Table I. Comparison of CW and SEFT Nmr Signal-to-Noise

| Compound[a] | CW nmr[b] Total time, min | S/N[e] | SEFT nmr[c] Total time, min | S/N[e] | Improvement[d] |
|---|---|---|---|---|---|
| Acetic acid | 17 | 12[f] | 2 | 44[f] | 11 |
| 3 *M* acetic acid (aq) | 53 | 4[f] | 6 | 11[f] | 8 |
| 1,3,5-Trimethylbenzene | 53 | 16[g] | 2 | 28[g] | 9 |
| Hexamethylbenzene, 21 mol % in $CHCl_3$ | 23 | 8[g] | 6 | 24[g] | 6 |

[a] Neat liquid unless otherwise indicated. Room temperature. [b] At 15.07 MHz. See text and ref 7. 11.6-mm i.d. sample tubes were used. Sweep width was 2000 Hz. Sweep time was 50 sec/scan. [c] At 9.8 MHz. See text and ref 6. 12.8-mm i.d. sample tubes were used. $\tau$ was 23 msec, there were 66 echoes per burst, and the recycle time between bursts was about 20 sec. The output filter time constant was 40 $\mu$sec. [d] Ratio of S/N values for SEFT and CW nmr, for equal total accumulation times. [e] Using the "practical" definition of 2.5 times the peak height divided by the peak-to-peak noise. [f] Carbonyl peak. [g] Inner peak of methyl quartet.

retical improvement,[1] but sufficient to be of great interest to the user of carbon-13 nmr.

We have also made some ordinary Fourier-transform nmr determinations. As expected, S/N ratios were appreciably lower than with SEFT for comparable total scan times, except in molecules with very short $T_1$ and $T_2$ values, such as glycerin, where ordinary FT nmr would be indicated.

Calculations by Waugh[8] indicate that under *optimum conditions* DEFT should be slightly more efficient than SEFT. The important advantage of SEFT, however, is that the signal at $t = 0$ (the time of the accumulated echo maximum) is not obscured by a strong rf pulse. Both in ordinary FT nmr and in DEFT, the rf pulse causes an uncertainty in $t = 0$ (the start of the accumulated free-induction decay) and a feedthrough of the excitation pulse, especially if long accumulation times are used. This causes frequency-dependent phase errors and spurious spectral features.[9] In using SEFT, we have found no base-line problems and no need for phase corrections. The cosine transform in Figure 2C is typical.

So far, we have made no measurements on samples more dilute than 1 *M* owing to a lack of field-frequency lock, which has prevented us from using accumulation times of more than about 15 min. We plan to do further SEFT experiments with improved instrumentation.

Finally, we wish to discuss those cases for which $T_1/T_2$ is appreciably larger than unity, and to present experimental evidence for the loss of effectiveness of Fourier-transform nmr in such cases, as predicted by Ernst and Anderson.[1] There are two possible contributions to $1/T_2$ that usually do not affect $1/T_1$. One is modulation of chemical shifts or coupling constants through intermolecular or intramolecular chemical exchange.[10] The other is residual broadening from scalar coupling to a quadrupolar nucleus undergoing rapid relaxation,[11] such as $^{35}Cl$ or $^{14}N$.

We believe we have encountered the effect of exchange in the case of cyclohexane, which yielded a relatively poor SEFT spectrum. Since much larger S/N ratios were obtained with cyclohexane-$d_{12}$, this is evidence for a modulation of carbon–hydrogen coupling by the chair–chair isomerization process, the effect being observable in spite of the very fast rate at room temperature.[12] Modulation of carbon–hydrogen coupling by chemical exchange will not affect the S/N ratio if proton decoupling is used.

In many instances carbons directly bonded to nitrogen or chlorine yielded relatively weak signals. Since the shortening of the carbon-13 $T_2$ by a quadrupolar nucleus is proportional to the relaxation time of the latter and the square of the coupling constant,[11] the loss of intensity can vary.

