electronic spectrum (DME) shows maxima at 380 (ca. log ε 4.12), 486 (ca. 3.66), and 625 nm (ca. 3.11).

Addition of a solution of 2 to water gave an 88%, yield of 1,2-dihydro-3,4:5,6:9,10-tribenzobicyclo·[6.2.0]decapentaene (3a), as colorless crystals (mp 150-· 153°). The spectral properties [mass, m/e 280, base peak; nmr (CCl₄) τ 2.6–3.3 (m, 11.9 H) 3.58 (d, 0.95 H), 5.82 (d, 0.95 H), 7.4 (m, 2.1 H); uv 264 (log ε 4.12), 294.5 (4.00), 301 nm (3.99)] were in accord with the assigned structure 3a. Treatment of 2 with deuterium oxide gave a 93% yield of the corresponding dideuterio com·· pound 3b, in which the mass (m/e 282, base peak) and nmr [(CCl₄) τ 2.7–3.3 (m, 12.2 H); 3.57 (s, 0.9 H), 7.16 (bs, 0.9 H)] spectra confirmed the incorporation of two atoms of deuterium. Hydrogenation (Pd–C, EtOAc) of 3a gave the known tetrahydro derivative 4a.[1,8]

The nmr spectrum of 2 shows the same type of pattern as that of the sym-dibenzocyclooctatetraenyl dianion (5).[4] However, the proton chemical shifts of 2 are at higher field than the analogous protons of 5, and, in par·· ticular, the singlet due to the proton H^E is now at higher field than the phenyl protons H^B, H^C. This displace·· ment of the proton chemical shifts to higher field is due to the induced paramagnetic ring current of the four·· membered ring.[9,10]

Interrupting the reaction by removing the solution of 1 from the potassium surface allows the course of the reduction to be followed. The sequence of events which occurs at 35° to the nmr spectrum of the solution is shown in Figure 1.[12] After initial contact with the potassium, the spectrum of 1 broadens and completely disappears, and a new spectrum (b) which is not that of 2 develops. This spectrum slowly increases in intensity on additional contact with potassium until it reaches a maximum resolution (c). On further contact the signal diminishes in intensity and disappears (d), and the final signal due to 2 appears (e).[13] This behavior is com· pletely different from that observed in the reduction of cyclooctatetraene[2] and sym-dibenzocyclooctatetraene,[4] and is most readily explained by assuming that the initial reduction occurs to give a nonplanar anion radical 6, which undergoes a rapid electron-exchange reaction with the hydrocarbon 1. Disproportionation or reduc· tion of 6 then gives the nonplanar dianion 7, the spec· trum of which is now observed (b, c). The high-field singlet (τ 5.76, 0.8 H) in the spectrum of 7 is attributed to the proton on the reduced double bond. Finally ring flattening occurs to give 2, which is assumed to un· dergo rapid electron exchange with the planar anion

6   7

8   2
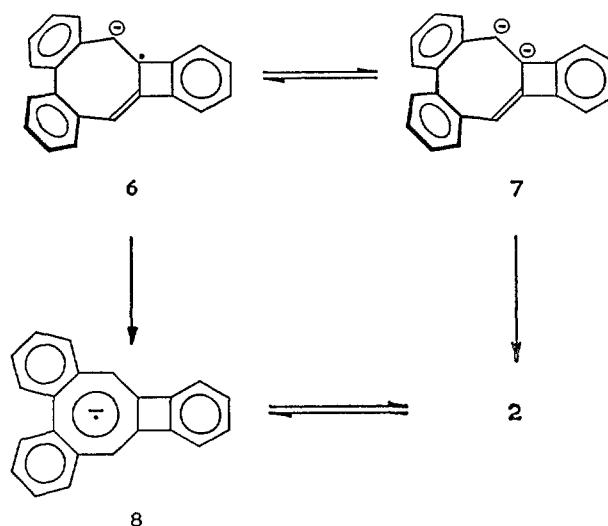
radical 8, since 2 does not appear until the spectrum of 7 has disappeared.[14]

This is the first observation of the formation of a non-planar, nonaromatic dianion in the reduction of a cyclo-octatetraenyl system. Whereas in the previous systems studied[3–5] the addition of the first electron was the rate-determining step,[4,15,16] the reduction of 1 appears to occur by two discrete one-electron additions in the non-planar conformation. The changed course of reduc-tion in this system we attribute to the increased barrier to ring flattening arising from the antiaromaticity of the cyclobutadienyl ring.

