predominance of the exo isomer.[7] The assigned endo isomer of **4**, R = CO_2Et, could be epimerized to the exo isomer using lithium *tert*-butoxide in DMSO at room temperature[8] demonstrating that the two compounds are epimeric and confirming the assignments of the exo and endo isomers of **3**, R = CO_2Et. Lithium aluminum hydride reduction of the *endo*-**3** ester (**1**, R_1 = CO_2Et) gives the corresponding *endo*-hydroxymethyl compound (**1**, R_1 = CH_2OH) shown to be identical with the minor product obtained by vpc collection of the original alcohol mixture. Similar reduction of the *exo*-**3** ester (**1**, R_2 = CO_2Et) gives *exo*-9-hydroymethylbicyclo[6.1.0]non-2-ene (**1**, R_2 = CH_2OH) whose nmr spectrum ($CDCl_3$) displays a hydroxymethylene doublet (J = 7 Hz) at τ 6.5 (2 H), an olefinic multiplet centered at 4.5 (2 H), and absorptions extending to 9.5 ppm. Injection of this compound into the vpc gives a single peak whose retention time is identical with the rearranged major product. Preparative collection of a sample from the vpc and spectral comparison confirmed the rearrangement to **2** (R_1, R_2 = H, CH_2OH) on the vpc column. Identical results can be obtained by injecting **3**, R = CH_2OH, onto a column filled with glass beads at 340° [9] under helium gas flow, limiting pyrolysis time to seconds instead of 15 min by vpc injection. The stereoselective pyrolytic rearrangement constitutes a facile synthesis of a 3-substituted 1,4-cyclononadiene in good yield from readily available starting material.

Acknowledgment. The financial support of the Petroleum Research Fund administered by the American Chemical Society (1207-G1), the Research Corporation (Frederick Gardner Cottrell Grant), and the Research Committee—UMSL is gratefully acknowledged.

[7] P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).

[8] Attempted epimerizations by standard techniques were surprisingly futile.

[9] Conversion was incomplete at lower temperatures with less than 10% conversion at 240°, the maximum temperature in the vpc system. Thus, the rearrangement in the vpc does not occur specifically in the injection port or detector.

David L. Garin
Department of Chemistry, University of Missouri—St. Louis
St. Louis, Missouri 63121

Received April 16, 1970

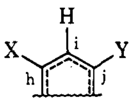
Nuclear Magnetic Resonance Spectroscopy. Studies of Carbon-13 Spectra of *n*-Alkyl Nickel(II) Aminotroponiminates[1]

Sir:

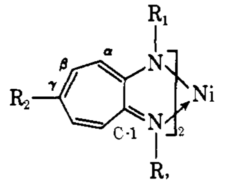
In a previous communication from these laboratories[2] we reported the ^{13}C nmr spectrum of nickel(II) N,N'-di(p-tolyl)aminotroponiminate and proposed that, at least qualitatively, the ^{13}C isotropic shifts were consistent with the propagation of unpaired spin density by way of both the π and σ electrons of the ligand. This analysis assumed that the π contribution to the ^{13}C hyperfine coupling constant, a^{C_i}, could be approximated by the Karplus–Fraenkel equation[3] (eq 1),

$$a^{C_i} = (S^C + Q_{C_iH}{}^C + Q_{C_iC_h}{}^C + Q_{C_iC_j}{}^C)\rho_{C_i}{}^\pi + Q_{C_hC_i}{}^C\rho_{C_h}{}^\pi + Q_{C_jC_i}{}^C\rho_{C_j}{}^\pi \quad (1)$$

where S^C is the proportionality factor for the polarization of the 1s electrons and the Q's are the proportionality factors for the 2s electrons.[4] The spin density in the p_π orbital centered at C_i of the molecular fragment **1** is $\rho_{C_i}{}^\pi$, while $\rho_{C_h}{}^\pi$ and $\rho_{C_j}{}^\pi$ are for the adjacent atoms h and j. We have now extended our studies to include the N-alkyl-substituted aminotroponiminates **2a** and **2b** and the results provide further evidence for the propagation of unpaired spin density through the σ electronic framework of the ligand.