In some compounds, such as amino acids, both the exchange and quadrupolar effects appear to be operating.[13]

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(8) J. S. Waugh, *J. Mol. Spectrosc.*, in press.
(9) I. Salmeen and M. P. Klein, presented in part at the 11th Experimental Nmr Conference, Pittsburgh, Pa., April 1970.
(10) C. S. Johnson, Jr., *Advan. Magn. Resonance*, **1**, 33 (1965).
(11) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, Oxford, 1961.
(12) A. Allerhand, F. M. Chen, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3040 (1965); F. A. L. Anet and A. J. R. Bourne, *J. Amer. Chem. Soc.*, **89**, 760 (1967).
(13) A. Allerhand and D. W. Cochran, unpublished.
(14) National Institutes of Health Predoctoral Fellow, 1967–1970.

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## Nuclear Magnetic Resonance Spectroscopy. Observation of Carbon-13 Resonances in a Paramagnetic Transition Metal Complex. Nickel(II) N,N′-Di(*p*-tolyl)aminotroponiminate[1]

*Sir:*

The discovery[2] of the extraordinary chemical shifts of the proton magnetic resonances of paramagnetic Ni(II) aminotroponiminates has been of great value for probing the nature of metal–ligand bonding especially because sharp resonances are observed as the result of the short electronic relaxation times of the tetrahedral forms[3] which are associated with the square-planar (diamagnetic) $\rightleftharpoons$ tetrahedral (paramagnetic) equilibria. These complexes are expected to provide a useful starting point for natural-abundance $^{13}C$ nmr studies of paramagnetic transition metal complexes. We report in this study observation of eight of the possible nine carbon resonances of the N,N′-di(*p*-tolyl) derivative **1**, and present evidence for nonzero spin density in the $\sigma$ framework of the ligand.

Typical carbon spectra of the complex and the ligand are shown in Figure 1, and a summary of the

(1) Supported by the National Science Foundation and by the Public Health Service (Grant No. 11072), Division of Research Grants, National Institutes of Health.
(2) (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962); (b) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, **85**, 397 (1963); (c) D. R. Eaton, A. D. Josey, and R. E. Benson, *ibid.*, **89**, 4040 (1967); (d) for a review, see R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969).
(3) G. N. La Mar, *J. Amer. Chem. Soc.*, **87**, 3567 (1965).

Table I. Proton and Carbon-13 Spectral Data for Ni(II) N,N′-Di(*p*-tolyl)aminotroponiminate and the Free Ligand

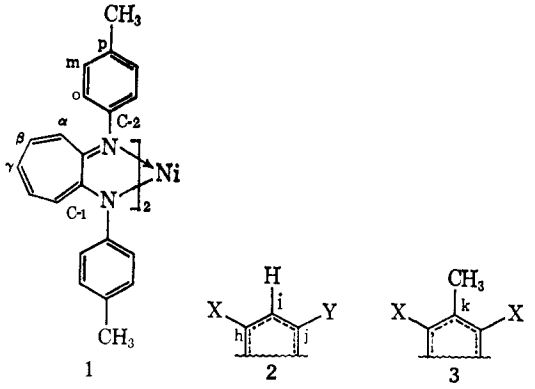
| | Proton resonances | | | | | |
|---|---|---|---|---|---|---|
| | α-H | β-H | γ-H | *o*-H | *m*-H | $CH_3$ |
| Chemical shifts[a] in ligand (ppm) | −6.7 | −6.7 | −6.7 | −7.1 | −7.1 | −2.3 |
| Chemical shifts[a] in complex (ppm) | +69.2 | −45.2 | +97.4 | +6.9 | −21.0 | −25.9 |
| Proton isotropic shifts (ppm) | +75.9 | −38.5 | +104.1 | +14.0 | −13.9 | −23.6 |

| | Carbon resonances | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | α-C | β-C | γ-C | *o*-C | *m*-C | $CH_3$ | *p*-C | C-1 | C-2 |
| Chemical shifts[b] in ligand (ppm) | −37.3 | −55.9 | −44.2 | −45.2 | −52.6 | +56.3 | −55.9 | −74.9 | −65.4 |
| Chemical shifts[b] in complex (ppm) | −1236.0 | +349.3 | u | −281.5 | +40.4 | +110.0 | −184.8 | −142.7 | −76.8 |
| One-bond $J_{CH}$ (Hz)[e] | 150d | 148d | u | 163d | 157d | 125q | | | |
| Carbon isotropic shifts | −1198.7 | +405.2 | u | −236.3 | +93.0 | +53.7 | −128.9 | −67.8 | −11.4 |
| π spin density[c] at $C_i$ | +0.042 | −0.021 | +0.058 | +0.008 | −0.008 | | +0.011 | −0.015 | −0.006 |

