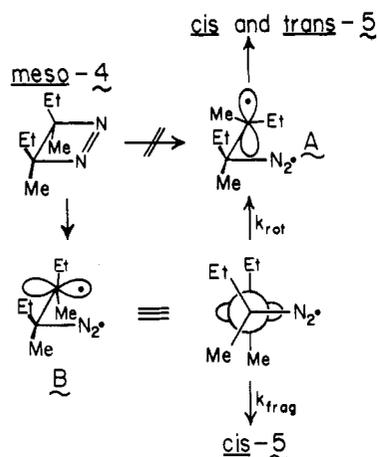


Scheme III



diradical B k_{frag} may well exceed k_{rot} ; i.e., the observation of overall cis elimination of N_2 from diazine 4 does not exclude a stepwise decomposition mechanism for diazines, e.g., via diradical B.¹⁹

In summary, these results (a) indicate the unimportance of electronically excited states in this highly exothermic reaction, (b) exclude one of the most probable of the possible synchronous modes of decomposition, (c) place severe constraints on the nature of the lifetime of a diradical derivable by a stepwise mode of decomposition.

References and Notes

- (1) Supported, in part, by the National Science Foundation and the National Institutes of Health.
- (2) (a) S. Patai, Ed., "The Chemistry of the Hydrazo, Azo and Azoxy Groups", Wiley, New York, 1975; (b) T. Koenig in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 3.
- (3) (a) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *J. Am. Chem. Soc.*, **91**, 5668 (1969): first report calling attention to orbital symmetry questions in diazine decompositions. (b) F. D. Greene and K. E. Gilbert, *J. Org. Chem.*, **40**, 1409 (1975): first report of a monocyclic alkyl diazine (tetramethyldiazine). (c) P. S. Engel, R. A. Hayes, L. Kelfer, S. Szilagyi, and J. W. Timberlake, *J. Am. Chem. Soc.*, **100**, 1876 (1978): includes kinetics and thermochemical results on tetramethyldiazine.
- (4) (a) See G. B. Schuster, N. J. Turro, H.-C. Steinmetzer, A. P. Schaap, G. Falser, W. Adam, and J. C. Liu, *J. Am. Chem. Soc.*, **97**, 7110 (1975), and references therein; K. A. Zaklika, P. A. Burns, and A. P. Schaap, *ibid.*, **100**, 318 (1978). (b) See also C. R. Jones and P. B. Dervan, *ibid.*, **99**, 6772 (1977).
- (5) Satisfactory combustion and spectral data were obtained for the new compounds in this study. Analysis of the isomer composition of dinitrohexane 1 was made by GC on a 15% SE-30, Chromosorb W column. The *meso*-1 (chunky rosettes) has mp 87–88 °C; *dl*-1 (plates) mp 85–86 °C. Separation of the isomers of diazine *N*-oxide (3) or diazine 4 could not be effected under a variety of GC conditions examined. Compounds 1, 2, 3, 4, and 8 all showed some differences in the ¹H NMR for *meso* and *dl* forms, from which it was clear (as expected) that all of these interconversions occurred without loss of stereochemical integrity.
- (6) This compound has been considered to be the *meso*-diol: W. Reeve and M. Karickhoff, *J. Am. Chem. Soc.*, **78**, 6053 (1956).
- (7) D. M. Reichel, Ph.D. Thesis, University of Maryland, 1970; *Chem. Abstr.*, **75**, 62997n (1971). The assignment of *cis* and *trans* olefin stereochemistry in this thesis should be reversed since it is based on the erroneous designation of diol stereochemistry in ref 6, above. We wish to thank Dr. Reeve (University of Maryland) for spectra of the two pure olefins (*cis*- and *trans*-5) and for information on the GC separation of these isomers.
- (8) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).
- (9) Relative retention times on 25% dimethylsulfolane on Chromosorb P: octane (1.0), *trans*-5 (1.50), *cis*-5 (1.63). Other evidence in support of these olefin assignments: J.-G. Duboulin and B. Jousseau, *J. Organomet. Chem.*, **44**, C1 (1972); Dr. Greenlee of Chemical Samples Co., acetate pyrolysis data (private communication to F. D. Greene).
- (10) The limits of analysis were set by the proximity of the NMR peaks in *meso*- and *dl*-4 and by the (small) overlap of the peaks for *cis* and *trans* olefins 5 in the GC trace.
- (11) $\Delta H_{\text{rot}}^{\ddagger} = \Delta H_{\text{rot}}^{\ddagger}(\text{tetramethylethylene}) - \Delta H_{\text{rot}}^{\ddagger}(10) = -16.4 - 35.9^{\text{sc}} = -52.3 \text{ kcal/mol}$.
- (12) (a) The T_1 state is expected to lie <75 kcal/mol above the S_0 state of the hexene 5 (e.g., see S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973). (b) The branching ratio for triplet 2-butene is 1.02; see E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968). (c) Based on lack of absorption at wavelengths >210 nm (see also G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966, p 533).
- (13) Crossing to a T_1 state of a product does appear to take place in the thermal

