

Resolvable multiplet structure in the spectra of the 1-naphthyl- and 2-naphthylazo derivatives provides insufficient data for complete spectral assignment. However, valence bond calculations have proved sufficiently reliable in these chelate systems[14] that the final details of assignment can

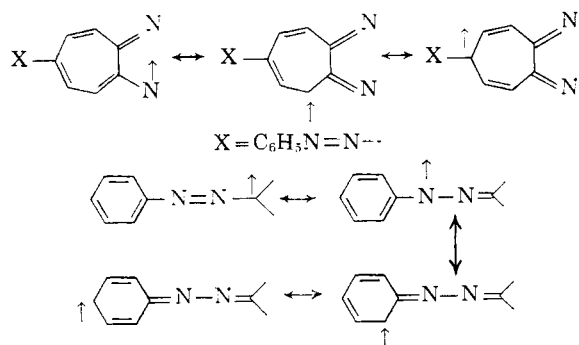(14) D. R. Eaton, Y. K. Kim and W. D. Phillips, to be published.

Fig. 1.

Fig. 2.—Proton nuclear magnetic resonance spectrum of nickel(II) γ-phenylazo-N,N'-diphenylaminotroponeimineate, determined at 60 Mc./s. in deuteriochloroform and internally referenced to tetramethylsilane.

be made with some confidence on the basis of calculated spin density distributions.

Spin Density Distributions and Valence Bond Calculations.—Negative spin densities arise from electron correlation effects in molecules. Determinations of signs and magnitudes of spin densities provide one of the few experimental approaches whereby such correlation effects can be directly measured. One of the principal aims of the present study is to obtain experimental data pertinent to this problem. Thus we have reported[2] previously the spin density distribution on the p-phenylazophenyl group attached to the nitrogen atom of the aminotroponeimineate. It is of interest to compare this earlier determination with the present results with regard not only to the transmission of spin density through the azo linkage, but also to electron correlation effects as reflected in the relative values of the positive and negative spin densities. It may be expected that the effectiveness of the azo group as a conjugating linkage will be reflected in the attenuation of spin density between the point of linkage (in this case the γ-position) and the p-position of the phenyl ring. Spin densities at the points of substitution may be estimated from calculated values (vide infra) or by comparison with the unsubstituted compounds. On this basis, the azo linkage produces an attenuation of 6 for the present compounds and 8 for the N-substituted azo compounds studied previously. These attenuation factors are sufficiently similar to suggest that such an approach may be generally used to assess the conjugative ability of different linkages.

Comparison of the relative values of the positive and negative spin densities for the N-(p-phenylazophenyl) and γ-phenylazo compounds reveals significant differences. Experimental spin density distributions are given in Table II. Valence bond calculations have been carried out on the fragment
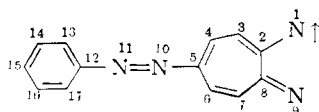

The fifteen principal Kekulé structures were included in the calculation. Exchange integrals other than those between nearest neighbors were neglected and the values $\gamma_{1,2} = \gamma_{8,9} = 1.2\gamma$ and $\gamma_{10,11} = 1.4\gamma$ were assumed. All other exchange integrals were taken to be γ. Matrix elements, eigenvalues and eigenvectors were evaluated by standard procedures[15] and spin densities were calculated from

the eigenvectors by the method of McConnell and Dearman.[16] The results of this calculation and of a similar one on the fragment
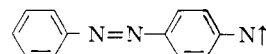
are included in Table II. The ratio of experimental to calculated spin density represents the fraction of an electron delocalized onto this part of the ligand, and the constancy of these ratios indicates the quality of the fit between theory and experiment. It is apparent that the valence bond method employed here overestimates electron correlation for the γ-arylazo compound. Two molecular orbital methods of calculating spin densities with allowance for correlation are those employed by Hoijtink[17] and by Pople and Nesbet.[18]

McLachlan[19] has compared the results of such MO calculations with those of VB calculations and shown that the latter generally provide for more correlation than the former. It appears, therefore, that the present results on the γ-arylazo derivative fit fairly well within the current theoretical framework. The present calculations indicate that $1/_{10.7}$ of an electron is delocalized from nickel to each ligand, and this figure is in good agreement with previous results for nickel(II) N,N'-diethylaminotroponeimineate.[4]

Spin density distributions on the γ-(1-naphthylazo) and γ-(2-naphthylazo) compounds are quite similar to those of the corresponding N-substituted derivatives except that the negative spin densities are relatively smaller. The above remarks are, therefore, equally applicable.

