of **2** and polymer, the methanol–benzene mixture was reduced in volume to 25% of the original on a rotary evaporator. The residual solution was analyzed on an LKB-9000 gas chromatograph–mass spectrometer. The chromatograph was fitted with a 6 ft × 0.5 in. glass column packed with 3% OV-1 on high performance Chromosorb W, and operated at a helium flow rate of 30 ml/min with a programmed temperature of 5°/min from 90 to 200°.

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Nuclear Magnetic Resonance Spectroscopy. Nitrogen-15 and Carbon-13 Spectra of Complexes of Ethylenediaminetetraacetic Acid (EDTA) with Closed-Shell Metal Ions[1]

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Abstract: The ^{15}N and ^{13}C chemical shift changes have been determined for ethylenediaminetetraacetic acid (EDTA) as the result of changes in pH and complex formation with closed-shell metal ions. The carboxyl-carbon ^{13}C shifts in parts per million resulting from complex formation with metal ions are generally smaller than the concomitant shifts of the ^{15}N resonances which themselves are not large. The comparatively small ^{15}N chemical shift changes of EDTA upon metal complex formation are probably due to near-cancellation of variations in local paramagnetic and diamagnetic shielding terms. This may be a general phenomenon for ligands lacking a large local paramagnetic contribution to the shielding of the nitrogen donor atoms.

The binding of metal ions to amino acids and proteins is a subject of very considerable biochemical importance into which studies using nuclear magnetic resonance (nmr) spectroscopy can be expected to lead to significant insight. For initial studies by ^{13}C and ^{15}N nmr spectroscopy of the interactions of amino acids and proteins with metal ions, ethylenediaminetetraacetic acid (EDTA) provided a quite convenient model system. EDTA is an outstanding complexing agent for metal ions,[2] and a great deal of information is available about its complexes. Much of this has come from proton nmr spectra,[3-10] although a ^{23}Na nmr study of the Na(I)–EDTA complex has emphasized the importance of nitrogen binding in the complexation of sodium.[11]

Because the protons of the EDTA ligand are more distant from the atoms intimately involved in bonding to the metal ion, it seemed possible that ^{13}C and ^{15}N nmr spectroscopy of metal–EDTA complexes would reveal effects that do not appreciably affect proton nmr spectra. This expectation is heightened by the presence of the 2p electrons of carbon and nitrogen, which allows for paramagnetic contributions to the nuclear shielding[12] and makes for the much larger chemical shift ranges of ^{13}C and nitrogen nmr by comparison with proton nmr.[13-15]

Results and Discussion

Chemical Shifts. There was some initial controversy over the sites of protonation of EDTA tetraanion;[2] later studies by proton nmr strongly indicated that the first two protons added to the tetraanion primarily go on to the nitrogens.[3,16,17]

To check this conclusion, we have measured the ^{13}C chemical shift changes of the carboxyl group upon protonation of acetate ions, glycinate ions, and the tetraanion of EDTA. These data are given in Table I and support the conclusions drawn by earlier workers from proton nmr results. The key finding here is that the upfield shifts of the carboxyl ^{13}C resonance upon pro-

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Table I. Carboxyl ^{13}C Chemical Shift Changes upon Protonation of EDTA, Glycine, and Acetic Acid

Protonation step	Change in carboxyl ^{13}C chemical shift,[a] ppm
$Y^{4-} \rightarrow H_2Y^{2-}$	−8.4
$H_2NCH_2COO^- \rightarrow H_3N^+CH_2COO^-$	−8.4
$H_3N^+CH_2COO^- \rightarrow H_3N^+CH_2COOH$	−2.5
$CH_3COO^- \rightarrow CH_3COOH$	−4.0

[a] Positive values correspond to downfield shifts on protonation.

tonation of acetate ion and the carboxyl group of the zwitterion of glycine are both much smaller than the identical shifts observed for protonation of the amino group of the glycine anion and diprotonation of the tetraanion of EDTA.[18]

The ^{15}N chemical shifts upon diprotonation of the tetraanion of EDTA are given in Table II. The changes in the nitrogen resonance position with addition of each proton are of comparable magnitude to the downfield shift in the range of 20–23 ppm upon protonation of aliphatic amines.[19,20] Furthermore, studies of the pH dependence of the ^{15}N chemical shift of glycine have shown that there is a downfield shift of about 12 ppm on protonating the nitrogen atom, but an upfield shift of 2 ppm as the carboxyl group is protonated.[21] Thus our ^{15}N data also support the conclusion that the first two protons which combine with the tetraanion of EDTA bind to the nitrogen atoms.

