an optical train through either sample cell or solvent-filled cells. This latter method employed a ferrioxalate actinometer.[21] The sensitized isomerization of piperylene was used not only as an actinometer but also to measure intersystem crossing efficiencies of model compounds. To determine photochemical conversion and to perform product analysis we used an F & M gas chromatograph with a 6 ft × 1/8 in. column packed with Apiezon L on Chromosorb W. Analysis of isomeric piperlyene mixtures was performed with a 20 ft × 0.25 in. column of triscyanoethoxypropane on Chromosorb W. A dual-flame ionization detector was used with both columns. Ir and uv spectra were recorded in double beam with a Beckmann Model IR5A and a Cary Model 15 spectrophotometer, respectively. Nmr spectra were recorded on a Hitachi-Perkin-Elmer H-16 spectrometer. Emission spectra were obtained on an Aminco-Bowman spectrophotofluorometer in frozen EPA at 77°K.

3′,6′-Dimethoxybenzonorbornadiene was prepared from cyclopentadiene–benzoquinone adduct, aqueous sodium hydroxide, and dimethyl sulfate as described by Meinwald and Wiley[8] for methylation of 3′,6′-dihydroxybenzonorbornadiene.

5,8-Dimethoxy-*endo,exo*-1,4:9,10-dimethano-1,4,6,7,9,10-hexahydroanthracene (2). In a sealed tube were placed 11.3 g of 3′,6′-dimethoxybenzonorbornadiene and 5.6 g of dicyclopentadiene. The tube was heated at 195° for 6 hr. The resultant oil crystallized from heptane to give 8.4 g (60%) of an off-white solid. Several recrystallizations from heptane gave colorless needles: mp 128–129°; ν_{KBr} 3030, 2950, 2850, 1490, 1480, 1430, 1350, 1270, 1250, 1175, 1105, 1080, 1060, 990, 910, 900, 850, 820, 795, 785, 755, 730, and 705 cm^{-1}; nmr (CCl_4) δ 6.27 (2 H, $H_{6,7}$, singlet), 5.98 (2 H, $H_{2,3}$, triplet), 3.63 (6 H, OCH_3, singlet), 3.20 (2 H, $H_{9,10}$, triplet), 2.90–2.57 (3 H, $H_{1,4,15a}$, complex), 2.19 (2 H, $H_{13,14}$, broad singlet, and 1.70–0.95 ppm (3 H, $H_{15s,16a,16s}$, complex).

5,8-Dimethoxy-*endo,exo*-1,4:9,10-dimethano-1,2,3,4,6,7,9,10-octahydroanthracene (6). Hydrogenation of 0.3 g of **2** was accomplished in a low-pressure hydrogenation apparatus in 50 ml of methanol over 0.1 g of palladium black. After charging the mixture with hydrogen, the reaction was magnetically stirred for 1 hr at room temperature. The catalyst was filtered, the solvent evaporated, and the residue recrystallized from ethanol as white crystals: mp 123–124°; ν_{KBr} 3080 (bridge (C–H)); nmr (CCl_4) δ 6.31 (2 H, $H_{6,7}$, singlet), 3.68 (6 H, OCH_3, singlet), 3.27 (2 H, $H_{9,10}$, triplet), and 1.2–2.2 ppm (10 H, complex). The compound gave a negative permanganate test for unsaturation.

8,11-Dimethoxytetracyclo[5.4.0^{2,4}.0^{3,6}]undeca-1,8,10-triene (3). **1** (2 g) in 200 ml of ether was irradiated for 2 hr with a 450-W Hanovia medium-pressure Hg arc. After evaporation of the ether, the residue, a dark yellow oil, was chromatographed on a silica gel column with benzene. The resulting yellow solid was recrystallized from ethanol and then from heptane as light yellow crystals: mp 65–66.5°; nmr (CCl_4) δ 6.40 (2 H, $H_{9,10}$, singlet), 3.76 (3 H, OCH_3, singlet), 3.64 ppm (3 H, OCH_3, singlet), complex patterns further upfield.

11,12-*o*-[1′,4′-Dimethoxybenzeno]pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{5,9}]-dodec-11-ene (4). **2** (1 g) in ether was irradiated through a Pyrex filter for 20 hr with light from a 450-W Hanovia medium-pressure Hg arc. Evaporation of the ether gave a quantitative yield of off-white crystals which were recrystallized from heptane to give white cubic crystals: mp 88–88.5°; ν_{KBr} 2950, 2875, 2700, 1600, 1490, 1460, 1350, 1320, 1280, 1260, 1190, 1140, 1110, 1090, 1065, 1020, 990, 975, 805, 795, and 710 cm^{-1}; nmr (CCl_4) δ 6.25 (2 H, $H_{2',3'}$, singlet), 3.66 (3 H, OCH_3, singlet), 3.6 ppm (3 H, OCH_3).

***exo*-3,6-Dimethoxytetracyclo[6.3.1.0^{2,7}.0^{9,11}]undeca-2,4,6-triene (7).** An ethereal solution of 0.30–0.35 g of diazomethane was distilled into a cooled, stirring mixture of 0.5 g of **1**, 0.05 g of cuprous chloride, and 30 ml of ether. After the addition was complete, the solution was stirred for another 30 min, filtered, and evaporated to dryness. The residue was recrystallized from ethanol: mp 97–98°; nmr (CCl_4) δ 6.32 (2 H, aromatic H, singlet), 3.69 (6 H, OCH_3, singlet), 3.39 (2 H, benzylic H, complex), and 0.5–1.5 ppm (6 H, aliphatic H, complex).