Fluorine Double Bonding.—Application of F^{19} contact shifts to the study of fluorine double bonding has been discussed in a previous paper,[3] and the present results on the γ-(fluorophenylazo)-derivatives provide further opportunity for assessing the importance of fluorine conjugation with π-systems. It is convenient to define a parameter Q_{CF} such that

$$a_F = Q_{CF}\rho_C \qquad (5)$$

However, it has been shown[3] that Q_{CF} is not a constant in the sense that Q_{CH} of eq. 2 is, but is a

(15) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949.

(16) H. M. McConnell and H. H. Dearman, J. Chem. Phys., **28**, 51 (1958).

(17) G. J. Hoijtink, Mol. Phys., **1**, 157 (1958).

(18) J. A. Pople and R. K. Nesbet, J. Chem. Phys., **22**, 571 (1954).

(19) A. D. McLachlan, Mol. Phys., **3**, 233 (1960).

TABLE II
### Comparison of Experimental and Calculated Spin Densities

Position	Calcd.[a]	Exptl.	Ratio[b]	Position	Calcd.[a]	Exptl.[c]	Ratio[b]
α	+0.36774	+0.0383	9.6	$ortho_1$	+0.2877	+0.0076	37.9
β	− .22531	− .0210	10.7	$meta_1$	− .1943	− .0096	20.2
ortho	+ .07515	+ .00756	9.9	$ortho_2$	+ .0916	+ .00078	117
meta	− .03780	− .00263	14.4	$meta_2$	− .0495	− .00108	45.8
para	+ .06274	+ .00872	7.2	$para_2$	+ .0903	+ .00128	70.5

[a] These spin densities, calculated by the valence bond procedure, assumed a full unpaired electron on the ligand.   [b] The reciprocal of this ratio of calculated to experimental spin densities is the actual fraction of an electron transferred from nickel-(II) to the ligand (see text).   [c] Ref. 2.

function of the C–F bond order owing to contributions of resonance structures such as
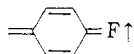
to the electronic structure of the molecule. C–F bond orders were calculated using simple Hückel MO theory treating the fragments
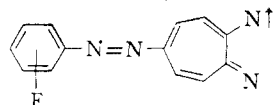
as 19 electron problems. Coulomb and resonance integrals were estimated from

$$\alpha_X = \alpha_C - E_C + E_X$$
$$\beta_{C-X} = (S_{CX}/S_{CC})\beta_{CC} \quad (6)$$

Overlap integrals, S_{CX}, were obtained from the tables of Mulliken, Rieke, Orloff and Orloff.[20] The parameters used were

$$\alpha_C = \alpha \qquad \beta_{CC} = \beta$$
$$\alpha_N = \alpha + 1.3\beta \qquad \beta_{CN} = 0.836\beta$$
$$\alpha_F = \alpha + 2.5\beta \qquad \beta_{CF} = 0.619\beta$$
$$\beta_{NN} = 0.885\beta$$

Bond orders are defined by eq. 7

$$p_{ij} = \sum_r n_r C_{ir} C_{rj} \quad (7)$$

Experimental and theoretical results are collected in Table III.

We have previously postulated[3] that

$$Q_{CF} = a_F/\rho_C = Q^C{}_{CF} + Q^F{}_{FC} (A p_{CF}) \quad (8)$$

where A is a constant of the order unity. Further justification for eq. 8 is provided by plotting all "experimental" values for Q_{CF} we have so far obtained against the corresponding calculated values for p_{CF}. This plot is shown in Fig. 3 and leads to the constants $Q^C{}_{CF} = -83$ gauss and $A Q^F{}_{FC} = +580$ gauss; $Q^C{}_{CF}$ is a measure of the indirect π-σ polarization of a ·C–F fragment similar to that of a ·C–H fragment discussed by McConnell and Chesnut,[9] and is negative. Spin density centered on fluorine as a result of participation by fluorine in conjugation produces the positive $Q^F{}_{FC}$ contribution to Q_{CF}. One ambiguity in the bond order calculations should, however, be noted. In the Hückel calculation for the γ-(m-fluorophenylazo) compound, the orbital which contains the odd electron in the corresponding ortho and para derivatives is re-

