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The Dielectric Properties of Acetylenic Compounds. VII. Alkyl- and Arylpropiolnitriles. Resonance in the Acetylene Triple Bond

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The low moments of the halogenoacetylenes in comparison to those of the alkyl halides point to a probable resonance of the classical structures with the form $R—C^{-}=C=X^{+}$. Resonance of the $—C\equiv C—$ group could be established more definitely by the examination of a class of compounds wherein the effect would be to increase the moment. The acetylenic nitriles offer a good test for this resonance in that the two forms contributing to the molecule would be $R—C\equiv C—CN$ and $R—C^{+}=C=C=N^{-}$. That the comparison of the moments of acetylenic halides and nitriles is further opposite is evident from an analysis of the data of Table I. In these compounds the polarity of which is influenced only by induction, the increase in moments from the acids to the substituted butanes is seen to be roughly parallel. The inductomeric polarizabilities of the —CN and —Cl groups are thus very nearly the same.

TABLE I

ELECTRIC MOMENTS OF ALKYL CHLORIDES AND CYANIDES[1] $\times 10^{18}$

	Chlorides	$\Delta\mu$	Cyanides	$\Delta\mu$
Hydrogen	1.03	0.83	2.65	0.79
Methyl	1.86	0.18	3.44	0.13
Ethyl	2.04		3.57	
Propyl	2.04		3.57	
Butyl	2.04		3.57	

Preparation of Compounds.—The butyl-, amyl- and phenylpropiolnitriles were prepared by the reactions of the corresponding acetylene magnesium bromides with cyanogen chloride.[2] The *p*-tolyl propiolnitrile was prepared by the following method. *p*-Tolylaldehyde was converted into *p*-methyl ethyl cinnamate by the action of ethyl acetate in the presence of sodium.[3] The cinnamate was brominated in the cold, dehydrohalogenated with alcoholic potassium hydroxide, acidified with hydrochloric acid, and the resulting *p*-tolylpropiolic acid esterified with methyl alcohol. The ester was dissolved in excess alcoholic ammonium hydroxide and allowed to stand in a stoppered flask for one month. The alcohol was then removed by distillation, and the amide was first dried and then converted into the nitrile by the action of phosphorus pentoxide.[4] The phenyl- and *p*-tolylpropiolnitriles were purified by repeated crystallizations from petroleum ether in a bath of liquid ammonia, and dried for a few hours by a current of dry air before being placed in a desiccator over calcium chloride. The polarizations at infinite dilution were obtained by the method of Hedestrand.[5] The value of the electronic polarization of phenylpropiolnitrile was obtained from the literature, and from this the value for *p*-tolylpropiolnitrile was calculated.

TABLE II

PHYSICAL CONSTANTS OF $R—C\equiv C—CN$

R	°C.	n_{D25}	d^{25}_{4}
C_4H_9	B. p. 69.7–70.5 (25 mm.)	1.44673	0.84124
C_5H_{11}	B. p. 74–75 (12 mm.)	1.45021	.84325
C_6H_5	M. p. 38	....	....
p-$CH_3C_6H_4$	M. p. 52	....	....

TABLE III

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF ACETYLENIC NITRILES

Solvent, benzene; temp. 25°

c_2	ϵ	d
	Butylpropiolnitrile	
0.00000	2.2760	0.87340
.01763	2.7103	.87251
.02156	2.8070	.87200
.02224	2.8271	.87196
	Amylpropiolnitrile	
0.00000	2.2760	0.87340
.01994	2.7715	.87236
.02238	2.8301	.87231
.02384	2.8673	.87210
	Phenylpropiolnitrile	
0.00000	2.2760	0.87364
.01435	2.6928	.87671
.01463	2.7018	.87717
.01807	2.7968	.87730
	p-Tolylpropiolnitrile	
0.00000	2.2760	0.87364
.01697	2.8596	.87601
.02188	3.0205	.87747
.02259	3.0432	.87770

TABLE IV

POLARIZATIONS AND MOMENTS OF ACETYLENIC NITRILES

--Propiolnitrile	P_∞	MR_D	P_{A+M}	$10^{18}\mu$
Butyl	400.6	33.99	366.6	4.21
Amyl	406.8	38.61	368.2	4.22
Phenyl	462.1	42.39	419.7	4.50
p-Tolyl	543.4	47.01	496.4	4.90

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(1) Cowley and Partington, *J. Chem. Soc.*, 604 (1935).

