ORGANIC SECTION

Dipole Moments and Molar Refractions of Some Substituted Cinnamonitriles

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The dipole moments and molar refractions are reported for the *p*-fluoro (2.88 D, 43.3 ml.), *p*-chloro (2.73 D, 49.1 ml.), *p*-bromo (2.80 D, 52.0 ml.), *p*-iodo (3.00 D, 54.5 ml.), and *p*-cyano (1.01 D, 52.2 ml.) derivatives of *trans*-cinnamonitrile.

A PREVIOUS PAPER (*3*) reported the dipole moments and molar refractions of the *p*-halo- and *p*-cyano-substituted β-nitrostyrenes. We now report these properties for the analogous cinnamonitriles.

In both the β-nitro and β-cyano series the magnitude of the dipole moments of the *p*-halo derivatives varies with the *p*-substituent and follows the order of I > F > Br > Cl. The moment of each of the *p*-halocinnamonitriles is approximately 0.2 D less than for the corresponding *p*-halo-β-nitrostyrene.

A comparison of the observed dipole moments with values calculated from group moments indicates that the substituted phenyl group and the β-cyano group are trans to each other.

The rather large dipole moment obtained for *p*-cyanocinnamonitrile is consistent with dipole moments reported for similar compounds with two powerful electron-withdrawing groups opposing each other (*1, 2, 3*).

EXPERIMENTAL

Compounds. The substituted cinnamonitriles were prepared by a method described by Dolter *et al.* (*2*) for the preparation of substituted cinnamonitrile.

Dipole Moments. The dipole moments were measured and calculated by the method described by Dolter *et al.* (*2*). Standard deviations of the slopes and intercepts σ_{x_i} were calculated for the lines fitted by the method of least squares to the dielectric constant–weight fraction, density–weight fraction, and index of refraction–weight fraction data. These were used to calculate the standard

Table I. Melting Points, Formulas, and Analyses of Compounds

Compound	M.P., ° C.	Formula	Analysis			
			Calculated		Found	
			%C	%H	%C	%H
p-Fluorocinnamonitrile	69–69.5	C_9H_6FN	73.46	4.11	73.29	4.23
p-Chlorocinnamonitrile	87	C_9H_6ClN	66.07	3.70	66.02	3.88
p-Bromocinnamonitrile	106.5–7	C_9H_6BrN	51.92	2.91	52.03	2.75
p-Iodocinnamonitrile	130–130.5	C_9H_6IN	42.38	2.37	42.49	2.39
p-Cyanocinnamonitrile	228–9	$C_{10}H_6N_2$	77.91	3.92	77.82	4.10

Table II. Slope-Intercept Data for Dilute Solutions of Substituted Cinnamonitriles in Benzene at 25° C.

$p\text{-}XC_6H_5CH=C(CN)H$

X	ϵ_1	α	d_1	β	n_1	γ
F	2.2737	6.33	0.8735	0.218	1.4981	0.074
Cl	2.2748	5.25	0.8727	0.249	1.4976	0.106
Br	2.2728	4.34	0.8757	0.371	1.4982	0.100
I	2.2724	4.20	0.8716	0.504	1.4978	0.126
CN	2.2687	1.051	0.8723	0.152	1.4968	0.114

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Table III. Observed Molar Polarizations, Molar Refractions, and Dipole Moments for Substituted Cinnamonitriles

X	$_\infty P_2$	R_D	μ	σ_μ
F	212.9	43.3	2.88	0.01
Cl	201.4	49.1	2.73	0.08
Br	210.4	52.0	2.80	0.02
I	238.6	54.5	3.00	0.04
CN	73.9	52.2	1.01	. . .

deviation of the dipole moment, σ_μ, according to the expression

$$\sigma_\mu = \left[\sum_i \left(\frac{\partial\mu}{\partial x_i}\right)^2 \sigma^2 x_i\right]^{\frac{1}{2}}$$

where μ is the dipole moment and x_i is the ith slope (or intercept).

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RECEIVED for review October 14, 1968. Accepted August 8, 1969. Work was supported by the National Science Foundation Undergraduate Research Participation Program.

Diesters from Trialkylacetic Acids and Glycols

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Diesters from trialkylacetic acids and the following glycols were prepared: straight-chain α,ω-glycols, β,β-disubstituted propanediols, lower molecular weight polyethylene glycols, and 2,2,3,3,4,4-hexafluoropentanediol. Viscosities at 212°, 100°, and −40° F., ASTM viscosity slopes, and pour points were determined and compared.

TRIALKYLACETIC ("neo") acids have recently become commercially available, and their structures have been described (*6*). Their esterification requires more rigorous conditions than those employed for conventional acids. The esters are much more resistant toward both acid and base hydrolysis than conventional esters (*1*), and the preparation and physical properties of several types of monoesters have been described (*3*). The synthesis of diesters from straight-chain α,ω-glycols, β,β-disubstituted propanediols, polyethylene glycols, and 2,2,3,3,4,4-hexafluoropentanediol is reported here. Viscosities, ASTM viscosity slopes between 212° and 100° F., and pour points were determined and compared.

EXPERIMENTAL

Starting materials were used as received. In general, the method of Coopersmith *et al.* (*1*) was used for the esterifications. Products of Type III and IV could be prepared by using toluene in place of xylene as azeotroping agent. Instead of *p*-tolenesulfonic acid, products of Type III were prepared with sulfuric acid catalyst. When this was the case, the catalyst was neutralized with an excess of solid calcium hydroxide, followed by filtration. This avoided contact with aqueous bases, which might have resulted in losses due to water solubility.

Products of Type II were especially difficult to prepare. Water formation usually stopped before the theoretical amount had azeotroped. When this occurred, the reaction mixture was cooled, additional catalyst was added, and azeotroping was resumed. If necessary, this procedure was repeated until the theoretical amount of water was obtained. Most products were obtained in analytical purity by vacuum distillation through a vacuum-jacketed Vigreux column, 5.5 inches long. Products of Type III were usually slightly yellow after one distillation and were redistilled. Most yields could be improved.

Physical properties were determined by ASTM methods: kinetic viscosity by method D 445-65, ASTM slope between 212° and 100° F. by method D 341-43, and pour point by method D 97-57. Only one cooling bath, dry ice–acetone, was used for the pour points. The approximate densities of Table IV were determined by weighing 10 ml. of the product in a graduated cylinder at room temperature.

DISCUSSION

Diesters from Straight-Chain α,ω-Glycols (I, Table I). The first six products contained identical acyl groups ($R_1 = R_2$). At constant $R_1 = R_2$, increasing the glycol chain length from $x = 4$ to $x = 8$ increased the viscosities, but gave lower ASTM slopes (runs 1 to 4). Increasing the glycol chain length from $x = 4$ to $x = 10$, while simultaneously decreasing the acid chain length, gave lower viscosities at −40° F. and lower ASTM