***exo,endo,exo*-11,14-Dimethoxyhexacyclo[7.6.1.1^{3,7}.0^{4,6}.0^{2,8}.0^{10,15}]-heptadeca-10,12,14-triene (8).** This compound was prepared from **2** the same way as **7** from **1**, white crystals: mp 91.5–92°; nmr δ 6.27 (2 H, aromatic H, singlet), 3.66 (6 H, OCH_3, singlet), 3.39 (2 H, benzylic H, complex), and 0.5–2.7 ppm (12 H, aliphatic H, complex).

Acknowledgment. This work was supported by the Atomic Energy Commission on Contract No. AT-40-01-3797.

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[21] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235** 518 (1956).

Spin-Density Distribution in Some Heterocyclic Systems

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Abstract: Nmr contact shift measurements have been made on a number of Ni(II) aminotroponeiminates containing heterocyclic substituents. From these measurements the spin-density distributions in the heterocyclic moieties have been evaluated. The spin densities are compared with those previously reported for analogous aromatic fragments and are discussed in terms of the valence bond formalism. Both odd alternant and even alternant systems are considered. In general, the results demonstrate the participation of ionic resonance structures in heterocyclic compounds, and qualitative estimates of the importance of such structures are presented. Competitive π bonding in mixed Ni(II) aminotroponeiminates enables a quantitative measurement of the electron-accepting or -donating properties of a heterocyclic group relative to a phenyl group to be obtained. Results for several such groups expressed in terms of the Hammett σ parameter are presented.

We have previously reported the use of nmr contact-shift measurements on the ligands of paramagnetic transition metal chelates to study conjugation[1] and hyperconjugation.[2] In the present paper this approach is extended to heterocyclic systems. It has long been recognized that pyridine and furan, for example, have chemical properties similar to aromatic molecules

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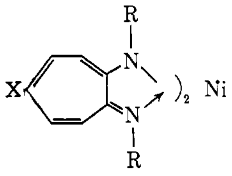
[1] (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, 37, 347 (1962); (b) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discuss. Faraday Soc.*, 34, 77 (1962).

[2] (a) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Amer. Chem. Soc.*, 84, 4100 (1962); (b) D. R. Eaton, A. D. Josey, and R. E. Benson, *ibid.*, **89**, 4040 (1967).

and hence that the heteroatoms participate in the π system. However, the extent of this participation has in many cases remained an open question. The measurement of spin-density distributions provides a direct approach to this problem. In general, we have tried to compare analogous molecules with and without heteroatoms to investigate the effect of heteroatom substitution. Spin-density distributions in both alternant and nonalternant conjugated systems have been examined.

The paramagnetic complexes used throughout this work are Ni(II) aminotroponeiminates of structure I.



I

The heterocyclic substituents are placed at either X or R. These nickel chelates can exist in either square planar (diamagnetic) or tetrahedral (paramagnetic) forms.[3] In solution there is a rapid interconversion of the two forms, and the nmr lines appear at frequencies intermediate between those expected for the diamagnetic and paramagnetic structures. (There is no evidence that any of these chelates form octahedral complexes. Thus the present shifts do not depend on concentration even when there is a pyridine substituent and previous work[3] has shown that the shifts are unchanged in coordinating solvents such as pyridine.) It has been shown that in the paramagnetic tetrahedral form about 10% of the spin is delocalized from the d orbitals of nickel to the π system of the ligands.[1] Hyperfine interactions between this delocalized electron spin and the nuclear spins of the ligand protons give rise to large contact shifts in the nmr spectra according to eq 1 and 2.

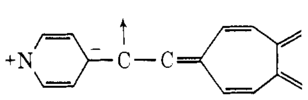
$$\frac{\Delta H_i}{H_0} = -a_i\frac{\gamma_e}{\gamma_N}\frac{g\beta S(S+1)}{3kT(e^{\Delta G/kT}+1)} \qquad (1)$$

$$a_i = Q\rho_i \qquad (2)$$

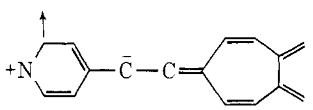
In these equations ΔH_i is the chemical shift at applied field H_0, a_i is the hyperfine coupling constant, γ_e and γ_N are the magnetogyric ratios of the electron and nucleus, respectively, and ΔG is the free-energy difference between the singlet and triplet states. The p–π spin density at the *i*th atom, ρ_i, is related to the hyperfine coupling constant by eq 2, where Q is a constant approximately equal to -22.5 G for aromatic protons. Thus, eq 1 and 2 enable the spin-density distribution in the π system to be calculated from the observed contact shifts. (We do not wish to imply that the observed shifts arise *entirely* from π spin densities. We believe, however, that the weight of evidence from this study and from previous work supports the contention that this is the *predominant* effect and justifies *qualitative* discussion of the data in these terms.) To obtain absolute spin densities it is necessary to study the temperature dependence of the shifts in order to find ΔG. For relative spin densities, measurements at room temperature suffice, and the present results are based on such experiments. Extensive previous work[1,2] with Ni(II) aminotroponeiminates has shown that the spin density at the β position of the seven-membered ring lies in the range -0.021 to -0.023, and this information can be used to normalize the spin densities at other positions. However, the qualitative arguments developed in the discussion depend only on the relative spin densities.

Results and Discussion

The spin-density distributions for Ni(II) aminotroponeiminates are presented in Table I. Compounds **1–4** were chosen to demonstrate directly the effect of heteroatom substitution in the aromatic ring. The substituents are well removed from the nickel atom, and previous results have shown that direct isotropic dipolar interactions with the unpaired electrons on the nickel are negligible for such substituents. Therefore, the observed shifts are a reliable measure of the spin densities. Comparison of the spin densities of compounds **1–3** with those of the phenyl derivative **4** shows that the effects of hetero substitution are comparatively small. The most notable difference is the lower negative spin densities at the meta positions. This feature is consistent with the participation of ionic structures in addition to the usual Kekule-type structure in the valence-bond formulation, *e.g.*, structures II and III.

