

Further analyzing the core-(σ valence) ZDO approximation, we note that the relatively modest error in the bond-order matrix results from the fact (also verified directly) that the approximate Fock matrix is rather accurate. The accuracy is achieved because the neglected nuclear-attraction integrals essentially cancel against the main energy contributions arising from the neglected (hybrid) electron-repulsion integrals. The elimination of the corresponding exchange integrals produces minor effects. This cancellation depends on the fact that the electron-repulsion energy is multiplied by 2 in the Fock matrix, thereby causing the electron-repulsion energy to be approximately equal in magnitude to the electron-nuclear attraction energy. In contrast, the electron-repulsion contribution to the total molecular energy has approximately one-half the magnitude of the electron-nuclear attraction energy, causing ZDO calculations of the total energy to be more seriously in error.

One way to remedy the error imbalance in the energy computation is to build a total energy expression from quantities not subject to large errors. Writing the total energy in the form⁴

$$E_{\text{total}} = \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) + E_{\text{nuc rep}}$$

where $H_{\mu\nu}$, $F_{\mu\nu}$, and $P_{\mu\nu}$ are the one-electron energy, Fock, and bond-order matrix elements, we meet our objective by taking $P_{\mu\nu}$ and $F_{\mu\nu}$ from the ZDO calculation while using values of $H_{\mu\nu}$ in which no integrals are neglected (balanced ZDO). For CO, this procedure leads to greatly improved and qualitatively satisfactory results (curve 4). Corresponding results are obtained for the other first-row diatomic molecules and for the 1s-1s two-center ZDO approximation in diatomic hydrides. If all the one-electron integrals, and two-electron hybrid integrals involving core-(σ valence) two-center charge distributions are retained, most of the remaining error is removed. This result further supports our argumentation.

Even the last procedure described in the preceding paragraph failed to enable us to obtain reliable results from valence-valence ZDO approximations near the equilibrium internuclear separations. However, we note that at typical second-neighbor separations in polyatomic molecules, valence-valence overlaps are comparable to the core-valence overlaps treated above. We therefore expect that the balanced ZDO procedure should be applicable to all but nearest-neighbor valence-valence overlaps. This method has the important advantage of automatically satisfying the requirement of invariance under axes rotation.⁵

(4) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, pp 41-46.

(5) Reference 4, pp 60-62.

(6) National Institutes of Health Fellow, 1968-1970.

John M. Herbelin,⁶ Frank E. Harris*

Departments of Chemistry and Physics
University of Utah, Salt Lake City, Utah 84112

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The Carbon-13 Intensity Problem. Elimination of the Overhauser Effect with an Added Paramagnetic Species

Sir:

The spectral simplification and increase in effective S/N produced by proton "decoupling" in ¹³C nmr

spectroscopy¹ is frequently accompanied by signal enhancement due to the operation of a ¹³C-¹H Overhauser effect.² The magnitude of the Overhauser enhancement ordinarily differs for different ¹³C nuclei, so the simple relationship between resonance intensity and the number of ¹³C nuclei no longer holds. ¹³C spectroscopy cannot therefore be generally employed for quantitative analysis, and spectral interpretation is made more difficult.

It was suggested by La Mar³ that the ¹³C-¹H Overhauser polarization might be eliminated by the presence of a paramagnetic species in solution. A theoretical analysis showing that the Overhauser effect should indeed be reduced by paramagnetic species is presented herein, and the criteria which govern the extent of the reduction are included. The existence of such reduction has been confirmed experimentally.³

The enhancement factor $(C_z - C_0)/C_0$ of ¹³C nuclei (C) due to proton (H) irradiation in the presence of unpaired electrons (E) is given⁴ by

$$\frac{C_z - C_0}{C_0} = \left[\frac{f_{\text{CH}} \rho_{\text{CH}} - f_{\text{CE}} \rho_{\text{CE}} f_{\text{EH}} \rho_{\text{EH}}}{1 - f_{\text{CE}} \rho_{\text{CE}} f_{\text{EC}} \rho_{\text{EC}}} \right] \frac{\gamma_{\text{H}} S_{\text{H}}}{\gamma_{\text{C}}} \quad (1)$$