Table II. Protonation and Complexation Chemical Shift Changes[a] of EDTA

Complex[b]	Change in carboxyl ^{13}C chemical shift	Change in ^{15}N chemical shift	Change in ^1H methylene chemical shift
Y^{4-}	(0.0)	(0.0)	(0.00)
HY^{3-}	−4.2[c]	+5.3[c]	+0.47[c]
H_2Y^{2-}	−8.4	+17.0	+0.91
LiY^{3-}	+0.8	−5.1	−0.03
NaY^{3-}	+0.2	−1.3	−0.18
MgY^{2-}	+0.1	−0.3	−0.04
CaY^{2-}	+0.9	+4.4	−0.19
SrY^{2-}	+0.4	+5.6	−0.22
BaY^{2-}	+0.3	+8.6	−0.28
ZnY^{2-}	−0.7	+0.2[c]	+0.13
CdY^{2-}	−1.2	+3.3[c]	−0.03
HgY^{2-}	−3.0	+15.3	+0.12[c]

[a] In ppm, downfield shifts positive. Measured relative to the protons of the tetramethylammonium ion, and given with respect to the signals of the EDTA tetraanion (Y^{4-}). The estimated errors are: δ_C, ±0.1 ppm; δ_N, ±0.3 ppm; and δ_H, ±0.02 ppm. [b] Tetramethylammonium ion is the positive counterion. [c] Error approximately twice that quoted above in footnote *a*.

The ^{15}N, carboxyl ^{13}C, and methylene ^1H chemical shifts of EDTA upon protonation and complexation with metal ions are also presented in Table II. The chemical shifts of the acetate protons of ethylenediaminetetraacetic acid are not reported, as the signal from the acetate protons sometimes overlapped with the resonance of the tetramethylammonium ion which we were using as an internal reference. Our values for the proton chemical shifts of the methylene protons are in fair agreement with the data of a previous study[3] when it is considered that we have used internal rather than external chemical shift referencing, and that the anions of the metal salts differ in a number of cases between the two studies.

Data are available in the literature for the pK's[3,9,22] and association constants[22] of EDTA complexes. Our chemical shift measurements were made at pH values that differed by at least 2 units from the pK's. In some cases the carboxyl ^{13}C chemical shifts have been investigated over a wider pH range (free EDTA, pH 4.5–12.7; Mg(II), pH 6.3–9.3; Ca(II), pH 6.5–9.2; Zn(II), pH 4.7–10.5; Cd(II), pH 4.5–12.2), but the ^{13}C results are similar to the proton chemical shifts.[3]

For complexes showing rapid ligand exchange, the shifts were determined as a function of the metal-to-ligand ratio, and the result for the 1:1 molar ratio is reported in Table II. A plot of the carboxyl ^{13}C chemical shift of the strontium(II) complex *vs.* this ratio does not change in slope in the region of a 1:1 molar ratio. For barium(II) and mercury(II) it was impossible to obtain results for metal-to-ligand ratios larger than 1.05 because of lack of solubility.

Within experimental error, the ^{15}N chemical shift of EDTA showed a linear dependence with the concentration of potassium chloride or cesium chloride, with the resonance moving to lower field as the salt concentration increased. It is here assumed that neither of these cations complexes significantly with EDTA. The ^{15}N chemical shifts of all the methylammonium species have recently been shown to depend linearly upon the total chloride concentration, with a downfield shift as the chloride concentration is increased.[20]

All the chemical shifts depend to some extent upon the salt concentration. For example, when a 0.7 M EDTA solution (pH ≈ 12) was made 4 M in tetramethylammonium chloride, the proton chemical shifts and the carboxyl ^{13}C chemical shift moved upfield relative to the signal of the tetramethylammonium ion protons [by 0.10 ppm (methylene and acetate protons of EDTA), 0.14 ppm (water protons), and 0.63 ppm (carboxyl ^{13}C)]. Salt effects are rather large in relation to the observed range of proton and ^{13}C chemical shifts; consequently, 0.5 M solutions of EDTA were used for comparison purposes except for the cadmium(II) and mercury(II) complexes where, because of solubility problems, only 0.4 M solutions could be employed.