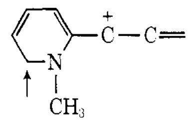


II



III

Structure III places positive spin at a position that has negative spin from nonionic valence bond structures and hence, insofar as it is of importance, is expected to diminish the observed negative spin. It is apparent that this effect is of minor importance except in the case of the pyridinium ion **3**, for which the contribution of structure IV is apparently sufficient to neutralize the expected negative spin density almost completely. It is interesting to note that the effect of substituting a heteroatom in the ring is no greater than that produced by an external substituent. This is illustrated by the aromatic spin densities in the *p*-chlorophenyl derivative **9** compared with those of the carbon analog **4**. The shift for CH_3 in **3** is to low field, indicating positive spin on the nitrogen, as expected. This assumes that Q_{NCH_3} is positive, as is Q_{CCH_3}.[2] It may be noted that the absolute contact shifts of **3** are smaller than those of compounds **1** and **2**, showing that the equilibrium is more toward the diamagnetic form of the chelate. This is in accord with the electron-withdrawing properties of the positively charged ion.[3]



IV

The next series of compounds **5–8** differs from those above and from aminotroponeiminates discussed in previous papers[1,2] in that structures can be written placing positive spin at all positions of the heterocyclic ring. Thus, for **5** we have the structures V–XI.

Structures VII–XI place spin at the proton-bearing positions. The resonance for position 2 can be as-

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[3] D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, **85**, 397 (1963).

Table I. Contact Shifts and Spin Densities

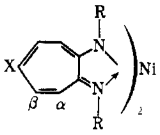
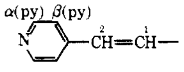
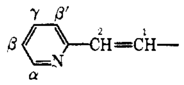
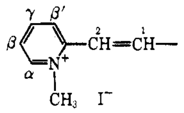
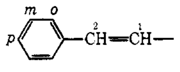
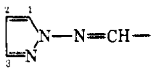
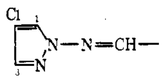
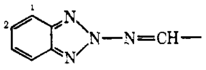
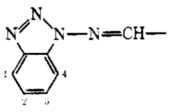
Compd no.	Position	R	 X	Contact shift, Hz	Spin density, ρ
1	α	C_2H_5		+5746	+0.0390
	β	$CDCl_3$		−3239	−0.0220
	CH_2			−9325	
	CH_3			−761	
	CH (1)			−2689	−0.0183
	CH (2)			+4247	+0.0288
	β (py)			+913	+0.0062
	α (py)			−177	−0.0012
2	α	C_2H_5		+5817	+0.0388
	β	$CDCl_3$		−3296	−0.0220
	CH_2			−9388	
	CH_3			−749	
	CH (1)			−2750	−0.0183
	CH (2)			+4254	+0.0284
	β′ (py)			+838	+0.0056
	α (py)			−196	−0.0013
	γ (py)			−224	−0.0015
	β (py)			+970	+0.0065
3[a]	α	C_2H_5		+3886	+0.0357
	β	DMSO		−2396	−0.0220
	CH_2			−8657	
	CH_3			−696	
	CH (1)			−1486	−0.0136
	CH (2)			+3296	+0.0303
	β′ (py)			+685	+0.0063
	α (py)			−11	−0.0001
	γ (py)			−50	−0.0004
	β (py)			+870	+0.0080
	NCH_3			−437	
4[b]	α	C_2H_5		+5894	+0.0387
	β	$CDCl_3$		−3352	−0.0220
	CH_2			−9465	
	CH_3			−710	
	CH (1)			−2890	−0.0190
	CH (2)			+4207	+0.0276
	Ortho			+908	+0.0060
	Meta			−254	−0.0017
	Para			+1007	+0.0066
5[b]	α	C_2H_5		+5393	+0.0413
	β	$CDCl_3$		−2870	−0.0220
	CH_2			−9164	
	CH_3			−807	
	CH			−1243	−0.0095
	1			+651	+0.0050
	3			+483	+0.0037
	2			+245	+0.0019
6[b]	α	C_2H_5		+5234	+0.0413
	β	$CDCl_3$		−2792	−0.0220
	CH_2			−9042	
	CH_3			−798	
	CH			−1155	−0.0091
	1			+619	+0.0049
	3			+454	+0.0036
7[b]	α	C_2H_5		+4807	+0.0431
	β	$CDCl_3$		−2452	−0.0220
	CH_2			−8723	
	CH_3			−874	
	CH			−572	−0.0051
	1			+224	+0.0020
	2			+335	+0.0030
8[b]	α	C_2H_5		+5048	+0.0415
	β	$CDCl_3$		−2677	−0.0220
	CH_2			−8930	
	CH_3			−824	
	CH			−975	−0.0080

Table I (*Continued*)