C_z and C_0 are magnetizations with and without proton irradiation, respectively. (Overhauser enhancements are often quoted as C_z/C_0 .) S_{H} is the degree of saturation of the proton absorption such that

$$S_{\text{H}} = 1 - \frac{1}{1 + \gamma_{\text{H}}^2 H_2^2 (T_1 T_2)_{\text{H}}} \quad (2)$$

where γ_{H} , H_2 , T_1 , and T_2 are the gyromagnetic ratio, irradiation field strength, and spin-lattice and spin-spin relaxation times, respectively, of the protons. ρ_{CH} describes the nature and effectiveness of the dynamic coupling⁵ between the C and H spins, and the other ρ terms are defined analogously. f_{CH} is that fraction of the total C relaxation due to coupling with the H spins and is given by⁴

$$f_{\text{CH}} = 1 - \frac{T_{1\text{C}}(\text{LEH})}{T_{1\text{C}}(\text{LE})} \quad (3)$$

where $T_{1\text{C}}(\text{LEH})$ and $T_{1\text{C}}(\text{LE})$ are the spin-lattice relaxation times of the C spins in the presence and absence, respectively, of the H spins. L refers to the lattice. Definitions of the other f terms follow analogously.

Only a negligible fraction of the electron relaxation proceeds *via* C and H, so f_{EC} and f_{EH} are approximately zero. Equation 1 therefore simplifies to

$$\frac{C_z - C_0}{C_0} = f_{\text{CH}} \rho_{\text{CH}} \frac{\gamma_{\text{H}} S_{\text{H}}}{\gamma_{\text{C}}} \quad (4)$$

The important ¹³C spin-lattice relaxation processes are illustrated in Figure 1. Thus

$$\frac{1}{T_{1\text{C}}(\text{LE})} = \frac{1}{T_{1\text{CL}}} + \frac{1}{T_{1\text{CE}}} \quad (5)$$

(1) R. E. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

(2) K. F. Kuhlmann and D. M. Grant, *J. Amer. Chem. Soc.*, **91**, 7355 (1969).

(3) G. N. La Mar, private communications; *J. Amer. Chem. Soc.*, **93**, 1040 (1971).

(4) D. F. S. Natusch, R. E. Richards, and D. Taylor, *Mol. Phys.*, **11**, 421 (1966).

(5) A. Abragam, "Principles of Nuclear Magnetism," Clarendon Press, Oxford, England, 1961, pp 333-346.

and

$$\frac{1}{T_{1C}(\text{LEH})} = \frac{1}{T_{1CL}} + \frac{1}{T_{1CE}} + \frac{1}{T_{1CH}} + \frac{\alpha'}{T_{1HE}} \quad (6)$$

where α' describes the efficiency with which the electrons relax C *via* H (i.e., the so-called three-spin effect⁴). T_{1CH} thus refers to C-H relaxation in the absence of electrons. Substituting eq 5 and 6 into eq 3 and writing⁴ $1/T_{1CE} = k[E]$ and $\alpha'/T_{1HE} = \alpha[E]$, eq 4 becomes

$$\frac{C_z - C_0}{C_0} = \rho_{CH} S_H \gamma_H \left[\frac{\frac{1}{T_{1CH}} + \alpha[E]}{\frac{1}{T_{1C}(\text{LH})} + (k + \alpha)[E]} \right] \quad (7)$$

[E] is the concentration of electron spins and

$$\frac{1}{T_{1C}(\text{LH})} = \frac{1}{T_{1CL}} + \frac{1}{T_{1CH}}$$

Equation 7 thus describes the effect of electron spins on the ^{13}C Overhauser enhancement factor during proton irradiation.

The effect of electron spins on the observed ^{13}C line width ($\Delta\nu_{1/2}$) is given by $\Delta\nu_{1/2} = [\pi T_{2C}(\text{LEH})]^{-1}$ where

$$\frac{1}{T_{2C}(\text{LEH})} = \frac{1}{T_{2CL}} + \frac{1}{T_{2CH}} + \delta k[E] + \alpha[E] \quad (8)$$

δ is the ratio T_1/T_2 for the C-E coupling and is normally a little greater than unity⁶ since dynamic scalar coupling operates between ^{13}C nuclei and electrons.⁷

Substitution of the condition $4\gamma_H^2 H^2 \gg \pi^2 J_{CH}^2$ for complete proton decoupling⁸ into eq 2 and evaluation of $(T_1 T_2)_H$ *via* eq 6 and 8 as outlined for ^{13}C shows that decoupling always implies $S_H \approx 1$ unless J_{CH} is very small (~ 3 Hz).