| | $^{13}C$ shift compared with | | | | |
|---|---|---|---|---|---|
| | α-H | β-H | *o*-H | *m*-H | $CH_3$ |
| Predicted[d] | −8.4 | −18.1 | −10.6 | −12.0 | −2 |
| Observed | −14.9 | −10.5 | −16.9 | −6.7 | −2.3 |

[a] Proton shifts relative to TMS were taken from ref 2a,b, + = upfield, − = downfield; μ = unobserved; d = doublet; q = quartet. [b] Carbon-13 chemical shifts are relative to chloroform used as solvent. [c] π spin densities are those reported in ref 2a and were determined from the proton isotropic shifts, assuming a pure π delocalization of unpaired spin density. The C-1 and C-2 $\rho_\pi$ spin densities are calculated values, while that for the *p*-C was determined from the *p*-H shift in the diphenyl analog. [d] Computed using eq 3-6. [e] Coupling constants are accurate to ±5 Hz.

spectral data, which is featured by $^{13}C$ chemical shifts extending over *~24,000 Hz (~1600 ppm)*, is given in Table I. The assignments of resonance lines to the α-, β-, *ortho-*, *meta-*, and methyl carbons were made from intensities and multiplicities in the undecoupled spectrum combined with single-frequency proton decoupling experiments.[4] These assignments seem quite certain. The *para*-carbon resonance was assigned by its intensity relative to the *meta*-carbon and the expected magnitude of the downfield isotropic shift. The resonances of C-1 and C-2 were assigned by default and could be reversed. As expected, no C,H couplings were observed for the lines assigned to C-1, C-2, and the *para*-carbon in the undecoupled spectrum. There is a monotonic, but not very linear, correspondence with a negative slope between the contact shifts observed for the carbons and the directly attached hydrogen. On the average, the carbon shifts are about ten times those of the directly attached hydrogens.



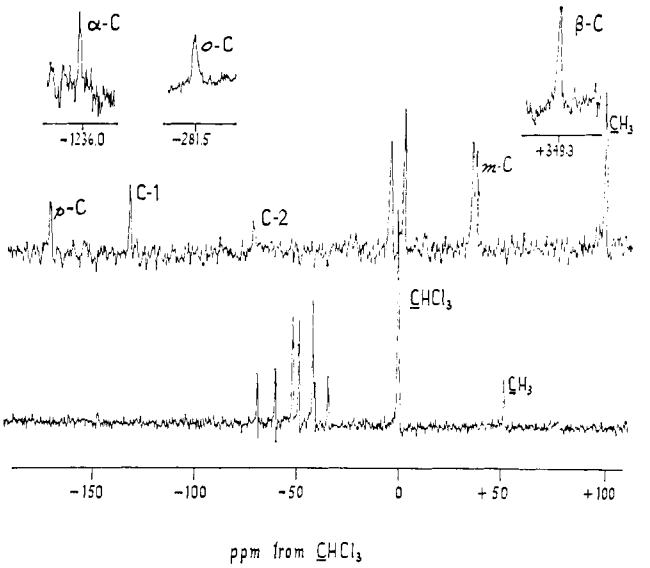




Figure 1. Upper trace: single-frequency proton-decoupled (centered at methyl resonance) $^{13}C$ spectrum of nickel(II) N,N′-di(*p*-tolyl)aminotroponiminate in $CHCl_3$ (1000 scans). Lower trace: noise-decoupled $^{13}C$ spectrum of N,N′-di(*p*-tolyl)aminotroponimine in $CHCl_3$ (50 scans). The total width of each spectrum is 5000 Hz.

