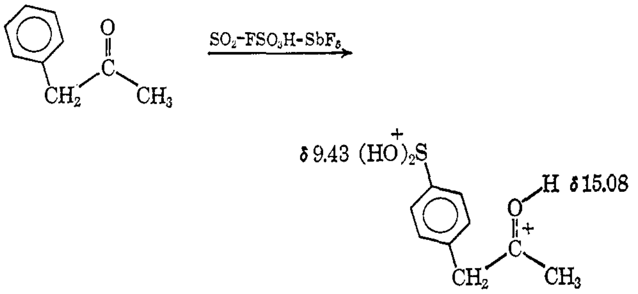
makes itself evident by the appearance of a two-proton $S(OH)_2^+$ peak[8] for the protonated sulfinated ketone. With phenylacetone, which is partially sulfinated in the SO_2–FSO_3H–SbF_5 medium, the $S(OH)_2^+$ signal is at δ 9.43 ppm and a new very-low-field C=O—H signal is observed at δ 15.08 ppm. The latter signal has the same general appearance as does the incompletely resolved quartet for the C=O—H proton of the *anti* isomer of the protonated unsulfinated phenylacetone. The $S(OH)_2^+$ group is evidently sufficiently deactivating for π hydrogen bonding that the *anti* form is quite dominant over the *syn* isomer in the diprotonated sulfinated phenylacetone.



Above −30°, in media with or without SO_2, other modes of decomposition, leading to still unknown and possibly polymeric products, become significant with several of the β-phenyl ketones investigated.

Acknowledgment. We thank Dr. Maurice St. Jacques for instrumental aid and Mr. Philip Warner for a sample of 2-indanone.

George C. Levy, S. Winstein
Contribution No. 2248, Department of Chemistry
University of California, Los Angeles, California 90024
Received April 22, 1968

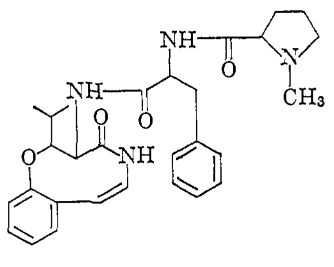
The Structure of Ceanothine-B

Sir:

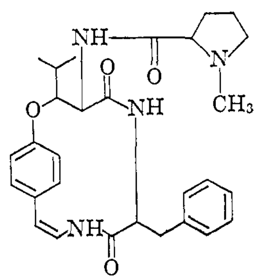
Recent structure elucidation studies have dealt with the alkaloids of *Ceanothus americanus* root bark.[1,2] On the basis of chemical and spectroscopic data other workers assigned[2b] structure I to one of these alkaloids, ceanothine-B. Although much of their structure proof was convincing, the evidence for the *ortho*-fused oxazacyclononadiene ring and the amino acid sequence was equivocal. We now present data which establish a new structure of ceanothine-B.

Our sample of ceanothine-B was obtained from dried, ground *C. americanus* root bark;[3] its properties, as well as those of dihydroceanothine-B, were in agreement with those reported.[2] High-resolution mass spectrometry and acid and alkaline hydrolysis followed by automatic amino acid analysis[4] of both ceanothine-B and dihydroceanothine-B confirmed the reported molecular formula, $C_{29}H_{36}N_4O_4$, and the presence of phenylalanine, β-oxygenated leucine, either an *o*- or a *p*-alkoxystyrylamine, and N-terminal N-methylproline.[5]

Ozonolysis of ceanothine-B followed by trimethyl phosphite decomposition of the ozonide and uv spectrophotometric analysis of the carbonyl products established that the alkoxy residue was fused *para* to the styryl double bond (λ_{max} 275 mμ; λ_{sh} 282, 290 mμ).[1] Since the seven bridging atoms of the *ortho* ring fusion of structure I are insufficient for *para* bridging, this observation required inclusion of the phenylalanine residue in the macrocycle and, consequently, attachment of the terminal N-methylproline residue to the leucine α-amino group. Revised structure II for ceanothine-B accommodates these requirements.