- decomposition of dioxetanes.^{4a}
- (14) P. S. Engel, *J. Am. Chem. Soc.*, **98**, 1972 (1976).
- (15) A $2_a(N_2)$ would involve 180° rotation about the N–N bond in the process of decomposition of 4; "partial $2_a(N_2)$ " would involve 90° rotation about the N–N bond.
- (16) See H. Fischer in "Free Radicals", Vol. 2, J. K. Kochi, Ed., Wiley, New York, 1973, p 482–483 and references cited.
- (17) A. Tsolis, S. G. Mylonakis, M. T. Nieh, and S. Seltzer, *J. Am. Chem. Soc.*, **94**, 829 (1972).
- (18) N. A. Porter, G. R. Dubay, and J. G. Green, *J. Am. Chem. Soc.*, **100**, 920 (1978). See also A. R. Lepley and G. L. Closs, "Chemically Induced Magnetic Polarization", Wiley, New York, 1973, p 112–117.
- (19) Of interest is the comparison of the predominance of *cis* elimination of N_2 in this study with the low selectivity observed in some cyclic peroxide, six-membered-ring disubstituted systems;^{4b} see also P. B. Dervan and T. Uyehara, *J. Am. Chem. Soc.*, **98**, 1262 (1976).
- (20) American Association of University Women Fellow, 1975–1976.

Dabney K. White,²⁰ Frederick D. Greene*

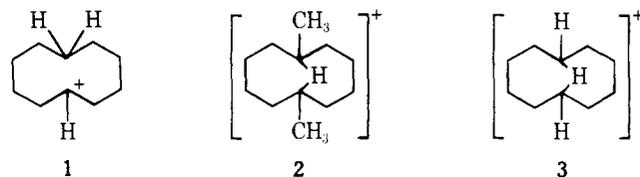
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received May 26, 1978

The Observable Cyclodecyl Cation. A Novel "Secondary" Hydrogen-Bridged Carbocation

Sir:

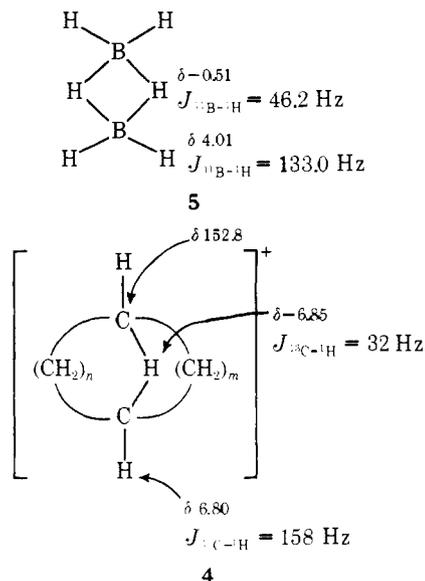
The cyclodecyl cation (conventionally written as 1), a well-studied¹ reactive intermediate noted for its ability to undergo transannular hydride shifts, has now been prepared and characterized in strong acid solution and we describe herein the very unusual features of both the ¹H and ¹³C NMR spectra which lead us to conclude that this cation, like the previously described 1,6-dimethyl analogue 2,² possesses a 1,6- μ -hydrido structure 3.



