parts of water a blood-red coloration. A characteristic property of this acid is the formation of a calcium salt on boiling its aqueous solution with animal charcoal. This salt crystallizes from water in plates with well-defined, diamond-shaped end faces.

Anal. Calcd. for $C_8H_5O_6N$: C, 45.50; H, 2.37; N, 6.63. Found: C, 45.29; H, 2.56; N, 6.83. *Mol. wt.* Subs., 11.503 mg.; camphor, 118.4 mg.; Δt, 18. Calcd. for $C_8H_5O_6N$: mol. wt., 211. Found: mol. wt., 216. *Titration.* Subs., 16.848 mg.: 9.20 cc. of 0.0257 *N* NaOH. Calcd. for $C_8H_5O_6N$ as tribasic acid: 9.33 cc.

Summary

1. A hydroaromatic base, $C_{16}H_{25}N$, isolated from the crude kerosene distillate as produced at the Oleum Plant of the Union Oil Company of California, is described along with a number of characteristic salts.

2. This base is regarded as 4-methyl-1,4-ethenopiperidine, condensed at 2,3 as well as at 5,6, with methylcyclopentane. In addition to the two cyclopentane nuclei, this structure presents two tetrahydropyridine complexes within the piperidine periphery, so that in all five rings are involved.

3. Corresponding to the structural formula proposed, the $C_{16}H_{25}N$ compound, apart from possessing the properties of a tertiary amine, behaves similarly to methyl cyclopentane.

4. The term "Naphthenic Bases" is proposed for bases like the $C_{16}H_{25}N$ compound of the cyclopentane type, in order to emphasize their relationship to the so-called naphthenes.

5. The claim previously advanced that "*petroleum offers the greatest wealth of nitrogen compounds of any natural source*" is strengthened by the results reported in this paper and the isolation, proof of structure and even synthesis of a host of so-called petroleum bases only await a realization of the attractive field of research presented.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE WEST VIRGINIA UNIVERSITY]

FLUOSILICATES OF ORGANIC BASES. II

BY C. A. JACOBSON[1]

RECEIVED SEPTEMBER 24, 1930 PUBLISHED MARCH 6, 1931

Continuing the work of Jacobson and Pray,[2] eleven new fluosilicates have been prepared and analyzed.

In general, the preparation of these compounds was similar to that recorded in the first paper. The purest Eastman Kodak Co. bases were

[1] The Author wishes to acknowledge the assistance of the following persons in the completion of the present work: H. McMillen and C. W. Weaver on *o*-tolidine fluosilicate; E. Stutzman on di-α-, and di-β-naphthylamine fluosilicate; Christine Arnold on di-diphenylamine and *m*-phenylenediamine fluosilicates; C. G. Rollins on the fluosilicates of ethylaniline, *p*-nitrosodiphenylamine, *p*-aminoazobenzene and *p*-aminobenzoic acid.

[2] Jacobson and Pray, THIS JOURNAL, 50, 3055 (1928).

used and always recrystallized if the microscopic examination showed impurities present.

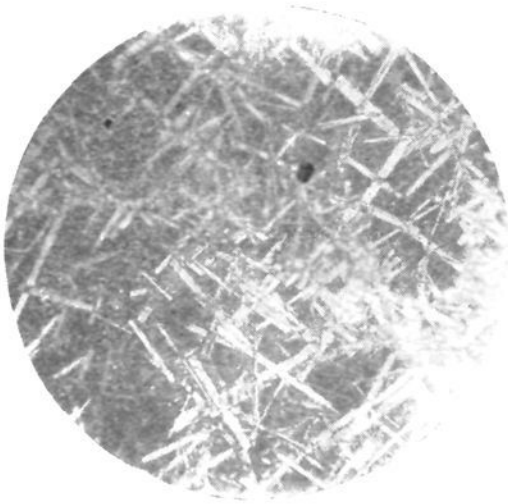

Fig. 1.—*o*-Tolidine fluosilicate.

