contanone-20 melting at 90–92.5° resulted. After treatment with charcoal to remove a yellow discoloration and two recrystallizations from light petroleum (b. p. 70–80°) the ketone melted at 91.2–91.4°.[1]

The long X-ray spacing (melted specimen) was 51.5 Å., indicating that this ketone, like the lower homologs, crystallizes with vertical molecules.

Anal.[2] Calcd. for $C_{39}H_{78}O$: C, 83.1; H, 13.9. Found: C, 83.1; H, 13.9.

***n*-Nonatriacontane.**—1.9 grams of the ketone, 48 g. of amalgamated zinc, 48 cc. of concentrated hydrochloric acid and 10 cc. of glacial acetic acid were boiled under reflux. Every sixth hour the mixture was cooled, the liquid decanted and fresh hydrochloric acid, glacial acetic acid and zinc (10 g.) added. The reduction was followed by determination of the m. p. of the product. After eighty hours the m. p. became constant at 79.0–79.4°. The hydrocarbon was collected and purified by treatment with concentrated sulfuric acid at 130° for two hours.[3] Considerable darkening occurred and the process was repeated until on the fourth treatment darkening no longer took place. The hydrocarbon was carefully washed with hot water and treated with charcoal in benzene. It crystallized from benzene in small white lustrous plates and after three crystallizations from this solvent the m. p. was 80.0–80.2°. The phenomena observed on heating and cooling the hydrocarbon through the m. p. are similar to those observed for the lower homologs.[3] On heating the opaque crystalline material a transition is observed at approximately 75° (change into a transparent form with vertical rotating chains). The s. p. on cooling the melt lies at 79.8°. At this point transparent needles are formed in the melt. On further cooling to 75°, the transparent solid is changed to an opaque form stable at lower temperatures.

The X-ray investigation of the hydrocarbon, crystallized from benzene and pressed on to glass, gave a long spacing of 51.3 Å., corresponding to the normal (A) form with vertical molecules. A specimen melted on to glass by means of the hot-wire technique gave, however, a different diffraction pattern with a long spacing of 47.1 Å., indicating tilted molecules. Odd number hydrocarbons containing more than eleven carbon atoms have previously been found to crystallize only in the A form with vertical molecules.[3] The dimorphism of *n*-nonatriacontane was therefore unexpected, and the compound provides an exception to the rule[4] that a longer chain and an odd number of carbon atoms (and also a higher temperature and the presence of impurity) favors crystallization in vertical forms.

Anal.[2] Calcd. for $C_{39}H_{80}$: C, 85.4; H, 14.6. Found: C, 85.1; H, 14.6.

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[1] The m. p.'s and s. p.'s were determined in capillary tubes using a glycerol bath and totally immersed calibrated Anschütz type thermometers. Heating and cooling were carried out very slowly.

[2] Microanalysis by Dr. Max Möller, Copenhagen.

[3] S. A. Piper, A. C. Chibnall, S. J. Hopkins, A. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2072 (1931).

[4] *Cf.* J. C. Smith, *Ann. Reports*, **35**, 259 (1938).

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RECEIVED MARCH 3, 1944

COMMUNICATIONS TO THE EDITOR

STERIC STRAIN AND THE ANOMALOUS BASE STRENGTH OF THE NORMAL ALIPHATIC AMINES

Sir:

The strength of the normal aliphatic acids and amines changes with chain length in a peculiar manner. Thus K_a decreases for the first three members, but increases for the fourth (Table I). This curious behavior has been ascribed in the case of the carboxylic acids to hydrogen bond formation between the end methyl group of butyric acid (or of the γ-methylene group of the higher acids) with the carbonyl oxygen of the carboxyl group.[1] A similar explanation could be used for the amines.

As part of a study of generalized acids and bases in gaseous systems,[2] the measurement of the base strength of the normal aliphatic amines with trimethylboron as the reference acid was undertaken. The base strength thus measured (Table I) first increases markedly from ammonia to methylamine, then decreases with ethylamine, rises again with propylamine and then increases regularly. This behavior is so similar to that of the normal aliphatic acids and of the corresponding amides that it is not unreasonable to seek one fundamental explanation for the phenomena.

TABLE I

ACIDITY CONSTANTS FOR THE NORMAL ALIPHATIC ACIDS AND AMINES

R	RCOOH at 25°[a]	RNH_3^+ at 25°[b]	$RNH_2:BMe_3$ at 100°
H	17.12×10^{-5}	5.38×10^{-10}	4.62
CH_3	1.75	0.229	0.036
C_2H_5	1.33	.214	.071
n-C_3H_7	1.38	.263	.060
n-C_4H_9	1.32	.229	.047
n-C_5H_{11}	1.28	.228	.042

[a] From Dippy, ref. 1. [b] From Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932), and from Hoerr, McCorkle and Ralston, *ibid.*, **65**, 328 (1943).

One important difference will be noted between the order obtained with trimethylboron and the orders obtained by classical methods. With trimethylboron the irregularity appears with the third member of the series, $C_2H_5NH_2:BMe_3$, rather than with the fourth. Since ethylamine cannot form a hydrogen bridge of the type postulated to account for the behavior of butyric acid and propylamine in aqueous solution, it is reasonable to seek some other explanation. (It might also be pointed out that according to the hydrogen bridge hypothesis the order should be independent

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[1] Dippy, *Chem. Rev.*, **25**, 151 (1939).

