Other reactions using the cyclic system described will be reported in a full paper.

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Dynamic Nuclear Magnetic Resonance Studies on Complex Spin Systems. Degenerate Valence Isomerization of a 3,4-Diazanorcaradiene

Sir:

Dynamic nmr spectroscopy (dnmr) has been a standard and often indispensable tool for many years, but applications to chemical rate processes have frequently been suffering from a notorious unreliability.[1] Arrhenius parameters and enthalpies and entropies of activation obtained by this technique are particularly prone to be in error[1,2] and many workers therefore restrict themselves to reporting only free energies of activation. On theoretical grounds we recently concluded[3,4] that certain inherent shortcomings of nmr line-shape analyses could sometimes be alleviated by deliberately choosing to study more complicated spectra. We now wish to report experimental evidence in support of our claim.[5]

At −25.1°[6] the cyclopropyl protons of 2,5-dicarbomethoxy-3,4-diazanorcaradiene (**1**) (15% solution in $CDCl_3$), obtained from 3,6-dicarbomethoxy-1,2,4,5-tetrazine[7] and cyclopropene, give rise to an A_2BC nmr spectrum[8] (Figure 1, top), whose least-squares analysis (Figure 2, top) yields the chemical shifts (at 60 MHz downfield from internal TMS) $\nu_A = 183.07 \pm 0.06$ Hz, $\nu_B = 136.60 \pm 0.06$ Hz, $\nu_C = -1.62 \pm 0.06$ Hz, and coupling constants $J_{AB} = 8.92 \pm 0.07$ Hz, $J_{AC} = 4.75 \pm 0.07$ Hz, $J_{BC} = -3.85 \pm 0.08$ Hz. At higher temperatures the rate of an $A_2BC \rightleftarrows A_2CB$ mutual-exchange process becomes commensurate with the nmr time scale (Figure 1). Using linear least-squares functions for the temperature dependence of the static parameters (Figure 3), extrapolated to the broadened region,[9] rates were calculated (Figure 2) by the com-

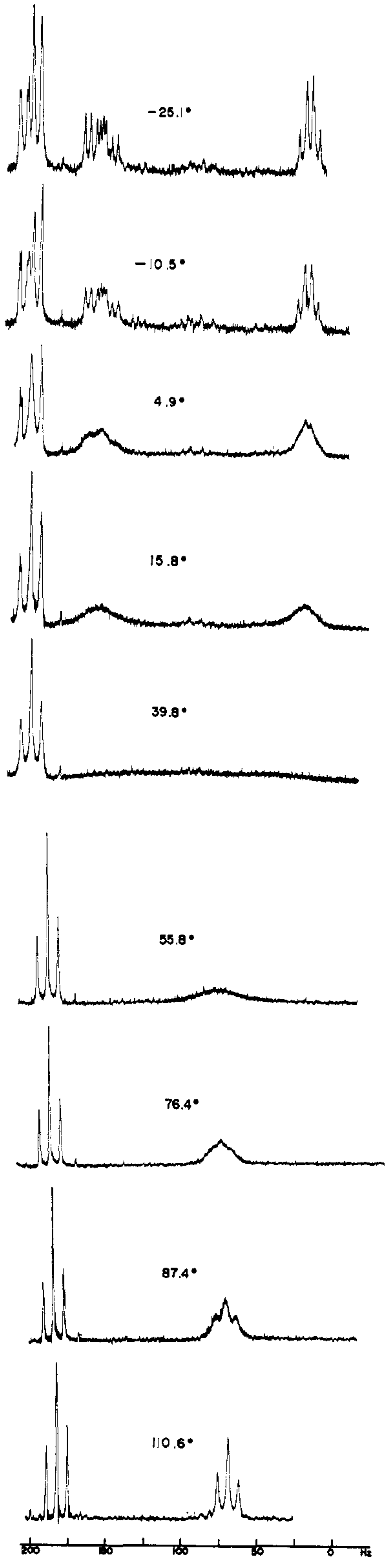

Figure 1. Experimental dnmr spectra of **1**.

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[1] For a recent review see G. Binsch, *Top. Stereochem.*, 3, 97 (1968).

[2] A. Allerhand, H. S. Gutowsky, J. Jonáš, and R. A. Meinzer, *J. Amer. Chem. Soc.*, 88, 3185 (1966).

[3] G. Binsch, *ibid.*, **91**, 1304 (1969).

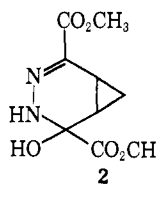
[4] D. A. Kleier and G. Binsch, *J. Mag. Resonance*, in press.

[5] Dr. K. I. Dahlqvist and Professor S. Forsén (Lund Institute of Technology, Sweden) have kindly informed us of experiments that lead to similar conclusions.