Nuclear shielding can be regarded as the sum of three terms[13,14,23,24]

$$\sigma^A = \sigma_d{}^A + \sigma_p{}^A + \sum_{B \neq A} \sigma^{AB} \qquad (1)$$

where σ^A is the shielding constant of the nucleus concerned, $\sigma_d{}^A$ is the local diamagnetic term (which is a function of the ground state only), $\sigma_p{}^A$ is the local para-

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magnetic term (involving matrix elements between the ground state and all excited states of suitable symmetry), and the $\Sigma_{B \neq A}\sigma^{AB}$ term (normally considered to be small for first-row elements, and therefore neglected, although it can also influence proton chemical shifts) arises from the shielding effects of other atoms in the molecule and from medium effects. The $\sigma_p{}^A$ term of eq 1 is expected to make no contribution to proton chemical shifts, because the hydrogen electrons are in s orbitals.[12] For carbon and nitrogen, it is possible (neglecting the third term in eq 1) to estimate $\sigma_p{}^A$, a quantity not easy to calculate from first principles, if $\sigma_d{}^A$ can be calculated, because σ^A is proportional to the experimental chemical shifts. Recently, a simple method for calculating the diamagnetic contribution to nuclear shielding has been published[25–28]

$$\sigma_d(k) = \sigma_d(\text{free atom/free ion}) - \frac{e^2}{3m}\sum_{\alpha}{}' \frac{Z_\alpha}{r_\alpha} \text{ [in SI units]} \tag{2}$$

where $\sigma_d(k)$ is the local diamagnetic contribution to the shielding of the kth nucleus in a molecule, σ_d(free atom/free ion) is the diamagnetic shielding of the appropriate free atom or ion (depending upon whether the atom in question bears a formal charge), Z_α is the atomic number of the αth nucleus, r_α is the distance between nuclei k and α, and the summation runs over all atoms directly bound to nucleus k.

It is expected that the $\sigma_d{}^N$ values for the various metal ion complexes of EDTA that we have studied will vary quite markedly. Equation 2 is most reliable when the electronegativity difference between directly bonded atoms is zero or small.[27] Where X-ray crystal structures are available for metal–ion complexes of EDTA,[29] the metal ion–nitrogen-atom distances are usually in quite close agreement with the values predicted by adding *atomic* (rather than *ionic*) radii for the metals[30] to the nitrogen radius (0.74 Å) appropriate for singly bonded nitrogen.[31] This suggests that electron donation from the six coordinating sites of the EDTA ligand to the metal ion results in little net charge on the metal ion. This is a fortunate occurrence, as the $\sigma_d{}^N$ values can probably thus be calculated with quite reasonable accuracy.

Table III. Local Diamagnetic and Paramagnetic Components of the ^{15}N Chemical Shifts of EDTA Complexes of Metal Ions

Complex	δ_N, ppm[a]	$\sigma_d{}^N$, ppm[b]	$\sigma_p{}^N$, ppm[a]
Y^{4-}	0.0	−440	0
HY^{3-}	5.3	−438	3
H_2Y^{2-}	17.0	−436	13
LiY^{3-}	−5.1	−439	−6
NaY^{3-}	−1.3	−466	25
MgY^{2-}	−0.3	−475	34
CaY^{2-}	4.4	−496	60
SrY^{2-}	5.6	−550	115
BaY^{2-}	8.6	−608	176
ZnY^{2-}	0.2	−563	123
CdY^{2-}	3.3	−629	192
HgY^{2-}	15.3	−762	337

[a] Downfield from EDTA tetraanion (Y^{4-}). [b] Downfield from bare nitrogen nucleus.