1



2a, $R_1 = CH_3$; $R_2 = H$
2b, $R_1 = CH_2CH_3$; $R_2 = CHO$
2c, R_1 = p-tolyl; $R_2 = H$

The spectral data for the complexes **2a** and **2b** are summarized in Table I. Observation and assignment of the ^{13}C spectrum of **2a** was straightforward, consistent with the known, large (square planar)/tetrahedral ratio of the forms of the complex.[5a,b] However, **2b** is largely in the paramagnetic tetrahedral form[6] with concurrent difficulties in observing and assigning its ^{13}C resonances. For this complex, only the carbon resonances corresponding to the β-C and the CH_2 and CH_3 groups could be assigned with certainty by single-frequency proton-decoupling experiments.[2] The carbon resonances, tentatively assigned to the α-C and CHO group, were observed with proton noise decoupling in the appropriate proton region of the spectrum. As with **2c**, no resonances assignable to the γ-C or C-1 were observed. Normally, 1000 scans of a $\approx$0.4 M sample were required to give satisfactory resonance peaks.

Previously,[2] eq 2 was used to predict ratios of the ^{13}C and ^1H isotropic shifts for the ring positions of the cycloheptatriene moiety, using the spin densities $\rho_{C_i}{}^\pi$ of the paramagnetic form of the complex computed from the proton isotropic shifts,[5,6] the equilibrium for the paramagnetic $\rightleftarrows$ diamagnetic interconversion, and the McConnell equation.[7] The results of the same procedure for **2a** and **2b** are given in Table II which also includes the experimental values determined from the shifts in Table I. Values for **2c** are included for comparison.[2]

$$\sigma_{con}{}^{C_i}/\sigma_{con}{}^{H_i} \approx -6.2 + 2.5(\rho_{C_h}{}^\pi + \rho_{C_j}{}^\pi)/\rho_{C_i}{}^\pi \quad (2)$$

---

[1] Supported by the National Science Foundation, and by the Public Health Service, Grant No. 11072, from the Division of General Medical Services.

[2] D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 4484 (1970).

[3] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

[4] We have taken the Q's to be independent of the nature of the complex, although they are in fact expected to be sensitive to structural parameters.[3]

[5] (a) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, **85**, 397 (1963); (b) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

[6] D. R. Eaton, A. D. Josey, and R. E. Benson, *J. Amer. Chem. Soc.*, **89**, 4040 (1967).

[7] H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).

Table I. Proton and Carbon-13 Spectral Data for Nickel(II) Aminotroponiminates **2a**, **2b**, and the Corresponding Free Ligands

	Carbon, ppm						
	α-C	β-C	γ-C	C-1	CH_2	CH_3	CHO
			2a				
Proton isotropic shift[a]	+2.15	−1.17	−3.00			−3.95	
^{13}C shift in ligand[b]	−56.1	−79.1	−63.7	−100.1		+20.7	
^{13}C shift in complex[b]	−83.3	−65.0	−86.5	−84.2		+4.8	
^{13}C isotropic shifts	−27.2	+14.1	−22.8	+15.9		−15.9	
			2b				
Proton isotropic shift[a]	+77.2	−36.4			−146.4	−14.3	+18.8
^{13}C shift in ligand[b]	−54.6	−81.7	−72.4	−99.8	+12.7	+39.0	−136.8
^{13}C shift in complex[b]	−666.8	+594.6	*c*	*c*	−614.5	−200.8	−533.6
^{13}C isotropic shifts	−612.2	+676.3	*c*	*c*	−627.2	−239.8	−396.8

[a] Proton isotropic shifts for **2a** and **2b** were taken from ref 5b and 6, respectively; + = upfield, − = downfield. [b] Carbon-13 shifts are relative to the carbon resonance of CH_2Cl_2 used as solvent. The solutions were 0.4 *M* and, with the proton noise decoupler on the sample temperatures were about 40°. The observing frequency was 15.08 MHz. [c] Unobserved.

Table II. Predicted and Experimental Values for $\sigma_{con}{}^{C_i}/\sigma_{con}{}^{H_i}$ for the Paramagnetic Forms of the Nickel(II) Aminotroponiminates

	Ligand Position					
	α-C	β-C	γ-C	CH_2	CH_3	CHO
			Predicted[a]			
	−8.4	−18.1	−8.0			
			Experimental			
2a	−12.65	−12.05	−7.60		+4.03	
2b	−7.93	−18.58	*b*	+4.28	+16.68	−21.11
2c	−14.9	−10.5	*b*			

[a] Predicted values are the result of using the same set of $\rho_{C_i}{}^{\pi}$'s for each complex. There are only minor changes[5,6] in the experimental values between the complexes. The set used is $\rho_{C\text{-}\alpha}{}^{\pi} = +0.040$, $\rho_{\beta\text{-}C}{}^{\pi} = -0.020$, $\rho_{\gamma\text{-}C}{}^{\pi} = +0.055$, and $\rho_{C\text{-}1}{}^{\pi}$ (from ref 5b) = −0.015. [b] Unobserved.