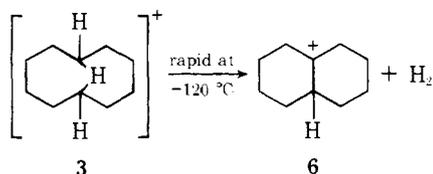
Addition of 1-chlorocyclodecane to a solution of either 1:1 $\text{SbF}_5\text{-FSO}_3\text{H}$ or pure SbF_5 in a mixture of $\text{SO}_2\text{ClF-SO}_2\text{F}_2$ at ca. -140 °C or the addition of either *cis*- or *trans*-cyclo-decene to the 1:1 $\text{SbF}_5\text{-FSO}_3\text{H}$ mixture³ results in a light yellow solution showing similar NMR features.⁴ The proton spectrum measured at -130 °C⁵ is the most informative and is characterized in particular by two broad peaks,⁶ one at δ 6.80 and a second of one half the area at δ -6.85 , a unique high-field position range shown previously² to be characteristic of the bridging hydrogen in 2. These two peaks can therefore be assigned to the terminal and bridging hydrogens of a μ -hydrido structure, i.e., partial structure 4. Coupling, if any, between these protons is obscured by the broadness of the peaks.⁷ The remaining 16 protons in 3 form a broad envelope of overlapping peaks from ca. δ 1–3.⁸

The lowest field ¹³C peak (-130 °C) is found at δ 152.8⁹ and is assignable to the two carbons involved in the hydrido bridge. Careful selective ¹H decoupling experiments¹⁰ show that this ¹H coupled ¹³C peak is a doublet of doublets with remarkably different coupling constants, $J_{13\text{C}-1\text{H}} = 158 \pm 5$ and 32 ± 5 Hz, the former from coupling to the δ 6.8 ¹H peak and the latter the coupling of this carbon to the high-field " μ -hydrido" proton.¹¹ The completed NMR characterization of the bridged region in 3 can be compared with the corresponding parameters in diborane, cf. 4 vs. 5.¹¹

Quenching experiments have been carried out on the cyclodecyl cation by adding the cation solution to vigorously



stirred 2-methylbutane- K_2CO_3 slurry at -130°C . In all cases, a mixture of *cis*- and *trans*-decalin is recovered in good yield.¹² The quench reaction probably involves the decalyl cation **6** since similar quench products are obtained when this cation is quenched under the same conditions.¹³ The cyclodecyl cation **3**, in our strong acid solvents,¹⁴ rearranges quantitatively and rapidly into H_2 and the decalyl cation **6** at -120°C and it is conceivable that this rearrangement rate is even faster under the quench conditions.

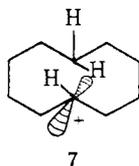


There are two major uncertainties concerning our cyclodecyl cation structure assignment. One question involves the position of the transannular bridging, i.e., are m and n in structure **4** equal ($m = n = 4$)? Secondly, what is the nature of the potential barrier involving the bridging hydrogen—is it symmetrical or a rapidly equilibrating structure?

The μ -hydrido bridge has been assigned a 1,6 position, i.e., **3**, for two reasons: (1) this 1,6 bridging also exists in cation **2**, where it can be positionedally fixed, and (2) the very ready formation of the decalyl cation can be explained by the loss of the bridging hydride and a terminal proton in a concerted reaction.¹⁵

Concerning the potential barrier, we favor a symmetrical μ -hydrido structure for the following reasons.

(1) The very high-field chemical shift observed for one of the transannular protons if **1** were a conventional secondary cyclodecyl cation could only be rationalized if there existed a cation conformation where this proton was located directly in the face of the empty p_z orbital (shielding region) of the cation (structure **7**). The rapid transannular shift of this hydrogen



(ΔG^\ddagger would have to be ≤ 4 kcal/mol¹⁶) would complete this hypothetical picture. We feel, however, that such a possible conformation is too stable to be explained solely by steric arguments.¹⁷ For example, there is no detectable interchange

of the two transannular protons shown in **7** (ΔG^\ddagger for this barrier ≥ 8 kcal/mol), nor do we observe any clearcut indication¹⁸ for 1,2-hydride shifts, expected to be very rapid in a conventional secondary cycloalkyl cation.¹⁹

(2) The observed coupling between the proposed hydrido hydrogen and the attached carbons is much smaller than can be accommodated for in an equilibrating structure, 32 ± 5 vs. ca. 65 Hz.²¹ Note also the similarity here to the diborane situation and also to cation **2**.