Because X-ray crystal structures do not appear to be available for the particular complexes that we have studied,[29] the metal–nitrogen distances required in order to calculate $\sigma_d{}^N$ values from eq 2 have been estimated using an atomic radius of 0.74 Å for nitrogen[31] and tabulated metal atomic radii.[30] The C–N bond lengths of EDTA have been used.[32] The calculated $\sigma_d{}^N$ values[33] are given in Table III; we should stress that the values are subject to error because of errors in estimation of bond lengths and metal–nitrogen electronegativity differences, but they are probably sufficiently accurate for the purpose for which we wish to use them. In any case, the $\sigma_d{}^N$ values, as expected, correspond to increasing shielding with increasing atomic number of the metal. Table III presents the $\sigma_p{}^N$ values found by subtracting $\sigma_d{}^N$ values from the observed ^{15}N chemical shifts, δ_N. The calculations show that the $\sigma_p{}^N$ terms would cause shifts to lower field with increasing atomic number within each series of complexes of similar metal ions, and upon successive protonation of the tetraanion of EDTA. The $\sigma_p{}^N$ values show trends similar to those in a preliminary report, wherein paramagnetic shielding was found to increase across rows and down columns of the periodic table as the ligand about the ^{13}C nucleus of interest is changed.[36] The important conclusion to be drawn fron Table III is that the diamagnetic terms are expected to be large, and the only way that the chemical shifts can remain so relatively invariant as the metal ion is changed is through near-cancellation of the metal substituent effects on the local diamagnetic and paramagnetic screening terms for nitrogen. This suggests that, although nitrogen nmr spectroscopy may be very useful in studying complexation of other nitrogen ligands with metal ions, with aliphatic amines (where the paramagnetic shielding of nitrogen nuclei is fairly small[14]), opposite and nearly canceling diamagnetic and paramagnetic shielding terms might well result in little change in the nitrogen chemical shifts upon complex formation. Perhaps pseudoaromatic nitrogen heterocycles which show a large spread of nitrogen chemical shifts[14] (and $\sigma_p{}^N$ values[37]) will give more impressive nitrogen chemical shifts upon complexation. However, for the one case for which data are available, it is reported that small nitrogen chemical shift changes were observed with adenosine triphosphate in the presence of Zn(II) ions,

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(33) In calculating $\sigma_d{}^N$ for the tetraanion of EDTA, a C–N bond length of 1.47 Å[34] was used. It was assumed in the case of the trianion of EDTA that the proton on nitrogen was associated with one particular nitrogen atom (rather than being symmetrically held between the two nitrogen atoms) but that it was rapidly chemically exchanged so that effectively each nitrogen atom was screened by half a proton 0.97 Å[32] away. The C–N bond length of the tetraanion was taken to be 1.49 Å;[32,34] an average of the shielding of a free nitrogen atom and a free nitrogen cation[35] was used for σ_d (free atom/free ion).

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but no significant change occurred with added Mg(II) ions.[38] It was concluded therefore that Zn(II) binds to nitrogen in the adenine ring of ATP, but that Mg(II) binds to phosphate. This conclusion may be correct but it is hardly supported by the fact that only very small ^{15}N shifts are produced by complexation of EDTA with Mg(II) and Zn(II) where the nitrogen is surely involved.

The carboxyl ^{13}C chemical shifts of EDTA complexes given in Table II are remarkably constant; changes in them can be considered to reflect changes in $\sigma_p{}^C$ values, because the diamagnetic contributions to the carboxyl ^{13}C shifts are likely to be small with the metal ions two bonds away.

Apart from the protonation effects on the carboxyl ^{13}C chemical shifts of EDTA metal complexes, the other chemical shift changes are generally too small to warrant rationalization. Discussion of the details of ^{15}N chemical shift trends is also speculative. Possibly upon protonation of EDTA, and with the complexes of heavier metal ions, the $\sigma_p{}^N$ shielding term predominates over the $\sigma_d{}^N$ term so that the observed ^{15}N shifts are downfield of EDTA. With a lighter metal ion, however, such as Li(I), the effect of $\sigma_d{}^N$ predominates over that of $\sigma_p{}^N$ so that the complex is more shielded than EDTA itself. An alternative viewpoint might consider the effect upon the chemical shifts of increases in the size of the cation.

It is already known that coordination of the tetraanion of EDTA to metals ions occurs by means of comparatively strong bonds to the nitrogen sites, and weaker bonds to the carboxyl-group sites.[5] Drawing an analogy between protonation of the EDTA tetraanion and formation of complexes with metal ions, a large downfield shift (of the order of 8 ppm; *cf.* ^{15}N data upon protonation of Table II) is expected on formation of each metal-to-nitrogen bond, and a small upfield shift (of about 2 ppm; *cf.* the glycine result[21] cited earlier) for each metal-to-oxygen bond that is formed. The overall pattern of results can then be explained by assuming that, in the comparatively large mercuric cation (and to a lesser extent in the case of the large strontium(II) and barium(II) cations), the observed ^{15}N chemical shift is dominated by the interaction between the metal ion and the nitrogen atoms (leading to a large downfield shift), and that this contribution is not markedly offset by interaction between the metal ion and the carboxyl group (giving a small upfield shift for each interaction). The anomalous behavior of the EDTA complex of the mercuric ion has already been noted.[2] With small cations such as lithium(I), the ligand can wrap around the ion effectively, so that the effect upon the nitrogen chemical shift of the metal–nitrogen bond is more than compensated for by the opposing effect of metal–oxygen bond formation. The ^{13}C shifts of the EDTA complexes are smaller than the ^{15}N shifts and inferences based on them are more uncertain, but by comparison with the carboxyl ^{13}C shifts of the other complexes the mercuric complex has a ^{13}C shift that is closer to those of mono- and diprotonated EDTA tetraanion. This would be consistent with comparatively loose metal–carboxyl coordination, but strong metal–nitrogen coordination.