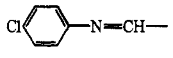
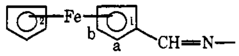
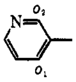
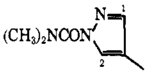
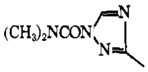
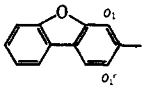
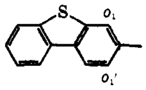
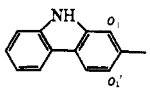
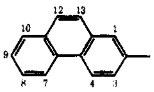
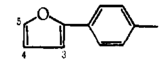
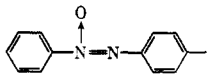
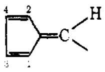
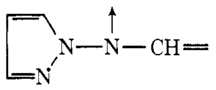
Compd no.	Position	R	X	Contact shift, Hz	Spin density, ρ
	1			+57	+0.00046
	2			+123	+0.00107
	3			+34	+0.00069
	4			+91	+0.00075
9	α	C_2H_5		+5204	+0.0417
	β	$CDCl_3$ (CS_2)		−2747	−0.0220
	CH_2			−9016	
	CH_3			−803	
	CH			−757	−0.0061
	Ortho			+613	+0.0049
	Meta			−240	−0.0019
10[c]	α	C_2H_5		+6126	+0.0395
	β	$CDCl_3$		−3412	−0.0220
	CH_2			−9977	
	CH_3			−671	
	CH			+2750	+0.0177
	Ferrocene 1a			+57	+0.0004
	Ferrocene 1b			+213	+0.0014
	Ferrocene 2			+74	+0.0005
11	α		H	+3149	+0.0393
	β			−1684	−0.0210
	X			+4405	+0.0549
	Ortho$_1$			+493	+0.0062
	Ortho$_2$	$CDCl_3$		+633	+0.0079
	Meta			−665	−0.0083
	Para			+841	+0.0105
12[d]	α		H	+819	+0.039
	β			−433	−0.0210
	X			+1190	+0.0577
	H_1	Mixed $CDCl_3$		+236	+0.0114
	H_2				
	CH_3			−18	
13[d]	α		H	+2894	+0.0387
	β			−1570	−0.0210
	X			+4730	+0.0633
	H	Mixed $CDCl_3$		−1704	−0.0228
	CH_3			−39	
14	α		H	+1932	+0.0412
	β			−985	−0.0210
	X			+2685	+0.0572
	Ortho$_1$			+450	+0.0096
	Ortho$_1'$	$CDCl_3$		+279	+0.0059
	Meta$_1$			−387	−0.0083
	Ortho$_2$			+57	+0.0012
	Meta$_2$			−42	−0.0009
	Para$_2$			+113	−0.0024
15	α		H	+2911	+0.0409
	β			−1495	−0.0210
	X			+4040	+0.0567
	Ortho$_1$			+690	+0.0097
	Ortho$_1'$	CS_2		+450	+0.0063
	Meta$_1$			−594	−0.0083
	Ortho$_2$			+90	+0.0013
	Meta$_2$			−102	−0.0014
	Meta$_2'$			−74	−0.0010
	Para$_2$			+175	+0.0025
16	α		H	+5765	+0.0412
	β			−2936	−0.0210
	X			+7865	+0.0563
	Ortho$_1$			+1263	+0.0090
	Ortho$_1'$	DMSO		+829	+0.0059
	Meta$_1$			−1128	−0.0081
17	α		H	+2355	+0.0414
	β			−1194	−0.0210
	X			+3264	+0.0574
	H_1			+641	+0.0113
	H_3	CS_2		+279	+0.0049
	H_4			−456	−0.0080
	H_7			+129	+0.0023
	H_8			−145	−0.0025

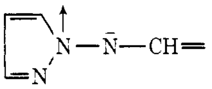
Table I (*Continued*)

Compd no.	Position	R	X	Contact shift, Hz	Spin density, ρ
	H_9			+117	+0.0021
	H_{10}			−85	−0.0025
	H_{12}			−65	−0.0011
	H_{13}			+41	+0.0007
18	α		H	+3760	+0.0408
	β			−1934	−0.0210
	X			+5212	+0.0566
	Ortho	$CDCl_3$		+713	+0.0078
	Meta			−791	−0.0086
	H_3			+279	+0.0030
	H_4			−102	+0.0011
	H_5			+213	+0.0023
19	α		H	+5079	+0.0407
	β			−2622	−0.0210
	X				
	$Ortho_1$	CS_2		+985	+0.0079
	$Meta_1$			−1178	−0.0094
	$Ortho_2$			+81	+0.00065
	$Meta_2$			−75	−0.00061
	$Para_2$			+92	+0.00074
20[b]	α	C_2H_5		+5353	+0.0370
	β	CS_2		−3041	−0.0210
	CH_2			−8860	
	CH_3			−773	
	CH			−3775	−0.0261
	H_1			+138	+0.0010
	H_2			+97	+0.0007
	H_3			+1750	+0.0120
	H_4			+1865	+0.0129

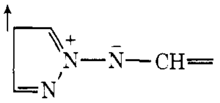
[a] Satisfactory elemental analytical data were not obtained for this compound. However, the nmr data are clearly in accord for the proposed structure. [b] A. D. Josey, U. S. Patent 3,385,874 (May 28, 1968). [c] Satisfactory elemental analytical data were obtained for the ligand; no data were obtained for the chelate. [d] Satisfactory elemental analytical data obtained for ligands. Chelates were not isolated and were prepared by exchange reaction of ligand with Ni(II) *N*,*N*′-diethylaminotroponeiminate.[5]



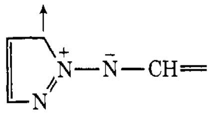
V



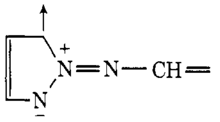
VI



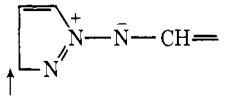
VII



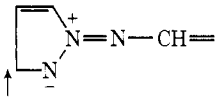
VIII



IX



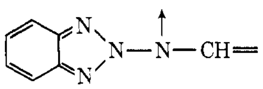
X



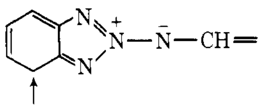
XI

signed by comparison with the chloro derivative **6**. The correct assignments of protons 1 and 3 are uncertain. However, it is significant that position 2 has the smallest spin density. This is qualitatively predictable since two valence-bond structures can be written placing spin at either position 1 or 3, but only one such structure (VII) can be written placing spin at 2. Previous results,[1] *e.g.*, with *N*,*N*′-dinaphthyl derivatives, have shown that this type of qualitative argument seems to have general validity. It is also interesting to compare the absolute magnitudes of the spin densities of **5**, for which only ionic structures can be written to place spin on the ring, with those of compound **4** in which the relevant structures are nonionic. The comparable spin densities indicate that ionic structures play an important role in these heterocyclic systems.

