Dipole Moments and Configurations of Triaryl Acrilonitriles

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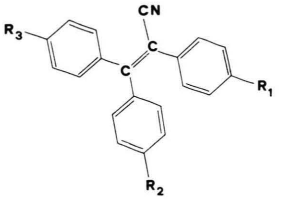
The electric dipole moments of *trans*-1,2 diaryl acrilonitrile **1** and of a series of triaryl acrilonitriles **2–14** were measured in benzene solution at 25 °C. A mesomeric moment of 0.4 D was found to act between the phenyl- and the nitrile groups through the vinylic bond in triaryl acrilonitrile **2**. For this molecule the direction of action of the total molecular moment was calculated and used to evaluate theoretical moments for the possible **E** and **Z** configurations of some unsymmetrical derivative compounds of the series. The configuration was settled for each compound on the basis of comparison between experimental and calculated dipole moment values.

Introduction

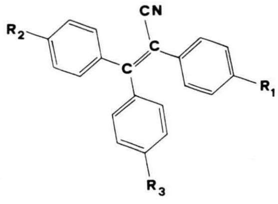
Triaryl acrilonitriles are a widely known class of compounds, from a synthetic point of view, due to the estrogenic potency of several derivatives [1], that also have chemotherapeutic effects on gland tissues [2] as well as on malignant tumor cells [3]. Their synthesis is in general accomplished *via* condensation of diaryl ketones with sodio derivatives of arylacetonitriles in anhydrous ether [4]. When unsymmetrical diaryl ketones are used, two stereo-isomeric nitriles can be produced: at present configurational assignments for the unsymmetrical derivatives described in literature are still lacking.

In the present note we wish to report, together with dipole moment measurements for the triaryl acrilonitriles, the application of this technique to the first configuration assignments for some unsymmetrical derivatives prepared by using the described synthetic procedure [4]. To this end, the compound **2–14**, having the general formula schematized below, have thus been prepared and their dipole moments measured (in benzene solution) and analyzed, for compounds **8–14**, in terms of **E** and **Z** configurations.

For purposes of comparison in this study, the *trans*-1,2-diaryl acrilonitrile **1** (m.p. 88 °) was prepared [5] and its dipole moment measured.



E



Z

2 $R_1 = R_2 = R_3 = H$ (m.p. 167 °);
3 $R_1 = Cl, R_2 = R_3 = H$ (m.p. 150 °);
4 $R_1 = H, R_2 = R_3 = Cl$ (m.p. 156 °);
5 $R_1 = H, R_2 = R_3 = CH_3$ (m.p. 178 °C);
6 $R_1 = Cl, R_2 = R_3 = Br$ (m.p. 206 °);
7 $R_1 = Cl, R_2 = R_3 = CH_3$ (m.p. 153 °);
8 $R_1 = R_3 = H, R_2 = Cl$ (m.p. 144 °);
9 $R_1 = R_3 = H, R_2 = Br$ (m.p. 177 °);
10 $R_1 = R_3 = H, R_2 = CH_3$ (m.p. 122 °);
11 $R_1 = R_2 = Cl, R_3 = H$ (m.p. 161 °);
12 $R_1 = Cl, R_2 = Br, R_3 = H$ (m.p. 182 °);
13 $R_1 = CH_3, R_2 = Br, R_3 = H$ (m.p. 174 °);
14 $R_1 = CH_3, R_2 = CH_3, R_3 = H$ (m.p. 150 °).

Experimental

The samples of *trans*-1,2-diarylacrilonitrile **1** and triaryl acrilonitriles **2–14** were prepared according to literature methods [4, 5].

The data required for the calculation of the electric dipole moments by the Halverstadt-Kumler method [6], were determined in benzene solution at 25 ° ± 0.01 °, using methods described in detail elsewhere [7]. The polarization data and experimental μ values (μ_{exp}, in Debye units) are collected in Table 1, where all symbols have the meaning as in ref. 7. The accuracy of the μ data is ± 0.01 D.