Coupling Constants. The geminal coupling constants ($^{2}J_{^{13}C-C-^{1}H}$) between the carboxyl ^{13}C nuclei and the acetate protons range between 4.5 and 5.1 Hz (standard variation ~0.2 Hz) for a series of EDTA complexes, but show no definite trends.

Mercury and cadmium have spin $^1/_2$ isotopes. Rapid exchange prevented observation of spin coupling to the metal ion for the mercury–EDTA complex. Spectra of the Cd(II)–EDTA complex showed coupling to the cadmium, although the signals for ^{111}Cd and ^{113}Cd could not be separately resolved. The average coupling constants are 12.7 ± 0.1 Hz to the carboxyl ^{13}C nuclei and 81 ± 1 Hz to the ^{15}N nuclei; the signs of the coupling constants were not determined.

The reduced Cd–N coupling constant[24] in the EDTA complex ($^{1}K_{Cd-N} = 3.1 \times 10^{21}$ N A^2 m^{-3}) is of comparable magnitude to the reduced Cd–C coupling constant in dimethylcadmium[39] ($^{1}K_{Cd-C} = 8.0 \times 10^{21}$ N A^2 m^{-3}). We are only aware of one other one-bond coupling constant between nitrogen and a metal;[13] $^{1}K_{Pt-N}$ is 23.0×10^{21} N A^2 m^{-3} for *cis*-[Pt(NCS)$_2$-(Bu$_3$P)$_2$].[40] It is unexceptional that this reduced coupling constant should be an order of magnitude greater than that in the Cd(II)–EDTA complex, as the magnitudes of reduced coupling constants generally increase as the atomic numbers of the coupled nuclei increase.[24]

Experimental Section

All samples used in the nmr studies of metal complexes were prepared from EDTA, a 25% aqueous solution of tetramethylammonium hydroxide, reagent grade metal salts, and water to give solutions that were 0.5 *M* in EDTA (except that the EDTA concentration was 0.4 *M* in the case of the cadmium and mercury experiments).

The metal salts used were: the chlorides of Li(I), Na(I), K(I), Cs(I), Mg(II), Ca(II), and Ba(II); the bromide of Sr(II); and the nitrates of Zn(II), Cd(II), and Hg(II).

The pH dependence of the chemical shifts was followed by preparing a starting solution at high pH, and then adding small amounts of 6 *M* hydrochloric acid. The pH measurements were made with a Beckman Model G pH meter, calibrated using Beckman buffer solutions.

The ^{13}C and ^{15}N nmr spectra were taken on the DFS-60 spectrometer[41] using about 2 ml of solution in 10-mm precision-bore sample tubes. The ^{13}C and ^{15}N resonance frequencies were measured at a magnetic field strength such that the water protons of the samples came at exactly 60 MHz; the water proton resonance was used to provide an internal heteronuclear lock for the spectrometer, and thus proton decoupling could not be used. Because water is not a satisfactory chemical shift reference, proton nmr spectra (taken on a Varian A-60 spectrometer) were used to measure the frequency separation of the tetramethylammonium ion and water signals. The water protons move upfield with respect to the tetramethylammonium ion proton signal as the temperature is increased. Generally about 100–400 scans were accumulated on a Varian C-1024 time-averaging computer. The Cd–^{15}N and Cd–^{13}C coupling constants were measured from proton-decoupled spectra.

The glycine and acetic acid solutions used for the ^{13}C nmr spectra were prepared from the reagent grade acids, 25% aqueous tetramethylammonium hydroxide solution, and water to give solutions 2.0 *M* in glycine and acetic acid, respectively, at high pH. The solutions at lower pH were obtained by addition of 6 *M* hydrochloric acid.

Synthesis of Ethylenediamine-$^{15}N_2$-tetraacetic acid. 1,2-Diphthalimidoethane-$^{15}N_2$ was prepared by heating potassium phthalimide-^{15}N (Merck, Sharp and Dohme of Canada; 96.0% ^{15}N) and

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the di-*p*-toluenesulfonate of ethylene glycol in a Carius tube.[42] The purified material melted at 235–237° (lit.[42] mp 233–234°).

