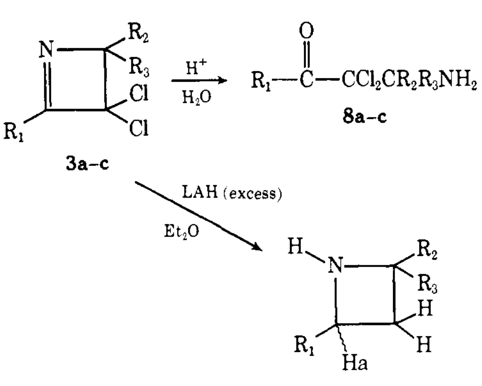

no other products present. The structures of azetidines **9a–c** were obvious from their ir, nmr, and mass spectra. That the geminal hydrogens were in the 3 position in **9a** and **b** was indicated by the low-field (τ 5.4) broad triplet for H_a. In **9c** H_a could not be resolved, but the mass spectra showed the expected α cleavage at *m/e* 43 ($CH_3CH{=}NH\cdot^+$) and no peak at *m/e* 30 ($CH_2{=}NH\cdot^+$).

The regioselectivity in the formation of **3** over **4** and **5** cannot be equated with conformational effects[9] governing a concerted loss of N_2 with ring enlargement, since the conformers of **2** are expected to be of nearly equal stability and should produce a mixture of **3**, **4**, and **5**.

The driving force for ring expansion in preference to formation of a cyclopropylimine **5** (Ph migration) must be relief of ring strain in going from a three- to a four-membered ring. Apparently, the reaction involves selective migration of the electron richer CH_2 (or CR_2) rather than the CCl_2 ring residue to the electron-deficient nitrogen atom.

Rate data on the pyrolysis of cyclopropyl azides **2** (Table I) indicate that in general cis substituents (see **2b** and **2c**) accelerate the reaction. This implies that the rate-determining step cannot be loss of N_2 unless the reaction is concerted. A concerted ring expansion with loss of nitrogen is in fact suggested by the negative entropy of activation ($\Delta S^{\ddagger} = -18$ eu for **2c** $\rightarrow$ **3c**) and is in accord with data on pyrolysis of simple alkyl azides.[10]

Acknowledgment. Support of this work by a grant (CA 04474) from the National Cancer Institute (Public Health Service) is gratefully acknowledged.

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(9) Different migratory aptitudes in the photolysis of organic azides have been ascribed to ground-state conformational preferences; see R. M. Moriarty and R. C. Reardon, *Tetrahedron*, **26**, 1379 (1970).

(10) W. Lwowski, "Nitrenes," Interscience, New York, N. Y., 1970, Chapters 3 and 4.

(11) NIH Predoctoral Fellow, 1968–1971.

A. B. Levy,[11] A. Hassner*
Department of Chemistry, University of Colorado
Boulder, Colorado 80302

Received December 5, 1970

Effect of CH Scalar Coupling on ^{13}C Transverse Relaxation Times

Sir:

In view of the increasing interest in ^{13}C nmr spectroscopy, we wish to report some preliminary relaxation studies of ^{13}C-enriched compounds. We find that the transverse relaxation times, T_{2C} ($\equiv R_{2C}^{-1}$), are usually shorter than the longitudinal relaxation times, T_{1C} ($\equiv R_{1C}^{-1}$). This result influences the sensitivity and resolution in both conventional and Fourier transform (FT) ^{13}C spectra and, in particular, affects the signal enhancement obtainable by the use of refocusing schemes such as driven equilibrium and spin–echo Fourier transform (DEFT and SEFT) techniques.[1–3]

The T_{2C} measurements were performed at 15.08 MHz by the usual Meiboom–Gill[4]-modified Carr–Purcell[5] technique on a high-resolution magnet with external fluorine lock. The π pulse width was 6 μsec and the inhomogeneity over the sample gave a free-induction decay constant $T_2^* \sim 100$ msec. Degassed and sealed sample tubes were constricted below the liquid surface to minimize interchange between liquid and vapor. T_{1C} and T_{1H} values were measured by π–τ–$\pi/2$ pulse sequences, T_{1C}'s at 15.08 MHz, T_{1H}'s at 23.2 MHz. The T_1 and T_2 values were obtained by the usual least-squares fitting procedures.

Table I. Relaxation Times[a] for 60% ^{13}C-Enriched Compounds at 25°

	T_{1C}, sec	T_{2C}, sec	T_{1H},[b] sec
$^{13}CH_3I$	13.4	3.9	10.9[c]
$^{13}CH_3COOCD_3$[d]	19.2	6.1	12.5
$^{13}CS_2$	48[e]	38	

[a] The experimental error is estimated to be ~5%. [b] T_{1H} for 100% enriched compounds will be less than these values. [c] T_{1H} for $^{12}CH_3I$ at 25° is reported [M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **69**, 659 (1965)] to be 12.5 sec. [d] Deuterium enrichment is 99%. [e] T_{1C} = 30 sec (15 MHz, 26–28°) was measured by rapid adiabatic passage: A. Olivson, E. Lippmaa, and J. Past, *Eesti NSV Tead. Akad. Toim.*, **16** 390 (1967).

