NOTES

The Group Refraction of the Carbon–Carbon Triple Bond

By Kenneth N. Campbell and Sylvester L. Eveslage

Considerable uncertainty has been attached to the values published for the group refraction of the carbon–carbon triple bond.[1,2] Auwers[3] recalculated the group refraction for the D line from selected literature data, and found that the value varied considerably, depending on whether the triple bond was present in a hydrocarbon or carbinol, and on whether it was a terminal or non-terminal triple bond. Furthermore, he found wide deviations within any one class; for example, in the case of non-terminal acetylenic hydrocarbons the deviations from the mean varied from +17 to −18%.

There are two possible explanations for these deviations. The first is, of course, structural. The structural effect may be overlaid, however, by the presence of impurities. Acetylenes as usually prepared are apt to contain small amounts of other unsaturated hydrocarbons and of unreacted halides, which can only be removed completely by careful fractionation of relatively large amounts through efficient columns. Furthermore, acetylenes form peroxides with great ease, and unless the physical constants of the hydrocarbon are determined immediately after distillation they are apt to be in error. In the older work these precautions were probably not always observed.

In recent years, since Auwers published his values, several straight-chain acetylenic hydrocarbons have been made in quantity, and purified by careful fractionation through highly efficient columns; accurate physical constants have been determined on the pure products.[4,5] It seemed of interest to use these recent, more accurate data to recalculate the group refraction of the triple bond (for the D line).

In making these calculations, 2.418 was used for the atomic refraction of carbon, and 1.100 for that of hydrogen.[6] The group refraction of the triple bond in straight-chain, terminal acetylenic hydrocarbons was found to be fairly constant, and is a little lower, 2.267, than the value found by Auwers,[3] 2.325. The group refractions calculated from the most recent physical constants[4,5] of 1-pentyne through 1-octyne are given in Table I, and plotted in Fig. 1; the maximum deviation from the mean was found to be ±2.5%.

Table I

Terminal, Straight-Chain Acetylenes

Compound	n^{20}_D	d^{20}_4	Triple bond value	Ref.
1-Pentyne	1.3852	0.6908	2.226	4
1-Hexyne	1.3990	.7156	2.257	4
	1.3984	.7152	2.237	5
1-Heptyne	1.4088	.7325	2.318	4
	1.4084	.7338	2.235	5
1-Octyne	1.4159	.7460	2.315	4
	1.4157	.7463	2.282	5

In non-terminal, straight-chain acetylenes the group refraction was found to increase as the triple bond is moved in from the end of the chain; this increase continues at least up to the 5-position. Thus for straight-chain 2-acetylenes the average value is 2.534, for 3-acetylenes 2.696, for 4-acetylenes 2.735 and for 5-acetylenes 2.767.

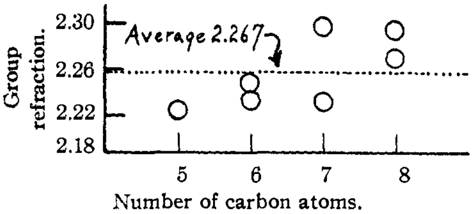

Fig. 1.—Group refraction of the triple bond in terminal, straight-chain acetylenic hydrocarbons.

These values are plotted in Fig. 2 and the data from which they were obtained are shown in Table

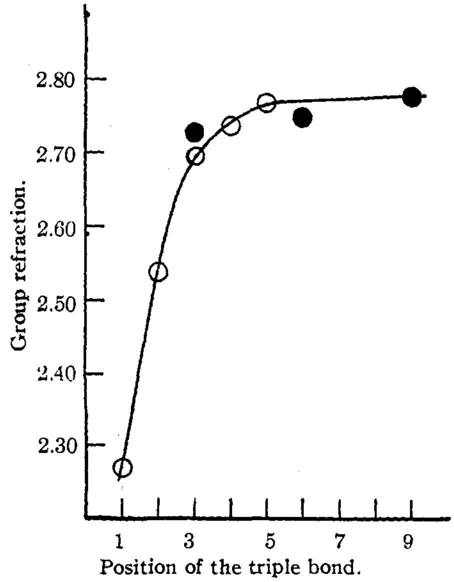

Fig. 2.—Group refraction of the triple bond in non-terminal straight-chain acetylenic hydrocarbons.

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(1) Auwers, *Ber.*, **65**, 146 (1932).

(2) Straus and Kuhnel, *ibid.*, 154 (1932).

(3) Auwers, *ibid.*, **68**, 1635 (1935).

(4) Henne and Greenlee, This Journal, **67**, 484 (1945).

(5) Campbell and Eby, *ibid.*, **63**, 2683 (1941).

(6) Gilman, "Organic Chemistry," Vol. II, 2nd ed., John Wiley and Sons, New York, N. Y., 1943, p. 1751.

II. Since Auwers[3] did not take into consideration the relative position of the triple bond in nonterminal acetylenes, these results explain in part the wide deviations found by him.

The group refraction of the triple bond was calculated from some of the older data, also.[7,8] In many cases the values found did not agree with those reported above, but in a few cases there was good agreement. The values so found are indicated in Fig. 2 by dark circles; they were not used in computing the averages.