Ethylenediamine-$^{15}N_2$ dihydrochloride was obtained by heating a suspension of 1,2-diphthalimidoethane-$^{15}N_2$ in 6*M* hydrochloric acid in a Carius tube at 180° for 3 hr. The crude product obtained from the filtrate and washings of the reaction mixture by freeze-drying was used in the next stage of the synthesis.

The ethylenediamine-$^{15}N_2$ dihydrochloride was allowed to react with sodium iodoacetate at 45° with concomitant addition of sodium hydroxide solution to keep the pH at 10 ± 0.3. When the reaction was complete, as judged by the fact that the pH no longer dropped on addition of base, the mixture was quickly cooled to about 5°, and hydrochloric acid was added rapidly to bring the pH to 1.2. The precipitate was removed by filtration, leached with water, and air dried. The ethylenediamine-$^{15}N_2$-tetraacetic acid so obtained melted at 232–235° (lit.[43] mp 242° dec).

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Nitrogen-Centered Free Radicals. VI. Electron Spin Resonance Studies of *N*-Alkoxy-*N*-alkylamino, *N*-Alkoxy-*N*-arylamino, and *N*-Alkoxy-*N*-carboethoxyamino Radicals in Solution[1]

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Abstract: A variety of substituted *N*-alkoxyamino radicals, RNOR′, have been generated and studied by esr spectroscopy. The oxygen substituent, R′, has been *tert*-butyl in most cases; the nitrogen substituent, R, categorizes the radical into one of three different classes. One such class, the *N*-alkoxy-*N*-alkylamino radicals (R = alkyl), is formed by photolysis of *tert*-butyl *N*-alkylperoxycarbamates, by hydrogen abstraction from appropriately substituted hydroxylamines, or by direct photolysis of solutions of these latter compounds. The ability of the alkoxy substituent to delocalize the unpaired electron is discussed; INDO calculations were performed on the *N*-methoxy-*N*-methylamino radical and the results were compared with experiment. Speculation as to the mechanism of N–O bond formation is also presented. A second category of paramagnetic species, the *N*-alkoxy-*N*-arylamino radicals (R = aryl), was also studied. A variety of these radicals with both electron-donating and -withdrawing substituents in the meta and para positions were generated from either the appropriate *tert*-butyl *N*-arylperoxycarbamate (electron-withdrawing substituents) or by photolysis of a solution of di-*tert*-butyl peroxide and the substituted aniline (electron-donating substituents). It was found that both para-electron-donating and para-electron-withdrawing substituents were effective in delocalizing the unpaired electron and that the *N*-alkoxy-*N*-arylamino radicals could be assigned to Walter's "class S" based on the nitrogen hyperfine coupling constant. The addition of a small amount of *tert*-butyl hydroxperoxide to solutions which normally afforded the alkoxyarylamino radicals produced, instead, the corresponding alkoxy aryl nitroxides. The nitrogen hfsc's in these radicals could be correlated with Hammett σ constants exhibiting the anticipated "class O" behavior. A final class of radicals, the *N*-alkoxy-*N*-carboethoxyamino species (R = carboethoxy), was generated and found to possess a Π-electronic ground state on the basis of the esr parameters.

Recent interest in neutral amino free radicals has led to several electron spin resonance (esr) investigations in this area.[1a,b,2–8] Photolysis of 2-tetrazenes directly in the esr cavity produced isotropic solution spectra of the simple dialkylamino radicals,[2] while the aziridino and azetidino radicals were formed by N–H abstraction from the parent heterocyclic amine by *tert*-butoxyl radicals.[3] Several amido radicals have been generated by the photolysis of *N*-chloramides.[1a] The anilino radical was prepared in an adamantane matrix by X-irradiation[4] while the 2,4,6-tri-*tert*-butylanilino species was produced by flash photolysis of 2,4,6-tri-*tert*-butylaniline.[5] Several alkylimino radicals have been prepared by the photoinduced decomposition of aminoalkyl radicals in an adamantane matrix[6,7] and two *N*-methoxyamino radicals were produced by hydroxyl radical addition to oxime *O*-methyl ethers.[8] During the course of this investigation, esr studies of *N*-*tert*-butylanilino[9] and *N*-*tert*-butoxyamido radicals[10] were reported which have a direct relationship to certain of the results herein.

In an earlier communication we reported that the photolysis of *tert*-butyl *N*-alkylperoxycarbamates pro-

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