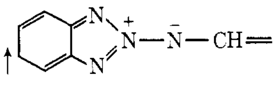
Compounds **7** and **8** represent a similar situation. In these cases no alternations of spin densities are predicted on the six-membered rings. Thus for compound **7** we can write structures such as XII–XV. It is apparent that positive spin can be placed at all four observable positions of the six-membered ring. In agreement with this, the shifts are all to high field, but since the spin–spin splitting was not resolved, individual assignments cannot be made with certainty. In compound **8** the shifts for the protons of the benzo group are also all to high field, and individual resonances can be discerned for each of the four positions. The resonances appear as two doublets and two triplets, as expected, but this does not suffice for an unambiguous assignment.



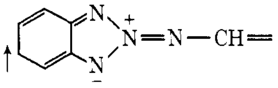
XII



XIII

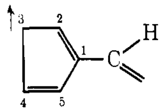


XIV

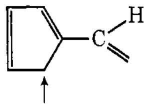


XV

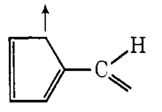
Since we have not previously observed π-electron spin densities that do not alternate in sign, it was considered desirable to have an example of such behavior in a system that does not contain heteroatoms. Such an example is provided by compound **20**. For this substituent, the four valence-bond structures XVI–XIX



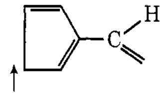
XVI



XVII

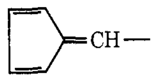


XVIII



XIX

give rise to positive spin at each of the proton-bearing positions of the five-membered ring. As expected, all four positions show high-field shifts. Thus, this phenomenon is not specifically associated with the presence of heteroatoms. It may be noted that the shifts for protons 3 and 4 are very much larger than those for protons 2 and 5. The implication is that structures XVI and XIX are energetically favored over structures XVII and XVIII. This is quite reasonable since the fulvene structure XX has short bond lengths in the 2,3 and 4,5 positions. Therefore, structures XVI and XIX contain one short and one long double bond, whereas XVII and XVIII have two long double bonds. The assignments of protons 2 and 5 and protons 3 and 4 are unambiguous since the former are doublets and the latter are triplets. Individual assignments are based on comparisons with previous results with styryl and phenylbutadienyl substituents.[1] For the styryl derivative it is found that the coupling constant for the protons trans to the phenyl ring is larger than that for the cis proton, and for the phenylbutadienyl compound the trans–trans coupling is larger than that of the trans–cis. By analogy, we expect the coupling constant for 4 to be greater than that of 3.

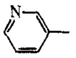
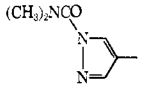
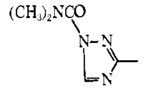


XX

Compound **10** was synthesized specifically to investigate the interaction of two π systems *via* the metal atom in ferrocene. Theory predicts that the top-filled orbitals in ferrocene will be the a_{1g} and e_{2g} metal orbitals and the e_{1u} orbital that is predominantly ligand. We assume that this orbital scheme is not significantly perturbed by the aminotroponeiminate substituent. In **10**, spin is placed in the e_{1u} orbital that mixes only with the 4p orbitals of iron. The question is whether this mixing suffices to make the e_{1u} orbital a π orbital common to both cyclopentadienyl fragments or whether the coupling will be indirect, *i.e.*, by polarization of the strongly bonding e_{1g} orbital of the type postulated by Levy and Orgel[4] to account for the contact shifts in vanadocene. In the latter case, it is expected that the sign of the contact shifts on the two rings will be different. In the former case, the signs should be the same. Experiment supports the direct mechanism. Thus, some participation of the Fe 4p orbitals in the bonding is indicated, although it is not necessarily implied that this is energetically important.

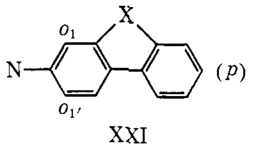
The next three compounds (**11–13**) illustrate a rather different approach to the question of spin delocalization in heteroaromatic systems. We have previously demonstrated the competitive nature of the π bonding in Ni(II) aminotroponeiminates comprised of ligands with different substituents.[5] The spin distributed to each of the ligands depends directly on the electron-donor properties of the substituent. A suitable plot of the relative spin densities on the competing ligands against the Hammett σ values of substituted phenyl groups was found to be linear.[5] Therefore, one may use this correlation to estimate Hammett σ values for heterocyclic moieties. The advantages of this approach are (1) that the relative contact shifts required can be easily measured with high precision and (2) that there is a very simple and direct physical interpretation of the measurement. Thus, there is a minimal probability that the resulting σ values will be distorted by extraneous factors. Also, the spin density on the ligand is a direct measure of the charge donated from the π system to the nickel, and in the competitive situation the relative spin densities are a direct measure of the relative donor properties of the ligands. Hammett σ values derived in this way are shown in Table II. The pyridine substituent was chosen to provide a basis for comparison. The observed value of +0.42 falls well within the range of σ values obtained by other techniques.[6] It is interesting to note that the triazole function **13** appears to be a very strong electron-withdrawing group (+0.89).