Equations 7 and 8 predict the following significant points. (1) Addition of increasing amounts of a paramagnetic species reduces (or increases) the ^{13}C Overhauser enhancement to a constant value before significant broadening of the ^{13}C line occurs. This is true for a wide range of k values. (2) When $(k + \alpha)T_{1C}(\text{LH})[E] \gg 1$ the enhancement factor is $1.988 S_H \alpha / (k + \alpha)$. Thus, when $\alpha = 0$ (which commonly occurs^{8,4}), the Overhauser effect is completely eliminated. (3) The initial enhancement factor ($[E] = 0$) is $1.988 S_H T_{1C}(\text{LH})/T_{1CH}$ as for the two-spin case.⁴ (4) Absolute values of k , α , $T_{1C}(\text{LH})$, and T_{1CH} (and thus T_{1CL}) can be obtained by fitting eq 7 to a plot of $(C_z - C_0)/C_0$ *vs.* $[E]$ unless $T_{1CH} \approx T_{1C}(\text{LH})$ or $k = 0$. (5) $k \propto r_{CE}^{-3}$, where r_{CE} is the ^{13}C -E distance. For a given value of $[E]$, therefore, the Overhauser enhancements of those ^{13}C nuclei closest to the paramagnetic species will, in general, be preferentially reduced. This effect is observed at values of $[E]$ at least two orders of magnitude lower than the observation of preferential line broadening.⁹

The validity of the theory is indicated by the fact that La Mar's experimental results for *p*-dioxane³ are de-

(6) R. A. Dwek, J. G. Kenworthy, D. F. S. Natusch, and R. E. Richards, *Mol. Phys.*, **13**, 27 (1967).

(7) D. F. S. Natusch and R. E. Richards, *Chem. Commun.*, 579 (1966).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

(9) R. Mathur and N. C. Li, *J. Amer. Chem. Soc.*, **86**, 1289 (1964).

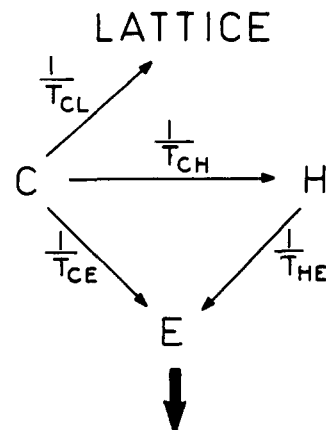


Figure 1. ^{13}C relaxation processes in a three-spin system.

scribed quantitatively by eq 7 and 8 if account is taken of the oxygen dissolved in his samples. The effects of dissolved oxygen, complex formation, and radical dimerization will be discussed elsewhere.

The theory suggests that any soluble, nonreactive paramagnetic species will reduce the Overhauser enhancement almost to zero when α is small. Preference can therefore be given to readily available, stable, easily handled materials. In cases where α is appreciable its value (and thus C_0) can be obtained by curve fitting. It appears feasible, therefore, to obtain the number of ^{13}C nuclei contributing to a given resonance by addition of a paramagnetic species to the sample. In addition the preferential reduction of ^{13}C Overhauser enhancements can be used to establish the binding sites of paramagnetic metal ions and spin labels in labile complexes.

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David F. S. Natusch

School of Chemical Sciences, University of Illinois
Urbana, Illinois 61801

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The Mechanism of the Chlorination of Anilines and Related Aromatic Amines. The Involvement of Nitrenium Ions¹

Sir:

The careful work of Neale and coworkers² and of Haberfield and Paul³ has firmly established the intermediacy of *N*-chloramines in the chlorination of aromatic amines by reagents such as *N*-chlorosuccinimide and calcium hypochlorite.⁴ Although there is little doubt about the initial step in the reaction being N-

(1) Paper XVI in a series on the Chemistry of Nitrenium Ions. For previous papers in this series, see P. G. Gassman and A. Carrasquillo, *Tetrahedron Lett.*, 109 (1971), and P. G. Gassman and J. H. Dygos, *ibid.*, 4749 (1970), and references therein.

(2) R. S. Neale, R. G. Schepers, and M. R. Walsh, *J. Org. Chem.*, **29**, 3390 (1964).

(3) P. Haberfield and D. Paul, *J. Amer. Chem. Soc.*, **87**, 5502 (1965).

(4) Various other chlorinating agents have been used. For additional synthetic applications, see T. A. Foglia and D. Swern, *J. Org. Chem.*, **33**, 4440 (1968); J. M. Muchowski, *Can. J. Chem.*, **48**, 422 (1970); and A. M. Pinchuk, L. N. Markovskii, and I. M. Kosinskaya, *Zh. Obshch. Khim.*, **38**, 1008 (1968).