In complexes such as **1** the observed proton shifts have been assumed to originate primarily from contact interactions which result from the transmission of π-unpaired spin density to the carbons. On this basis, the expected shift value of nucleus N is related to the electron–nucleus hyperfine coupling constant $a^N$ by eq 1.[2] Thus, for the ratio of shifts between carbon

$$\sigma_{con}{}^{N} = -a^{N}(\gamma_e/\gamma_N)(g_e\beta_e S[S+1]/3kT) \times (\exp[\Delta G/RT]+1)^{-1} \quad (1)$$

and hydrogen, we would have

$$\sigma_{con}{}^{C_i}/\sigma_{con}{}^{H_i} = a^{C_i}\gamma_H/a^{H_i}\gamma_C \quad (2)$$

(4) Single proton-decoupling frequencies could be fitted to previously assigned[2a,b] resonances in the proton spectrum to within ±15 Hz. The $^{13}C$ spectra were determined as described by F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967).

If spin density in the $\pi$ framework were the only mechanism causing the shifts, the following relationships are expected to apply, which relate the carbon-13 and proton isotropic shifts to the appropriate $a^C$ and $a^H$ value for the ring positions of the molecular fragments **2** and **3**, where $\rho_{Ci}^{\pi}$ is the spin density in the $p_\pi$ orbital centered at $C_i$.[5]

$$\sigma_{con}^{C_i}/\sigma_{con}^{H_i} = (\gamma_H/\gamma_C)(35.5\rho_{C_i}^{\pi} - 14.0[\rho_{C_h}^{\pi} + \rho_{C_i}^{\pi}])/(-22.5\rho_{C_i}^{\pi}) \quad (3)$$

$$\approx -6.2 + 2.5(\rho_{C_h}^{\pi} + \rho_{C_i}^{\pi})/\rho_{C_i}^{\pi} \quad (4)$$

$$\sigma_{con}^{CH_3}/\sigma_{con}^{CH_3} = (\gamma_H/\gamma_C)(-14.0\rho_{C_k}^{\pi}/27.5\rho_{C_k}^{\pi}) \quad (5)$$

$$\approx -2.1 \quad (6)$$

Because only the resonances of the $\alpha$-, $\beta$-, *ortho*-, *meta*-, and methyl carbons were assigned with real certainty, the following discussion will be centered around these positions. It is readily seen that the predicted ($\sigma_{con}^{C_i}/\sigma_{con}^{H_i}$) and observed ($\sigma_{obsd}^{C_i}/\sigma_{obsd}^{H_i}$) values are in major disagreement for the $\beta$ and *meta* positions whereas good agreement is obtained for $\sigma_{con}^{CH_3}/\sigma_{con}^{CH_3}$. However, in all cases, the signs of the ratio, predicted to be negative because $(\rho_{C_h}^{\pi} + \rho_{C_i}^{\pi})/\rho_{C_i}^{\pi}$ is negative, of the carbon and corresponding proton isotropic shifts are reproduced experimentally. No experimental determinations for the ratio are possible for the $\alpha$ and *ortho* positions because $\rho_{C\text{-}1}^{\pi}$ and $\rho_{C\text{-}2}^{\pi}$ are unknown; however, if the calculated values[2a] of these parameters are used it is readily seen that the predicted ratios are too low. The discrepancies between the predicted and observed ratio of contact shifts for carbon and hydrogen are sizable but might be regarded as tolerable in view of the approximate nature of the Karplus–Fraenkel treatment[5b] and the serious reservations that have been suggested for its application.[5b] However, in our view, the discrepancies fall into a pattern which indicates that there is an additional important mechanism contributing to the isotropic shifts and involve transmission of spin density by the $\sigma$ framework of the ligand. The argument is based on the expectation that positive spin density arising from $\sigma$ delocalization at the $\beta$ and *meta* position would reduce the predicted upfield carbon shifts and increase the downfield proton isotropic shifts.[6] The overall result would be to reduce $\sigma_{con}^{C_i}/\sigma_{con}^{H_i}$ for these two positions, in agreement with experiment. The reverse situation is expected for the $\alpha$ and *ortho* positions, again in accord with experiment. The methyl group should exhibit a ratio in better agreement with theory, because effect of $\sigma$ delocalization should be markedly reduced at this position as the result of attenuation through the intervening bonds. Because a tetrahedral Ni(II) complex has only unpaired electrons of $\pi$ symmetry available for interaction with the ligand, a likely pathway of introducing spin density into the $\sigma$ framework would be an indirect $\pi$–$\sigma$ polarization.