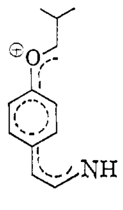


I

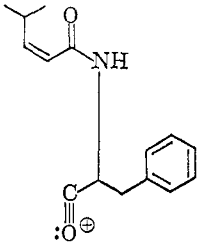


II

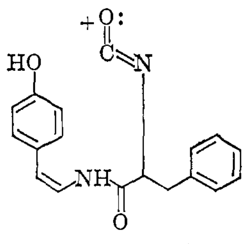
Mass spectra of ceanothine-B and dihydroceanothine-B are completely and uniquely explicable on the basis of structure II and are irreconcilable with the amino acid sequence of structure I. Peaks at *m/e* 189, 244, 308, and 337 are consistent only with the sequence of structure II. High-resolution measurements of the latter three peaks verified the empirical formulas of the associated fragment ions.



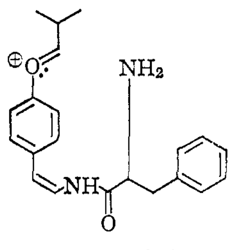
$C_{12}H_{15}NO^+$
m/e 189



$C_{15}H_{18}NO_2^+$
m/e 244



$C_{18}H_{16}N_2O_3^+$
m/e 308



$C_{21}H_{25}N_2O_2^+$
m/e 337

Thus ceanothine-B is correctly represented by structure II. Moreover, our mass spectral and ozonolytic analyses of many different alkaloid fractions isolated from *C. americanus* root bark suggest strongly that among the constellation of alkaloid structures present

---

[1] F. K. Klein and H. Rapoport, *J. Am. Chem. Soc.*, **90**, 2398 (1968).

[2] (a) E. W. Warnhoff, S. K. Pradhan, and J. C. N. Ma, *Can. J. Chem.*, **43**, 2594 (1965); (b) E. W. Warnhoff, J. C. N. Ma, and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **87**, 4198 (1965).

[3] Plant material was furnished by Flint, Eaton and Co., Decatur, Ill. (now Baxter Laboratories, Morton Grove, Ill.).

[4] Automatic amino acid analyses were very generously conducted by Dr. Jonathan Dixon of the Hormone Research Laboratory, University of California Medical Center, San Francisco, Calif.

[5] Details of the methodology employed and the basis for these interpretations are given in ref 1.

in this plant material, the dominant, if not exclusive, mode of ring fusion is *para*.[6]

(6) Subsequent to the submission of our manuscript we received a communication from Dr. Warnhoff that upon his later discovery of *para*-substituted benzene rings in two related *Ceanothus* alkaloids, he became suspicious that ceanothine-B might be similarly *para* fused and that his original assigned structure was incorrect.

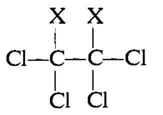
(7) Woodrow Wilson Honorary Fellow; National Institutes of Health Predoctoral Fellow.

Frederick K. Klein,[7] Henry Rapoport
Department of Chemistry, University of California
Berkeley, California
Received April 19, 1968

Nuclear Magnetic Resonance Spectroscopy. Conformations and Conformational Equilibration of Bis(trifluoromethyl)tetrachloroethane[1]

Sir:

The factors which influence conformational populations and barriers to rotation in halogenated ethanes do not yet seem well understood. While the favored form for 1,1,2,2-tetrachloroethane (**1a**) has the hydrogens *gauche*,[2] 1,2-difluorotetrachloroethane (**1b**) has a slight preference for fluorines *trans*[3] and 1,2-dimethyltetrachloroethane (**1c**) has a strong preference for methyls *trans*.[4] The effect of trifluoromethyl groups has now been determined by investigating the temperature variation of the ^{19}F nmr spectrum of bis(trifluoromethyl)tetrachloroethane (**1d**) (obtained from the Pierce Chemical Co.) with the aid of a Varian A-56/60A spectrometer and a V-6040 variable-temperature accessory.



$$Cl\text{—}\overset{X}{\underset{Cl}{C}}\text{—}\overset{X}{\underset{Cl}{C}}\text{—}Cl$$