(3) Molecular orbital calculations on C_2H_7^+ and related systems²² show a single minimum, symmetrical hydrogen structure. The bridging hydrogen carries a slight negative charge in these calculations²³ and we feel that this can in the main account for the experimentally observed high-field NMR position.

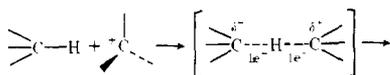
Experiments are in progress on related cyclic and acyclic carbocations to find out if these bridging structures are unique to the 10-membered rings. In particular, we feel that the C-H-C bond may be bent in the cyclodecyl case, for steric reasons, and that a more favorable geometry might be found for linear bonding.

Acknowledgments. We thank the National Research Council of Canada for generous financial support. Cities Service Co., Cranbury, N.J., generously provided the cyclodecane starting material.

References and Notes

- (a) V. Prelog in "Perspectives in Organic Chemistry", Interscience, New York, 1956, p 96; (b) V. Prelog, *Rec. Chem. Prog.*, **18**, 247 (1957); (c) V. Prelog, *Angew. Chem.*, **70**, 145 (1958); (d) V. Prelog, *Bull. Soc. Chim. Fr.*, 1433 (1960); (e) V. Prelog and J. G. Traynham in "Molecular Rearrangements", Vol. 1, P. de Mayo, Ed., Interscience, New York, 1963, p 593; (f) A. C. Cope, M. M. Martin, and M. A. McKervey, *Q. Rev.*, **20**, 119 (1966); (g) H. H. Westen in "Conformational Analysis, Scope and Present Limitations", G. Chiurdoglu, Ed., Academic Press, New York, 1971, p 259.
- R. P. Kirchen and T. S. Sorensen, *J. Chem. Soc., Chem. Commun.*, submitted for publication. The μ -hydrido proton is found at -3.9 and -5.8 (average) in two isomeric forms of this cation which have been assigned a *cis* and *trans* geometry, respectively.
- Use of a chlorine-free precursor rules out the possibility of any chlorine containing cation, etc.
- Using the cycloalkenes, the spectra are not as clean—extra peaks are present.
- All spectra must be obtained at temperatures lower than -120°C . In the case of ^{13}C spectra, fresh samples must be continuously provided for the various decoupling experiments.
- Half-width is ~ 30 – 35 Hz and this does not change appreciably as the temperature is varied from -140 to -117°C . Both the acid solvent peaks and the rearranged decalyl cation peaks are much sharper than this.
- Mutual decoupling of either the δ 6.8 or -6.85 peak fails to sharpen up the other.
- This region integrates for more than 16 protons (compared with the 2 H:1 H area of the bridging region hydrogens) and this varies with experiment. In all cases, some decalyl cation **6** is formed in the preparation and all of the protons from this cation are found in the δ 1–3 region.
- This is the major peak and only this one is under discussion. Two, much smaller peaks are also present in this region at δ 150.1 and 146.6, each ~ 10 – 15% of the large peak area. These peaks are from species which seem to be in equilibrium with **3** (similar peak ratios exist in spectra where more than 50% rearrangement to the decalyl cation has occurred), but we do not know whether they possess bridging hydrogens (only one high-field ^1H peak is observed; so superimposition of peaks would be necessary if they do). In the high field ^{13}C region, four distinct, viscosity broadened peaks are present at δ 47.8, 41.2, 34.3, and 30.8, ratios $\sim 1:2:4:2$, based on 2 C for the δ 152.8 peak. The latter three peaks are probably from the major species. It should be pointed out that possibilities exist for both the *cis* and *trans* isomer of **3,2** each of these having various ring conformation possibilities.
- The δ 152.8 ^{13}C peak was recorded, each a number of times, with selective, low power, ^1H decoupling at δ 6.8, at δ -6.85 , and in the δ 1–2 region. These were compared to the completely coupled ^{13}C spectrum.
- To our knowledge, the bridgehead and bridging hydrogens show the most divergent ^{13}C - ^1H coupling constants and chemical shifts (13.7 ppm) for two protons bonded to the same carbon. The diborane situation is not as extreme: J. B. Leach, C. B. Ungermann, and T. P. Onak, *J. Magn. Reson.*, **6**, 74 (1972).
- The *trans*/*cis* ratio was variable but close to 2:1 from four separate experiments.
- Same temperature and quench conditions. In four separate runs, the same $\sim 2:1$ *trans*/*cis* ratio was observed.
- Also reported when cyclodecanol is added to FSO_3H - SbF_5 at -80°C : G. A. Olah, D. P. Kelly, and R. G. Johanson, *J. Am. Chem. Soc.*, **92**, 4139 (1970). We find the rate of this reaction ($t_{1/2} = \sim 1$ h at -130°C) to be essentially independent of ion concentration or the strong acid system used.