Results and Discussion

The data obtained for molecules **1** and **2** indicate that the total moment of **2** is enhanced by about 0.4 D with respect to that of **1**, due to the additional (apolar) phenyl group. This may be considered as corresponding to the mesomeric moment arising from the interaction between the phenyl ring and the C≡N group in *trans* position to each other with respect to the vinylic double bond.

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Table 1. Polarization Data for and Dipole Moments of *trans*-1,2-Diarylacrylonitrile (**1**) and Triaryl Acrylonitriles (**2**–**14**) Determined in Benzene Solution at 25°. Experimental (μ_{exp}) and calculated (μ_{calcd}) Dipole Moments for **E** and **Z** Configurations of **8**–**14**.

Compound	α	β	$P_{2\infty}/cm^3$	R_D/cm^3	μ_{exp}/D	μ_{calcd}/D	
						E	**Z**
1	7.36	– 0.283	336.20	69.5	3.61		
2	6.70	– 0.280	426.20	96.0	4.01		
3	6.20	– 0.475	430.49	100.8	4.01		
4	4.07	– 0.400	345.38	104.4	3.43		
5	7.33	– 0.120	513.64	104.4	4.47		
6	2.25	– 0.803	244.46	115.2	2.51		
7	6.91	– 0.270	529.53	109.5	4.53		
8	4.29	– 0.817	285.48	100.9	3.00	2.60	4.60
9	7.06	– 0.228	568.04	105.5	4.75	2.43	4.59
10	6.17	– 0.413	405.39	101.0	3.86	4.38	4.10
11	5.79	– 0.553	442.79	108.4	4.04	4.01	4.58
12	5.81	– 0.220	539.41	102.8	4.62	2.62	4.01
13	8.58	– 0.104	719.42	111.2	5.45	2.53	4.79
14	6.83	– 0.526	428.04	105.8	3.97	4.32	4.01

To determine the direction of the action of the dipole moment of **2**, its μ_{exp} value was compared to that of the chloro-substituted derivative **3**. By classical vector subtraction, the conclusion was drawn that the former lies at an angle of 41.3° to the axis of the C–C double bond, i.e., at 14.8° to the C≡N axis. All the calculations were accomplished by assuming bond angles as those given by microwave studies for vinyl cyanide [8] and substituent group moments from literature data [9].

Theoretical dipole moments (μ_{calcd}) for **E** and **Z** configurations of the unsymmetrical compounds **8**–**14** were thus calculated by simple vector addition of μ_{exp} of **2** and the pertinent group moment of the substituent moieties.

The results of the calculations (Table 1) show that the two configurations of **8**, **9**, **12**, **13** can be unambigously distinguished and assigned by their dipole moments as **E**, **Z**, **Z**, **Z**, respectively. Some differences, from 0.4 to 0.6 D, between μ_{exp} and μ_{calcd} for the assigned configurations may be attributed to enhanced (by conjugative interaction) polarization of the substituent-CN group bond, combined with the inherent inaccuracy of the method (assumed as ranging from 0.2 to 0.4 D).

Although the small differences between the μ_{calcd} values for the **E** and **Z** configurations of **10**, **11**, **14** do not constitute too strong an evidence, stereochemical assignment may be made in favor of the form **E** for **11**, due to the analogy with **8**, as well as to the better agreement of μ_{exp} with μ_{calcd} for this configuraton, where the R_1 and R_2 substituents may cancel and the total moment is expected to be equal to that of the unsubstituted molecule **2**. On this basis, in fact, μ_{calcd} for **11** in the **E** configuration seems indeed in better agreement with μ_{exp}. The configurations of **10** and **14** are still questionable, although it may be inferred to be **Z** for both molecules, as suggested by the better agreement of μ_{exp} with μ_{calcd} for the **Z** configurations.

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