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 $\sim$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 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.

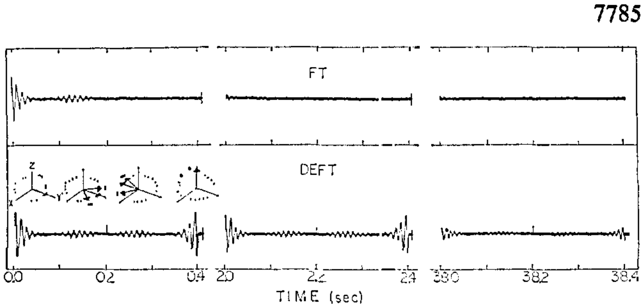

Figure 1. Response to pulse sequences for ^{13}C in 60% enriched $CH_3{}^{13}COOH$ (neat liquid). Upper trace shows signals obtained for a normal Fourier transform experiment in which 90° pulses are applied at 2-sec intervals. Responses to the 1st, 2nd, and 20th pulses are shown. Lower trace shows signals 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.

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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(3) A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961.

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

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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(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).

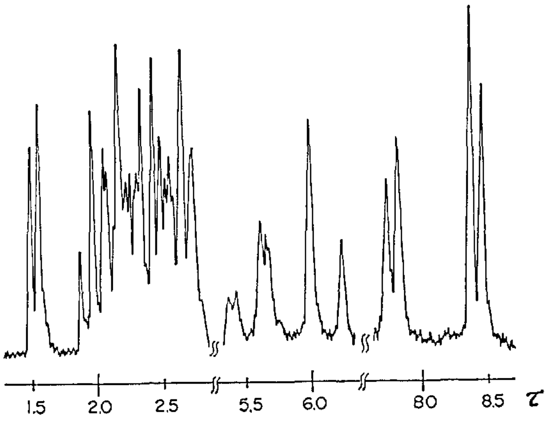


Figure 1. The 100-MHz nmr spectrum of II (temperature *ca.* −85°, sweep width = 1000 Hz) in FSO_3H-SO_2ClF (1:2, v/v); $CHDCl_2$ internal standard (τ 4.70).

+ 2 (n = 2) aromatic, 1,6-methanocyclodecapentaene (I), to give the corresponding $4m$ (m = 2) π-electron cation (II), potentially antihomoaromatic.[2]

Extraction of I from a CD_2Cl_2 solution into a FSO_3H-SO_2ClF (1:2, v/v) solution at −78° in an nmr tube proceeds smoothly to give II.[5] That the carbon skeleton of I remains intact is shown by the fact that quenching of the acid solution in sodium bicarbonate buffered methanol at −78° gives 85–90% recovery of I. Vogel has previously reported that treatment of I with a mixture of deuteriotrifluoroacetic acid in ether containing a catalytic amount of deuteriosulfuric acid results in deuterium incorporation at the 2, 5, 7, and 10 positions (the four α positions).[6] Therefore, we *a priori* expected protonation to occur at the 2 position, and the nmr spectrum (60 and 100 MHz) of the dark red solution is in complete accord with these expectations. Thus the methylene protons of the bridge appear at τ 7.78 and 8.42 ($J_{11a,11b}$ = −9.3 ± 0.3 Hz),[7] while the methylene protons attached to C_2 appear as an AB quartet at τ 5.54 and 6.10 ($J_{2a,2b}$ = −24.9 ± 0.1 Hz)[7] with the lower half doubled due to coupling with H_3 ($J_{2a,3}$ = 5.8 ± 0.2 Hz). The seven olefinic protons appear as complex absorptions in the τ 1.5–2.7 region (see Figure 1).

The solution of the olefinic pattern was made possible through the use of protonated I-α-d_4 (see Figure 2) and extensive decoupling experiments, all at 100 MHz. The only assumption made was that H_9 absorbs at lower field than H_8, which is quite reasonable since C_9 bears charge directly whereas C_8 does not. The derived chemical shifts and coupling constants are compiled in Table I.

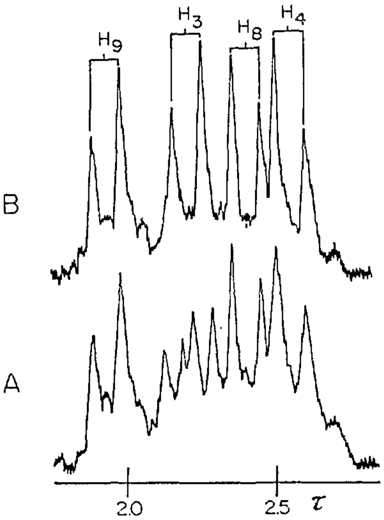
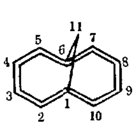


Figure 2. The 100-MHz nmr spectra (temperature *ca.* −85°, sweep width = 500 Hz): A, olefinic region of protonated I-α-d_4 in FSO_3H-SO_2ClF (1:2, v/v); deuterons decoupled; B, same as A, but with proton at C_2 also decoupled. [Additional decoupling of doublet centered at τ 1.96 (H_9) results in collapse of the doublet centered at τ 2.43 (H_8).]