Table II. Hammett σ Values Calculated from Contact Shifts

	+0.42[a]
	+0.32
	+0.89

[a] Literature values; 0.62 (p*K* of pyridines), 0.34 (infrared intensity of nitrile group), 0.55 (hydrolysis of benzamides with base), 0.62 and 1.3 (hydrolysis of ethyl benzoates with base), and 0.27–0.40 (nuclear quadrupole resonance studies).[6]

The final group of compounds (**14–19**) involves a rather different approach to the study of the involvement of heteroatoms in conjugated systems. Thus, spin densities in a substituent such as XXI are compared with those in the biphenyl substituent. If X can participate in the π system, there will be an additional conjugative pathway and this will be manifested in the spin



XXI

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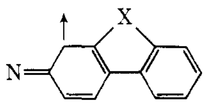
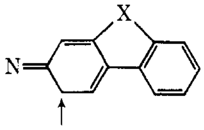
[4] D. A. Levy and L. E. Orgel, *Mol. Phys.*, 3, 583 (1960).

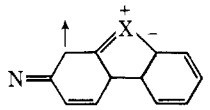
[5] D. R. Eaton and W. D. Phillips, *J. Chem. Phys.*, 43, 392 (1965).

[6] With the exception of one value, the reported range is 0.27–0.62 (H. H. Jaffe and H. L. Jones, *Advan. Heterocycl. Chem.*, 3, 209 (1964)).

densities. We have previously reported results for the compound with X = CH$_2$, and now extend this series to include X = O, X = S, X = NH, and X = CH═CH. The latter compound provides a comparison with a "fully conjugated" bridge. Primarily, we are looking for two effects. Structures XXII, XXIII, and XXIV place spin on the ortho positions of the first ring. Only the first two are available to the biphenylyl derivative and lead to equal spin densities at both ortho positions. To the extent that X is involved in the π system, we expect to find inequalities in these ortho spin densities. The positions can be distinguished since ortho_1 gives a singlet and ortho_1' gives a doublet.

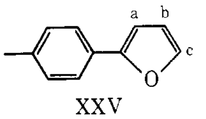

XXII


XXIII

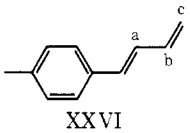

XXIV

For the biphenylyl compound, both ortho carbons have a spin density of +0.0078; for X = O, ortho_1 is +0.0096 and ortho_1' is +0.0059. As anticipated, the imbalance is largest for X = CH═CH (ortho_1 = +0.0113, ortho_1' = +0.0049), but it is rather surprising that the results are very similar for X = CH$_2$, O, S, and NH. This leads to the conclusions that the sulfur d orbitals do not play an important role in this type of conjugation (in agreement with earlier contact-shift results) and that the hyperconjugation in fluorenyl substituent is rather surprisingly effective. The second effect concerns the spin density of the para carbon (*p*) of the second ring. For all substituents this is about twice as large as in the biphenylyl example, and this is ascribed to the enforced coplanarity of the two aromatic rings. Thus, it may be deduced that nonplanarity reduces the effectiveness of conjugation in biphenyl by about 50%.

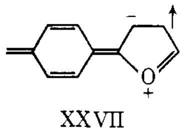
The interest in compound **18** is somewhat similar. The relevant comparison is between XXV and the phenylbutadienyl group XXVI. In XXV the butadiene moiety has been forced into cis configuration and bridged with oxygen. At the three comparable positions, XXV and XXVI have spin densities of +0.0030 and +0.0042 (position a), −0.0011 and −0.0022 (position b), and +0.0023 and +0.0034 (position c), respectively. The immediately obvious point is that all the spin densities are smaller in the furan derivative, and this probably reflects the lower electron-donating ability of the group arising from the presence of the electronegative oxygen. The negative spin density at position b has been reduced proportionately more than the positive spin densities. This is consistent with the participation of ionic structures such as XXVII that tend to place positive spin at b. In this case, the ionic structures are not sufficiently important to put positive spin densities at all positions. This is consistent with the relatively small resonance energy of furan.



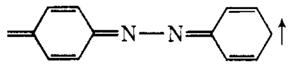
XXV

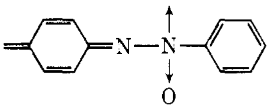


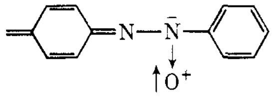
XXVI


XXVII

Finally, compound **19** raises a slightly different question regarding the effect of a heteroatom in conjugative systems. Whereas in the bridged compounds **14–17** the heteroatom provided an additional conjugative pathway, in this case there is a competing pathway. The comparison is between the azo compound with valence-bond structures such as XXVIII and the azoxy compound with structures such as XXIX and XXX.


XXVIII


XXIX


XXX

In these two compounds the spin densities of the first phenyl ring are virtually the same (ratios 1.04 and 0.98 for ortho and meta, respectively). On the second ring the ratios for the azoxy to azo compounds are 0.83, 0.56, and 0.58 (average 0.66) for ortho, meta, and para positions, respectively. Thus, in the azoxy compound only about two-thirds as much spin is transmitted to the second ring as in the azo compound. In structure XXIX the half-filled p–π orbital on the nitrogen can gain an electron either from the phenyl π system or from the lone p–π pair on the oxygen. Intuitively, it seems that these processes would be competitive and hence that the presence of the oxygen will modify the conjugative system.

Conclusions

The qualitative deductions from this work, *e.g.*, that the π system of pyridine is much the same as that of benzene, are unlikely to surprise many organic chemists. We have chosen to discuss these results in terms of valence-bond structures rather than in terms of the more popular molecular orbital theory although this has been used almost exclusively for calculating spin densities. Molecular orbital treatments would be quite straightforward, but we feel that for these rather complicated molecules a more useful end is achieved demonstrating the consistency of the results with the qualitative ideas of experimental chemists, as exemplified by valence-bond structures, than would be effected by extensive numerical calculations. It appears from the above results that, providing ionic structures are considered, this approach can be applied with some success to heterocyclic molecules as well as to the aromatic and aliphatic systems previously discussed.

Experimental Section

A. **Synthesis of Aminotroponeimines.** Several general methods were used for the synthesis of substituted aminotroponeimines. These are illustrated below, and the physical constants of the products obtained are given in Table III.

