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Abstract

Full Text

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Dipole Moments and the Structure of Some Fluorine-Substituted Styrenes

If the routes for the synthesis of fluorostyrenes substituted in the side chain have been studied fairly well, the question of the configuration of these compounds still remains open. We investigated the structure of a series of fluorine-substituted styrenes by the method of dipole moments.

The dipole moments were measured by us in benzene at 25° by the beat method. The results of the measurements are given in Table 1, where the following notation is used: P_∞ is the polarization at infinite dilution, P_E is the electronic polarization, taken to be equal to the molecular refraction; μ is the dipole moment in debyes, calculated by the formula

$$\mu = 0.22\sqrt{P_\infty - P_E}.$$

All the compounds studied were synthesized by us according to procedures described in the literature. All substances were carefully purified by repeated distillation to a constant refractive index n_D^{20}.

Table 2 gives the constants of the substances and references to the literature. Some compounds were synthesized by analogy. In all cases a complete organic analysis of the substance was carried out.

It is known that molecules with conjugated bonds tend to be planar, since only in this case is the mutual—

Table 1

No.	Compound	Structural formula	P_∞	P_E	$\mu \cdot 10^{-18}$
1	1,1-Difluoroethylene	$CH_2{=}CF_2$	–	–	1.96*
2	1,1,2-Trifluorohexene-1	$C_4H_9CF{=}CF_2$	97.81	29.4	1.82

No.	Compound	Structural formula	P_∞	P_E	$\mu \cdot 10^{-18}$
3	1,1,2-Trifluorooctene-1	$C_6H_{13}CF{=}CF_2$	118.59	38.6	1.97
4	1,1,2-Trifluorodecene-1	$C_8H_{17}CF{=}CF_2$	122.82	47.9	1.90
5	β-Fluorostyrene	$C_6H_5{-}CH{=}CHF$	73.16	34.9	1.36
6	β-Chlorostyrene	$C_6H_5{-}CH{=}CHCl$	–	–	1.4*
7	β-Bromostyrene	$C_6H_5{-}CH{=}CHBr$	91.13	41.0	1.56
8	ω-Fluoro-α-vinylnaphthalene	α-naphthyl-CH=CHF	88.68	50.3	1.36
9	α,β-Difluorostyrene	$C_6H_5{-}CF{=}CHF$	148.13	34.9	2.36
10	α,β,β-Trifluorostyrene	$C_6H_5{-}CF{=}CF_2$	115.60	34.7	1.98
11	p-Methyl-α,β,β-trifluorostyrene	p-$CH_3C_6H_4{-}CF{=}CF_2$	149.25	39.3	2.31
12	o-Methyl-α,β,β-trifluorostyrene	o-$CH_3C_6H_4{-}CF{=}CF_2$	118.29	39.3	1.95
13	α,β-Difluoro-β-chlorostyrene	$C_6H_5{-}CF{=}CFCl$	126.89	39.6	2.05
14	p-Methyl-α,β-difluoro-β-chlorostyrene	p-$CH_3C_6H_4{-}CF{=}CFCl$	190.32	47.2	2.63
15	β,β-Dichlorostyrene	$C_6H_5{-}CH{=}CCl_2$	118.53	36.0	2.0

* Literature data.

Table 2

No.	Compound	Structural formula	B.p., °C	n_D^{20}	Literature data
1	1,1,2-Trifluorohexene-1	$C_4H_9CF{=}CF_2$	70	1.3481	(3)
2	1,1,2-Trifluorooctene-1	$C_6H_{13}CF{=}CF_2$	120	1.3751	(3)
3	1,1,2-Trifluorodecene-1	$C_8H_{17}CF{=}CF_2$	91 (90 mm)	1.3928	(3)
4	β-Fluorostyrene	$C_6H_5{-}CH{=}CHF$	75–76.5 (50 mm)	1.5257	(4)
5	α, β-Difluorostyrene	$C_6H_5{-}CF{=}CHF$	88–90 (60 mm)	1.5060	(4)
6	ω-Fluoro-α-vinylnaphthalene	naphthyl-CH=CHF	molecular distillation	1.5901	(5)
7	α, β, β-Trifluorostyrene	$C_6H_5{-}CF{=}CF_2$	62–63 (75 mm)	1.4760	(6)
8	*p*-Methyl-α, β, β-trifluorostyrene	*p*-$CH_3C_6H_4{-}CF{=}CF_2$	91.5 (70 mm)	1.4810	(6)
9	*o*-Methyl-α, β, β-trifluorostyrene	*o*-$CH_3C_6H_4{-}CF{=}CF_2$	79 (75 mm)	1.4688	(6)
10	α, β-Difluoro-β-chlorostyrene	$C_6H_5{-}CF{=}CFCl$	71 (20 mm)	1.5220	(7)
11	*p*-Methyl-α, β-difluoro-β-chlorostyrene	*p*-$CH_3C_6H_4{-}CF{=}CFCl$	71 (7 mm)	1.5190	(7)
12	β-Bromostyrene	$C_6H_5{-}CH{=}CHBr$	109	1.6094	(8)
13	β, β-Dichlorostyrene	$C_6H_5{-}CH{=}CCl_2$	96 (10 mm)	1.5899	(9)

