Summary

This paper reports the isolation of 2,8-dimethylquinoline from the kerosene distillate of California petroleum.

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The Nitrogen Compounds in Petroleum Distillates. VII. New Reactions of the Naphthenic Base, $C_{16}H_{25}N$.[1] A New Naphthenic Base, $C_{13}H_{21}N$

BY B. F. ARMENDT AND J. R. BAILEY

Introduction.—Unrefined California petroleum distillates yield, along with aromatic bases, in preponderant amount a host of non-aromatic bases.[2] Since these non-aromatics represent, not only new substances, but also new structural types, their investigation may be considered of unusual scientific interest. In this connection, it may be mentioned, work is in progress to obtain experimental evidence of a possible structural relationship between the non-aromatic bases and petroleum hydrocarbons.

Because both the isolation and proof of structure of the low-boiling non-aromatic bases might be expected to present the least experimental difficulty, an investigation of fractions within the boiling point range of 215–216° was undertaken. Three barrels of kero bases originally available gave only 708 cc. of this material and from this 20 g. (0.004% of the three barrels) of a base of the formula $C_{13}H_{21}N$ was obtained. Research on this product has been limited to a comparison of its general behavior with that of the $C_{16}H_{25}N$ base.

All attempts to hydrogenate both the $C_{13}H_{21}N$ and the $C_{16}H_{25}N$ base ended in failure. They also resist dehydrogenation, a stability hardly to be expected of true *hydroaromatic* bases, and prolonged heating with alkaline permanganate has no oxidizing effect. The $C_{16}H_{25}N$ compound reacts readily with methyl iodide, but the methiodide of the $C_{13}H_{21}N$ compound is not formed under similar conditions. Attempts to employ the Hofmann reaction in degradation of the $C_{16}H_{25}N$ base were unsuccessful, probably due to rearrangement of the quaternary base to a pseudo form.

From the many theoretical possibilities, there has been selected provisionally formula I, for the $C_{13}H_{21}N$ base and the original structural interpretation of the $C_{16}H_{25}N$ base has been changed to II.

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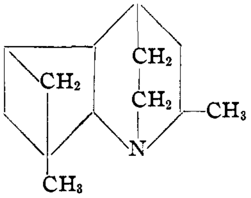
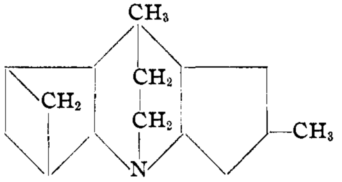
(1) W. C. Thompson and J. R. Bailey, THIS JOURNAL, **53**, 1002 (1931).

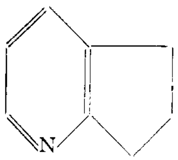
(2) Shale and bones on distillation yield exclusively aromatic bases and the same applies to coal with one exception [Decker and Dunant report the isolation of dihydroacridine from a coal tar distillate, *Ber.*, **42**, 1178 (1909)].



I



II



III

The n_D^{20} value, 1.4850, of I, as compared with the n_D^{20} value, 1.5129, of II, is accounted for by one more ring nucleus in a pyridindacine than in a pyrindine. Furthermore, the refractive difference here of 0.0279 is of the same order as that of 0.0342 between pyridine, where n_D^{20} is 1.5068, and 5,7-dihydropyrindine,[3] III, where n_D^{20} is 1.5410.

An unexpected observation was that the $C_{16}H_{25}N$ base, just like a quinoline methylated at 2, condenses readily with phthalic anhydride to produce a phthalone.[4] On the other hand, attempts to prepare a phthalone of the $C_{13}H_{21}N$ base gave a negative result. The phthalone of the pyrindacine is of a light orange color and sublimes undecomposed. The presence of a $CH(CO)_2$ complex was established through the preparation of a deep orange colored sodium salt which necessarily involved in its formation enolization of CHCO to C=COH.

