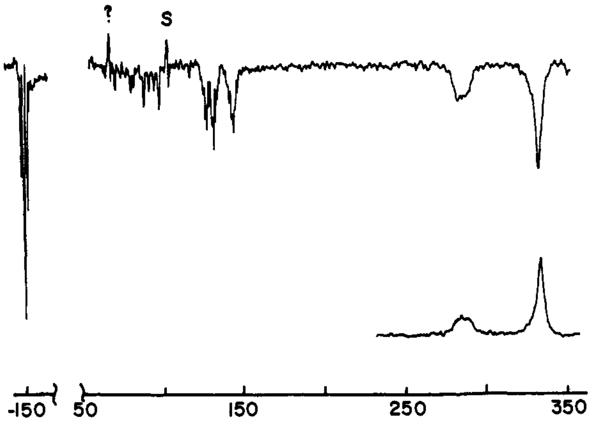

Figure 1. Spectra of 0.14 M cycloheptanone in chloroform at 60 MHz: lower trace, dark spectrum; upper trace, spectrum obtained during irradiation. Chemical-shift scale is in hertz from $CHCl_3$. S denotes ^{13}C satellite of solvent.

intersystem crossing in II. As has been pointed out previously,[2] $T_{\pm}$–S mixing, in contrast to T_0–S mixing, does not depend on the signs of the hyperfine couplings nor on any differences in the g factor of the individual electron spins.

Comparison of the signal intensities of the olefinic and aldehyde protons in III with those of the α and β protons in I, after correction for the nuclear relaxation times, is a direct measure of the ratio of forward and return reaction. For Ib a value of 3 ± 1 : 1 was found in favor of regenerating starting material.[7,8]

Most interesting is the observation of a strong solvent effect on the signal intensities. Figure 2 shows that the intensities of the aldehyde proton in IIIb decrease with the solvent sequence $CHCl_3$, CH_2Cl_2, C_6H_{12}, with no observable signal in benzene. In chloroform–benzene mixtures, 1 M benzene results in a sixfold reduction in signal intensity while the reaction rate is only diminished by a factor of two. We believe this effect to be a reflection of the average singlet–triplet splitting between the zero-order states.[9] Solvent–diradical interaction may lead to preferential stabilization of either the singlet or triplet state. At present we prefer not to speculate on the nature of this interaction.

As expected, variation of ring size and structure has a large influence on the CIDNP signal intensities. While cyclohexanone (Ia) showed no detectable emission, very weak aldehyde proton emissions were observable from 2-methyl- (IVa) and 2-phenylcyclohexanone (IVb). The maximum signal intensity was observed for cycloheptanone (Ib), with decreasing intensities for Ic–e. Presumably this is at least in part[10] a reflection of the decreasing singlet–triplet splitting with increasing chain length of the biradical. A maximum signal is expected for the intermediate with the closest match of the Zeeman and singlet–triplet splittings.

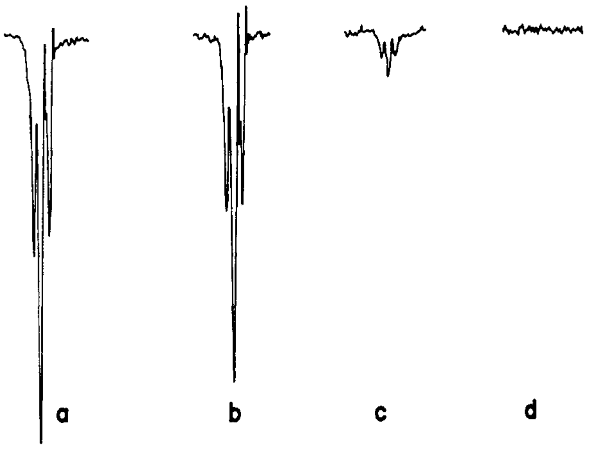

Figure 2. Aldehyde proton signal of IIIb in: (a) $CHCl_3$; (b) CH_2Cl_2; (c) cyclohexane; (d) benzene.

That the average exchange coupling is not only dependent on the formal length of the chain but also on structural features is demonstrated rather convincingly by the strong signals obtained from bicyclo[3.2.1]-octanone (V) which gives a 1,6 diradical, and the weak but easily detectable signal from camphor in which a 1,5 diradical is the intermediate. The bridging in the biradicals derived from the latter two compounds is presumably preventing an easy approach of the two ends.

