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HINDERED ROTATION OF UNSUBSTITUTED AMINO GROUPS OF FLUORINATED

β -AMINOVINYL THIONES

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Previously we had shown [1, 2] that a hindered rotation of the unsubstituted amino group around the N-C= bond is characteristic for fluorinated β -aminovinyl ketones (β -AVK) with a gem arrangement of the R_F and NH_2 groups. For unfluorinated β -AVK and β -aminovinyl thiones (β -AVT) a similar rotation was studied only in the case of the N,N-disubstituted compounds [3-5].

In the present paper the NMR method was used to study the structure and determine the barriers of hindered rotation of the unsubstituted amino group around the N-C= bond in fluorinated β -AVT (I)-(IV) (Table 1).

EXPERIMENTAL

The PMR spectra were recorded on a Varian HD-100D/15 spectrometer (100 MHz) for (I)-(III) and a JEOL JNM FX-100 spectrometer (100 MHz) for (IV). The compounds were studied as 5% solutions in perfluorotoluene in the temperature range from -40° to $100^\circ C$. The accuracy of the thermostating was $\pm 0.5^\circ C$. The $\Delta G^\ddagger_{\text{expt}}$ values were calculated using the equation: $\Delta G^\ddagger_{\text{expt}} = 4.57 (10.32 + \log T/K) T$ [6], and the function $\Delta G^\ddagger_{\text{expt}} = f(T)$ was estimated using the method of least squares. The K values were calculated as an approximation of slow exchange. In calculating the activation parameters the quadrupole broadening as a function of the temperature was neglected. The IR spectra as a function of the concentration were obtained on a UR-20 spectrophotometer for 5, 1, and 0.2% solutions of the β -AVT in CCl_4 .

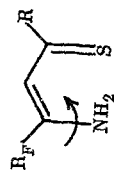
1-Phenyl-4,4,4-trifluoro-3-amino-2-buten-1-thione (I). To a stirred solution of 4.1 g (10 mmoles) of 2,4-bis(4-methoxyphenyl)-2,4-dithio-PV, PV-1,3,2,4-dithiophosphetane (V) in 100 ml of refluxing xylene was added 4 g (18 mmoles) of 1-phenyl-4,4,4-trifluoro-3-amino-2-buten-1-one. The heating was stopped after 2-5 min (TLC control). The solvent was distilled off. The residue was chromatographed on a silica gel column, using a 1:2 $CHCl_3$ -n- C_6H_{14} mixture for elution. The solvent was distilled off and the residue was recrystallized from n- C_6H_{14} to give 2.45 g (57% yield) of (I) as red crystals, mp $92^\circ C$. Found: C 50.00; H 3.34; F 24.10; N 6.00; S 14.10%. $C_{10}H_8F_3NS$. Calculated: C 50.64; H 3.50; F 24.64; N 6.06; S 13.86%.

1-Phenyl-4,4,5,5-tetrafluoro-3-amino-2-pentene-1-thione (II) and 1-Phenyl-4,4,5,5,6,6,6-heptafluoro-3-amino-2-hexen-1-thione (III) were obtained similarly. Yield of (II) 38%, mp $90^\circ C$. Found: C 50.36; H 3.18; F 28.54; N 5.51; S 12.18%. $C_{11}H_9F_4NS$. Calculated: C 50.19; H 3.45; F 28.87; N 5.32; S 12.19%. Yield of (III) 36%, mp $51^\circ C$. Found: C 43.46; H 2.25; F 40.77; N 4.50; S 9.69%. $C_{12}H_8F_7NS$. Calculated: C 43.51; H 2.43; F 40.15; N 4.23; S 9.68%.

1,1,1,5,5,5-Hexafluoro-2-amino-2-pentene-4-thione (IV). To a stirred solution of 1.46 g (3.62 mmoles) of (V) in 4 ml of refluxing anhydrous xylene was added 2.5 g (7.25 mmoles) of

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TABLE 1. Spectral Characteristics and Activation Parameters of Hindered Rotation of Amino Group in β -Aminovinyl Thiones



Compound	R _F	R	PMR, δ , ppm				T _m °C	ΔH^\ddagger , kcal/mole	ΔS^\ddagger , entropy units	ΔG^\ddagger , kcal/mole
			N-H...S	N-H	NH ₂	=CH-				
(I)	CF ₃	Ph	12.5 a	6.0 a	9.2 b	6.79	35	41.3	-1.1	14.7
(II)	HCF ₂ CF ₂	Ph	12.8 a	6.1	9.4 b	6.85	40	9.8	-1.8	15.2
(III)	C ₆ F ₇	Ph	12.7 a	6.4	9.4 b	6.75	35	13.9	-0.8	14.6
(IV)	CF ₃	CF ₃	12.65 c	7.27 c	9.5 d	6.93	85	6.9	-2.9	17.5

a 10°, b 50°, c 25°, d 100°.