duced in energy so as to be no longer the highest occupied orbital. This situation did not occur in previous calculations[3] on the analogous N-fluorophenyl compounds. In view of the known inadequacy of the Hückel approximation with respect to energies, this inversion was neglected and the odd electron placed consistently in the same orbital for the three γ-(fluorophenylazo) derivatives. With due reservations as to the justification of this procedure, the present results may be said to provide confirmation for our previous analysis[3] of the dependence of fluorine contact shifts in fluoroaromatics on fluorine conjugation.

Methyl Hyperconjugation.—A similar variation in the experimental Q_{CCH_3} values for the ·CCH₃ bonding situation has been reported[3] previously and the present results provide further confirmation. The success of the above treatment for fluorine suggests that similar calculations involving hyperconjugation of the CH₃ group may be worth while. Following Crawford and Coulson,[21] the CH₃ group was considered as C≡X and calculations were carried out on the fragments
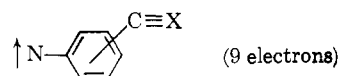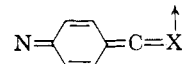

and
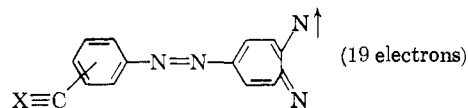
The integrals of Crawford and Coulson were used, namely

$$\alpha_X = \alpha - 0.5\beta \text{ and } \beta_{C=X} = 2.5\beta$$

For carbon of C≡X, $\alpha_C = \alpha - 0.1\beta$ and $\beta_{CC}' = 0.7\beta$ were used.[21,22] The nitrogen integrals used previously again were employed. Spin is placed on the methyl protons by structures of the type
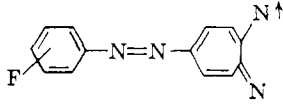

and the Q_{CCH_3} value may be expected to vary with the C≡X bond order. Experimental and theoretical results are presented in Table IV. In this case the indirect mechanism which gave the negative contribution to Q_{CF} must operate through two bonds, and may, therefore, be anticipated to be

(20) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, J. Chem. Phys., 17, 1248 (1949).

(21) C. A. Coulson and V. A. Crawford, J. Chem. Soc., 2052 (1953).
(22) D. B. Chesnut, J. Chem. Phys., 29, 43 (1958).

zero or small. A rough correlation of Q_{CCH_3} with $p_{C=X}$ is apparent. It may be noticed that the variation in $p_{C=X}$ is very small (0.01 unit) and that the poorest correlation of Q_{CCH_3} with bond order occurs with the *meta* substituents where the MO results are expected to be poor. Similar deviations from constancy for Q_{CCH_3} recently have been observed in the e.p.r. hyperfine splittings of anion and cation radicals of methylated anthracenes.[23]

TABLE III

FLUORINE CONTACT SHIFTS[1]

$$F\text{—}\underset{}{\bigcirc}\text{—}N{=}N\text{—}\underset{N}{\overset{N\uparrow}{\bigcirc}}$$

F position	F[19] contact shift[a]	ρ_C	Q_{CF}, gauss	C–F bond order
ortho	−2112	+0.00880[b]	+38.5	0.2067
meta	+1148	− .00250[b]	+73.8	.2717
para	−3227	+ .00960[b]	+52.6	.2173

[a] $f_{Ni\ chelate} - f_{ligand}$ in c.p.s. at 56.4 Mc./sec. in CS_2 at 25° and internally referenced to 1,2-difluorotetrachloroethane.
[b] Averaged values taken from unsubstituted positions, see Table I.