All the fluosilicates prepared are recorded in the table, giving name, formula, properties and analytical values. They were all recrystallized from 95% ethyl alcohol except Nos. 1 and 9. *o*-Tolidine fluosilicate was recrystallized from 75% ethyl alcohol and di-nitrosodiphenylamine fluosilicate from a mixture of 95% ethyl alcohol and acetone. The analyses of these compounds indicate that they are all composed of two molecules of the base with one of the acid except Nos. 1, 6 and 7, which have a one to one ratio. This fact is indicated by applying the prefix di- to the name of the compound.

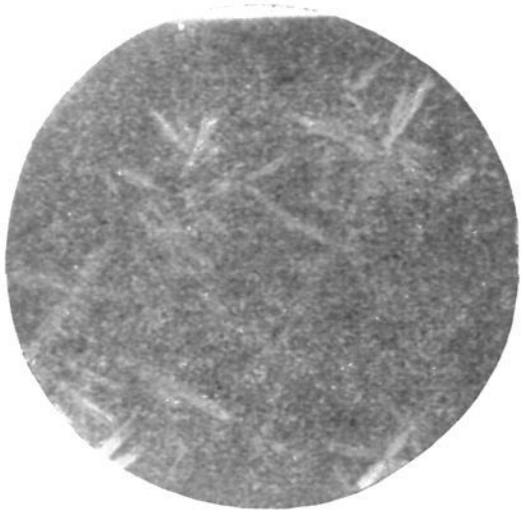

Fig. 2.—Di-α-naphthylamine fluosilicate.

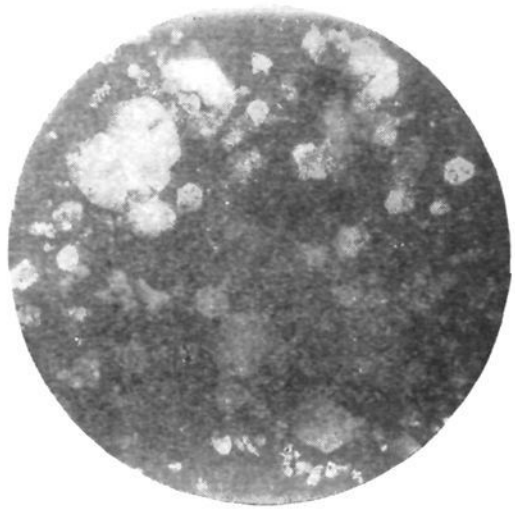

Fig. 3.—Di-β-naphthylamine fluosilicate.

TABLE I

COMPOUNDS AND DATA

No.	Fluosilicate of	Formula	Crystal form	M. p., °C.
1	*o*-Tolidine	$(CH_3NH_2C_6H_3)_2H_2SiF_6$	Tiny microscopic prisms	268–269
2	Di-α-naphthylamine	$(C_{10}H_7NH_2)_2H_2SiF_6$	Rosets of needles	218 (dec.)
3	Di-β-naphthylamine	$(C_{10}H_7NH_2)_2H_2SiF_6$	Hexagonal plates	236.3
4	Di-*m*-nitraniline	$(C_6H_4NO_2NH_2)_2H_2SiF_6$	Rhomboidal plates	200
5	Di-diphenylamine	$[(C_6H_5)_2NH]_2H_2SiF_6$	Rods forming rosets	169
6	*m*-Phenylenediamine	$C_6H_4(NH_2)_2H_2SiF_6$	Long needle-like prisms	243–244
7	*p*-Phenylenediamine	$C_6H_4(NH_2)_2H_2SiF_6$	Six-sided irregular plates	Dec.
8	Di-ethylaniline	$(C_6H_5NHC_2H_5)_2H_2SiF_6$	Pointed prisms	165.3
9	Di-nitrosodiphenylamine	$[(C_6H_5)_2N{=}NO]_2H_2SiF_6$	Butterfly-shaped	124.5 (dec.)
10	Di-*p*-aminoazobenzene	$(NH_2C_6H_4N_2C_6H_5)_2H_2SiF_6$	Long needles	220 (dec.)
11	Di-*p*-aminobenzoic acid	$(NH_2C_6H_4COOH)_2H_2SiF_6$	Long narrow prisms	240–245