[6] Temperatures were calculated from the chemical shift difference between the methylene and hydroxyl resonances of an equimolar mixture of ethylene glycol and methyl-d_3 alcohol plus 0.03% of concentrated hydrochloric acid,[5] contained in a sealed capillary within the sample. The standard deviation of the temperature measurements was ±0.3°.

[7] M. Avram, I. G. Dinulescu, E. Marica, and C. D. Nenitzescu, *Chem. Ber.*, 95, 2248 (1962); J. Sauer and G. Heinrichs, *Tetrahedron Lett.*, 4984 (1966); G. Heinrichs, H. Krapf, B. Schröder, A. Steigel, T. Troll, and J. Sauer, *ibid.*, in press.

[8] Compound 1 is accompanied by *ca.* 3% of the hydrate 2, which could not be removed by recrystallizations.



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[9] This extrapolation predicts the time-averaged chemical shift of protons B and C at +125° to within 0.3 Hz of the measured value.

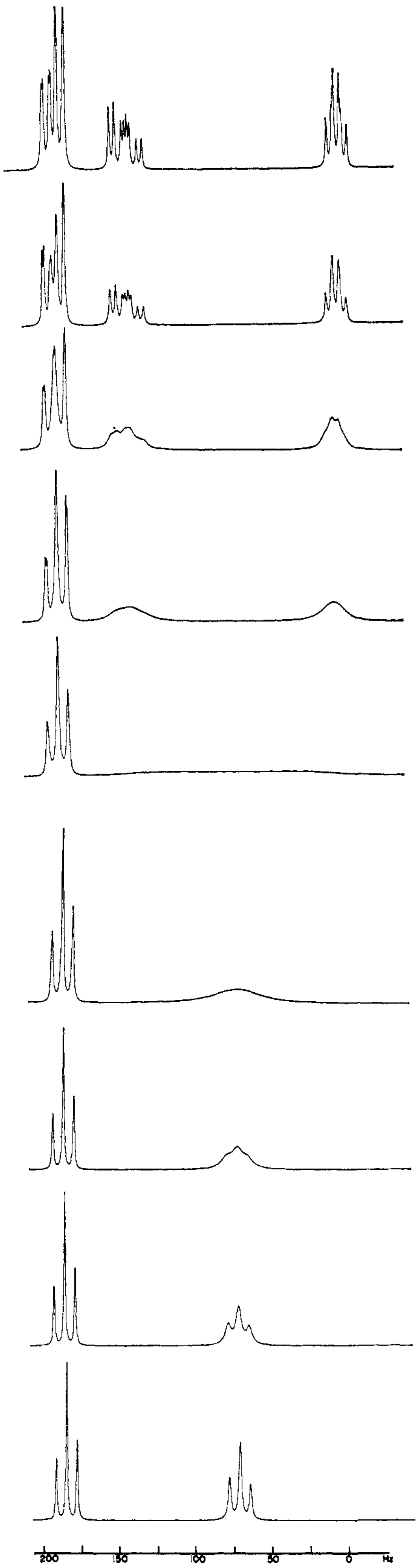

Figure 2. Computed dnmr spectra of **1**.

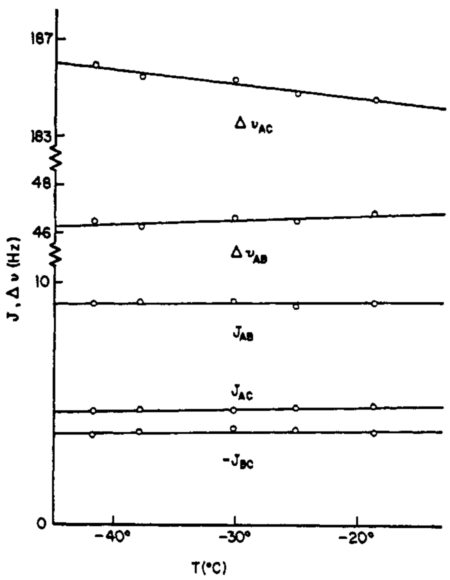

Figure 3. Temperature dependence of the static parameters of **1**.

puter program DNMR3.[10] An Arrhenius plot (Figure 4) yielded $E_a = 15.30 \pm 0.10$ kcal/mol and $\log A = 13.12 \pm 0.07$ and an analogous plot[1] of ln (k/T) *vs.* $1/T$, the Eyring parameters $\Delta H^{\ddagger} = 14.67 \pm 0.11$ kcal/mol and $\Delta S^{\ddagger} = -0.61 \pm 0.34$ eu.