TABLE IV

COMPARISON OF Q_{CCH_3} VALUES FOR N,N'-DITOLYL- AND
γ-(TOLYLAZO)-N,N'-DIETHYLAMINOTROPONEIMINEATES

Position	ρ_C	Q_{CCH_3} gauss	C≡H$_3$ bond order
γ*ortho*	+0.00854	+14.9	0.9739
γ*meta*	− .00250	+27.0	.9787
γ*para*	+ .00920	+22.1	.9725
N*meta*	− .00792	+ 8.3	.9776
N*para*	+ .0107	+27.7	.9689

Spin Densities and Chemical Reactivity.—Figure 4 shows the experimental spin density distribution in the 2-naphthyl group when observed either in the nickel(II) chelate of N,N'-di-(2-naphthyl)-aminotroponeimine[4] or of γ-(2-naphthylazo)-N,N'-diethylaminotroponeimine.

It is clear that quantitatively spin density distributions are not the same for the 2-naphthyl group in the two different electronic environments, but the over-all patterns are similar. For example, in both cases at sites of positive ρ, the magnitudes decrease in the order $C_1 > C_6 > C_3 > C_8$, and at sites of negative ρ, the order is $C_4 > C_5 > C_7$. Minor differences in spin density distribution which occur within the general pattern now established for the 2-naphthyl group are not surprising. In the 2-naphthylazo derivative above, the naphthalene ring is a part of the π-system which includes the azo group and the seven-membered ring. On the other hand, it has become clear from studies of many N-aryl aminotroponeimineates that the aryl group in this position is not significantly conjugated with the seven membered ring. These differences are reflected in the models chosen for valence bond calculations of spin density distributions (see above).

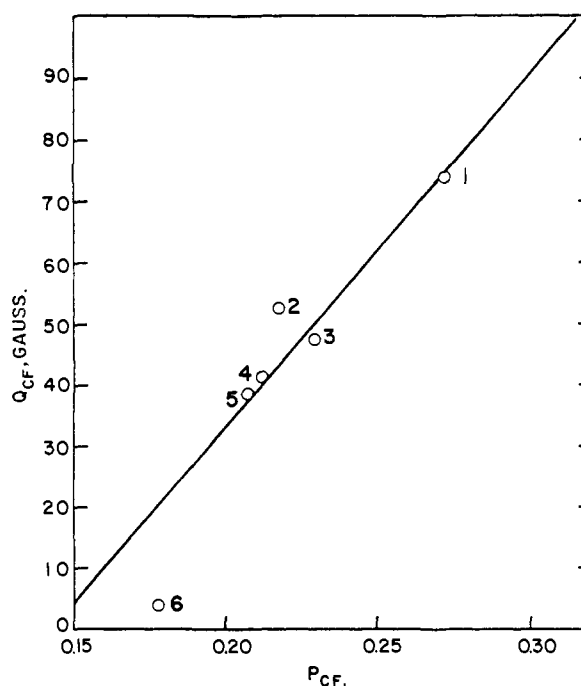(23) J. R. Bolton, A. Carrington and A. D. McLachlan. *Mol. Phys.*, **5**, 31 (1962).

Fig. 3.—Variations of Q_{CF} with C–F bond order for several nickel(II) aminotroponeimineates: 1, γ-(*m*-fluorophenylazo)-; 2, γ-(*p*-fluorophenylazo)-; 3, N-(*p*-fluorophenyl)-; 4, N-(*o*-fluorophenyl)-; 5, γ-(*o*-fluorophenylazo)-; 6, N-(*m*-fluorophenyl)-.
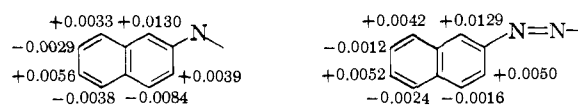

Fig. 4.

Some conclusions can be drawn from the data of Fig. 4 regarding the substitution reactions of 2-naphthyl derivatives. Spin density values are best related to free radical substitution reactions with the site of highest spin density the most susceptible to attack. The same considerations are not strictly applicable to the choice, for example, of a favored point for electrophilic substitution in the unsubstituted ring of a 2-naphthyl derivative. However, the results do show that a substituent at C_2 affects more strongly the spin densities at C_6 than any other site in the second ring. Accordingly, it might be suspected that, in reactions not subject to steric control, an electron-donating group at C_2 will direct an entering electrophilic group to C_6, while an electron-withdrawing group at C_2 selectively deactivates C_6 and C_8 and should direct the entering group to C_5 or C_7. While these predictions are borne out in a number of substitution reactions in the naphthalene series,[24] more data are required before the extent of agreement between electron spin densities and positions of attack by electrophilic species in aromatic systems can be assessed.