Further evidence in support of positive spin density in the $\sigma$ framework of the ligand comes from previous pmr studies. It has been noted[2a,c] that, if the *p*-tolyl group is replaced by ethyl or *n*-propyl, large negative contact shifts are observed for the $CH_2$ and $CH_3$ groups of the chain. The only reasonable mechanism of placing spin density at these positions is *via* the $\sigma$ framework, and thus it is not unreasonable to expect nuclei at ring positions to also exhibit isotropic shifts resulting from such a mechanism. On this basis, the observed small isotropic shifts of C-1 and C-2 seem quite reasonable. The $\sigma$ and $\pi$ effects, though large, should be opposite in sign and could be close to equivalence at these positions. The present results indicate that spin densities calculated from proton isotropic shifts, assuming purely $\pi$ delocalization, are likely to be unreliable.

This study is the first reported of the $^{13}C$ nmr spectrum of a paramagnetic transition metal complex capable of showing multiple resonances, and although not all of the carbon resonances were observed, it seems clear that $^{13}C$ contact shifts will be extremely useful in probing the nature of metal–ligand interactions.

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(5) (a) H. M. McConnell, *J. Chem. Phys.*, 24, 632, 764 (1956); *Proc. Nat. Acad. Sci.*, 43, 741 (1957); (b) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 35, 1312 (1961); G. K. Fraenkel, *Pure Appl. Chem.*, 4, 143 (1962).

(6) The predictions about the direction of the shifts are based on consideration of $\pi$–$\pi$ configurational interactions[2a] which suggest that negative spin density at the carbon will produce positive spin density at the proton and a downfield shift.

## The Structure of a Novel Lipid from the Antibiotic Diumycin

*Sir:*

The isolation and characterization of a new group of phosphorus-containing antibiotics, the diumycins, have been reported.[1,2] The antibiotics are highly active *in vitro* against gram-positive bacteria and exhibit a remarkable duration of action *in vivo*. A single dose of 6.7 mg/kg of diumycin, administered subcutaneously to mice 14 days prior to challenge with a lethal dose of *Streptococcus pyogenes* $C_{203}$, provides protection to 50% of the mice injected.[1]

Recently, structures have been assigned to the optically inactive lipids obtained by hydrolysis of the related antibiotics prasinomycin[3] and moenomycin.[4] We now wish to present evidence for the structures of the

(1) E. Meyers, D. S. Slusarchyk, J. L. Bouchard, and F. L. Weisenborn, *J. Antibiot.*, 22, 490 (1969).

(2) The diumycins are members of a family of antibiotics that includes: prasinomycin,[2a] moenomycin,[2b] 11,837RP,[2c] 8036RP,[2d] 19,402RP,[2e] and macarbomycin.[2f] (a) F. L. Weisenborn, J. L. Bouchard, D. Smith, F. Pansy, G. Maestrone, G. Miraglia, and E. Meyers, *Nature (London)*, 213, 1092 (1967); (b) G. Huber, U. Schacht, H. L. Wiedenmuller, J. Schmidt-Thome, I. Duphorn, and R. Tschesche, *Antimicrob. Ag. Chemother. 1965*, 737 (1966); (c) Rhone-Poulenc, Belgian Patent 653,168 (1965); (d) Rhone-Poulenc, South African Patent 65/6204 (1966); (e) Rhone-Poulenc, Netherlands Patent 68,02093 (1968); (f) S. Takahashi, A. Okanishi, R. Utahara, K. Nitta, K. Maeda, and H. Umezawa, *J. Antibiot.*, 23, 48 (1970).

(3) W. A. Slusarchyk and F. L. Weisenborn, *Tetrahedron Lett.*, 659 (1969).

(4) R. Tschesche, F.-X. Brock, and I. Duphorn, *ibid.*, 2905 (1968); R. Tschesche, F.-X. Brock, and I. Duphorn, *Justus Liebigs Ann. Chem.*, 720, 58 (1968).