Method A. Preparation of Substituted Ethylenes. Ethylenes bearing the aminotroponeimine substituent were prepared by condensation of 4-formyl-*N*,*N*′-diethylaminotroponeimine with the appropriately substituted arylmethylenetriarylphosphonium chloride. The reaction is illustrated by synthesis of the ligand used for the preparation of **2**.

Table III

Compd no.	Method of preparation, % yield	Mp, °C, color	Solvent for recrystallization	Ligand							Chelates						
					Anal.							*Anal.*					
					Calcd			Found				Calcd			Found		
				Formula	C	H	N	C	H	N	Formula	C	H	N	C	H	N
1	A, 39	152.0–152.5, red plates	Ethanol–water	$C_{18}H_{21}N_3$	77.38	7.58	15.04	77.51	7.73	14.70	$C_{36}H_{40}N_6Ni$	70.26	6.55	13.66	70.61	7.13	13.62
2	A, 49	119.0–119.5, orange plates	Ethanol–water	$C_{18}N_{21}N_3$	77.38	7.58	15.04	77.67	7.66	14.88	$C_{36}H_{40}N_6Ni$	70.26	6.55	13.66	70.50	6.90	13.42
3	A, 62	220.0–221.0, red needles	Ethanol	$C_{19}H_{24}N_3I$	54.16	5.74	9.97 (I, 30.12)	53.67	5.73	9.46 (I, 29.26)	$C_{38}H_{46}N_6I_2Ni$	50.75	5.16	9.35 (I, 28.22)	49.77	5.33	8.9 (I, 27.14)
4[a]	A, 64	139.0–139.8, orange plates	Ethanol–benzene	$C_{19}H_{22}N_2$	81.97	7.97	10.16				$C_{38}H_{42}N_4Ni$	74.40	6.90	9.13	74.6	6.88	8.86
5[a]	B, 20	115.1–115.5, orange needles	Ethanol–water	$C_{15}H_{19}N_5$	66.88	7.11	26.01	66.90	7.93	26.23	$C_{30}H_{36}N_{10}Ni$	60.52	6.10	23.52	60.74	6.43	23.38
6[a]	B, 35	139.0, red needles	95% ethanol	$C_{15}H_{18}N_5Cl$	59.30	5.97	23.05 (Cl, 11.67)	59.21	5.92	22.70 (Cl, 11.43)	$C_{30}H_{34}N_{10}Cl_2Ni$	54.24	5.16	21.09 (Cl, 10.67)	54.54	5.15	21.22 (Cl, 10.65)
7[a]	B, 65	154.0–155.0, red needles	Ethanol	$C_{18}H_{20}N_6$	67.47	6.29	26.24	67.49	6.45	26.52	$C_{36}H_{38}N_{12}Ni$	61.99	5.49	24.10	61.51	5.81	24.13
8[a]	B, 65	149.0–149.5, red needles	Ethanol–water	$C_{18}H_{20}N_6$	67.47	6.29	26.24	67.97	6.54	26.22	$C_{36}H_{38}N_{12}Ni$	61.99	5.49	24.10	62.08	5.72	24.17
9	A, 59	120.4–121.8, orange needles	Acetonitrile	$C_{18}H_{20}N_3Cl$	68.89	6.42	13.39	69.48	6.51	13.4	$C_{36}H_{38}N_6Cl_2Ni$	63.18	5.60	12.28	63.75	5.92	12.0
10	A, 60	141.4–141.6, maroon plates	Ethanol	$C_{22}H_{25}N_3Fe$	68.23	6.51	10.85 (Fe, 14.4)	68.4	6.45	11.0 (Fe, 14.2)							
11	C, 27	117–118, yellow needles	Methanol	$C_{17}H_{14}N_4$	74.43	5.14	20.42	74.5	4.96	20.4	$C_{34}H_{26}N_8Ni$			18.51			18.9
12	C, 38	175.0–176.0, orange	Benzene–cyclohexane	$C_{19}H_{22}N_8O_2$	57.85	5.62	28.41	58.23	5.48	27.98							
13	C, 29	171.5–172.5, yellow-orange	Benzene–cyclohexane	$C_{17}H_{20}N_{10}O_2$	51.51	5.09	35.34	51.78	5.13	34.71							
14	C, ?	214–215.2, red prisms	Benzene	$C_{31}H_{20}N_2O_2$	82.28	4.46	6.19	82.5	4.59	5.96	$C_{62}H_{38}N_4O_4Ni$	77.4	3.98	5.83	77.0	3.94	6.05
15	C, 77.5	200–202, red needles	Benzene	$C_{31}H_{20}N_2S_2$ $\cdot C_6H_6$	76.85 78.97	4.16 4.66	5.78 4.98	79.0	4.70	5.31	$C_{62}H_{38}N_4S_4Ni$			5.46			5.42
16	C, 56	>300, wine-red needles	Benzene	$C_{31}H_{22}N_4$			12.44			12.4	$C_{62}H_{42}N_8Ni$			11.70			11.70
17	C, 55	240.0–240.2, orange	Benzene	$C_{35}H_{24}N_2$	88.95	5.12	5.93	89.3	5.18	5.60	$C_{70}H_{46}N_4Ni$	83.92	4.63		83.9	4.82	
18	C, 18	133–135, orange needles	Ethanol–benzene	$C_{27}H_{20}N_2O_2$	80.18	4.98	6.93	80.4	4.92	7.13	$C_{54}H_{38}N_4O_4Ni$	74.93	4.42	6.47	74.4	4.60	6.43
19	C, 32	165.0–166.0, red	Benzene–hexane	$C_{31}H_{24}N_6O_2$	72.64	4.72	16.40	72.73	4.99	16.51	$C_{62}H_{46}N_{12}O_4Ni$	68.83	4.29	15.54	69.52	4.60	14.94
20[a]	D, 81	101.5–102, red needles	Ethanol	$C_{17}H_{20}N_2$	80.91	7.99	11.10	81.3	8.08	11.0	$C_{34}H_{38}N_4Ni$	72.74	6.83	9.98	72.9	6.73	10.3

[a] A. D. Josey, U. S. Patent 3,385,874 (May 28, 1968).