Table I shows that T_{2C} is substantially shorter than T_{1C}[6] for methyl iodide and methyl-d_3 acetate-^{13}C. We would like to point out that short T_{2C}'s occur when relaxing spin-$^1/_2$ nuclei, *e.g.*, protons, are coupled to ^{13}C such that

$$A \equiv 2\pi J \gg R_{1H} \qquad (1)$$

where $R_{1H} \equiv 1/T_{1H}$. Gutowsky, Vold, and Wells[8] have pointed out the analogy between chemically exchanging, equally populated, uncoupled two-site systems and relaxing, scalar-coupled AX systems. They suggest that the two cases are related by the simple substitution of $\Omega \rightarrow A/2$ and $k \rightarrow R_{1X}$, where Ω is half the chemical shift between the two sites, k the exchange rate, and R_{1X} the spin–lattice relaxation rate of X.

Scalar contributions to R_{2A} for a general AX_n system originate from relaxation processes within the X manifold which preserve the spin state of A while changing the scalar coupling energy by a nonzero multiple of J. These processes randomly alter the precession frequency

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(1) E. D. Becker, J. A. Ferretti, and T. C. Farrar, *J. Amer. Chem. Soc.*, **91**, 7784 (1969).

(2) A. Allerhand, *ibid.*, **92**, 4482 (1970).

(3) J. S. Waugh, *J. Mol. Spectrosc.*, **35**, 298 (1970).

(4) S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **29**, 688 (1958).

(5) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

(6) We realize that T_1 is not rigorously defined for strongly coupled AX_n systems (see, *e.g.*, ref 7, p 295) but we could detect no deviation from exponential behavior.

(7) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 311.

(8) H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, **43**, 4107 (1965).

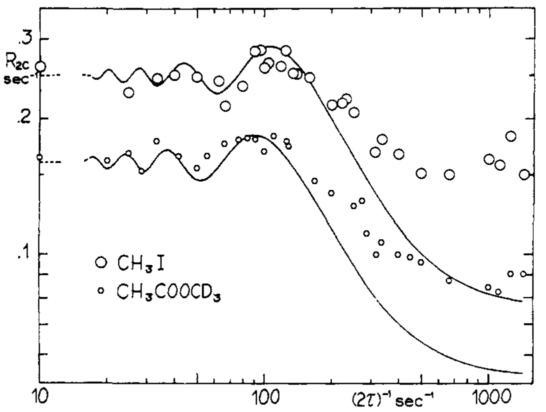

Figure 1. Apparent ^{13}C transverse relaxation rates *vs.* Carr–Purcell pulse repetition rate $(2\tau)^{-1}$ for 60% enriched $^{13}CH_3I$ and $^{13}CH_3COOCD_3$. The theoretical curves assume the model of a two-spin AX system, where $R_{2C}{}^0 = R_{1C}$ and $\bar{R}$ is chosen to agree with the slow pulse limit. This model is based on $\Delta I_H = \pm 1$ transition only; however, inclusion of $\Delta I_H = \pm 2$ would improve the agreement in the region above $(2\tau)^{-1} = 100$ sec^{-1}.

of A causing irreversible decay of the magnetization in the transverse plane. In particular, for $^{13}CH_3I$ and $^{13}CH_3COOCD_3$, whose T_1's are dominated by intramolecular dipolar effects, the scalar contribution to R_{2C} is determined by the rate, $\bar{R}$, averaged over all states, of such H transitions. One might guess that $\bar{R} = 3R_{1H}$; however, R_{1H} is based not only on the number of such transitions, but also on the ability of these to produce thermal equilibrium. Thus, for example, a $\Delta I_H = \pm 2$ transition is a more effective T_{1H} process than $\Delta I_H = \pm 1$, whereas $\bar{R}$ considers both equally. This implies that $\bar{R} < 3R_{1H}$ for a CH_3 system; to be more quantitative is beyond the scope of this communication.