Determination of the magnetic field dependence of signal intensities should give information in the scope and limitations of CIDNP as a tool to study biradicals. Such experiments are in progress.

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[7] The large uncertainty may have its origin in the fact that the relaxation times prevailing during the reaction can be expected to differ substantially from those measured on the static compounds. The reason for this discrepancy is the presence of a relatively high steady-state concentration of free radicals during the reaction.

[8] P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969), deduced the reversibility of the reaction by quantum yield studies; see also W. C. Agosta and W. L. Schreiber, *ibid.*, **93**, 3947 (1971).

[9] A solvent dependence of the magnitude of exchange interactions has previously been noted by S. Glarum, *J. Chem. Phys.*, **47**, 1374 (1967).

[10] The type I cleavage becomes less pronounced with increasing ring size of the cyclic ketones and therefore part of the reduction in signal intensities must be attributed to a diminished quantum yield.

Detection of Trace Amounts of Sodium by Fluorescence Emission Excited by a Continuous Wave Organic Dye Laser

Sir:

Organic dye lasers have been used by several workers to increase the detectability of trace amounts of materials.[1–6] The high intensity of a continuous wave (cw) dye laser concentrated in a line width comparable to atomic and ionic absorption widths combined with its highly directional properties and tunability makes it an excellent source for fluorescence excitation.[7] In this communication, we describe the use of a cw organic

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[1] N. C. Peterson, M. J. Kurylo, W. Braun, A. M. Bass, and R. A. Keller, *J. Opt. Soc. Amer.*, **61**, 746 (1971).

[2] R. A. Keller, E. F. Zalewski, and N. C. Peterson, *ibid.*, **62**, 319 (1972).

[3] R. J. Thrash, H. Von Weyssenhoff, and J. S. Shirk, *J. Chem. Phys.*, **55**, 4659 (1971).

[4] M. B. Denton and V. H. Malmstadt, *Appl. Phys. Lett.*, **18**, 485 (1971).

[5] L. M. Fraser and J. D. Winefordner, *Anal. Chem.*, **43**, 1694 (1971); **44**, 1444 (1972).

[6] J. Kuhl and G. Marowsky, *Opt. Commun.*, **4**, 125 (1971).

[7] For a review of cw dye lasers, see A. L. Bloom, *Opt. Eng.*, **11**, 5 (1972), and references cited therein.

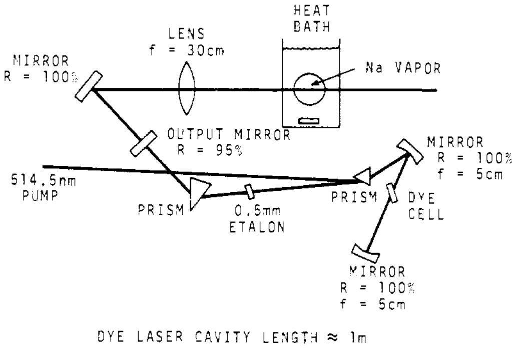

Figure 1. Block diagram of experimental apparatus showing cw dye laser configuration and sodium vapor cell for observing the sodium fluorescence.

dye laser to detect 0.016 fg (1 fg = 10^{-15} g) of sodium vapor.

The apparatus used in these experiments is shown in Figure 1. The laser configuration is similar to that described by Dienes, *et al.*[8] Two prisms and a 0.5-mm uncoated etalon in the cavity reduced the band width of the laser emission to 3 GHz (0.03 Å). The wavelength used in these experiments was 5896 Å and corresponds to the longest wavelength member of the sodium doublet. An output power of approximately 50 mW was obtained when the laser was pumped with 1.7 W of 5140-Å radiation from the Ar ion laser. The laser emission was focused into the sodium cell with a 30-cm focal length lens to give a beam diameter inside the cell of approximately 0.5 mm. The sodium was contained in an evacuated 2-in. spherical flask completely submerged in a well-stirred glycerine temperature bath. The pressure of the sodium vapor was obtained by measuring the temperature of the bath at its coldest point and using the vapor pressure *vs.* temperature data of Gordan.[9] Temperature gradients in the cell were less than 5°. Fluorescence from the sodium vapor in the cell was easily detected by visually observing the narrow line source excited by the passage of the laser beam through the sample cell.