[2] THIS JOURNAL, **66**, 431, 435 (1944).

of the reference acid, a conclusion which is contrary to the observed facts.)

We suggest that the origin of this behavior is steric in nature—the observed weakening of the base occurring with the first member of the series in which the alkyl group of the base can interfere with the acid (H^+ or BMe_3). It is obvious that the point in the series at which the weakening is observed will depend upon the size of the reference acid. In the case of a large acid, such as trimethylboron, such interference occurs in a base having a shorter chain than in the case where the acid is the small proton. It would be expected that an even larger acid, *e. g.*, triethylboron or tri-*n*-propylboron, would lead to a shift of the irregularity to methylamine, or even to ammonia. This prediction is now being tested.

The assistance afforded by a grant from the Penrose Fund of the American Philosophical Society is gratefully acknowledged.

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MODDIE D. TAYLOR

RECEIVED APRIL 19, 1944

THE RELATIONSHIP OF STRUCTURE TO ACTIVITY OF SULFANILAMIDE TYPE COMPOUNDS

Sir:

Kumler and Daniels[1] have suggested that the resonating form of the *p*-amino group with a separation of charge is a fundamental factor for the bacteriostatic activity of sulfanilamide type compounds. The experimental evidence for this suggestion is "that sulfanilamide has a higher (ultraviolet) extinction coefficient in base than in water."[2]

Because of the theoretical importance placed on this single observation, and since previous studies in this Laboratory[3] were not in agreement with it, we have repeated the work using a more suitable instrument (Beckman Spectrophotometer Model DU).[4] The data obtained for sulfanilamide are recorded in Fig. 1 and Table I. The additive function $-\log_{10}T$ was used in Fig. 1 to demonstrate the reliability of the method of correcting for solvent absorption.

TABLE I

ULTRAVIOLET SPECTRAL DATA ON SULFANILAMIDE

Form	Wave length of peak absorption, Å.	Extinction coefficient
Molecular (1 *N* NaCl)	2585	16,380 ± 49[a]
Ionic (1 *N* NaOH)	2505	16,150 ± 48
Difference	80	230 ± 97
Per cent. difference		1.42 ± 0.6

[a] The limits of error are those encountered in quadruplicate determinations.

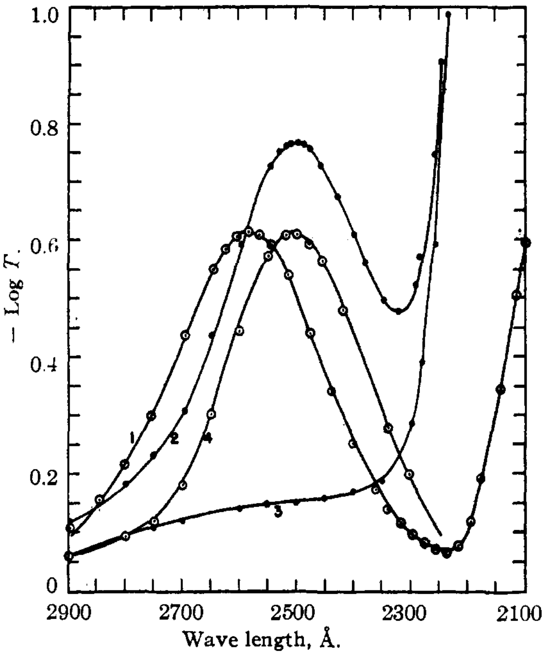

Fig. 1.—Log_{10} of per cent. light transmitted by a 1-cm. sample of: 1, 3.78×10^{-5} *M* sulfanilamide in 1 *N* NaCl, 1 *N* NaCl blank; 2, 3.78×10^{-5} *M* sulfanilamide in 1 *N* NaOH, water blank; 3, 1 *N* NaOH, water blank; 4, 3.78×10^{-5} *M* sulfanilamide in 1 *N* NaOH, solid line obtained by subtracting curve 3 from 2, and points -⊙- from measurements with 1 *N* NaOH blank.

These results do not confirm those of Kumler and Strait, and there appears to be no adequate experimental basis for the assumption that the resonating form with a separation of charge contributes more in a sulfonamide ion. Moreover, the lack of correlation between the base constants and bacteriostatic activity of sulfanilamide type compounds in general[5] does not support the hypothesis that the base weakening resonance form is a fundamental factor for activity.

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(1) Kumler and Daniels, THIS JOURNAL, **65**, 2190 (1943).

(2) Kumler and Strait, *ibid.*, **65**, 2349 (1943).

(3) E. J. Robinson and D. Richardson, personal communication.

(4) This instrument was made available to us through the courtesy of Dr. V. du Vigneaud and Dr. W. Summerson, Department of Biochemistry, Cornell University Medical School, New York, N. Y.

(5) Bell and Roblin, THIS JOURNAL, **64**, 2905 (1942).

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RECEIVED MARCH 15, 1944

SYNTHETIC THIOPHANE DERIVATIVES

Sir:

Karrer and Schmid[1] have recently described the synthesis of thiophanone-3 and of 2-methylthiophanone-3. Results essentially in agreement with those of the Swiss investigators have been obtained in this Laboratory.

(1) Karrer and Schmid, *Helv. Chim. Acta*, **27**, 116, 124 (1944).