DIPOLE MOMENTS AND CONFORMATIONS OF 2-(4-PYRIDYL)ETHYL ALKYL(ARYL) SULFIDES

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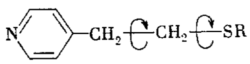
Determination of the spatial structures of compounds containing two geminal axes of internal rotation is an interesting problem in conformational analysis. In principle, the dipole moment method (DM) can be used here, provided the substituents in the nonregular groups of the molecule are polar and thus variously oriented with respect to one another in the different conformations. Cases do arise, however, in which the relative dipole orientations are the same in different conformations, and a correct choice of conformations cannot be made [1, 2]. Good results have been obtained by following the Exner method [5], varying the aryl substituents in the nonregular groups [3] or molecular skelton [4]. The available data on the structures of molecules containing several nonregular groups attached to a single atom are largely limited to the case of compounds with identical geminal groupings [2-4, 6-8].

It seemed of interest to study rotation in molecules with two different geminal bonds, more specifically, cases in which rotation can be realized in different ways. Moreover, it is necessary to decide what information concerning molecular structures can be obtained by varying the polarity of one of the nonregular substituents.

We have therefore studied the conformations of 2-(2-pyridyl)ethyl propyl sulfide (I) and various 2-(4-pyridyl)ethyl aryl sulfides (II)-(V)



R = C_3H_7 (I), C_6H_5 (II), $C_6H_4CH_3$-*p* (III), C_6H_4Br-*n* (IV); C_6H_4F-*p* (V)

These compounds were prepared by the addition of propyl mercaptans and thiophenols to 4-vinylpyridine. The additions of mercaptans and certain thiophenols to 2-vinylpyridine have been described in [9, 10], and the addition to dialkylphosphoric acids to 4-vinylpyridine in [9]; in each case the product obtained is a β-addition compound.

The NMR spectra of compounds (I)-(V) also indicated addition in apparent violation of the Markovnikov rule. These spectra contained signals for the CH_2 group protons, but not for the extremal CH_3 groups. Dipole moments were determined for compounds (I)-(V), and the values obtained then used to calculate, by an additive scheme, DM's for conformers resulting from rotation around the C−C and C−S bonds. There are five possible spatial structures (at least, if the optical isomers are left out of account for the compounds in question), these differing in the trans and gauche orientations of the S−Ar group with respect to the C−C bond, and the C−Py group with respect to the C−S bond (Fig. 1). In our abbreviated symbolism, the first letter designates the aryl group orientation and the second the pyridyl group orientation.

The DM calculations were based on the group moment m(CH_2−S) = 1.12 D (calculated from the experimentally determined DM for dimethyl sulfide [11]) and the C−S−C valence angle, the latter equal to 99° according to [12]. Group moments, m (p-XC_6H_4−S), for various X were calculated from data on the thioanisoles [11].

X = H 0.98 D; X = CH_3 1.41 D; X = Br−1.16 D; X = F−0.93 D. The C_3H_7−S group moment (1.23 D) was obtained from the experimentally determined DM for dipropyl sulfide [11], while the CH_2−Py group moment was assumed equal to the experimentally determined DM for 4-picoline [11]. Experimental and calculated DM's for various conformations of compounds (I)-(V) are shown in Table 1.

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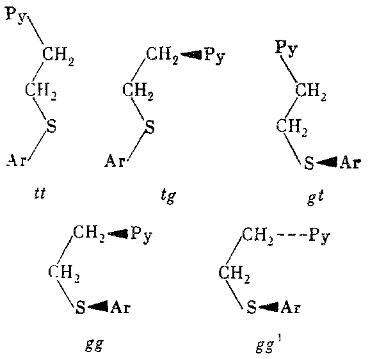

Fig. 1. Possible orientations of the C−Py and S−Ar groups 2-(4-pyridyl)ethyl alkyl(aryl) sulfides.

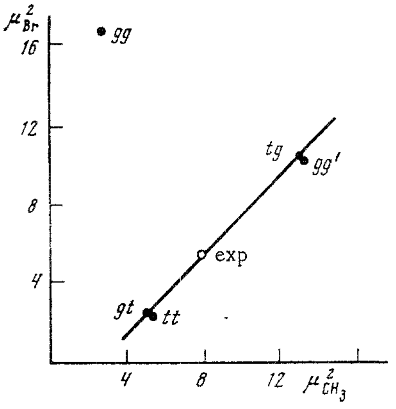

Fig. 2

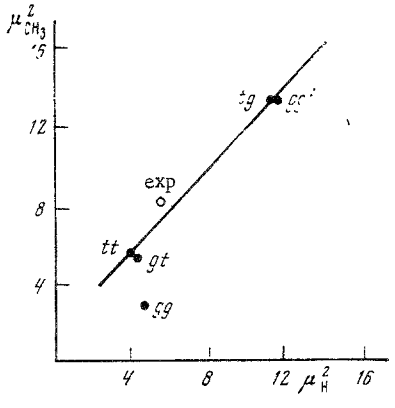

Fig. 3

Fig. 2. Comparison of the second-power experimental and calculated DM for (III) and (IV).