From a quantitative point of view the four-spin spectra of Figures 1 and 2 offer the following advantages over the simpler AB $\rightleftharpoons$ BA exchange process, to which the present problem could be reduced by deuterating the positions 1 and 6 in **1**. (1) The two additional nuclei, though not participating in the exchange by themselves, introduce a desirable complexity that renders the shape of the spectra more sensitive to slight changes in the rate constant; in particular, these nuclei prevent the spectra from collapsing into a single line, at which point the total spectrum would essentially be determined by a single parameter, *i.e.*, the line width. (2) The various line separations in the spectra of Figures 1 and 2 may be regarded as a collection of individual clocks, running on different time scales, that become successively tuned to the changing rate of the molecular process, whereas for a simple spectrum with only a single clock reliable rate determinations may be limited to a narrow range around the "coalescence point." In the present example, for which dynamic measurements could be performed for a temperature range of 121°, spanning no less than four powers of ten in the rate constant, the sensitivity of the method was actually highest toward both ends of the range. (3) In complicated exchange-broadened spectra there may be transitions that are not noticeably affected by the rate constant varying in certain limits. Such lines can easily be identified by examining the real components of the complex spectral vector[3] and can then serve as an internal calibration of the apparent line width in the absence of exchange. In the spectra of Figures 1 and 2 lines of this type could be found throughout the entire temperature range.

With the availability of a general theory of exchange-broadened nmr line shapes[3,4] the mathematical and computational obstacles for treating reasonably complex spectra no longer exist. The computation of a spectrum in Figure 2 consumed 21 sec of central

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[10] DNMR3 is a more sophisticated version of DNMR2[11] that makes explicit use of the invariance properties[4] of the line-shape equation.

[11] G. Binsch and D. A. Kleier, "The Computation of Complex Exchange-Broadened NMR Spectra," Program 140, Quantum Chemistry Program Exchange, Indiana University, 1969.

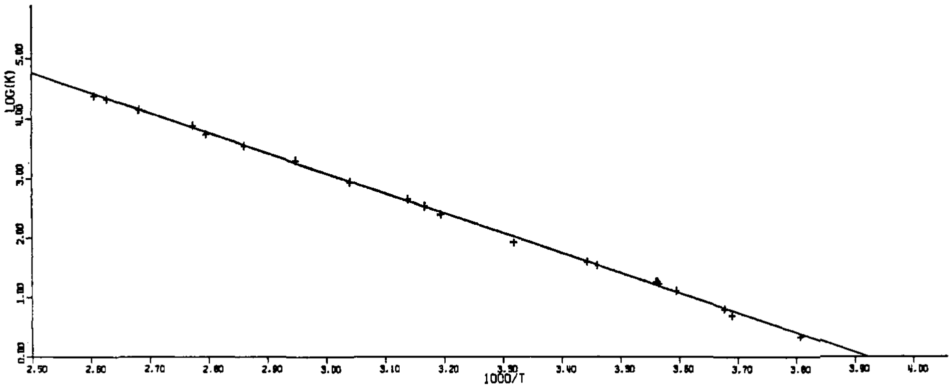
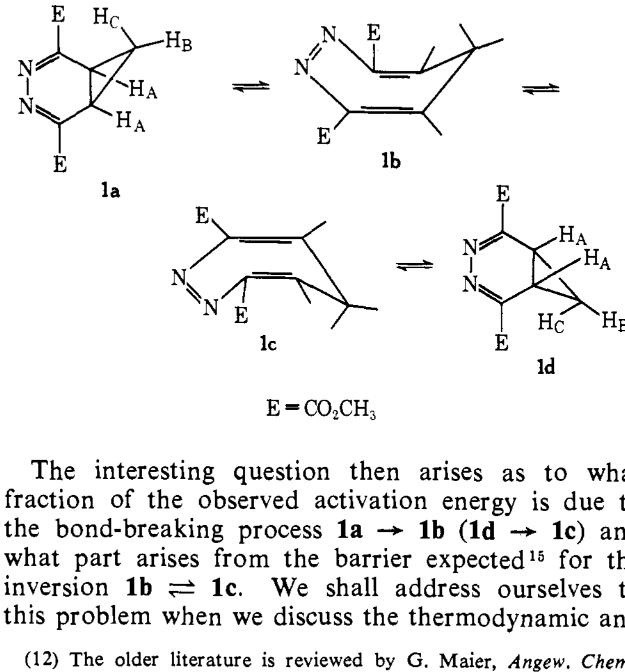


Figure 4. Arrhenius plot for the **1a** ⇌ **1d** exchange process.

processor time on a UNIVAC 1107 computer, which would be reduced to a fraction on the third-generation computers now in operation at many institutions.

On the basis of the extensive literature on the norcaradiene–cycloheptatriene problem[12,13] and its hetero analogs[12,14] it seems likely that the interconversion **1a** ⇌ **1d**, which is responsible for the temperature-dependent nmr spectra, proceeds through the diazacycloheptatrienes **1b** and **1c** as intermediates.



