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 (22) The INDO program⁷ employs an EHT calculation as an initial guess for the molecular orbitals which are then populated according to their energies. These populated orbitals are strongly lowered in energy relative to the unoccupied orbitals by the SCF procedure. Subsequent calculations at new geometries during the minimization utilize the previous density matrix. Therefore, once a particular electronic state has been chosen its energy surface in parameter space (bond lengths and angles) can be calculated by our program although there exists a state of lower energy.
- The following conditions must, however, be met: (a) the energy of the excited state being calculated must not be too greatly above the ground state or the lowering effect of the SCF procedure will be overcome; (b) the symmetry of the excited state must be sufficiently different from that of the ground state so that significant mixing will not occur. Condition (a) is easily satisfied for species with near electronic degeneracies such as the substituted benzene anions and cations. Condition (b) is obviously met for the A and S states of the benzene ion problem; however, distortions which remove the planes of symmetry can result in convergence to the ground state (e.g., the methyl group is not a large enough perturbation, but putting one of the ring carbons out of the plane by 0.1 Å is). We have modified our INDO program to allow selection of the initial population so that the "trick" method described in the experimental section is no longer necessary. In any case the INDO results reported herein for toluene radical anion correspond to the same S and A states known from HMO, EHT, and ASMO-CI calculations.
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Quantitative Carbon-13 Fourier Transform Nuclear Magnetic Resonance. Limitations of Spin Relaxation Reagents

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Abstract: There are several problems associated with the use of paramagnetic relaxation reagents such as chromium (tris)acetylacetonate ($\text{Cr}(\text{acac})_3$) to quantify ^{13}C NMR spectral data. In medium and large sized organic molecules ^{13}C - ^1H NOE suppression will be incomplete and variable owing to the fact that efficient ^{13}C - ^1H dipole-dipole relaxation is able to successfully compete with electron-nuclear relaxation to the $\text{Cr}(\text{acac})_3$. For these molecules the use of $\text{Cr}(\text{acac})_3$ actually can degrade the performance of the experiment. These conclusions are illustrated with a complete spin-lattice relaxation study at 67.9 MHz on cholesteryl chloride as a representative organic compound. Another finding of this study is that at the high field employed (63 kG) the chemical shift anisotropy (CSA) mechanism accounts for 60% of the spin-lattice relaxation of the nonprotonated olefinic carbon, C-5. The calculated anisotropy of the C-5 chemical shift tensor is somewhat higher than previously observed for sp^2 carbons not attached to heteroatoms, 340 ppm.

Theory

Paramagnetic relaxation additives such as chromium tris(acetylacetonate) ($\text{Cr}(\text{acac})_3$) are being utilized increasingly to shorten long spin-lattice relaxation times and to eliminate the nuclear Overhauser effect (NOE) in proton decoupled ^{13}C NMR studies.^{1,2} These reagents have also been found to be valuable in spectral analyses complementing or replacing lanthanide chemical shift reagents³ and in NMR of other nuclei like silicon-29 and nitrogen-15 where the negative magnetogyric ratios could cause signals to vanish (negative NOE ≈ -1).⁴

The most widely reported application of these paramagnetic relaxation reagents (PARR), however, has been to

quantify spectral results in ^{13}C FT NMR.² The main purpose of this paper is to show that the use of PARR materials in these analyses *should be strongly restricted* because NOE's may not be effectively suppressed in the general case.

Early studies evaluated NOE quenching and enhanced spin-lattice relaxation for nonprotonated carbons or for other carbons in small molecules where rapid molecular tumbling makes the normal ^{13}C - ^1H dipole-dipole relaxation process, R_1^{DD} , inefficient. In these restricted cases a relaxation contribution of ca. 0.3 sec to T_1^{obsd} ($\approx 3 \text{ sec}^{-1}$ to the relaxation rate, R_1^{obsd}) from a 0.1 M solution of $\text{Cr}(\text{acac})_3$ is able to effectively suppress all NOE's and essentially equalize all T_1 's for protonated and nonprotonated