- (15) Labeling experiments are underway to test for this possibility.
- (16) Carbon peak (δ 152.8) half-width = 25.8 Hz at -130°C and assuming a separation of 300 ppm for the two carbons in a conventional secondary cation two-site NMR exchange.
- (17) The existence of these bridged cations may be related to the favorable energy release involved in forming a decalin-type geometry from the strained cyclohexyl system. However, we believe that the "extra" electronic stabilization of a symmetrical bridged species creates an even more stable conformation.
- (18) Up to -117°C , there is no substantial further line broadening in either the 2 H low-field peak or the 1 H high-field peak, $k_{\text{exchange}} \leq 50 \text{ sec}^{-1}$, $\Delta G^\ddagger \geq 8 \text{ kcal/mol}$ for a possible 1,2-H shift, based on simulated line-broadening curves calculated for this exchange.
- (19) For example, in the cyclopentyl cation, these shifts are so fast that only one carbon and one proton peak is observed, even at the lowest temperatures.²⁰
- (20) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).
- (21) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, pp 345-347.
- (22) (a) L. Radom, D. Poppinger, and R. C. Haddon, "Carbonium Ions", Vol. 5, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, 1976, Chapter 38; (b) A. Rauk, personal communication.
- (23) The term "hydride shift" in carbocation rearrangements has in the past been informally criticized on the grounds that the overall charge would likely be "smeared out" between the two carbons involved and the migrating hydrogen, i.e.



and hence that the term is useful only in an electron-bookkeeping sense. However, if our postulated bridged cations are any indication, the migrating hydrogen is indeed "hydride-like" at the midpoint of the transfer. These bridged cations emphasize the stability associated with charge alternation, i.e. $+ - +$. The higher field position of the bridging hydrogen in the secondary ion, compared with 2, suggests that more positive charge on carbon simply reinforces more negative charge on hydrogen.

R. P. Kirchen, T. S. Sorensen,* K. Wagstaff

The Department of Chemistry, University of Calgary
Calgary, Alberta, Canada T2N 1N4

Received June 23, 1978

"Tailored Detection" of Nuclear Magnetic Resonance Signals: Application to the Assignment of Carbon-13 Spectra

Sir:

We propose a new method for treating data in a Fourier transform NMR experiment in order to select signals which appear at certain predetermined frequencies and calculate their contribution to the total signal intensity. The technique might be used to determine the relative proportions of two components in a mixture, for monitoring the growth and decay of transient intermediates, or for comparing an unknown experimental spectrum with a library of stored spectra. It will also be shown to be useful for reducing the noise content of projections of two-dimensional Fourier transform spectra.¹⁻³ Several authors have described NMR experiments where the excitation is frequency selective or "tailored" to a particular requirement;⁴⁻⁶ the present method uses an equivalent "tailored detection" scheme.