(2) Grignard and Courtot, *Bull. soc. chim.*, **17**, 228 (1915).

(3) Marvel and King, "Organic Syntheses," **9**, 38 (1929).

(4) Moureu and Lazennec, *Bull soc. chim.*, **35**, 524 (1906).

(5) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

TABLE V

ELECTRIC MOMENTS OF CHLORIDES AND NITRILES

Compound	$10^{18}\,\mu$	Compound	$10^{18}\,\mu$
Chlorobutane	2.04	Valeronitrile	3.57
Chlorobenzene[6]	1.56	Benzonitrile[6]	3.91
Butylchloroacetylene[7]	1.23	Butylpropiolnitrile	4.21
Phenylchloroacetylene[8]	1.10	Phenylpropiolnitrile	4.50

Discussion

The large moments found for the acetylenic nitriles reveal the existence of resonance in these compounds as well as in the halogenoacetylenes. From Table V it can be seen that butylchloroacetylene has a lower moment than chlorobenzene, while butylpropiolnitrile has a higher moment than benzonitrile. These comparisons indicate that the forms $R—C^-{=}C{=}Cl^+$ and $R—C^+{=}C{=}C{=}N^-$ contribute to a greater extent to their respective molecules than do the forms $^-C_6H_5{=}Cl^+$ and $^+C_6H_5{=}C{=}N^-$. The electromeric polarizability of the acetylene triple bond is therefore greater than that of the phenyl group. A pronounced increase in moment is obtained by replacing a phenyl group for an alkyl group in the acetylenic nitriles despite the fact that the alkylacetylenes have higher moments than phenylacetylene. While this increase is due partly to the fact that the form $^+C_6H_5{=}C{=}C{=}C{=}N^-$ is more polar than $R—C^+{=}C{=}C{=}N^-$ it is also evidence of the strong resonance in phenylpropiolnitrile.

Summary

1. Electric moments have been determined for butyl-, amyl-, phenyl- and *p*-tolylpropiolnitriles.
2. The values obtained for these moments prove the existence of resonance in these molecules as well as in the alkyl and aryl halogenoacetylenes.
3. The electromeric polarizability of the acetylene triple bond is shown to be greater than that of the phenyl group.

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[6] Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, 1931, 203.

[7] Pflaum and Wenzke, THIS JOURNAL, **56**, 1106 (1934).

[8] Wilson and Wenzke, *ibid.*, **56**, 2024 (1934).

NOTES

Photosynthesis and the Absorption of Radiation by Plants

BY G. RICHARD BURNS

In the course of investigations on the amount of photosynthesis by white pine seedlings in different portions of the spectrum, a rather interesting correlation was found between the amount of photosynthesis and the color of the plant.

In an attempt to arrive at some value for the radiation absorbed by the plant the reflection of the plant was assumed to be the reflection of the needles to light of 45° incidence and the absorption, the absorption of the plant pigments in acetone solution with the concentration the same as in the plant. The absorption spectrum obtained from these two values might be called the "primary absorption spectrum" of the plant, defining the difference between this and the true absorption as the "secondary absorption." The values for the secondary absorption would be high where the primary is low due to reflection within the needle. Also the absorption of the pigments is shifted toward the blue when in solution. In determining the absorption and reflection values, each spectrometer reading covered a wide band of wave lengths and the front slit was 0.75 mm. wide so that the spectrum was rather blurred.

Graph I gives the percentage primary absorption for two types of seedlings, B for those grown in blue light and R for those grown in red. The stepwise curves indicate, approximately, the range of wave lengths covered at each reading. Assuming constant quantum efficiency and that only light thus primarily absorbed is effective in photosynthesis it is possible to cal-