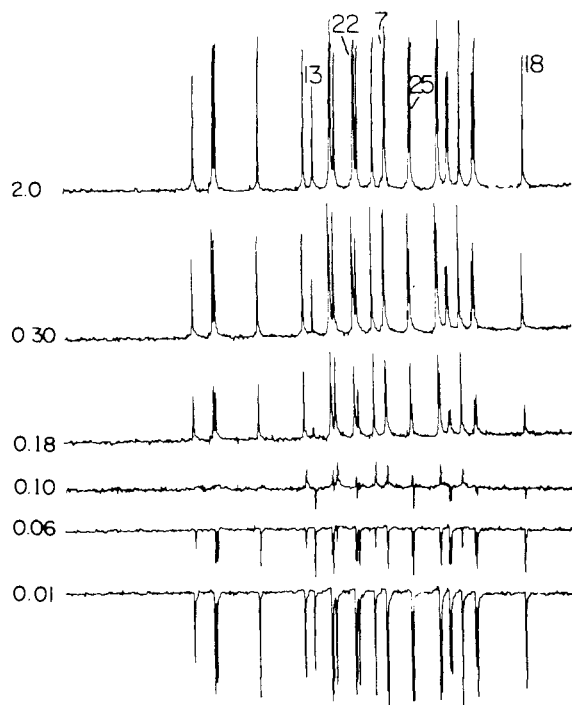
PRFT Spectra of Cholesteryl Chloride with added $\text{Cr}(\text{acac})_3$ 

Figure 1. Set of proton-decoupled PRFT spectra using the unmodified inversion-recovery sequence $(T-180^\circ-t-90^\circ)_n$ at 67.9 MHz and $38 \pm 2^\circ$. Peak intensities for the carbons indicated are plotted semilogarithmically in Figure 2. t values, the interval between the 180° and 90° pulses, are given to the left of the spectra. The recovery time, T , was set to 2.0 sec (200 scans, 5000 Hz spectral width shown). Additional PRFT spectra (not shown) covering the range of 0.010–2.0 sec were also obtained and used for the calculation of T_1 's (unfilled circles in Figure 2).

carbons. According to the theory, T_1^{DD} and T_1^{obsd} are related by the enhancement factor η as

$$T_1^{\text{DD}}/T_1^{\text{obsd}} = 1.988/\eta$$

where 1.988 is the maximum possible NOE.

If after addition of PARR T_1^{DD} still makes a significant contribution to the total rate, this relation reveals that the NOE factor will not be fully suppressed.

Most organic molecules of molecular weight ≈ 200 will undergo efficient ^{13}C - ^1H dipole-dipole relaxation ($T_1^{\text{DD}} \approx 1 \text{ sec}$)⁵ and addition of a relaxation reagent such as $\text{Cr}(\text{acac})_3$ to these solutions will not effectively quench NOE's at practical $\text{Cr}(\text{acac})_3$ concentrations. If a more effective relaxation reagent were used then a great deal of line broadening would of necessity result when NOE's were completely suppressed, since the T_1^e term would have to be much shorter than T_1^{DD} (on the order of 10 msec, typically).

Experimental Section

Materials. Cholesteryl chloride was obtained from Aldrich Chemical Company and chromium (tris)acetylacetonate, $\text{Cr}(\text{acac})_3$, was purchased from Alfa Products. These substances were used without further purification.

NMR Measurements. All ^{13}C NOE's and spin-lattice relaxation times were obtained with complete decoupling on a Bruker HX-270 (67.9 MHz) at $38 \pm 2^\circ$. Samples were not degassed since relaxation contributions from dissolved O_2 at atmospheric pressure are not significant with ^{13}C T_1 's $\approx 5 \text{ sec}$.^{5b}

The T_1 measurements were performed using an unmodified inversion-recovery pulse sequence $(T-180^\circ-t-90^\circ)_n$ using 8k transforms. As shown below with the T_1 data and NOE's the extreme narrowing approximation is still valid for this system at 67.9 MHz.

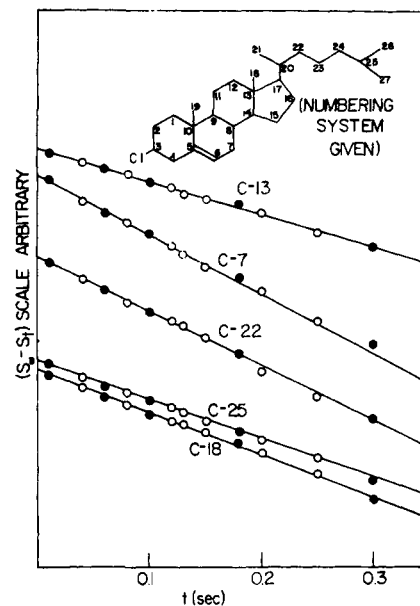


Figure 2. Semilogarithmic plot of $S_\infty - S_t$ for the carbons labeled in Figure 1.