The lowest temperature at which sodium fluorescence was visible was 80°. At this temperature, the vapor pressure of sodium is 1.5 × 10^{-8} mm.[9] The laser power used in these experiments was sufficient to saturate the sodium transition. This was demonstrated by observing that the intensity of the sodium fluorescence was not appreciably changed when the excitation beam intensity was attenuated by 90%. In this range of excitation intensities, the fluorescence intensity depends only upon the concentration of sodium atoms and not upon the light intensity.

The concentration of sodium atoms at a vapor pressure of 1.5 × 10^{-8} mm is 4.2 × 10^8 atoms/cc. Detection of the fluorescence was actually made in a volume of approximately 1 mm^3 which contained 4.2 × 10^5 molecules or 0.016 fg of material. Comparison of these data with other fluorescence excitation techniques is shown in Table I. Most of the data for Table I were taken from the recent work of Kuhl and Marowsky.[6] Inspection of Table I shows that the use of a cw organic dye laser as an excitation source for fluorescence analysis decreases the amount of sodium necessary for detection by two orders of magnitude.

Table I. Detectability Limits of Sodium by Different Analytical Techniques[a]

Technique	Limit[b]
Atomic absorption	
Hollow cathode lamp	12 ng/cm^3
Pulsed dye laser (sample inside cavity)[c]	2.0 pg/cm^3
Atomic fluorescence	
Hollow cathode lamp	33 ng/cm^3
Sodium vapor lamp	0.5 ng/cm^3
Pulsed dye laser (estimated)[d]	3 pg/cm^3
cw dye laser (present work)	16 fg/cm^3

[a] See ref 6. [b] Defined by Kuhl and Marowsky[6] as at a concentration where the signal to noise ratio is 2. The limit expressed in the present work is not a true limit in the sense that no signal to noise ratio was determined. [c] See ref 1: 10-cm path with pressure 3 × 10^{-7} mm ∼ 2.0 pg/cm^3. [d] Estimated by multiplying 12 ng/cm^3 by the ratio of the laser power necessary to obtain a minimum detectable signal in a 12-ng cm^3 sample to the maximum laser power available.[6] This assumes that the sodium absorption will not be saturated at the higher laser powers.

Photoelectric detection of fluorescence excited by cw dye lasers will permit quantitative determination of atomic and ionic species in amounts well under a femtogram. Corresponding improvements in the ability to detect molecular species are expected.

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Received August 4, 1972

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(8) A. Dienes, E. P. Ippen, and C. V. Shank, *IEEE J. Quantum Electron.*, **5**, 388 (1971).

(9) A. R. Gordan, *J. Chem. Phys.*, 4, 100 (1936).

Determination of Conformational Energy Barriers in Medium- and Large-Ring Cycloalkanes by ^1H and ^{13}C Nuclear Magnetic Resonance

Sir:

Until very recently it appeared that only cyclohexane[1] and cyclooctane[2] among the cycloalkanes, $(CH_2)_n$, had conformational energy barriers of magnitudes sufficient for direct measurement by nmr line-shape studies. The successful determination[3] of a conformational barrier in cyclononane by ^{13}C and high-frequency (251 MHz) ^1H nmr spectroscopy prompted us to investigate the higher cycloalkanes by these techniques, and we now report measurements of conformational barriers for cyclodecane, cyclododecane, and cyclotetradecane.

The ^1H 251-MHz spectra[4] of the C_{10}, C_{12}, and C_{14} cycloalkanes are single lines at room temperature. Below −100°, broadening of the lines occurs and a separation into more than one peak takes place at

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(1) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, **82**, 1256 (1960); F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *J. Chem. Phys.*, **41**, 2041 (1964); F. A. L. Anet and A. J. Bourn, *J. Amer. Chem. Soc.*, **89**, 760 (1967).

(2) F. A. L. Anet and J. S. Hartman, *ibid.*, **85**, 1204 (1963); F. A. L. Anet and M. St. Jacques, *J. Amer. Chem. Soc.*, **88**, 2585, 2586 (1966).

(3) F. A. L. Anet and J. J. Wagner, *ibid.*, **93**, 5266 (1971).

(4) The spectra were obtained on a superconducting solenoid nmr spectrometer: F. A. L. Anet, G. W. Buchanan, and C. H. Bradley, paper presented at the 11th Experimental Nuclear Magnetic Resonance Conference, Pittsburgh, Pa., April 1970.