Mabery and Wesson[5] in an investigation of "Nitrogen Bases of California Petroleum" found "phthalic anhydride condenses with the basic fractions in what is evidently a phthalone formation," and used this reaction in support of their claim that petroleum bases "consist mainly of alkylated quinolines (or isoquinolines)." It is now evident that phthalone formation cannot be accepted as an infallible test for quinoline bases.

Experimental Part. I

Isolation of the $C_{13}H_{21}N$ Base.—This product was first obtained in a preliminary experiment in an amount sufficient to determine its b. p. 225.6° and the n_D^{25} value, 1.4833. Also of importance was the m. p. of the picrate, 158.7°, along with its crystalline form and solubilities. The subjoined data pertain to the material assembled in quest of the $C_{13}H_{21}N$ base and represent combinations of distillation fractions in the order of boiling points:

No.	Cc.	B. p., °C.	n_D^{30}
I	163	215.3-218	1.4935-1.4972
II	190	220 -221.5	1.4875-1.4905
III	203	223 -224.5	1.4862-1.4880
IV	152	225 -226	1.4858-1.4865

Each of the four batches of bases was extracted with three successive portions of *N*

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[3] Takashi Eguchi, *Bull. Chem. Soc. Japan*, **3**, 239 (1928); *Chem. Zentr.*, **100**, 331 (1928); W. C. Thompson, THIS JOURNAL, **53**, 3160 (1931).

[4] *Cf.* A. Eibner, *Ber.*, **37**, 3605 (1904). M. Q. Doja, *Chem. Reviews*, **11**, 278 (1932), states: "A methyl group in a quinoline ring is known to lose its power of condensation with ketones or aldehydes when the ring is partially or wholly reduced."

[5] C. F. Mabery and L. G. Wesson, THIS JOURNAL, **42**, 1026 (1920).

sulfuric acid and the resulting 16 fractions were precipitated with a hot solution of picric acid in water or alcohol.

No.	H_2SO_4, cc.	G. picric acid In H_2O	G. picric acid In alc.	No.	H_2SO_4, cc.	G. picric acid In H_2O	G. picric acid In alc.
	Batch I				Batch III		
1	200	2	..	1	200	2	0
2	200	42	25	2	250	62	25
3	200	42	10	3	300	62	20
4	100	17	..	4	300	42	10
	Batch II				Batch IV		
1	200	2	0	1	150	2	0
2	250	52	25	2	200	42	0
3	300	52	20	3	250	62	10
4	300	42	0	4	250	21	0

All the picrates obtained from acid extracts 2, 3 and 4 of each batch were subjected to fractional crystallization from 95% alcohol, until crystalline products were obtained. Next a number of melting points and mixed melting points were made as controls on the seven fractions of picrate mixtures most insoluble in alcohol. Three serial numbers are employed in listing below these picrates; the first number indicates the distillation fraction, the second the acid extraction, and the third the picrate precipitation; *e. g.*, "231" applies to the product that came from the first picrate precipitation of the third acid extract of distillation fraction II. "A" refers to initial melting point of picrates and "B" to the melting point after one recrystallization from alcohol

Melting Points (uncorr.), °C. Picrate fractions	M. p. A	M. p. B	Mixed Melting Points (uncorr.), °C. Mixed picrate fraction	M. p. A	M. p. B
231	163–164	163–164	231 + 331	163.5–164.5	163.5–165
241	142–143	159–160	231 + 241	119–123	119–122
331	162–165	165–166	331 + 341	123–124	132–133
341	145–147	160–161	341 + 441	146–146.5	159.5–160.5
342	145–158	160–161	241 + 341	145.5–146	160–160.5
431	144–145	159–161	431 + 441	145.5–146	160.5–161
441	145–146	160–161	341 + 342	144–146	160–161
			342 + 441	144–146	160–161
			331 + 431	120–132	120–126

Preliminary experiments had disclosed that, where samples of two mixed picrates had an initial m. p. of 144–146.5° and, after recrystallization from alcohol, a m. p. of 159.5–161°, the $C_{13}H_{21}N$ base was present in high concentration. Accordingly picrates 241, 341, 342, 431 and 441 were combined and recrystallized from alcohol, and then from benzene. From 50 g. of pure picrate with m. p. 158.7°, 21.5 g. of the $C_{13}H_{21}N$ base was separated with ammonium hydroxide. From the reworked residues two other picrates, one of m. p. 115–118° and the other of m. p. 160°, were obtained but were not further investigated. No doubt the Perrin–Bailey method of cumulative extraction, which was perfected toward the close of the present investigation, will prove of service in developing the most practical procedure in isolation of the several bases in this temperature range.