Table I. ^{13}C Relaxation Behavior and NOE Factors for Cholesteryl Chloride in Benzene- d_6 with and without Added $\text{Cr}(\text{acac})_3$ (0.1 M, temp $38 \pm 2^\circ$)

Carbon	Chemical shift ^a	T_1^{obsd} , sec ^b	T_1^{obsd} , sec ^c	T_1^e	NOE ^b	NOE ^c
1	39.2	0.39	0.14	0.21	2.0	0.78
2	33.7	0.39	0.14	0.23	2.0	0.77
3	59.7	0.67	0.17	0.22	2.0	0.55
4	43.8	0.37	0.14	0.22	2.0	0.80
5	140.7	3.2	0.22	0.24	0.80 ^d	0.06
6	122.3	0.65	0.15	0.19	2.0	0.59
7	32.0	0.37	0.14	0.22	1.8	0.77
8	31.9	0.70	0.16	0.21	1.8	0.52
9	50.3	0.66	0.17	0.23	2.0	0.58
10	36.4	4.3	0.23	0.25	1.8	0.11
11	21.1	0.37	0.14	0.22	1.9	0.80
12	28.4	0.37	0.14	0.22	1.8	0.77
13	42.4	4.2	0.24	0.25	1.8	0.10
14	56.8	0.65	0.16	0.22	2.0	0.61
15	24.4	0.34	0.14	0.23	2.0	0.85
16	40.0	0.34	0.14	0.25	1.8	0.75
17	56.5	0.80	0.17	0.22	1.9	0.52
18	11.9	1.3	0.19	0.23	2.0	0.27
19	19.1	1.2	0.19	0.22	2.0	0.25
20	36.0	0.67	0.18	0.24	1.9	0.45
21	18.9	0.98	0.18	0.23	2.0	0.33
22	36.5	0.46	0.15	0.22	2.0	0.65
23	24.2	0.57	0.16	0.21	2.1	0.65
24	39.8	0.86	0.17	0.22	1.9	0.47
25	28.2	1.9	0.20	0.23	1.8	0.20
26	22.7	1.8	0.21	0.23	1.9	0.20
27	22.9	1.7	0.21	0.23	1.9	0.21

^a Ppm downfield from TMS. Assignments taken from ref 6. ^b Diamagnetic solution. ^c $\text{Cr}(\text{acac})_3$ added, 0.1 M. ^d Average of three runs, high and low field carrier position, ± 0.07 .

Results and Discussion

In order to experimentally confirm the arguments given above we have performed a high-accuracy spin-lattice relaxation study on a medium-sized organic molecule, cholesteryl chloride. The choice of this molecule was based in part on previously published work⁶ and because it has no functional group capable of intermolecular association.