In the analyses nitrogen was determined by the Kjeldahl method, and the fluosilicic acid radical by the author's own method recorded.[3]

TABLE II

SOLUBILITIES AND ANALYSES

No.	Solubilities in 100 cc. of 95% EtOH at 25°		Nitrogen, % Calcd.	Found			H_2SiF_6, % Calcd.	Found	
1	0.013	0.041 at 35°	9.85	9.17	9.06		40.44	40.52	
2	.1504		6.50	6.36	6.54	6.58	33.48	33.46	33.50
3	.0816	.1248 at 35°	6.50	6.60	6.54		33.48	33.13	33.16
4	.1210	.4736 at 35°	13.34	13.45	13.46		34.29	34.70	34.28
5	2.4492		5.81	6.06	5.84		29.87	29.72	29.74
6	0.065		11.11	11.39	11.26		57.13	57.27	(Av. of 3)
7	.014		11.11	11.89	11.51		57.13	57.43	56.96
8	.979		7.25	7.42	7.43		37.30	37.17	37.41
9	.84		10.37	10.15	10.41		(Colored soln. end-pt. indist.)		
10	.187		15.62	15.73	15.78		(Colored soln. end-pt. indist.)		
11	.91		6.94	6.71	6.89		34.45	34.59	34.67

All the above compounds are white in color except No. 6, which is chocolate-brown, No. 7 pinkish, No. 9 indigo and No. 10 cinnamon-brown. They are all stable in the air except No. 4, which turns yellow on long standing, and No. 5, whose surface becomes blue after some weeks exposure to the air.

All are stable in water solution except Nos. 2, 6 and 9. Nos. 3, 4 and 10 also decompose in the presence of water although more slowly. The remaining fluosilicates are all insoluble in water except Nos. 7, 8 and 11, which are readily soluble. No. 3 exhibits a high surface tension and at first floats on the water like lycopodium.

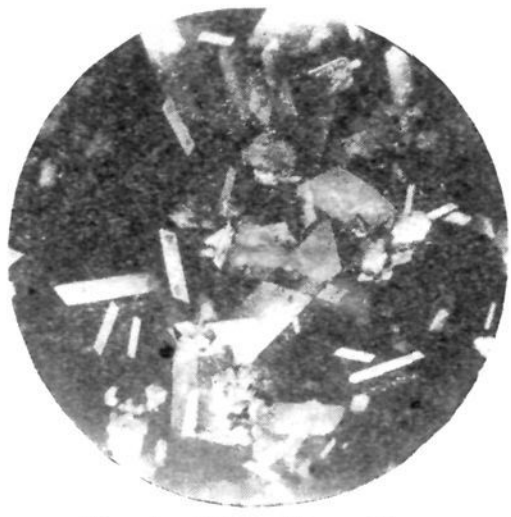

Fig. 4.—Di-*m*-nitroaniline fluosilicate.

Fig. 5.—Di-diphenylamine fluosilicate.

The fluosilicates are all crystalline compounds possessing definite and characteristic crystal forms, as shown in the accompanying micro photographs. In the case of No. 9, very fine hair-like crystals were obtained from 95% ethyl alcohol, while differently shaped crystals, as shown in

[3] Jacobson, *J. Phys. Chem.*, **28**, 506 (1924).

