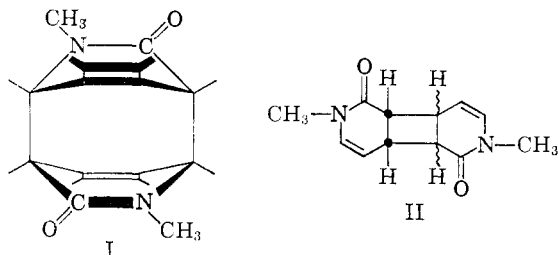## STRUCTURE STUDIES BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. I. THE PHOTODIMER OF N-METHYL-2-PYRIDONE

Sir:

Nuclear magnetic resonance (n.m.r.) evidence[1] indicates that ultraviolet irradiation[2] of an aqueous solution of N-methyl-2-pyridone yields the unique tricyclic octadiene, I. This dimer (m.p. 221.5–

222.0°) presumably results from the formation of novel cyclic 1,4-diradicals under the influence of the irradiation and the coupling of these diradicals in the favored head-to-tail transoid conformation.

We wish also to report a unique conformational interconversion inherent in the corresponding tetrahydro derivative, III.
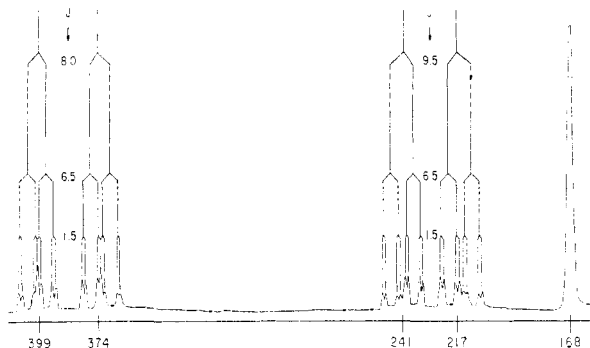
Cps. at 60 mc., from tetramethylsilane.

Fig. 1.—N.m.r. spectrum of photodimer of N-methyl-2-pyridone.

The dimer has been described previously by Taylor and Paudler,[3] who formulated it as the cyclobutane derivative, II, on the basis of ultraviolet absorption, dipole moment, hydrogenation, epoxidation, and pyrolytic data. Like II, structure I, because of its point of symmetry, would possess no dipole moment and would demonstrate no optical isomerism; Taylor's other published data also support the revised structure, I.

The n.m.r. spectrum of the dimer (Fig. 1) showed three types of hydrogens of relative abundances 4, 4, and 6, from area measurements, based on the dimeric empirical formula. The least shielded multiplets centered at 399 and 374 are in the region ordinarily assigned to olefinic hydrogens with additional unshielding groups[4] nearby. Closer

(1) Spectra were obtained on dilute solutions in deuteriochloroform with a Varian 4300-2 Spectrometer operating at 60 mc. The spectra were calibrated by the audiofrequency sideband technique against internal tetramethylsilane standard.

(2) A 200-watt unfiltered Hanovia lamp was employed.

(3) E. C. Taylor and W. W. Paudler, *Tetrahedron Letters*, No. 25, 1 (1960).

(4) Varian Associates Staff, "NMR and EPR Spectroscopy," Pergamon Press, New York, N. Y., 1960, p. 103.