effect of π-electrons. The molecule of monosubstituted β-fluorostyrene has a trans structure and is, apparently, planar. The trans structure of β-monohalogen-substituted styrenes, including β-fluorostyrene, was proved by Bergmann (1). The dipole moment of β-fluorostyrene had not previously been measured. The value obtained by us, 1.36 D, is in agreement with the dipole moments of β-halogen-substituted styrenes, for which the trans structure has also been proved.

C_6H_5-F $\mu = 1.45\,D$	$C_6H_5-CH=CHF$ $\mu = 1.36\,D$
C_6H_5-Cl $\mu = 1.70\,D$	$C_6H_5-CH=CHCl$ $\mu = 1.40\,D$
C_6H_5-Br $\mu = 1.71\,D$	$C_6H_5-CH=CHBr$ $\mu = 1.54\,D$

For styrenes with two halogen atoms in the β position, a planar arrangement of the molecule is impossible. If one considers the geometry of α, β, β-trifluorostyrene, then, as is evident from the scale drawing in Fig. 1, the cis-β fluorine atom and the ortho hydrogen atom of the phenyl ring (with the following structural parameters: length of the C=C bond 1.31 Å, C−F −1.32 Å, ∠FCF−125°, ∠CCF−124°) do not fit in one plane. With these structural parameters the distance between the centers of the hydrogen and fluorine atoms is 1.6 Å, whereas the sum of their van der Waals radii is 2.45 Å. Good confirmation of these geometrical calculations is provided by the dipole moments of these compounds given in Table 1.

For the molecule of α, β, β-trifluorostyrene, as a result of compensation of two C−F bonds, one might have expected a moment close to that of trans-β-fluorostyrene. As follows from Table 1, the dipole moment of this compound (1.98 D) differs considerably from the moment of trans-β-fluorostyrene (1.36 D). The dipole moment of α, β-difluorostyrene (2.36 D) indicates an asymmetric,

less favorable for the molecule, arrangement of the fluorine atoms. In the case of a symmetrical arrangement of the fluorine atoms in the molecule of α, β-difluorostyrene, the dipole moment should be close to the moment of styrene. Apparently, the steric hindrances created by the ortho hydrogen atom prevent the β fluorine atoms from occupying the cis position. For still greater certainty as to the correctness of our propositions concerning the noncoplanarity of α, β, β-trifluorostyrenes, we synthesized ortho-methyl-α, β, β-trifluorostyrene. As is known, the methyl group, with its van der Waals radius of ~ 2 Å, creates large steric hindrances for arrangement in one plane of the methyl group and the double bond. According to Suzuki' s data (2), the interplanar angle in ortho-methylstyrene is $\sim 31°$. The moments of α, β, β-trifluorostyrene and ortho-methyl-α, β, β-trifluorostyrene are the same (1.98 and 1.95), which indicates the presence of rotation already in the molecule of α, β, β-trifluorostyrene itself.

Fig. 1

The nonplanar, noncoplanar structure of α, β, β-trisubstituted fluorostyrenes is also confirmed by comparison of the dipole moments of trifluoroolefins and

Fig. 1

Figure 1: Fig. 1

α, β, β-trifluorostyrenes. The dipole moments of the four fluoroolefins (Nos. 1–4) given in Table 1 coincide with the dipole moments of α, β, β-trifluorostyrenes (Nos. 10, 11, 12), which is possible only on condition that in the latter there is no interaction of the olefinic grouping with the benzene ring.

The data we have obtained on the nonplanar structure of β, β-disubstituted fluorostyrenes may be extended to other styrenes with substituents in the β positions. It may be assumed that in β, β-disubstituted styrenes the benzene ring and the ethylenic grouping will not lie in one plane in the case where the van der Waals radius of the substituent group or atom in the cis-β position is greater than 1.35 Å, i.e., greater than the van der Waals radius of the fluorine atom.

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Note: Figure translations are in progress. See original paper for figures.