Fig. 3. Comparison of the DM for (II) and (III).

TABLE 1. Experimental and Calculated Dipole Moments for the 2-(4-Pyridyl)ethyl Alkyl(aryl) Sulfides

Compound	μ_{calc}, D					μ_{exp}, D
	tt	*tg*	*gt*	*gg*	*gg'*	
(I)	2.20	3.52	2,19	2.01	3,54	2,69
(II)	2.01	3,41	2,02	2.23	3,43	2,37
(III)	2.37	3,63	2,35	1,83	3,65	2,87
(IV)	1,51	3,17	1,52	4,24	3,15	2,29
(V)	1,43	3,12	1,44	4,01	3,11	2,78

The data of Table 1 can be worked up in various combinations, following the method of [5], but the best results are undoubtedly obtained by choosing pairs in which the p substituents DM's are oppositely directed [comparison of (II) or (III) with (IV) or (V)]. Each of the plots had the same general form. Figure 2, for example compares second-power experimental and calculated DM's for 2-(4-pyridyl)ethyl p-tolyl sulfide (III) and 2-(4-pyridyl)ethyl p-bromophenyl sulfide (IV). It is interesting to note (Fig. 3) that even the slight change in polarity which accompanies passage from the $CH_3-C_{sp^2}$ bond of compound (III) to the $H-C_{sp^2}$ bond of compound (II) makes it possible to construct a graph from which the same conclusions concerning the conformation can be read. It is seen from Figs. 1 and 2 that the gg conformation is not involved in the equilibrium state, a conclusion consistent with the predictions of the 1,3-parallel-interaction rule. The table also shows that the tt and gt, and the tg and gg', forms coincided in every case. These conformations are characterized by identical orientations of the pyridyl end of the molecule, and by the fact that the polarity is independent of rotation around the C−S bond. Thus definite conclusions can be drawn concerning the conformations resulting from rotation around the C−C bond. For the four compounds (II)-(V) which have been treated graphically, the form with the C−Py group trans oriented with respect to the C−S bond makes up 0.6-0.7 of the whole; for compound (I), $n_t \cong 0.7$.

Thus we have determined the conformation of that end of the molecule whose polarity remains constant. Further study will be needed in order to decide whether or not this is a special instance of a general rule.

EXPERIMENTAL*

2-(4-Pyridyl)ethyl Akyl(aryl) Sulfides. A quantity (0.023 mole) of 4-vinylpyridine was cooled and then added dropwise to 0.02 mole of propyl mercaptan or the corresponding thiophenol. The reaction product was separated by vacuum distillation. 2-(4-Pyridyl)ethyl propyl sulfide (I): bp 97-98°C (10 mm), n_D^{25} 1.5392, d_4^{25} 1.0266. Found: C 66.71; H 8.90%. $C_{10}H_{15}NS$. Calculated: C 66.60; H 9.20%.

2-(4-Pyridyl)ethyl phenyl sulfide (II): bp 139°C (10 mm), n_D^{25} 1.6080, d_4^{25} 1.1234. Found: C 73.09; H 6.43%. $C_{13}H_{13}NS$. Calculated: C 72.56; H 6.05%.

2-(4-Pyridyl)ethyl p-tolyl sulfide (III): bp 135-136°C (10 mm); n_D^{25} 1.6022; d_4^{25} 1.1214. Found: C 73.27; H 6.61%. $C_{14}H_{15}NS$. Calculated: C 73.27; H 6.65%.

2-(4-Pyridyl)ethyl p-bromophenyl sulfide (IV): bp 165-166°C (10 mm); n_D^{25} 1.6299, d_4^{25} 1.4294. Found: C 52.94; H 4.28; S 9.94%. $C_{13}H_{12}NSBr$. Calculated: C 53.06; H 4.08; S 10.88%.

2-(4-Pyridyl)ethyl p-fluorophenyl sulfide (V): bp 138-140°C (10 mm); n_D^{25} 1.5869; d_4^{25} 1.2108. Found: C 66.05; H 5.82; S 13.02%. $C_{13}H_{12}NSF$. Calculated: C 66.95; H 5.15; S 13.73%.

The identity of these compounds was checked by chromatography.

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CONCLUSIONS

Study of the 2-(4-pyridyl)ethyl akyl sulfides has shown that these compounds exist as equilibrated mixtures of structures with trans- and gauche-oriented C−Py and C−S fragments, the content of the first making up 0.6-0.7 fraction of the whole.

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*N. G. Abdullina participated in this part of the work.