1a, X = H
b, X = F
c, X = CH_3
d, X = CF_3

A set of spectra of **1d** taken between −73 and −150° is shown in Figure 1. The complexity of these spectra below −150° shows that, under these conditions, rotation about *all* of the carbon–carbon bonds must be slow on the nmr time scale. At −112° rotation about the carbon–trifluoromethyl bond is slow in the *gauche* isomer but rapid in the *trans* isomer. Integration of the spectral peaks at this temperature indicates that **1d** is comprised of 8% of the *trans* and 92% of the *gauche* conformations. The spectrum at −150° could be matched by trial-and-error calculations with LAOCOON II.[5] The resulting shift and coupling parameters which fit the spectrum (see Figure 1) are given in Table I. In the analysis, advantage was taken of the fact that the *trans* isomer **2** is expected to give an $(XY_2)(XY_2)'$ spectrum while the *gauche* isomer **3** is expected to give an (ABC)(ABC)′ spectrum. The fluorine resonances of the *trans* isomer were inferred as deviations from the calculated spectrum of the *gauche* isomer.[6] The magnetic environment of F_x in **2** is expected to be similar to that of F_c in **3**, and the same should be true of F_b and F_y. This was therefore taken as a basis for assigning the resonances in the *gauche* isomer to specific fluorines. The proximity of the trifluoromethyl group thus shifts the resonance of F_a downfield relative to F_b.

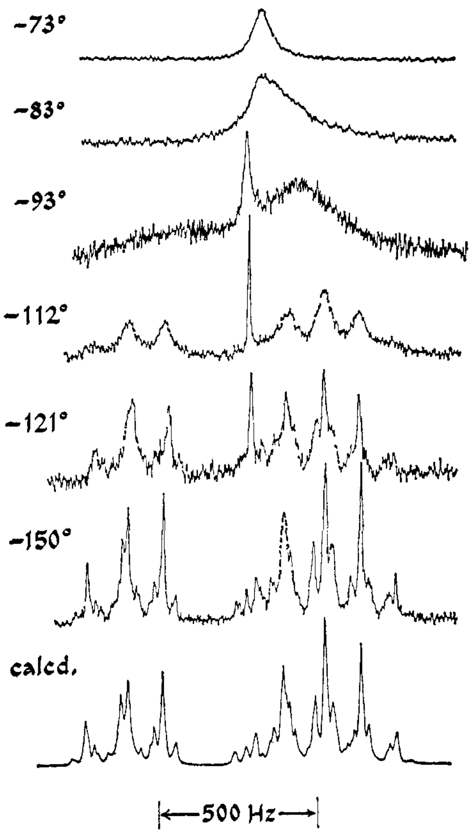


Figure 1. Experimental ^{19}F nmr spectra of bis(trifluoromethyl)tetrachloroethane in difluorodichloromethane at 56.4 MHz as a function of temperature. Bottom curve is a theoretical spectrum calculated for the *gauche* isomer using the shift and coupling parameters in Table I.

Table I. Chmeical Shifts and Coupling Constants of Bis(trifluoromethyl)tetrachloroethane

Fluorine	Chemical shift[a]	Fluorine couplings[b]	*J*, Hz
a	69.8	a,b	105
b	73.5	a,c	124
c	61.1	b,c	116
		a,a′	75
x	61 ± 2		
y	73 ± 2		

[a] In parts per million upfield from trichlorofluoromethane. [b] The average value of J_{FCCCCF} as determined from the ^{13}C satellites (J_{CF} = 285.6 Hz and ^{13}C isotope effect on the fluorine chemical shift = 0.13 ppm) of the spectrum of **1d** at room temperature was 8.6 Hz.

The presence of *one* and *only one* large, five-bond, fluorine–fluorine coupling (a,a′ which is between the

---

(1) Supported by the National Science Foundation.

(2) H. S. Gutowsky, G. C. Belford, and P. E. McMahon, *J. Chem. Phys.*, 36, 3353 (1962).

(3) R. A. Newmark and C. H. Sederholm, *ibid.*, 43, 602 (1965). This assignment has been confirmed by investigation of the F–F couplings in the ^{13}C satellite spectra for each isomer (11 Hz for the *trans* and 21 Hz for the *gauche*) at −100° by Mr. Vernon Cormier in unpublished work in this laboratory.

(4) S. Borčić and J. D. Roberts, unpublished results.

(5) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(6) At −150°, rotation of the *trans* isomer is probably not completely stopped on the nmr time scale. The chemical-shift difference is taken from studies of other trifluoromethyl groups.