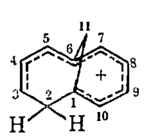
Table I. Nuclear Magnetic Resonance Data for the Olefinic Region of Protonated 1,6-Methanocyclodecapentaene[a]

Proton	Chem shift[b] (τ)	Coupling constant (Hz)
H_3	2.21	$J_{3,4}$ = 10.0 ± 0.5
H_4	2.56	$J_{4,5}$ = 6.5 ± 0.2
H_5	1.52	
H_7	2.12	$J_{7,8}$ = 9.0 ± 0.5
H_8	2.43	$J_{8,9}$ = 9.0 ± 0.5
H_9	1.96	$J_{9,10}$ = 8.0 ± 0.5
H_{10}	2.68	

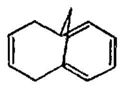
[a] In FSO_3H-SO_2ClF (1:2, v/v) at *ca.* −85°. [b] Chemical shifts measured relative to internal $CHDCl_2$ (τ 4.70).



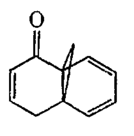
I



II



III



IV

Two main questions arise concerning the electronic structure of II. The first is whether or not II is antihomoaromatic. As indicated in II, no substantial C_1–C_3 interaction can be supported on the basis of the nmr spectrum. Thus the very large, presumably negative,[7,8a] $J_{2a,2b}$ indicates the C_1–C_2–C_3 bond angle is abnormally large[8b] (compare the much smaller geminal C_2 couplings of 13–16 Hz in III[10] and IV[6]), which makes $\beta_{1,3}$ very small. Apparently, II attempts to avoid 1,3 overlap,[11] which would destabilize it. This is borne out by the lack of any evidence for a paramagnetic ring current. The seven olefinic protons appear at an average chemical shift of τ 2.21, a mere 0.12 ppm higher than the average chemical shift of the seven olefinic protons of

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(2) To our knowledge, two other potentially antihomoaromatic systems have been reported. These are the protonated benzenes[3] and protonated *trans*-15,16-dimethyldihydropyrene.[4] The former show no evidence for antihomoaromaticity, while the data for the latter are not sufficiently complete to allow a decision.

(3) G. Olah, *J. Amer. Chem. Soc.*, 87, 1103 (1965).

(4) J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *ibid.*, **89**, 1704 (1967).

(5) The solution of II is quickly cooled in liquid nitrogen and the nmr spectrum observed at *ca.* −85°. If the solution is allowed to warm to −63°, a rearrangement to another species takes place ($t_{1/2}$ *ca.* 2 hr); this rearrangement will be the subject of a future report.

(6) E. Vogel in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 113.

(7) (a) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 85, 1899 (1963); (b) R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron, Suppl.*, 7, 355 (1966).

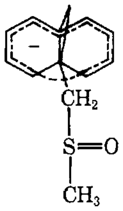
(8) (a) In so far as we know, $J_{2a,2b}$ is the largest negative H–H coupling constant yet reported. (b) $J_{^{13}C_2,H_2}$ = 115 ± 2 Hz (obtained, at 60 MHz, after summation of 180 scans by the Time Averaging Computer) supports this idea and also represents the lowest reported $J_{^{13}C,H}$.[9]

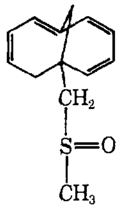
(9) W. McFarlane, *Quart. Rev.* (London), 23, 187 (1969).

(10) H. D. Roth, Ph.D. Dissertation, Köln, 1965, p 25.

(11) Inspection of models indicates the p orbitals at C_1 and C_3 can readily become virtually orthogonal.

monohomotropylium ion.[1] Furthermore, the average chemical shift of the bridge protons, τ 8.10, is only 0.24 ppm downfield from the average shift of the bridge protons of III, τ 8.34,[10] hardly an impressive deshielding when compared to the shielding of the bridge protons (2.88 ppm) of the homoaromatic V, relative to VI.[12]


V


VI

The second question of electronic structure is what is the extent of C_1–C_6 overlap (*i.e.*, what is the C_1–C_6 distance or the C_1–C_{11}–C_6 bond angle)?[13] The usual nmr criterion for such overlap is the size of $J_{11a,11b}$.[7b] Thus, since $|J_{11a,11b}|$ for II (9.3 Hz) is larger than for I ($|J_{11a,11b}|$ = 7.0 Hz),[14] one is tempted to conclude that there is less 1,6 overlap in II than I. Recently, however, some doubt was cast on the validity of the above concept by the report that the chromium tricarbonyl complex of I [I-Cr(CO)$_3$], whose C_1–C_6 distance is known[15] to be 0.12 Å shorter than that of I, has a larger $|J_{11a,11b}|$ (8.9 Hz)[16] than I. On the other hand, $J_{^{13}C_{11},H_{11}}$ (147 ± 1 Hz)[16] for I-Cr(CO)$_3$ is larger than that for I ($J_{^{13}C_{11},H_{11}}$ = 142 ± 2 Hz),[14] as is expected for a decreased C_1–C_6 distance. $J_{^{13}C_{11},H_{11}}$ (148 ± 1 Hz)[17] for II is also larger than that for I. In fact, the coupling constant data for C_{11} in II bear a strikingly close resemblance to those for C_{11} in I-Cr(CO)$_3$. Thus, we tentatively conclude that the C_1–C_6 distance in II may be smaller than in I. However, it seems clear that the extent of C_1–C_6 overlap in II is much less than in IV (same number of π centers in the ring), which exists in the closed form ($J_{11a,11b}$ = 4.5 Hz).[6] This smaller overlap is readily understood, since increasing the σ character of the C_1–C_6 interaction serves to localize charge on C_3, C_4, and C_5. This is particularly harmful since the charge is removed from C_1, which is a tertiary position (and thus best able to bear positive charge).