examination discloses that it is an AB multiplet[5] (doublet of doublets) with two additional splits. The large asymmetric split (J = 8 cps.) indicates *cis*-olefinic hydrogens.[6] The symmetrical second split (J = 6.5 cps.) is by an atom in the intermediate group and indicates the presence of a hydrogen atom α to the double bond[6] having a dihedral angle of 0 or 180 degrees.[7] Since both olefinic hydrogens are split thus, similar α-hydrogens are required on each side. The nature of the third split (J = 1.5 cps. symmetrical) indicates that this partner (also of the intermediate group) is the other α-hydrogen coupled through the double bond, thereby suggesting the system
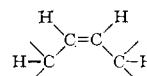
The intermediate multiplets at 241 and 217 cps. are also of the AB pattern[5] with two additional symmetrical splits. The large asymmetric split (J = 9.5 cps.) is indicative of an interaction of similar adjacent hydrogens[6] having a dihedral angle of 0 or 180 degrees. The two remaining symmetrical splits are the counterparts of those described above, and they require that these four AB type hydrogens all be α to the olefinic hydrogens, thus necessitating the 1,5-cyclooctadiene formulation.
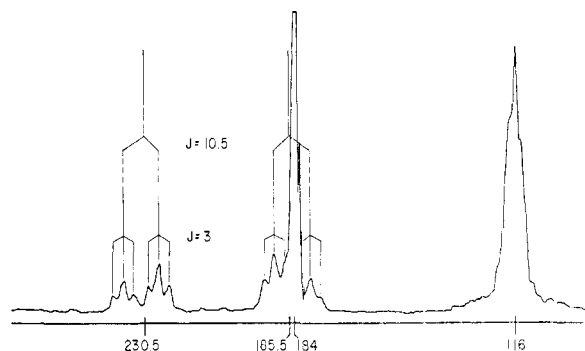
Cps. at 60 mc., from tetramethylsilane.

Fig. 2.—N.m.r. spectrum of tetrahydro derivative.

The presence of two equivalent N-methyl groups is confirmed by the sharp singlet at 168 cps.

The N-methyl amide residues must be attached to the 1,5-cyclooctadiene in a head-to-tail arrangement. The two adjacent tertiary hydrogens are now coplanar yet environmentally different, fulfilling the requirement for splitting, and the transoid conformation gives the compound the symmetry required by the n.m.r. spectrum and the dipole moment. *Thus only I conforms to all data.*[8]

This structure gained additional support from the n.m.r. spectrum of the tetrahydro derivative,

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 119.

(6) (a) *Ibid.*, p. 242; (b) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 85.

(7) F. M. Karplus, *J. Chem. Phys.*, **30**, 12 (1959); H. Conroy, *Advances in Organic Chemistry*, II, 311 (1960).

(8) The alternate cyclobutane structure, II, requires an ABX olefin pattern and A₂B or ABC patterns for the tertiary hydrogens. These well-known patterns are definitely absent in Fig. 1.
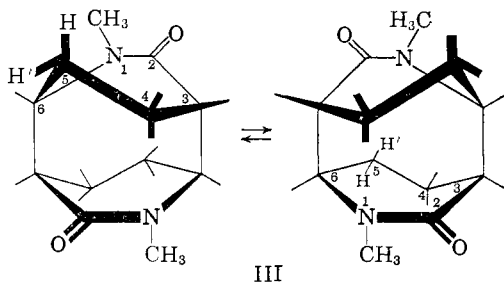
III (m.p. 284–285°)[3]. Three types of hydrogen absorption in an abundance of 4, 6, and 8 are present (cf. Fig. 2). The two tertiary hydrogen absorptions centered at 230.5 and 185.5 cps. are still a doublet of doublets (J = 10.5 cps.) but have additional splitting of each line into symmetrical triplets (J = 3 cps.) by the new methylene groups. This confirms that these tertiary hydrogen atoms were α to the double bond in the photodimer and further identifies this coupling in Fig. 1.

The N-methyl line has shifted to lower field because of the removal of the double bond with its diamagnetic anisotropy. The new ring methylenes show an absorption at 116 cps. which lacked the usual distinction between hydrogens in the axial and equatorial conformations. The formation of symmetrical triplets (J = 3 cps.) is of interest because it indicates that the coupling to both methylene hydrogens which have different conformations is identical and that the dihedral angles are about 45°.

The situation was clarified when a Dreiding Stereomodel was constructed and *the molecule was observed to undergo very facile ring interconversion between two boat forms of the two six-membered rings.* The third form, with the ring fusions in the flagstaff positions, is highly strained and is the transition state between the other two. It is of interest to observe that the two forms (cf. Structure III) are mirror images after rotation of one through 180°. During this process, the equatorial hydrogens become axial and *vice versa* (see III), the net effect averaging the methylene hydrogens (only one absorption frequency) and the dihedral angle to about 45° as required.

This reaction has proved to be general. The products present interesting problems in magnetic anisotropy effects, rates of conformation mobility, and chemical synthesis which are presently under active investigation.