NOE DETERMINATION : CHOLESTERYL CHLORIDE 67.9MHz, 38°C, 4kHz SHOWN

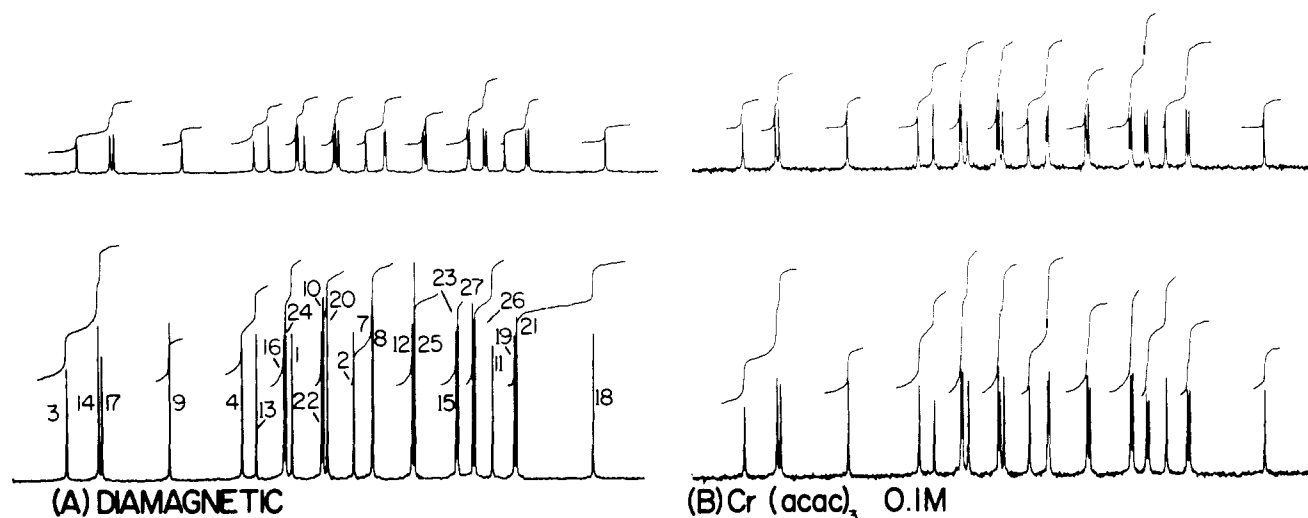


Figure 3. Upfield region in the ^{13}C FT NMR spectra of 1 *M* cholesteryl chloride in benzene- d_6 (A) and after addition of $\text{Cr}(\text{acac})_3$ (0.1 *M*) (B). All spectra: 128 scans with a recycle time of 25 sec, 4000 Hz spectral width shown using 16k transform. Note the lower signal-to-noise obtained with the paramagnetic reagent added. Bottom: proton-decoupled spectra (without instrumental NOE suppression). Top: pulse-modulated decoupled spectra (NOE suppression).

67.9 MHz SPECTRA

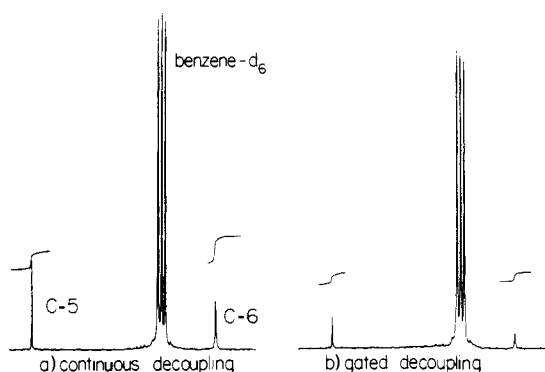


Figure 4. NOE determination at 67.9 MHz for the olefinic carbons in cholesteryl chloride.

With smaller molecules undergoing limited association the results would be similar.

Figure 1 shows a set of ^{13}C IRFT spectra for cholesteryl chloride with added $\text{Cr}(\text{acac})_3$ (at 0.1 *M*, the highest practical concentration for general use). This corresponds to the most difficult run experimentally; without paramagnetic doping the resolution and the sensitivity are significantly better. The data for five peaks assigned from Figure 1 are plotted semilogarithmically in Figure 2, to yield experimental T_1 's from the slopes. Note that the five peaks are chosen to show the entire range of line separations, from signals that are only slightly resolved to completely separated peaks. Even when line separation is small, as between C-7 and C-8, the internal estimated error is less than $\pm 10\%$; typically the T_1 's in this study could be considered to be accurate to $\pm 5\%$ (for the well resolved carbons C-13, C-18, etc.). Three separate runs for each sample produced internal T_1 deviations of less than 5–10%.⁷

The NOE measurements were performed using the gated decoupling technique⁸ where the decoupler is gated on only during the data acquisition periods. The pulse delays were set to approximately five times the T_1 for the slowest relax-

ing carbon.⁹ The NOE's for these runs were reproducible to ± 0.05 to ± 0.1 .

In Table I and Figure 3 we report T_1 's and NOE's for all carbons of cholesteryl chloride with and without paramagnetic doping. The observed enhancement factors show that within the limits of experimental accuracy in the diamagnetic solution all carbons except C-5 are totally relaxed by the dipole-dipole interaction; this includes even the quaternary carbons. The observed T_1 's for the CH and CH_2 carbons of the ring framework are in a rough ratio of 2:1 and we can assume that the rotational motion is not particularly anisotropic which is in accordance with the earlier reported results.⁶ Interestingly, Allerhand reported the nuclear Overhauser enhancement for the C-5 atom to be 2.1 ± 0.3 at 14 kG while we observed this factor to be 0.8 ± 0.07 (average of three runs) at 63 kG (see Figure 4). This indicates a competition between ^{13}C - ^1H interactions and the chemical shift anisotropy (CSA) mechanism at high field. A preliminary investigation in this laboratory at 21.1 kG gave a T_1 for C-5 of 5.6 sec ($\eta = 1.6 \pm 0.2$) compared with 3.2 sec ($\eta = 0.8 \pm 0.07$) at 63 kG. Using a $\tau_{\text{eff}} = 6.6 \times 10^{-11}$ sec obtained from the average T_1 at 63.3 kG ($NT_1 \equiv 0.72$) the chemical shift anisotropy factor, $\Delta\sigma$, was calculated to be ~ 340 ppm in this solvent at 38°. From the calculated shift anisotropy for C-5, T_1^{CSA} at 21.1 kG can be calculated in the standard way⁵ to be 48 sec and thus CSA relaxation would just give a minor contribution to T_1^{obsd} at the lower field.