Experimental

A.   Synthesis.—Reaction of aryldiazonium fluoroborates with aminotroponeimines is the preferred method for the

(24) L. Fieser and M. Fieser, "Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., third edition, 1956, pp. 743–746.

TABLE V

γ-ARYLAZO-N,N'-DISUBSTITUTED AMINOTROPONEIMINES Ar—N=N—[troponeimine, =NR, NHR]

R	Ar	Ligand Formula	Ligand M.p. °C	Calcd. C	Calcd. H	Calcd. N	Found C[b]	Found H	Found N	Chelate Formula	Chelate M.p. °C	Calcd. C	Calcd. H	Calcd. N	Found C[b]	Found H	Found N
C_2H_5	p-O₂NC₆H₄-	$C_{17}H_{19}N_5O_2$	174–176	62.7	5.88	21.5	62.7	5.95	21.2	$C_{34}H_{35}N_{10}O_4Ni$	>300	57.7	5.13	19.8	58.0	5.21	20.0
C_2H_5	1-C₁₀H₇-	$C_{21}H_{22}N_4$	101–102	76.3	6.71	17.0	76.5	6.80	17.1	$C_{42}H_{42}N_8Ni$	224–226	70.3	5.90	15.6	70.8	6.00	15.5
C_2H_5	2-C₁₀H₇-	$C_{21}H_{22}N_4$	135–136	76.3	6.71	17.0	76.5	6.76	16.8	$C_{42}H_{42}N_8Ni$	265–268	70.3	5.90	15.6	70.8	5.97	15.7
C_2H_5	o-CH₃C₆H₄-[a]	$C_{36}H_{42}N_8Zn$	232–233	66.3	6.49	17.2	66.8	6.55	17.2	$C_{36}H_{42}N_8Ni$	205–206	67.0	6.56	17.4	67.3	6.66	17.7
C_2H_5	m-CH₃C₆H₄-[a]	$C_{36}H_{42}N_8Zn$	252–254	66.3	6.49	17.2	66.5	6.57	17.3	$C_{36}H_{42}N_8Ni$	241–242	67.0	6.56	17.4	67.9	6.73	17.4
C_2H_5	p-CH₃C₆H₄-[a]	$C_{36}H_{42}N_8Zn$	261–262	66.3	6.49	17.2	67.2	6.64	17.0	$C_{36}H_{42}N_8Ni$	251–252	67.0	6.56	17.4	67.6	6.70	17.4
C_2H_5	o-FC₆H₄-	$C_{17}H_{19}N_4F$	124–125	68.4	6.42	18.8	68.3	6.26	18.5	$C_{34}H_{36}N_8F_2Ni$	230–231	62.5	5.56	17.2	62.8	5.84	17.3
C_2H_5	m-FC₆H₄-	$C_{17}H_{19}N_4F$	110–111	68.4	6.42	18.8	68.7	6.76	18.7	$C_{34}H_{36}N_8F_2Ni$	252–253	62.5	5.56	17.2	63.1	5.83	17.0
C_2H_5	p-FC₆H₄-	$C_{17}H_{19}N_4F$	120–121	68.4	6.42	18.8	68.4	6.78	18.7	$C_{34}H_{36}N_8F_2Ni$	259–260	62.5	5.56	17.2	63.0	5.50	17.3
C_6H_5	C₆H₅-									$C_{50}H_{38}N_8Ni$	254–255	74.2	4.73	13.8	74.5	4.96	13.9

[a] Isolated and analyzed as diamagnetic zinc chelates. [b] Complete removal of the recrystallization solvent (benzene) was not achieved even on drying at 120° for 48 hr. in a high vacuum. At higher temperatures, some decomposition occurred. These compounds were, however, uniquely characterized by their n.m.r. spectra which showed, in addition to the expected lines, a single sharp resonance of low intensity at $\tau = 2.84$ p.p.m. attributable to benzene.

preparation of γ-arylazoaminotroponeimines. Direct coupling with the diazotized amines can be used with the more highly electrophilic diazonium salts from aniline and p-nitroaniline. When isolated as the free bases, the azo compounds were obtained as deep red-maroon crystalline solids in 20–50% yield[25] after crystallization from ethanol. In some cases, the coupling reaction gave low melting products which were difficult to purify, and it was found convenient to isolate the products as the crystalline, diamagnetic zinc chelates.