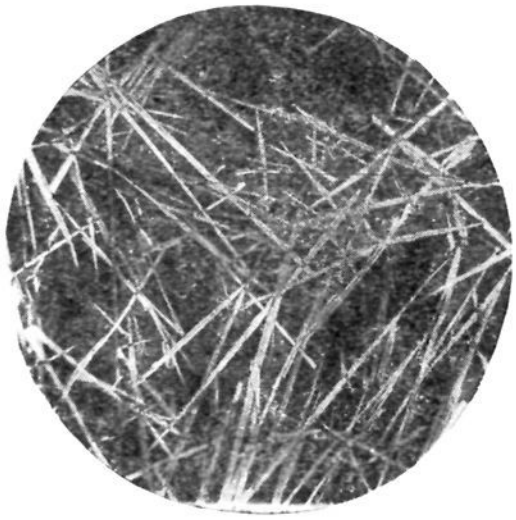

Fig. 6.—*m*-Phenylenediamine fluosilicate.

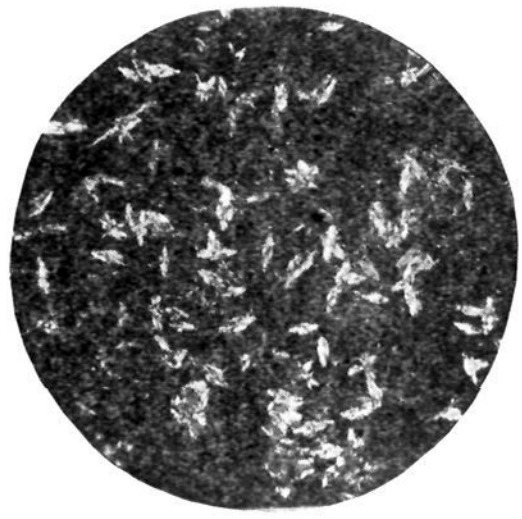

Fig. 7.—*p*-Phenylenediamine fluosilicate.

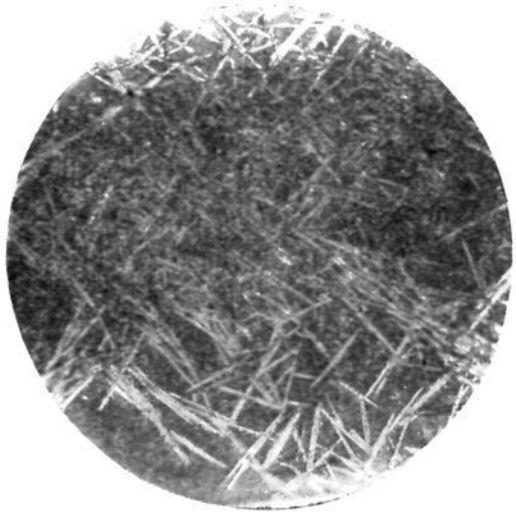

Fig. 8.—Diethylaniline fluosilicate.

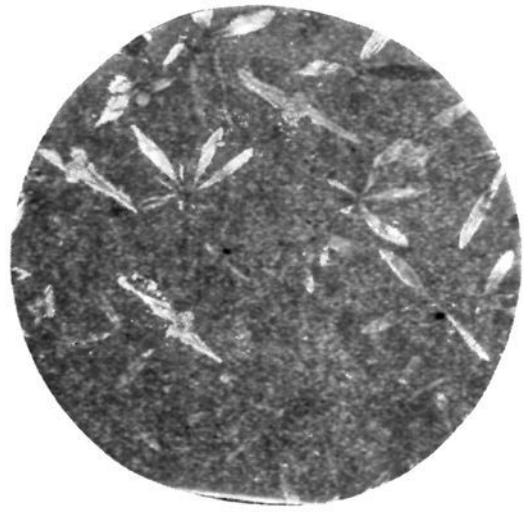

Fig. 9.—Di-nitrosodiphenylamine fluosilicate.

Fig. 10.—Di-*p*-aminoazobenzene fluosilicate.