$E = CO_2CH_3$

The interesting question then arises as to what fraction of the observed activation energy is due to the bond-breaking process **1a** → **1b** (**1d** → **1c**) and what part arises from the barrier expected[15] for the inversion **1b** ⇌ **1c**. We shall address ourselves to this problem when we discuss the thermodynamic and kinetic data for a series of substituted diazanorcaradienes in the full paper.

Acknowledgments. The A-60A nmr instrument used in this investigation was acquired under National Science Foundation equipment Grant No. GP-6875.

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(12) The older literature is reviewed by G. Maier, *Angew. Chem.*, **79**, 446 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967).

(13) For some recent references see E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454, 1458 (1967); J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, *ibid.*, **89**, 4076 (1967); J. A. Berson, D. R. Hartter, H. Klinger, and P. W. Grubb, *J. Org. Chem.*, **33**, 1669 (1968); T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Lett.*, 3581 (1967); T. Toda, M. Nitta, and T. Mukai, *ibid.*, 4401 (1969); M. Jones, Jr., *J. Org. Chem.*, **33**, 2538 (1968); *Angew. Chem.*, **81**, 83 (1969); M. Jones, Jr., A. M. Harrison, and K. R. Rettig, *J. Amer. Chem. Soc.*, **91**, 7462 (1969); M. Jones, Jr., and E. W. Petrillo, Jr., *Tetrahedron Lett.*, 3953 (1969); C. J. Rosteck and W. M. Jones, *ibid.*, 3957 (1969); D. Schönleber, *Angew. Chem.*, **81**, 83 (1969); *Chem. Ber.*, **102**, 1789 (1969); T. Tsuji, S. Teratake, and H. Tanida, *Bull. Chem. Soc. Jap.*, **42**, 2033 (1969); N. Görlitz and H. Günther, *Tetrahedron*, **25**, 4467 (1969).

(14) E. Vogel, *Angew. Chem.*, **79**, 429 (1967); M. A. Battiste and T. J. Barton, *Tetrahedron Lett.*, 1227 (1967); G. Maier and U. Heep, *Chem. Ber.*, **101**, 1371 (1968); H. Prinzbach and P. Vogel, *Helv. Chim. Acta*, **52**, 396 (1969).

(15) F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964); F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964); A. Mannschreck, G. Rissmann, F. Vögtle, and D. Wild, *Chem. Ber.*, **100**, 335 (1967).

(16) National Science Foundation Predoctoral Fellow.

(17) Alfred P. Sloan Research Fellow.

(18) The Radiation Laboratory is operated by the University of Notre Dame under contract with the U.S. Atomic Energy Commission. This is AEC Document No. COO-38-725.

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Solvent Assistance in the Solvolysis of Secondary Substrates. IV. The Solvolytic Behavior of the Di-*t*-butylcarbinyl System

Sir:

Highly crowded acyclic derivatives usually react rapidly in carbonium ion processes because of the opportunities for "B strain" relief in going from ground state to transition state.[1-4] On the basis of such reasoning and the very slow rate of $NaBH_4$ reduction of di-*t*-butyl ketone, Brown and Ichikawa[1b] predicted "a very fast rate of solvolysis for the tosylate of di-*t*-butylcarbinol." This prediction, though untested,[5] is supported by numerous theoretical arguments.[6] From the very low carbonyl stretching frequency of di-*t*-

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(1) (a) H. C. Brown and R. S. Fletcher, *J. Amer. Chem. Soc.*, **71**, 1845 (1949); 73, 1317 (1951); (b) H. C. Brown and K. Ichikawa, *ibid.*, **84**, 373 (1962).

(2) P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968), and earlier papers therein cited.

(3) (a) E. D. Hughes, *Quart. Rev. Chem. Soc.*, **5**, 245 (1951); *Bull. Soc. Chim. Fr.*, C39 (1951); (b) F. Brown, T. D. Davies, I. Dostrovsky, O. J. Evans, and E. D. Hughes, *Nature* (London), **167**, 987 (1951).

(4) V. J. Shiner, Jr., and G. F. Meier, *J. Org. Chem.*, **31**, 137 (1966).

(5) The earlier history is confused. Hughes[3] alluded several times to work with di-*t*-butylcarbinyl chloride (I, X = Cl), but full details were never published. The activation parameters for 80% ethanolysis of this compound were said to be "of quite the same order as for simpler secondary alkyl chlorides."[3b] Brown and Ichikawa were unable to prepare I (X = OTs), but quoted Hughes' work as showing that the corresponding chloride exhibited "unusually high reactivity."[1b] Apparently, the earlier reference was misread.

(6) A fuller analysis may be found in the Ph.D. Thesis of J. J. Harper, Princeton University, Princeton, N. J., 1968.