Properties of the $C_{13}H_{21}N$ Base.—It is a colorless oil, with a faint basic but not unpleasant odor, insoluble in water and miscible in all proportions with the common organic solvents. The following physical constants were determined: m. p. 24.5°; b. p. 225.6° at 750 mm.; d_4^{20} 0.8700; n_D^{25} 1.4833 and n_D^{30} 1.4811.

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.61; H, 10.98; N, 7.34. Found: C, 81.40; H, 11.03; N, 7.49. *Mol. wt.* Subs., 10.454 mg.; camphor, 206.452 mg.; Δt, 10.5°. Calcd. for $C_{13}H_{21}N$: mol. wt., 191; found: mol. wt., 185.

An attempt to prepare the methiodide by heating 0.5 cc. of base with 2 cc. of methyl iodide in a sealed tube for thirty hours at water-bath temperature gave a negative result. The base and phthalic anhydride, heated for four hours at 200°, did not react. Reduction experiments with the use of Adams catalyst were unsuccessful. In chloroform solution the base does not react with bromine even on warming, and it can be distilled over heated zinc dust unchanged. The base shows an unusual stability toward alkaline permanganate. In contrast to its stability in alkaline solution, the $C_{13}H_{21}N$ base in 1:5 sulfuric acid reduces permanganate readily. An attempt to effect nitration, in accordance with the procedure of Markownikoff for nitration of methylcyclopentane,[6] ended in failure.

Picrate.—This salt separates on addition of picric acid in water or alcohol to a solution of the acid sulfate and can be crystallized from benzene in yellow needles melting at 158.7°. It is readily soluble in alcohol, 50% acetic acid, acetone and ethyl acetate and only slightly soluble in water, ether and petroleum ether.

Anal. Calcd. for $C_{19}H_{24}O_7N$: C, 54.29; H, 5.71; N, 13.33. Found: C, 54.53; H, 5.61; N, 13.55.

Mercuric Chloride Salt.—This salt, prepared by addition of a solution of mercuric chloride to the base in dilute hydrochloric acid, is difficultly soluble in water and can be crystallized from alcohol in prisms melting at 131.6°.

Anal. Calcd. for $C_{13}H_{21}N \cdot HCl \cdot HgCl_2, H_2O$: N, 2.71; Cl, 20.60. Found: N, 2.85, 2.71; Cl, 20.64.

Chloroplatinate.—The chloroplatinate, prepared in dilute hydrochloric acid solution, crystallizes from dilute alcohol in well-defined rectangular plates, of an orange color and melting with decomposition at 205°. It is only moderately soluble in water and alcohol.

Anal. Calcd. for $C_{13}H_{21}N \cdot H_2PtCl_6$: Pt, 24.65; N, 3.45. Found: Pt, 24.32; N, 3.48.

Acid Sulfate.—This salt crystallizes out on dissolving the base in the calculated amount of sulfuric acid. It is very soluble in water and alcohol, difficultly soluble in ethyl acetate and can be crystallized from acetone in cubes melting at 155°.

Anal. Calcd. for $C_{13}H_{21}N \cdot H_2SO_4$: N, 4.84. Found: N, 4.82.