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THE RELATIVE SIGNS OF PROTON-FLUORINE COUPLING CONSTANTS IN ETHYL FLUORIDE

Sir:

There has been considerable interest recently in the relative signs and magnitudes of CH_3-X and CH_2-X coupling constants in compounds of the type $(CH_3CH_2)_nX$, where X is a nucleus of spin $1/2$.[1–4] We wish to report the analysis of the

(1) P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, 34, 1049 (1961).

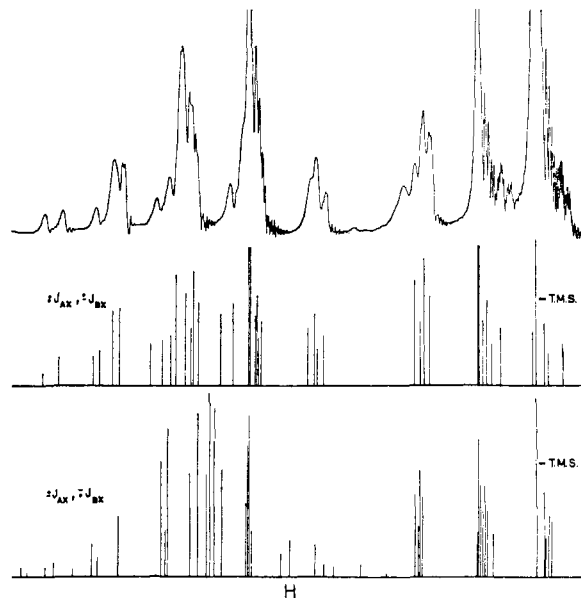Fig. 1.—High field portion of proton n.m.r. spectrum of CH_3CH_2F at 15.08 Mcps., with spectra calculated for like and opposite signs of J_{CH_3-X} and J_{CH_2-X}.

spectrum of CH_3CH_2F, an additional compound of this type. The relative signs and magnitudes of the proton–fluorine coupling constants in ethyl fluoride apparently are inconsistent with the trends suggested from previous measurements.

TABLE I

COUPLING CONSTANTS IN SOME $(CH_3CH_2)_nX$ COMPOUNDS

Compound	Atomic number	$J_{CH_3-CH_2}$, cps.	J_{CH_3-X} cps.	J_{CH_2-X}, cps.	Rel. signs of J_{CH_3-X} and J_{CH_2-X}	Ref.
$(CH_3CH_2)F^{19}$	9	6.9	25.2	46.7	Same	...
$(CH_3CH_2)_3P^{31}$	15	7.6	13.7	0.5	Opp.	1
$(CH_3CH_2)_4Sn^{117}$	50	~8.2	~68.1	~30.8	Opp.	1
$(CH_3CH_2)_4Sn^{119}$	50	8.2	71.2	32.2	Opp.	1
$(CH_3CH_2)_2Hg^{199}$	80	7.0	115.2	87.6	Opp.	1
$(CH_3CH_2)_3Tl^{205}$	81	~7.7	396	198	Opp.	4
$(CH_3CH_2)_4Pb^{207}$	82	8.2	125.0	41.0	Opp.	1

The n.m.r. spectrum of ethyl fluoride at 60 Mcps. is readily assigned from first order considerations. The coupling constants determined from this spectrum are given in the table. (Approximate coupling constants of J_{CH_3-F} ~ 20 cps. and J_{CH_2-F} ~ 60 cps. have been reported.[5]) The chemical shifts of the CH_3 and CH_2 protons are -1.24 and -4.36 ppm., respectively, relative to tetramethylsilane (these shifts have been reported previously[6] as 6.07 and 2.89 ppm. relative to benzene). The F^{19} chemical shift relative to CCl_3F is 214 ppm.

(2) P. T. Narasimhan and M. T. Rogers, *ibid.*, 31, 1430 (1959).
(3) P. R. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, 82, 34 (1960).
(4) J. P. Maher and D. F. Evans, *Proc. Chem. Soc.*, 208 (1961).
(5) H. S. Gutowsky, L. H. Meyer and D. W. McCall, *J. Chem. Phys.*, 23, 982 (1955).
(6) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, 77, 3977 (1955).