TABLE II

NON-TERMINAL, STRAIGHT-CHAIN ACETYLENES

Compound	n^{20}_D	d^{20}_4	Triple bond value	Average	Ref.
2-Pentyne	1.4040	0.7115	2.521		a
	1.4039	.7104	2.553		4
2-Hexyne	1.4135	.7317	2.511		5
2-Octyne	1.4278	.7596	2.562		4
	1.4270	.7592	2.522		5
				2.534	
3-Hexyne	1.4110	.7231	2.696		5
3-Heptyne[b]	1.415	.7335	2.698		7
3-Octyne	1.4250	.7522	2.714		4
	1.4250	.7529	2.679		5
3-Nonyne[b]	1.4295	.7616	2.729		c
				2.696	
4-Octyne	1.4248	.7509	2.763		4
	1.4243	.7512	2.708		5
				2.735	
5-Decyne	1.4332	.7688	2.767	2.767	5
6-Dodecyne[b]	1.4425	.787	2.748		8
9-Octadecyne[b]	1.4488	.8022	2.786		7

[a] Sherrill, THIS JOURNAL, **60**, 2563 (1938). [b] These data were not used in determining the averages. [c] Unpublished work, Campbell and Campbell.

Huggins has shown that the molecular refraction of saturated hydrocarbons and olefins is not strictly an additive function, but is influenced to some extent by the type and amount of branching.[9] In this connection it seemed of interest to ascertain whether the group refraction of the triple bond was affected by branching of the chain. Unfortunately, there are but few branched chain acetylenes known which have been made in large enough amounts for satisfactory purification, so any conclusions are tentative.

Where the branching is not adjacent to the triple bond, there seems to be little effect, judging from the value calculated from 5-methyl-1-hexyne (2.342)[4] and 7-methyl-3-octyne (2.695)[10] which are the only members of this class conforming to the requirements.

Where the branching is adjacent to the triple bond, calculations made from literature data[7,8] indicated a large increase in the group refraction. In the course of other work, however, we have had occasion to prepare 3,3-dimethyl-4-nonyne in large amounts, by the method of Campbell and Eby.[11] Careful fractionation of this material through a very good column showed that it contained a small amount of a hydrocarbon (probably an enyne) with almost the same boiling point, but with a much higher index of refraction. This impurity could only be removed by repeated distillations. From the physical constants of the purified material (n^{20}_D 1.43168, d^{20}_4 0.76666) the group refraction is 2.882; this shows a slight increase over the value for the straight-chain 4-acetylenes. The group refraction calculated from the data on *t*-butylacetylene[8] (2.57) likewise shows only a slight increase over the straight-chain acetylenes. The large increase found for other branched-chain acetylenes reported in the literature may well be due to small amounts of impurities, as most of these acetylenes have not been made in large enough amounts for efficient fractionation.

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[7] M. P. Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Co., New York, N. Y., 1942.

[8] Egloff, "Physical Constants of Hydrocarbons," A. C. S. Monograph, Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939.

[9] Huggins, THIS JOURNAL, **63**, 116, 916 (1941).

[10] Campbell and O'Connor, *ibid.*, **61**, 2897 (1939).

[11] Campbell and Eby, *ibid.*, **62**, 1798 (1940).

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RECEIVED AUGUST 6, 1945

N^1-Alkoxysulfanilamide Derivatives

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Among the large number of sulfanilamide derivatives reported, the greatest emphasis has been placed on N^1-substituted derivatives in which the substituent is an organic residue. Kharasch and Reinmuth[1] and Moore, Miller and Miller[2] have reported the preparation of N^1-hydroxysulfanilamide and the N^4-acylated derivatives. These compounds are relatively unstable[3] and it was thought desirable to prepare the more stable O alkyl ethers of sulfanilhydroxamide.

The acetyl derivatives of N^1-methoxysulfanilamide and N^1-benzyloxysulfanilamide were prepared from the corresponding hydroxylamine derivative and acetylsulfanilyl chloride. The hydrolysis of the acetyl derivatives was readily accomplished with aqueous hydrogen chloride.

The pK_a and pK_b of both compounds were determined potentiometrically. For N^1 methoxysulfanilamide pK_a is 4.27 and pK_b is 12.03. For N^1-benzyloxysulfanilamide pK_a is 3.86 and pK_b is 11.77. The bacteriostatic activity[4] lies generally between that of sulfanilamide and sulfathiazole, which is the approximate activity to be ex-

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[1] Kharasch and Reinmuth, U. S. Patent 2,097,415.

[2] Moore, Miller and Miller, THIS JOURNAL, **62**, 2097 (1940).

[3] Moore, Miller and Miller, ref. 2, have reported that N^4-hexanoylsulfanilhydroxamide hydrolyzed readily in cold aqueous alkali to give the corresponding sulfinic acid. See also Gilman "Organic Chemistry," Vol. 1, 1938, pp. 631, 632.

[4] The author is indebted to Dr. H. J. White of the American Cyanamid Laboratories, Stamford, Conn., for the bacteriological studies.