Experimental Part. II

The $C_{16}H_{25}N$ Base.—The $C_{16}H_{25}N$ base used in the following experiments was isolated from distillation fractions of kero bases, boiling in the temperature zone around 275°, by employment of the Perrin–Bailey cumulative extraction process.[7]

Phthalone.—The base and phthalic anhydride in molecular proportions are heated at 200° for four hours, the melt is dissolved in 15 cc. of concentrated sulfuric acid for each 10 cc. of base used, and the solution is poured onto crushed ice. In final purification the product is crystallized from 95% alcohol in thin rectangular plates, of a deep yellow color and melting at 208°. It dissolves readily in boiling glacial acetic acid, is more difficultly soluble in 95% alcohol, 50% acetic acid and ethyl acetate and is practically insoluble in water and dilute mineral acids. Like quinoline yellow, it sublimes undecomposed at 220° and 45 mm. Treated with sodium ethylate, it separates from alcohol in the form of a crystalline deep orange colored salt which hydrolyzes in water.

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(6) Markownikoff, *Ann.*, **307**, 352 (1899).

(7) See Paper IV of this series by Perrin and Bailey.

In all attempts to hydrolyze the phthalone with dilute sulfuric acid and alcoholic potassium hydroxide, it was recovered unchanged. In oxidation experiments only gums were obtained, from which no crystalline product containing nitrogen was isolated. Unlike quinoline yellow, the new phthalone cannot serve as a spirit-soluble dye and, furthermore, sulfonation experiments ended in failure.

Anal. Calcd. for $C_{24}H_{27}O_2N$: C, 79.77; H, 7.48; N, 3.88. Found: C, 79.75; H, 7.31; N, 3.75. *Mol. wt.* Subs., 0.1008 g.; camphor, 1.060 g.; Δt, 11°. Calcd. for $C_{24}H_{27}O_2N$: mol. wt., 361. Found: mol. wt., 316.

Attempt to Condense Methylcyclopentane with Phthalic Anhydride.—It was of some interest to determine whether a hydrocarbon of naphthenic structure would condense, like the naphthenic base, with phthalic anhydride. However, all attempts to condense methylcyclopentane with phthalic anhydride,[8] with and without the use of zinc chloride, were unavailing.

Hydrochloride of the Dibenzal Compound.—Five grams of base, 6.5 g. of benzaldehyde and 0.5 g. of zinc chloride are heated for eighteen hours in a sealed tube at 190–210°. The viscous reaction product dissolved in ether is precipitated as the hydrochloride (9 g.) by shaking the solution with dilute hydrochloric acid. After being washed with ether and acetone, it crystallizes from a mixture of alcohol and chloroform in long flat prisms, with pyramidal end faces and melting at 241–242°.

Anal. Calcd. for $C_{30}H_{34}NCl$: N, 3.16. Found: N, 2.98.

Dibenzal Compound.—This substance, freed from the hydrochloride with ammonium hydroxide, is insoluble in water and separates from alcohol in ill-defined crystals melting at 120–121°. In chloroform it absorbs an amount of bromine corresponding to two double bonds. It is very resistant to alkaline permanganate.

Anal. Calcd. for $C_{30}H_{33}N$: C, 88.45; H, 8.11; N, 3.44. Found: C, 88.37; H, 7.83; N, 3.71. *Mol. wt.* Subs., 9.187 mg.; camphor, 77.2 mg.; Δt, 11.9°. Calcd. for $C_{30}H_{33}N$: mol. wt., 407. Found: mol. wt., 400.

Picrate of the Dibenzal Compound.—On addition of an alcoholic solution of picric acid to the hydrochloride in chloroform, a granular product, highly insoluble in water and the common organic solvents, separates. It crystallizes from a mixture of alcohol and chloroform in microscopic long flat prisms, with pyramidal end faces and melting at 249–250° with decomposition.

Anal. Calcd. for $C_{36}H_{36}O_7N_4$: C, 67.92; H, 5.66; N, 8.81. Found: C, 67.52; H, 5.41; N, 8.60.

Summary

This paper describes a non-aromatic base of the constitution $C_{13}H_{21}N$ occurring in the crude kerosene distillation of California petroleum.

In further study of the previously isolated $C_{16}H_{25}N$ base, the unexpected discovery has been made that it condenses with phthalic anhydride to form a phthalone.

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[8] We are indebted to Dr. Edward W. Washburn of the U. S. Bureau of Standards for the methyl cyclopentane used in these experiments.