1,1,1,5,5,5-hexafluoro-2-amino-2-penten-4-one. The heating was stopped after 10-15 min. The reaction mixture was chromatographed on a silica gel column and eluted with CHCl_3 . The solvent was distilled off. The yield of (IV) was 0.8 g (56%) (dark red oily liquid). Found: C 26.88; H 1.54; N 6.08; S 14.50%. $\text{C}_5\text{H}_3\text{F}_6\text{NS}$. Calculated: C 26.91; H 1.36; N 6.28; S 14.37%.

DISCUSSION OF RESULTS

The signals of the protons of the amino group are not observed in the PMR spectra of the fluorinated β -AVT (I)-(III) at 35°C, but two one-proton singlet signals appear when the temperature is lowered to 10°C. The nonequivalence of the latter is caused by a retardation of the rotation of the NH_2 group around the $\text{N}-\text{C}=\text{S}$ bond. Heating up to 40-50°C leads to the appearance of a single very broad two-proton signal, which is located symmetrically with respect to the vanished signals of the nonequivalent protons of the amino group. For β -AVT (IV) with two fluoroalkyl groups the conditions of a slow (on the NMR time scale) exchange are fulfilled at higher temperatures (60°C), and the temperature at which the signals merge (T_m) is 85°C. The constant form and intensity of the NMR signals of the $\text{HC}=\text{S}$ and R_F fragments confirm the discussed nature of the dynamic transitions in (I)-(IV). A study of the concentration relationships in the IR spectra of compounds (I)-(IV) permits concluding that the contribution made by the intermolecular proton exchange in the observed dynamic process is negligibly small. As a result, the existence of specific hindered rotation of the amino group around the $\text{N}-\text{C}=\text{S}$ bond was shown for β -AVT (I)-(IV), and the possible realization of a cis-trans structure, i.e., rotation around the $\text{C}-\text{C}$ bond was excluded. A similar conclusion was obtained in [1, 2] for polyfluorinated β -AVK and it was shown that the β -AVK exist in the cis-S-cis form with an intramolecular hydrogen bond (IMHB).

Due to the quadrupole broadening of the proton signals on nitrogen and the low solubility of the compounds in perfluorotoluene the T_m cannot be determined more accurately than $\pm 5^\circ\text{C}$, which makes the error of determining ΔG^\ddagger equal to $\pm 4\%$ [7].

The obtained high values of the activation parameters of this process for the fluorinated β -AVT (see Table 1) testify to the existence of polar conjugation between the unshared electron pair of the N atom and the π electrons of the $\text{C}=\text{S}$ group [8]. Judging by the ΔG_m^\ddagger values, the degree of such conjugation in β -AVT (I)-(IV) is noticeably higher than in the isostructural β -AVK [1, 2] due to the greater polarizability of the $\text{C}=\text{S}$ bond. However, to make a quantitative estimate of the comparative contributions made by the polar conjugation and the IMHB to the value of the energy barrier of the hindered rotation of the amino group does not appear possible for the polyfluorinated β -AVK and β -AVT.

The value of such $n-\pi$ conjugation for β -AVT (IV) is higher than for (I)-(III), which reflects the joint effect of two fluoroalkyl groups. At the same time, the character of the fluoroalkyl substituent in β -AVT (I)-(III) exerts only a slight effect on the value of the barrier of rotation of the amino group.

CONCLUSIONS

1. The hindered rotation of the unsubstituted amino group around the $\text{N}-\text{C}=\text{S}$ bond in fluorinated β -aminovinyl thiones with a gem arrangement of the R_F and NH_2 groups was established.
2. The activation parameters of this process are but slightly dependent on the nature of R_F and increase when two R_F groups are inserted.

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