(14) When the experiment is carried out at −40°, the spectrum of a further intermediate, not 7, is observed, together with the spectrum of 2. When the experiment is carried out at −70°, the spectrum of the intermediate 7 is not well developed, and the signals of 2 are the first to be well resolved. However, if, after the spectrum of 2 has partially developed, the sample is allowed to warm to room temperature without further contact with the potassium, then a reexamination of the spec-trum at −70° shows the spectrum of 7 appearing coincidently with that of 2.

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(17) SRC Predoctoral Fellow, 1967 to present.

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(8) Hydrogenation of 3b gave 4b.

(9) H. P. Figeys, Chem. Commun., 495 (1967).

(10) Taking the value of the paramagnetic ring current of the cyclo-butadienyl ring to have the same value, but opposite sign to the diamagnetic ring current of benzene,[9] then a correction for the proton chemical shifts for the ring currents of directly adjacent rings was made using a modification[4] of the method of Shaefer and Schneider.[11] Cal-culations of the charge densities of the carbon atoms bonded to the pro-tons using this method overestimated the electronic charge (sum >2). If the value for the paramagnetic ring current is increased threefold, then the following values for the excess charge densities are obtained, C^A 0.09, C^B 0.18, C^C 0.15, C^D 0.11, C^E 0.19, C^F 0.10, C^G 0.14. This is a minimal estimate for the paramagnetic effect, since some charge is certainly localized on the carbons bearing no protons.

(11) T. Schaefer and W. G. Schneider, Can. J. Chem., 41, 966 (1963).

(12) (Preliminary studies (with Dr. B. P. Roberts) have also shown that changes occur to the esr spectrum during the course of the reaction.

(13) The signals due to the protonated solvent remain relatively sharp throughout the experiment. Hydrolysis of the solution when the spectrum was at stage c gave a 43% yield of 3a.

Driven Equilibrium Fourier Transform Spectroscopy. A New Method for Nuclear Magnetic Resonance Signal Enhancement[1]

Sir:

Fourier transform spectroscopy has attracted con-siderable attention as a means of attaining very signifi-cant improvements in the signal:noise ratio of high resolution nuclear magnetic resonance (nmr) spectra.[2] The technique consists of the application to the sample of a short, intense pulse of radiofrequency energy and the measurement as a function of time of the resulting free induction signal from the nuclear spins in the

(1) A preliminary report of this work was given at the 5th Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 7, 1969.

(2) R. R. Ernst and W. A. Anderson, Rev. Sci. Instrum., 37, 93 (1966).

sample. Fourier transformation of the free induction signal gives the ordinary high resolution spectrum.[2,3] The advantage of obtaining the spectrum by this indirect procedure is that the free induction signal is obtained rapidly, so that in a given length of time it is possible to apply the pulse repetitively and add the free induction signals coherently in a digital computer or time-averaging device. As a result, a given signal:noise level may be achieved in a much shorter time than with conventional time-averaging procedures. The theoretical saving in time is given approximately by Δ/r, where Δ is the total range of chemical shifts that must be covered and r is the width of a typical line.[2] For protons at 60 MHz this theoretical ratio is 500. In practice, a time saving of a factor of at least 100 (or equivalently an improvement in signal:noise of 10) has been demonstrated.[2]

The Fourier transform method should be even more valuable for nuclei other than hydrogen, where Δ is large and lines are often sharp. For example, for ^{13}C at 15 MHz, with 1-Hz line width, $\Delta/r > 3000$, and at 55 MHz $\Delta/r \sim 12,000$. However, application of the Fourier transform technique to nuclei, such as ^{13}C, with relatively long spin-lattice relaxation times (T_1) has been hampered by the fact that the time interval between successive pulses must in general be long relative to T_1 to permit the nuclear spin system to return to equilibrium. We demonstrate here a new method by which the equilibrium magnetization of nuclei with long T_1 may be restored rapidly and full advantage taken of the Fourier transform technique. We call the procedure the "driven equilibrium Fourier transform" (DEFT) method.