The theory for coupled AX systems presented by Gutowsky, *et al.*,[8] predicts a sigmoidal plot[8,9] of R_{2C} *vs.* $(2\tau)^{-1}$ for Carr–Purcell measurements with π pulse repetition rates $(2\tau)^{-1}$. Two limits are predicted. For rapid pulse rates

$$R_{2C} \rightarrow R_{2C}{}^0 \qquad (2\tau)^{-1} \gg A \qquad (2)$$

where $R_{2C}{}^0$ is the transverse relaxation rate in the absence of scalar coupling effects and is often very close to R_{1C}. For slow pulse rates

$$R_{2C} \rightarrow R_{2C}{}^0 + \bar{R} \qquad (2\tau)^{-1} \ll A \qquad (3)$$

and a damped oscillation is predicted[8,9] for $(2\tau)^{-1} \lesssim J$.

In Figure 1, R_{2C} for $^{13}CH_3I$ and $^{13}CH_3COOCD_3$ is plotted *vs.* $(2\tau)^{-1}$. The values of J_{CH} are 152 and 130 Hz, respectively, and there is good qualitative agreement between these curves and those predicted by theory.[8,9] A maximum in R_{2C} is predicted for $(2\tau)^{-1} = 2J/3$; we observe a maximum in the vicinity of this value. We also find a less rapid decrease in R_{2C} at higher pulse rates, which is consistent with the occurrence of intramolecular $\Delta I_z = \pm 2$ transitions between proton spin states resulting in coupling energy changes of $\pm 2J$. Pulse repetition rates faster than those experimentally available to us $[(2\tau)^{-1} > 1000$ sec$^{-1}]$ are necessary to pulse these effects completely away. An unsatisfactory feature of this graph is that the values of R_{2C} seem to plateau above R_{1C} at the higher pulse rates. For $^{13}CH_3I$ the scalar coupling to $^{127}I^7$ may result in $R_{2C}{}^0 > R_{1C}$; however, the higher limiting value of $R_{2C}{}^0$ observed for $^{13}CH_3COOCD_3$ cannot be explained this way. At these high pulse rates we may be exceeding the duty cycle of our transmitter; we plan to investigate compounds where the fast pulsing limit should occur well within our instrumental capabilities. In the slow pulsing limit our experimental values indicate, as expected, that $\bar{R} < 3R_{1H}$, when $R_{2C}{}^0 = R_{1C}$. Corrections required to account for scalar coupling effects from I in $^{13}CH_3I$ would decrease $\bar{R}$ even further. The small ^{13}C–D coupling in $^{13}CH_3COOCD_3$ can in principle contribute to R_{2C}, but any effect has been pulsed away in these measurements $[(2\tau)^{-1} \geq 10$ sec$^{-1}]$.

As expected, T_{2C} of $^{13}CS_2$ was found to be independent of the Carr–Purcell time. Experiments in this laboratory[10] have shown that spin rotation is the dominant relaxation mechanism for $^{13}CS_2$ at 15 MHz, in agreement with data reported elsewhere.[11]

In summary, it appears that the ultimate resolution in ^{13}C spectra will be of the order of the proton line widths, as long as eq 1 is satisfied for all coupled nuclei. Furthermore, the advantage predicted by the multiple-pulse, refocusing method[1,2] over the normal FT technique will be greatly reduced, since the promised sensitivity enhancement[3] was based on the assumption that $T_2 \approx T_1$.

The foregoing remarks relate to undecoupled spectra only. For pseudorandom proton noise decoupling the ^{13}C line widths should be a function of the H_2 rf level. At lower rf power, for which $A \gtrsim \tau_H{}^{-1}$, where τ_H is the effective lifetime of the proton spin states in the presence of H_2, R_{2C} should increase and reach a maximum as the rf power increases. For rf power sufficiently high that $A \ll \tau_H{}^{-1}$, R_{2C} should then decrease toward $R_{2C}{}^0$. The refocusing techniques might therefore still be useful under conditions of strong, random proton decoupling.

(9) A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, 42, 1587 (1965).

(10) T. C. Farrar, S. J. Druck, R. R. Shoup, and E. D. Becker, to be published.

(11) In general, our I_2 measurements are reproducible to $\sim\pm 5\%$; however, systematic errors may increase for very fast pulse rates and very long T_2's. The latter may account for the difference between T_{1C} and T_{2C} for $^{13}CS_2$.

R. R. Shoup*
National Institutes of Health
Bethesda, Maryland 20014

D. L. VanderHart
National Bureau of Standards
Washington D. C. 20234

Received November 30, 1970

Polarized Single-Crystal Absorption Spectrum of Cytosine Monohydrate

Sir:

In this communication we present polarized absorption spectra of single crystals of cytosine monohydrate. Callis and Simpson have recently reported a polarized reflectance study on cytosine monohydrate and 1-methylcytosine.[1] The results of these authors are in excellent agreement with our own, but our more sensitive direct absorption measurements using a microspectrophotometer permit additional and more quantitative

(1) P. R. Callis and W. T. Simpson, *J. Amer. Chem. Soc.*, 92, 3593 (1970).