The diazonium fluoroborates were prepared by a standard procedure[26] using sodium fluoroborate as the precipitant. A typical coupling reaction is described below since it incorporates some modifications of a procedure already described.[7]

γ-(o-Fluorophenylazo)-N,N'-diethylaminotroponeimine.— A solution of 4.77 g. (0.027 mole) of N,N'-diethylaminotroponeimine[4] in 120 ml. of absolute ethanol was combined with a solution of 4.06 g. (0.027 mole) of sodium acetate trihydrate in 27 ml. of water and cooled to 0 to −5°. o-Fluorobenzenediazonium fluoroborate (5.58 g., 0.027 mole) was added as the dry powder during 0.75 hr. After the addition was complete, 15 ml. of water was added and the mixture was stirred at 0° for 1.5 hr. The product was removed by filtration and washed successively with two 15-ml. portions of 50% aqueous ethanol and with water. Crystallization from ethanol gave 2.12 g. of γ-(o-fluorophenylazo)-N,N'-diethylaminotroponeimine as long red needles. Concentration of the liquors gave an additional 0.25 g., for a total of 2.37 g. (28.4%). The m.p. and analytical data are recorded in Table V.

For preparation of the nickel(II) chelate, 1.50 g. (0.005 mole) of the aminotroponeimine was dissolved in 50 ml. of warm ethanol, and a solution of 0.72 g. (10% excess) of nickel(II) acetate tetrahydrate in 5 ml. of water was added. After refluxing for 1 hr., the iridescent olive-green chelate was isolated by filtration and washed successively with hot ethanol, dilute ammonia, water and cold ethanol. After drying, the product weighed 1.42 g. (86.5%).

The nickel(II) chelate was recrystallized three times from benzene and dried at 120° (0.1 mm.) for 48 hr. The m.p. and analytical data are given in Table V.

γ-(Phenylazo)-N,N'-diphenylaminotroponeimine (Direct Coupling with Diazotized Amine).—A solution of 2.72 g. (0.01 mole) of N,N'-diphenylaminotroponeimine was prepared in 100 ml. of ethanol, 60 ml. of acetone and 10 ml. of water and chilled to 0°. Aniline (0.93 g., 0.01 mole) was dissolved in 2.9 g. of concentrated hydrochloric acid and 1.5 ml. of water and diazotized with 0.73 g. of sodium nitrite. The cold filtered diazonium salt solution was added rapidly to the aminotroponeimine, and a deep red color developed. After stirring 1 hr., an aliquot of the clear red solution was poured into water, but the gummy mass which separated could not be crystallized. The product was isolated by treatment of the reaction mixture with an aqueous solution of nickel(II) acetate. After 2 hr., the nickel(II) γ-(phenylazo)-N,N'-diphenylaminotroponeimineate was isolated and washed as described in the preceding experiment. The yield of dark maroon powder was 1.85 g. (46% based on the starting aminotroponeimine). A sample was obtained as large maroon prisms with a metallic luster after several crystallizations from methylene chloride. After drying in vacuo for 6–8 hr. at 60–80°, the sample retained one mole of methylene chloride of crystallization.

Anal. Calcd. for $C_{50}H_{38}N_8Ni \cdot CH_2Cl_2$: C, 68.5; H, 4.51; N, 12.5. Found: C, 68.9; H, 4.54; N, 12.5.

A sample free of solvent was obtained after a further crystallization from benzene followed by prolonged drying in vacuo at 90–100°. The analytical data are recorded in Table V.

B. Nuclear Magnetic Resonance Studies —Nuclear magnetic resonance spectra were obtained at 60 Mc./sec. for H[1] and 56.4 Mc./sec. for F[19] employing a Varian high resolution n.m.r. spectrometer. The usual side band modulation method of calibration was employed. Temperature control was achieved by using a standard Varian temperature probe. The contact shifts observed are given in Tables I and III.

(25) These yields are not necessarily optimum.
(26) "The Schiemann Reaction" by A. Roe, "Org. Reactions," Vol. V, Chapter 4, John Wiley and Sons, Inc., New York, N. Y., 1949.