Consider, with the aid of Figure 1, the behavior of the macroscopic magnetization M in a standard Fourier transform pulse experiment and in a DEFT experiment. Initially M lies along the z axis (the direction of applied field H_0). Application of a 90° pulse along the x axis in the coordinate frame rotating at the Larmor frequency causes M to tip into the xy plane and to lie along the y axis. The signal induced in the coil along the laboratory fixed y axis, shown also in Figure 1, decays both as a result of spin–spin relaxation in a time T_2 and as a result of magnetic field inhomogeneity, ΔH_0, in a time $T_2^* \approx \pi/\gamma\Delta H_0$. T_2^* is usually less than 2 sec, and for most liquid samples governs the decay rate of the signal. Thus spectral information can be accumulated after each 90° pulse for a period of ~ 2 sec at most. For nuclei in most small molecules $T_1 \approx T_2$, and in those cases where T_1 is not much longer than T_2^*, magnetization along the z axis is reestablished spontaneously by natural relaxation processes concurrently with the xy dephasing, and the pulse may be repeated. However, if $T_1 \approx T_2 \gg T_2^*$, repetition of the pulse after a time T_2^* results in a free induction signal that is severely attenuated.

Suppose that at a time τ immediately after decay of the initial free induction, a 180° pulse is applied. As Hahn[4] first showed, the dephasing due to field inhomogeneity is largely reversible, and at time 2τ the resultant refocussing causes an "echo"—two free induction signals back to back. We now propose that
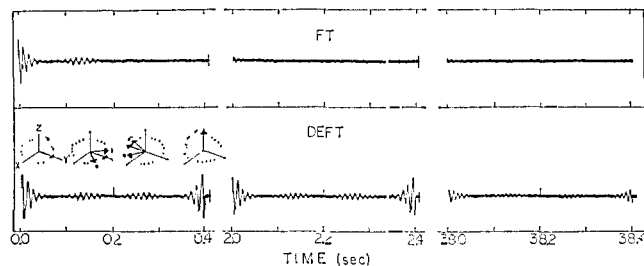

Figure 1. Response to pulse sequences for ^{13}C in 60% enriched CH$_3$^{13}COOH (neat liquid). Upper trace shows signals obtained for a normal Fourier transform experiment in which 90° pulses are applied at 2-sec intervals. Responses to the 1st, 2nd, and 20th pulses are shown. Lower trace shows signals obtained in a DEFT experiment, with an indication of the behavior of the magnetization vector. Each sequence, again spaced at 2-sec intervals, begins with a 90° pulse followed after 0.2 sec by a 180° (refocussing) pulse. At the peak of the echo an additional 90° pulse restores the magnetization to the z axis.

precisely at the peak of echo, as the nuclei are back in phase, a second 90° pulse be applied. M is then restored to the z axis. Its magnitude is nearly equal to the initial magnetization if T_2 is long, since little irreversible dephasing has occurred. Thus the DEFT method provides an almost complete reestablishment of the equilibrium magnetization in a time much less than T_1 and permits rapid initiation of a new pulse sequence.

Figure 1 shows a test of the DEFT method for ^{13}C in 60% enriched CH$_3$^{13}COOH, where $T_1 \approx 50$ sec. It is apparent that fast repetition of 90° pulses, as in the usual Fourier transform procedure, results in appreciable attenuation of the signal following the second and subsequent pulses. The DEFT method, on the other hand, gives almost undiminished signals even with fast repetition rates for the pulse sequence. The exact enhancement factor for DEFT relative to ordinary Fourier transform nmr depends upon T_1, T_2, and the effect of diffusion in a magnetic field gradient. Further details of the method will be published.

DEFT nmr promises to be a powerful technique in enhancing signals for many nuclei of spin $^1/_2$ which have long T_1 and T_2, low sensitivity, and in some cases occur at low natural abundance. In addition to ^{13}C, which has been studied here, other suitable nuclei include ^{15}N, ^{57}Fe in diamagnetic compounds, ^{31}P, and ^{183}W.

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Protonated 1,6-Methanocyclodecapentaene, a Potentially Antihomoaromatic Species

Sir:

There has been much interest recently in the protonation of the $4n$ ($n = 2$) polyene, cyclooctatetraene, to yield the homoaromatic $4m + 2$ ($m = 1$) species, monohomotropylium ion.[1] We now report the protonation of a $4n$

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(4) E. L. Hahn, *Phys. Rev.*, **80**, 580 (1950).

(1) For leading references, see S. Winstein in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 5; see also, S. Winstein, *Quart. Rev.* (London), 23, 141 (1969).