We find that dissolving I in FSO$_3$D–SO$_2$ ClF gives rise to II-d_1, where the deuteron replaces the proton whose resonance is at τ 5.54 (H_{2a}). The stereoselectivity is greater than 96% (60-MHz nmr integration). Unfortunately, it is not possible to determine which side of I the incoming proton attacks, since two final conformations are possible for II.[18] In the first, the methylene group (C_2) is tipped upward, toward C_{11}. If this is the conformation, then the incoming proton must attack from the bottom side of the molecule (*trans* to C_{11}). This might be favorable due to the greater electron density beneath I.[20] The other conformation has C_2 bent downward, away from C_{11}. If this conformation is the correct one, then the proton attacks from the top side of I. This latter conformation seems to allow better overlap among the p orbitals of C_5, C_6, and C_7. It is important to note that the data only allow one of the two conformations to be present in large amounts; however, examination of models indicates no great barrier should exist for their interconversion (*i.e.*, one conformer must be more stable than the other).

It would be interesting to observe the higher annulenes in strong acid. Work in that direction is currently in progress in these laboratories.

Acknowledgment. We are grateful to Dr. David Harris for assistance in taking the 100-MHz nmr spectra.

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[12] W. A. Böll, *Tetrahedron Lett.*, 5531 (1968).

[13] It is noteworthy that as C_1 and C_6 come together, they do so in a manner that increases the σ-type overlap of their p orbitals, ultimately resulting in the formation of a cyclopropane banana bond.

[14] H. Günther, *Z. Naturforsch.*, *B*, **20**, 948 (1965).

[15] P. E. Baikie and O. S. Mills, *Chem. Commun.*, 683 (1966).

[16] H. Günther, R. Wenzl, and W. Grimme, *J. Amer. Chem. Soc.*, **91**, 3808 (1969).

[17] Obtained, at 60 MHz, after summation of 100 scans by the Time Averaging Computer.

[18] This is based on the fact that H_{2b} and H_3 must have a dihedral angle of *ca.* 90°[19] between them, since $J_{2b,3}$ is *ca.* 0 Hz. The conformations were derived from examination of models.

[19] E. Garbisch, Jr., *J. Amer. Chem. Soc.*, **86**, 5561 (1964).

[20] In the analogous protonation of 1,6-methanocyclononatetraenyl anion [P. Radlick and W. Rosen, *ibid.*, **89**, 5308 (1967)], the incoming proton was found to attack from the bottom.

[21] National Science Foundation Predoctoral Fellow, 1966–1969.

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Evidence for a *cis,cis,cis,trans*-Cyclononatetraene in the Thermal Reorganization of 9-Ethyl-9-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene

Sir:

The facile thermal reorganization of *cis*-bicyclo[6.1.0]-nona-2,4,6-trienes to *cis*-8,9-dihydroindenes has stimulated a great deal of interest,[1,2] primarily because the most reasonable mechanism is not in accord with the orbital symmetry rules for concerted reactions.[3] We have recently reported the first example of the reorganization of a *cis*-bicyclo[6.1.0]nona-2,4,6-triene in which a *trans*-8,9-dihydroindene is obtained as the major product (**1a** → **2a**).[1] The mechanism of this reaction is of interest because there are several conceivable "symmetry allowed" pathways and also because its elucidation should provide additional insight into the mechanism of formation of *cis*-8,9-dihydroindenes.[2]

(*E*)- and (*Z*)-9-ethyl-9-methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene[4] (**1b** and **1c**, respectively) were obtained in 67% yield as a 1.5:1 mixture by the general method described previously.[1] The separation of these isomers was a difficult task but was successfully accomplished by employing two different gas chromatography (glpc) columns, *viz.* 20% DEGA on 80–100 Diatoport S and 20% Carbowax 20M on 100–120 silanized Chromosorb P. Both products exhibited negative distribution isotherms[5] (steep front peak edge) on the former column at 130°, which permitted the purification of **1b** (eluted first), and positive isotherms on the latter column at

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[1] S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969), and references cited therein.

[2] P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969).

[3] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[4] For a discussion of the nomenclature see J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

[5] A. I. M. Keulemans, "Gas Chromatography," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1959, Chapter 4.