A solution of 4.25 g (0.01 mol) of α-picolyltriphenylphosphonium hydrochloride[7] and 2.04 g (0.01 mol) of 4-formyl-*N*,*N*′-diethylaminotroponeimine in 105 ml of 0.2 *M* lithium ethoxide in ethanol was allowed to stand at room temperature for 7–10 days. The resulting deep red solution was poured onto 300 ml of ice-water and the resulting red mixture was extracted with three 300-ml portions of ether. The ether layers were combined, washed with water, and dried over anhydrous sodium sulfate. Distillation of the ether left a red, semisolid residue that was recrystallized from ethanol–water to give 1.35 g (49% yield) of orange plates. The nickel(II) chelate was prepared by reaction of the γ-substituted aminotroponeimine with a 10% excess of nickel acetate in aqueous ethanol. The product **2** was obtained in 77% yield as green clusters from benzene–ethanol. Ligands for the preparation of the chelates **1** and **3** were synthesized in a similar manner.

Method B. Preparation of Anils. The anils were prepared by condensation of 4-formyl-*N*,*N*′-diethylaminotroponeimine with the appropriate amine. The reaction is illustrated by the synthesis of the product derived from 4-chloro-1-aminopyrazole, which was converted to the chelate **6**.

To a solution of 1.0 g of 4-formyl-*N*,*N*′-diethylaminotroponeimine and 1.0 g of 4-chloro-1-aminopyrazole in 25 ml of benzene and 40 ml of absolute ethanol was added two drops of acetic acid. The solution was heated under reflux in such a manner that the alcohol was removed slowly by distillation. When 25 ml of distillate had been collected, 25 ml of absolute ethanol containing one drop of acetic acid was added to the distillation flask and the process was repeated until a total of 150 ml of distillate had been obtained. The remaining solvent was removed by distillation under vacuum and the residue was recrystallized from ether–petroleum ether to give 0.65 g of red needles, mp 135–137°. The product was converted to the nickel chelate **6** in the usual manner.

Method C. Preparation of *N*,*N*′-Diaryl-Substituted Aminotroponeimines. The general preparative method has been described previously.[1,2] It is illustrated by the preparation of *N*,*N*′-di(*p*-phenyl-α-azoxyphenyl)aminotroponeimine. A solution of 0.58 g (2.72 mmol) of *p*-phenyl-α-azoxyaniline,[8] 0.23 g (1.36 mmol) of tetrafluorocycloheptadiene (97% purity), and 0.54 g (5.44 mmol) of triethylamine in 25 ml of ethanol was refluxed for 5 hr. After cooling, the red solid was removed by filtration and recrystallized twice from benzene–cyclohexane to give 0.15 g of the substituted aminotroponeimine. The product was converted to the nickel chelate **19** in the usual manner.

B. Nmr. Proton nmr spectra were obtained at 60 MHz using a Varian HR-60 instrument. Except where otherwise stated, the solvent was deuteriochloroform. The chelate solutions were internally referenced to tetramethylsilane to avoid bulk susceptibility corrections. Calibration was by the usual audiofrequency sideband technique. Contact shifts are defined as the difference in frequency between corresponding protons in the nickel chelate and the diamagnetic zinc chelate or ligand. The assignments of the protons presented few ambiguities in the present compounds and are based on spin–spin multiplets (where observed), the relative intensities of the resonances, and intercomparisons among related compounds in the manner previously[1,2] described.

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Absence of Synergism in the Addition of Dichlorocarbene to Certain Oxygen-Functionalized Cyclohexenes

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Abstract: Reported are the relative reactivities toward CCl_2 addition at 80–85° of cyclohexene (1.00), cyclohexen-4-one ethylene acetal (0.44), 1-carboethoxycyclohexene (0.11), 2-carboethoxycyclohexen-4-one ethylene acetal (0.11), 1-carboethoxycyclohexen-4-one ethylene acetal (0.028), and cyclohexen-3-one ethylene acetal (0.012). No evidence is found for cooperative or synergistic addition of CCl_2 to these olefins, mediated by the ethylene acetal function. This conclusion is discussed in the light of a previous suggestion favoring such a mechanism. The reactivity data are analyzed in terms of substituent effects which operate mainly on a highly unsymmetrical transition state for CCl_2 addition.

Reactions of carbenes with heteroatomic substrates are of current interest.[2] Such reactive species as methylene and carboalkoxycarbenes react *via* ylide intermediates with a wide variety of substrates, including ethers, whereas *dihalocarbenes* are somewhat less avid. The latter do react with amines,[3] phosphines,[4] and sulfides,[5] and the "deoxidation" of alkoxides (or alcohols) may involve either a ylide or an alkoxydihalomethide anion.[6] CCl_2 is also able to strip oxygen from dimethyl sulfoxide[7] and pyridine *N*-oxide.[8] However, although reactions of CCl_2 with benzaldehyde[9] and benzophenone[10] appear to involve carbonyl ylides, similar reactions of CCl_2 with saturated ethers seem unknown. The following observations thus assume substantial importance.

The preference for CCl_2 addition to the central as opposed to the peripheral double bond of **1** decreases

(1) Fellow of the Alfred P. Sloan Foundation. Special Postdoctoral Fellow of the National Institutes of Health. This work was done at the Massachusetts Institute of Technology, while the author was a Visiting Scientist.

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