The pattern of the experimental ratios for **2a** is the same as that previously observed[2] for **2c**, and it is important to note that for **2a** good agreement is obtained for the γ position, which was not observed for **2c**, consistent with a rapid attenuation of σ delocalization with the intervening bonds. However, the results for **2b** are markedly different from those of the other two complexes, in showing close agreement between experimental and predicted values of $\sigma_{con}{}^{C_i}/\sigma_{con}{}^{H_i}$. The complexes **2b** and **2c** exhibit proton isotropic shifts within 2 ppm for the α and β positions, but the ^{13}C isotropic shifts differ by about a factor of two. It appears, therefore, that the mechanisms of the proton and ^{13}C isotropic shifts are markedly different in these complexes, with the proton ring position being less sensitive to structural change, as witnessed by the substantial constancy of the experimental $\rho_{C_i}{}^{\pi}$ values.[5,6] Again, it appears that propagation of spin density through σ bonds can be important in determining the direction and magnitude of the ^{13}C isotropic shifts, but is probably of less importance in determining the contiguous proton shifts. In **2b**, the situation is probably complicated by the formyl group which may interact strongly with the electrons in the π framework of the cycloheptatriene ring as proposed to explain the apparent anomalous positive isotropic shifts of the formyl proton.[6]

Further evidence demonstrating the sensitivity of the ^{13}C isotropic shifts to the σ spin density is apparent from the shifts of the carbons of the *N*-alkyl substituents of **2a** and **2b**. For the CH_3 group of **2a** and the CH_2 group of **2b** $\sigma_{con}{}^{C\mathrm{H}}/\sigma_{con}{}^{\mathrm{C}H}$ can be written as

$$\sigma_{con}{}^{C\mathrm{H}}/\sigma_{con}{}^{\mathrm{C}H} = \frac{\gamma^{\mathrm{H}}}{\gamma^{\mathrm{C}}}\frac{a^{C\mathrm{H}}}{a^{\mathrm{C}H}} = \frac{\gamma^{\mathrm{H}}}{\gamma^{\mathrm{C}}}\frac{Q_{\mathrm{NC}}{}^{\mathrm{C}}\rho_{\mathrm{N}}{}^{\pi} + k^{\mathrm{C}}\rho_{\mathrm{C}}{}^{\sigma}}{Q_{\mathrm{NCH}}{}^{\mathrm{H}}\rho_{\mathrm{N}}{}^{\pi} + k^{\mathrm{H}}\rho_{\mathrm{H}}{}^{\sigma}} \quad (3)$$

where $\rho_N{}^{\pi}$ is the p_{π} spin density at the nitrogen, and is positive.[5] $Q_{NC}{}^{C}$ and $Q_{NCH}{}^{H}$ are proportionality constants which are negative and positive, respectively. $\rho_C{}^{\sigma}$ and $\rho_H{}^{\sigma}$ are the σ spin densities at carbon and proton, respectively, while k^C and k^H are positive constants. Thus, the π and σ contributions to the ^{13}C isotropic shifts are of opposite sign, while they are of the same sign for the proton, consistent with the small experimental ratio. However, the σ contribution to the ^{13}C isotropic shift must be dominant, as witnessed by the observed downfield shift. Any π contribution to the shift of the CH_3 carbon in **2b** is expected to be small and σ effects appear to be dominant as judged by a fourfold increase in the ratio $\sigma_{con}{}^{C\mathrm{H}}/\sigma_{con}{}^{\mathrm{C}H}$ between the CH_2 and CH_3 groups. It can be seen from these results that the ^{13}C isotropic shifts of the alkyl group carbons are more sensitive to σ spin density than are the shifts of proton directly attached to the same carbon.

Acknowledgments. We are greatly indebted to Dr. R. E. Benson of the Central Research Department of E. I. du Pont de Nemours and Company for samples of the ligands and complexes.

(8) Address correspondence to this author.

David Doddrell, John D. Roberts[8]
Contribution No. 4072
Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109

Received June 11, 1970

Wavelength Dependence and Orbital Symmetry Controlled Sensitizer Selectivity in the Photochemistry of 2-Benzal-5-methylcyclopentanone

Sir:

A number of α,β-unsaturated carbonyl compounds undergo different photochemical reactions in solution with different wavelengths.[1] This behavior implies the existence of two or more reactive excited states which

(1) For leading references see (a) E. F. Ullman, *Accounts Chem. Res.*, 1, 353 (1968) and (b) E. F. Ullman and N. Baumann, *J. Amer. Chem. Soc.*, 90, 4158 (1968); in press. (c) N. Baumann, M. Sung, and E. F. Ullman, *ibid.*, 90, 4157 (1968).