Our T_1 data for the carbons on the ring backbone differ significantly from T_1 's reported earlier⁶ in carbon tetrachloride.¹⁰

Addition of the paramagnetic reagent to the solution of cholesteryl chloride decreased the observed T_1 's and NOE's but even this relatively high concentration of $\text{Cr}(\text{acac})_3$ (0.1 *M*) is not sufficient to equalize the spin-lattice relaxation times, NOE's, nor the resulting peak intensities. As seen from the electron-nuclear relaxation times, T_1^e , most carbons are equally affected by the paramagnetic chelate. Interestingly the T_1^e 's for the quaternary carbons are on the average somewhat longer and T_1^e for C-6 a little shorter compared with the values for the other carbons. This could be explained by a steric effect causing the quaternary car-

bons to be slightly less accessible to the paramagnetic chelate.

Conclusions

This investigation clearly points to the fact that some precautions must be taken before using paramagnetic additives such as $\text{Cr}(\text{acac})_3$ in order to obtain quantitative results in ^{13}C NMR. First, it is necessary to have a rough estimate of the spin-lattice relaxation times for the sample. This estimate of the T_1 's serves two purposes: (1) it would give supplementary evidence for spectral peak assignments and (2) it would indicate the amount of paramagnetic relaxation reagent (PARR) needed to quench the NOE. If the dipole-dipole interaction is efficient enough then it will be impossible to effectively suppress NOE's with relaxation reagents without causing considerable line broadening. Also, spectral sensitivity is lowered for this application of PARR materials, since it is in this case particularly that NOE's are at or near the theoretical maximum^{5,6} (Figure 3 is illustrative).

In addition to the problems cited above, there is the possibility of solution complex formation between the metal chelate and substrate functional groups (e.g., OH, NH_2 , CX_2H).^{1f,3} In this case the T_1 leveling effect is not present; relaxation times for carbons close to the site of complexation are shortened preferentially and individual carbon NOE's may be variably affected.

In cases where T_1 's are longer than several seconds this method can be valuable for obtaining quantitative ^{13}C NMR results, provided discretion is used in the design and execution of the experiment. Also chemical suppression will allow accurate and rapid calculation of nuclear Overhauser enhancements for these molecules in laboratories where instrumental NOE suppression is not available.

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al Science Foundation and Research Corporation is gratefully acknowledged. The Bruker HX-270 spectrometer was purchased through a grant from the National Science Foundation. Dr. U. Edlund is holder of a postdoctoral fellowship from the Swedish Natural Science Research Council.

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- (9) It has been suggested that longer pulse delays are required, up to $10(T_1)$, in order to fully suppress NOE's in gated ^1H experiments. This was not necessary for the present case as evidenced by the maximum NOE's observed for all carbons (except C-5, see text) with no $\text{Cr}(\text{acac})_3$ added.
- (10) The solution viscosities for cholesteryl chloride, 1 M, in CCl_4 at 42° and benzene- d_6 at 38° are 2.87 and 1.48 cP, respectively.

A Change in Mechanism During Fluorescence Quenching of Substituted Anthracenes by Triphenylphosphine

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Contribution from the Instituto de Quimica, Universidade de São Paulo, São Paulo, Brazil. Received September 11, 1974

Abstract: The rate constants, k_q , for the fluorescence quenching of anthracene and ten mono- and disubstituted anthracenes by triphenylphosphine have been measured. The k_q values are correlated with the singlet energies and half-wave reduction potentials of the anthracenes according to the treatments of Weller, Evans, and Hammond. It is found that the anthracenes substituted with electronegative groups undergo quenching by a charge transfer mechanism. The anthracenes with electro-positive groups are quenched by a different mechanism which probably involves formation of an excitation resonance stabilized exciplex.

It is known that the fluorescence of many aromatic molecules, A, which possess low-lying singlet states, is quenched by compounds, X, whose first excited singlets are much higher in energy.² Direct or indirect evidence has indicated that exciplexes, excited state complexes between electronically different molecules which are dissociative in the ground states, are often formed during the quenching process.² The nature of the binding energy in exciplexes and

the electronic nature of the nonclassical quenching step are still subjects of controversy. While Weller³ and Evans,⁴ especially, agree that charge transfer interactions contribute most, their mechanisms for exciplex formation differ. Hammond⁵ believes that charge transfer interactions need not always be important: in some cases, resonance excitation may be the dominant stabilizing force; in others, many factors may contribute.