CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR A. P. TERENT'EV, R. A. GRACHEVA, L. F. TITOVA,

1963

SovietRxiv

Abstract

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Corresponding Member of the Academy of Sciences of the USSR A. P. TERENT' EV, R. A. GRACHEVA, L. F. TITOVA,
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SPECTROPOLARIMETRIC STUDY OF SCHIFF BASES OF THE FURAN SERIES

The problem of the relationship between the optical activity of a substance and its chemical structure has long interested chemists. Schiff bases from optically active amines and substituted benzaldehydes are an interesting object for the study of this relationship. As is known, the azomethine group is responsible for the optical activity of Schiff bases. The introduction of various substituents into the benzene nucleus of the aldehyde makes it possible to study the influence of the latter on optical activity. All optically active Schiff bases of the indicated structure can be divided into two groups: in the first, the substituent in the benzene nucleus has a noticeable influence on optical activity; for Schiff bases of the second group, no such influence is observed.

In the work of one of us, the optical activity of Schiff bases from optically active (+) α-phenylethylamine and its derivatives, (+) α-benzylethylamine and (+) 2-aminobutane, was studied ([1]-[3]). In all cases the molecular rotation was measured only at the sodium D line ($\lambda = 589$ mμ). It was established that the character of the substituent in the benzene nucleus of the aldehyde has no substantial influence on the magnitude and sign of rotation of Schiff bases. F. Nerdel arrived at analogous conclusions; he measured the optical-rotation dispersion curves (ORD curves) for a series of Schiff bases from (−) α-phenylethylamine and substituted benzaldehydes ([4]). It turned out that the ORD curves are smooth and positive for all Schiff bases of this series.

Considerably earlier, M. Betti studied the optical activity of an extensive series of Schiff bases from (+) α-(β-naphthyl)-benzylamine and various substituted benzaldehydes ([5]-[8]). He established that the sign and magnitude of the molecular rotation depend strongly on the electronic character of the substituent in the benzene nucleus of the aldehyde (M. Betti carried out his measurements only at one wavelength, $\lambda = 589$ mμ).

We had at our disposal two amines of the furan series: (−) σ-α-furylethylamine with $[\alpha]_D^{20} = -22^\circ$ and (−) σ-α-(5-methylfuryl)ethylamine with $[\alpha]_D^{20} = -19^\circ$*, which in their structure are analogous to (−) σ-α-phenylethylamine. It was of interest to check the optical properties of the Schiff bases from these amines and to compare them with the properties of already known analogous compounds

Fig. 1. ORD curves

Figure 1: Fig. 1. ORD curves

from the indicated optically active amines.

We obtained two series of Schiff bases of the following general formula:

[structural formula]

$$
\begin{gathered}
R = H,\ CH_3 \\
X = n\text{-}N(C_2H_5)_2,\ n\text{-}OCH_3, \\
n\text{-}Br,\ n\text{-iso-}C_3H_7,\ n\text{-}NO_2,\ -H, \\
m\text{-}NO_2,\ o\text{-}NO_2,\ o\text{-}OH.
\end{gathered}
$$

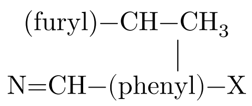
Along with this we also obtained Schiff bases from both amines and furfural.

* The preparation and resolution of α-(5-methylfuryl)ethylamine, and the preparation and properties of Schiff bases from (−)α-furylethylamine and (−)α-(5-methylfuryl)ethylamine will be described in detail later.

For all the Schiff bases obtained, ORD curves were recorded. The measurement results are presented in Figs. 1 and 2. On the basis of the studies carried out, the following preliminary conclusions may be drawn:

1. The substituent in the benzene nucleus of the aldehyde has a substantial influence on the direction of the ORD curve. Curves 1, 2, 10 (see Figs. 1 and 2) are smoothly positive, whereas curves 3, 4, 5, 6, 8, 9 are smoothly negative.

Fig. 1. ORD curves of



$$
\begin{array}{c}
\text{(furyl)}-\text{CH}-\text{CH}_3 \\
\quad\quad | \\
\text{N}=\text{CH}-\text{(phenyl)}-\text{X}
\end{array}
$$

in benzene (A), in ethanol (B), where

X : 1—p-$\mathrm{N(C_2H_5)_2}$; 2—p-$\mathrm{OCH_3}$; 3—p-iso-$\mathrm{C_3H_7}$; 4—p-Br;
5—p-$\mathrm{NO_2}$; 6—H; 7—furyl-CH $\cdot$ $\mathrm{CH_3}$ derivative; 8—m-$\mathrm{NO_2}$;
9—o-$\mathrm{NO_2}$; 10—o-OH.

2. The methyl group in the furan nucleus of the amine does not change the general course of the ORD curves of the Schiff bases, but shifts them toward positive values of the angle of rotation.

3. The solvent has no noticeable effect on the direction of the ORD curves of the Schiff bases.

Fig. 2. CD curves

Figure 2: Fig. 2. CD curves

Thus, Schiff bases from amines of the furan series differ in their optical properties from analogous Schiff bases from (−)-phenylethylamine and (+)-2-aminobutane; namely, the magnitude and sign of their rotation depend strongly on the electronic character of the substituent in the benzene nucleus of the aldehyde. It should also be noted that the Schiff bases from amines of the furan series and furfural show anomalous behavior—for both Schiff bases an inversion of the ORD curve is observed depending on the solvent (curve 7 in all figures). The ORD curve of furfural-α-furylethylamine without solvent is smoothly negative; in ethanol and methanol it is smoothly positive, and in benzene it is smoothly negative. The ORD curve of furfural-α-(5-methylfuryl)ethylamine without solvent is smoothly positive, in methanol smoothly positive, and in benzene and isooctane smoothly negative. The observed inversion of the ORD curve

reversible. An analogous phenomenon for Schiff bases had not previously been observed. In the UV spectrum of the Schiff base from (−)-(5-methylfuryl)ethylamine, a strong shift of the absorption maximum of the azomethine group is observed under the influence of the solvent: λ_{max} in methanol = 305 mμ, λ_{max} in isooctane = 268 mμ.

Fig. 2. CD curves of
CH_3—furyl—CH—CH_3—N=CH—phenyl-X,
in benzene (**A**), in methanol (**B**),

where X: 1 —p-N(C_2H_5)$_2$; 2 —p-OCH_3; 3 —p-iso-C_3H_7; 4 —p-Br; 5 —p-NO_2; 6 —H; 7 —CH_3—furyl—CH—CH_3—N=CH—furyl; 8 —m-NO_2; 9 —o-NO_2; 10 —o-OH.

Thus, Schiff bases of the furan series have characteristic features which are probably dependent on the specific influence of the furan nucleus on the asymmetric carbon atom directly bonded to it.

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named after M. V. Lomonosov

Received
19 VII 1963

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