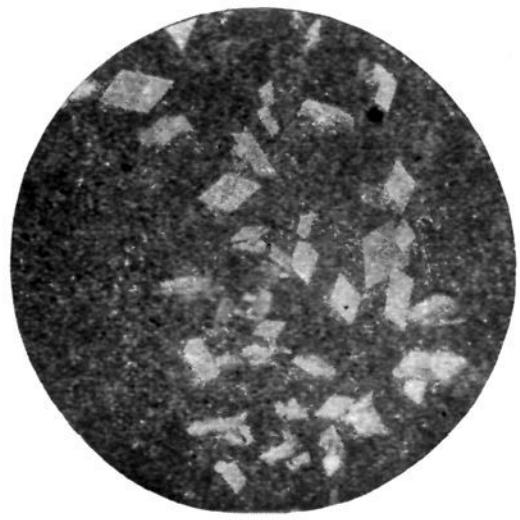

Fig. 11.—Di-*p*-aminobenzoic acid fluosilicate.

the cut, resulted when crystallized from a mixture of ethyl alcohol and acetone.

Fruitless attempts were made to prepare fluosilicates of the following substances: (1) triphenylamine, (2) *o*-nitroaniline, (3) *p*-nitroaniline, (4) succinimide, (5) dimethyl-α-naphthylamine, (6) benzamide, (7) dimethyl-*p*-toluidine.

Benzidine fluosilicate has been prepared but will be described later.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

LOCAL ANESTHETICS IN THE PYRROLE SERIES. II[1]

BY F. F. BLICKE AND E. S. BLAKE

RECEIVED OCTOBER 2, 1930 PUBLISHED MARCH 6, 1931

The structure of novocaine has been modified by a number of investigators in the hope that a better medicament might be obtained and also in order that more information might be acquired regarding the relationship between structure and local anesthetic action.[2] This has been accomplished by a variation in one or more of the three units A, B and C in the novocaine molecule (I).

(4) $\underset{\text{A}}{\underline{H_2N—C_6H_4—CO}}—O—\underset{\text{B}}{\underline{CH_2—CH_2}}—\underset{\text{C}}{\underline{N(C_2H_5)_2}}$

I

The primary object of our investigation was to determine, with regard to local anesthetic activity, the effect of a replacement of 4-aminobenzoyl by 2-pyrroyl and the result of a substitution of 1-pyrryl and 1-pyrrolidyl for the diethylamino group.[3] Thus in the analogs of novocaine which we obtained unit A is represented by benzoyl, 4-aminobenzoyl and 2-pyrroyl,

[1] This paper represents the second part of a dissertation submitted to the Graduate School by E. S. Blake in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan. The first part of the dissertation was published in THIS JOURNAL, **52**, 235 (1930).

This investigation was made possible by the grant of a fellowship by Frederick Stearns and Company and we wish to express our appreciation for the aid which has been given us.

[2] Fränkel, "Die Arzneimittel-synthese," J. Springer, Berlin, **1927**, p. 386–395; v. Braun and co-workers, *Ber.*, **52**, 2011 (1919); *ibid.*, **55**, 1666 (1922); McElvain and co-workers, THIS JOURNAL, **48**, 2179, 2239 (1926); *ibid.*, **49**, 2835 (1927); **51**, 887, 922 (1929); Barnes and Adams, *ibid.*, **49**, 1307 (1927); Marvel and co-workers, *ibid.*, **50**, 563 (1928); **51**, 915 (1929); Tréfuel, Tréfuel and Barbelet, *Bull. sci. pharmacol.*, **37**, 184, 240 (1930); *Chem. Abstracts*, **24**, 3502 (1930).

[3] Luft [*Ber.*, **38**, 4044 (1905)] has described the preparation of 4-(N-piperidyl)-antipyrine, while v. Braun and Lemke [*ibid.*, **55**, 3540, 3557 (1922)] prepared 4-(N-pyrrolidyl)- and 4-(N, Δ^3-pyrrolyl)-antipyrine. According to the latter investigators the pyrrolidyl is a stronger antipyretic than the piperidyl or the pyrrolyl derivative.