To illustrate the principle, consider the problem of making a quantitative comparison between an experimental spectrum and a reference spectrum, as in the example of a library search of NMR data to match an unknown spectrum. This may be achieved by multiplying the experimental free induction decay $E(t)$ with that of the reference $A(t)$ and integrating the product. The result is a measure of the overlap between the experimental and the reference spectrum. The idea may be extended to the multiplication of $E(t)$ with an artificial time-domain reference signal $A'(t)$, obtained by Fourier transformation and suitable weighting of a "stick spectrum" defined by the operator.⁷ The Fourier transform of $A'(t)$ resembles this stick spectrum but has finite line widths determined by the weighting function. It may be thought of as a "mask" $A'(f)$ constructed to pass certain frequency compo-

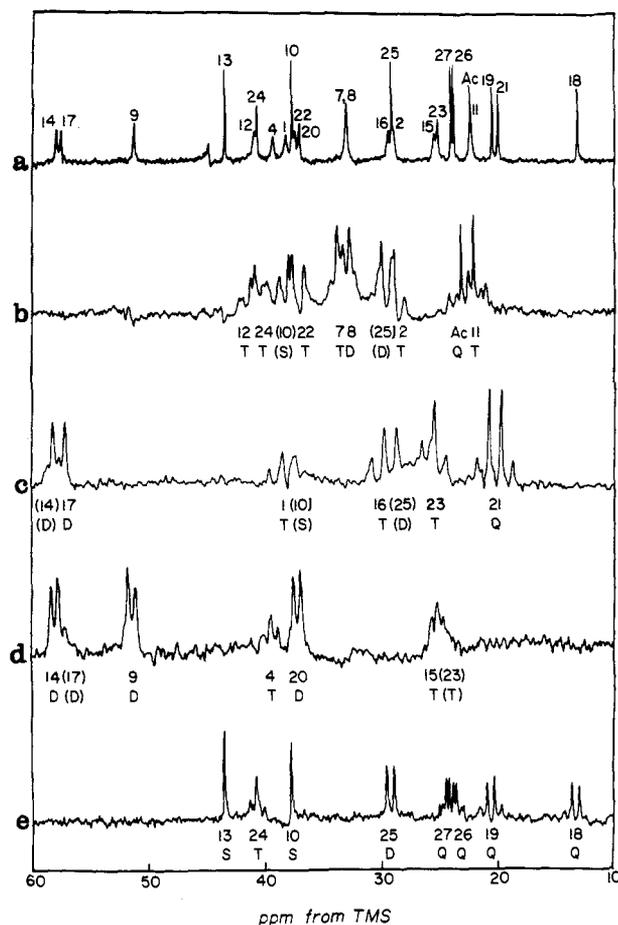


Figure 1. The ^{13}C NMR spectrum of the aliphatic region of cholesteryl acetate: (a) noise decoupled; (b-e) with selected resonances showing scaled-down proton-carbon splitting. The breakthrough of signals from nearby nonselected resonances is indicated by parentheses.

ponents of the spectrum $E(f)$, the Fourier transform of $E(t)$. The line widths of $A'(f)$ and $E(f)$ may be matched in order to optimize signal-to-noise ratio. Multiplication and integration of time domain signals has the twin advantages of speed (since the NMR signal may be processed as it is acquired) and economy of data storage (since the incoming free induction signal need not be stored). An "on-line" masking process necessarily leads to a loss of information; in some applications it might be preferable to store the entire experimental free induction signal and then later use suitable masks to extract various special types of information off-line.

We concentrate on a particular application—the improvement of signal-to-noise ratio in an experiment which presents ^{13}C NMR spectra in a form where all proton-carbon splittings are scaled down by a suitable constant factor R . This "J-scaling" experiment⁸ can considerably reduce the confusion caused by overlapping multiplets in conventional coupled ^{13}C spectra, and avoids some of the instrumental problems of off-resonance decoupling.⁹ The pulse sequence is described in detail elsewhere.⁸ The principle is to establish an evolution period t_1 during which proton-coupled carbon-13 precession takes place for a fraction $1/R$ of the time, broad band decoupling being used for the remainder of t_1 . A series of measurements of the NMR response is made over a range of values of t_1 , building up an "interferogram" $S(t_1)$. If the final J-scaled spectrum is to contain N significant points, then N separate measurements are needed to construct $S(t_1)$, a time-consuming operation which leads to poor sensitivity. The original version of the J-scaling experiment⁸ employed a refocusing method to improve the signal-to-noise ratio, but this