Chemistry

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Abstract

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On the Equilibrium of the Tetrazole and Azide Forms in Benzthiazolotetrazole

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The question of the structure of benzthiazolotetrazole has recently attracted the attention of researchers more than once (1–6).

As is known, compounds obtained from monohydrazines of *N*-heterocyclic compounds of the structure:

[chemical structure]

and nitrous acid, or from the corresponding 2-chloro derivatives

[chemical structure]

and sodium azide, may be tetrazoles or azides. It was established relatively recently that five-membered heterocycles containing sulfur occupy a special position and give compounds which in crystals are tetrazoles, while in solutions they represent an equilibrium mixture of two forms, tetrazole $\rightleftharpoons$ azide (4). Thus, for benzthiazolotetrazole in solutions the following equilibrium occurs:

[chemical equilibrium: tetrazole form   azide form]

In continuation of studies of hydrazines of benzazoles (7), and independently of Boyer’ s work (4–6), we recorded the IR spectra of benzthiazolotetrazole in crystals and in solutions*. In the spectra of solutions in various solvents, strong azide bands were found: a doublet of bands in the region $2155, 2120$ cm^{-1}, which is assigned to the asymmetric stretching vibration of the azide group, and a band in the region 1255 cm^{-1}, corresponding to the symmetric stretching vibration of this group (8). In the crystalline state (pastes with vaseline oil and perfluorohydrocarbon), the substance shows no azide bands in the spectra and has bands which in the literature are usually assigned to the tetrazole ring (bands in the region 1000—1100 cm^{-1} and 760 cm^{-1}) (9).

On examining the spectra of solutions and comparing them with the spectra of crystals (Fig. 1), it is easy to see that, depending on the nature of the solvent, the ratio of the azide and tetrazole forms in solutions is different. Thus, when benzothiazolotetrazole is dissolved in benzene or carbon tetrachloride, it exists

* The spectra were obtained with a UR-10 infrared spectrophotometer (Zeiss).

Fig. 1. Infrared spectra of benzothiazolotetrazole: 1 —in the crystalline state (pastes with Vaseline oil and polytrifluorochloroethylene); 2 —in pyridine solution; 3 —in dioxane solution; 4 —in CCl_4 solution.

Figure 1: Fig. 1. Infrared spectra of benzothiazolotetrazole: 1 —in the crystalline state (pastes with Vaseline oil and polytrifluorochloroethylene); 2 —in pyridine solution; 3 —in dioxane solution; 4 —in CCl_4 solution.

practically completely in the azide form (intense azide bands at 2155, 2120, 1255 cm^{-1} appear in the spectrum, while the bands observed in the crystalline compound and, consequently, characterizing the tetrazole structure are absent). In dioxane and especially in pyridine solutions, along with the bands characteristic of the azide form, there are also bands corresponding to tetrazole (1480, 1465, 1216, 760 cm^{-1}).

Thus, an increase in the polarity of the solvent shifts the equilibrium toward the tetrazole form.

When studying the spectra of pyridine and dioxane solutions of benzothiazolotetrazole at different temperatures (in the range 20—95°), we found a strong temperature dependence of the band intensities in the spectra; moreover, raising the temperature causes an increase in the intensity of all azide bands and a decrease in the intensity of the tetrazole bands. This indicates a shift of the tetrazole—azide equilibrium toward the azide form with increasing temperature. In solutions in CCl_4, no change whatever in the intensity of the bands is observed under these conditions, which agrees with the data already noted above on the existence of benzothiazolotetrazole in this solvent practically completely in the azide form.

Fig. 1. Infrared spectra of benzothiazolotetrazole: **1** —in the crystalline state (pastes with Vaseline oil and polytrifluorochloroethylene); **2** —in pyridine solution; **3** —in dioxane solution; **4** —in CCl_4 solution.

On the basis of the temperature dependence found, the thermal effect ($-\Delta H$) of the tetrazole—azide transformation was calculated; it proved to be 4650 cal/mole for the pyridine solution and 984 cal/mole for the dioxane solution. The tetrazole —azide equilibrium is completely reversible; the conversion of tetrazole to azide upon dissolution is also reversible: after removal of the solvent the crystals formed show no azide bands, while upon repeated dissolution strong azide bands again appear, etc.

This kind of opening and closing of the tetrazole ring during dissolution and crystallization suggested that, upon destruction of the crystal lattice in the molten substance, opening of the tetrazole ring and establishment of an equilibrium between the azide and tetrazole forms would likewise take place.

Indeed, in the IR spectra we obtained for melts of benzthiazolotetrazole (Fig. 2), at a temperature of 115-120° the bands of both the azide and the tetrazole

Fig. 2. Infrared spectra of benzthiazolotetrazole: 1 –in the crystalline state; 2 –in the melt (at 120°); 3 –in the crystalline film formed after the melt solidified

Figure 2: Fig. 2. Infrared spectra of benzthiazolotetrazole: 1 –in the crystalline state; 2 –in the melt (at 120°); 3 –in the crystalline film formed after the melt solidified

forms appear quite distinctly, the content of the latter being higher than in the pyridine solution. Evidently, the polarity of the medium in the melt is higher than in the pyridine solution, and this accounts for the further increase in the content of the tetrazole form.

Fig. 2. Infrared spectra of benzthiazolotetrazole: **1** –in the crystalline state; **2** –in the melt (at 120°); **3** –in the crystalline film formed after the melt solidified.

When the temperature of the melt is lowered until its complete crystallization, the azide bands disappear and the spectrum becomes identical with the spectrum of the initial crystals (Fig. 2). The process may be repeated several times; however, prolonged heating or a considerable increase in temperature (above 120°) leads to irreversible destruction of part of the substance. In this case new bands appear, and, upon solidification of the melt, the bands of the azide group do not disappear completely.

The example presented of equilibrium isomerism, consisting in the opening and closing of the tetrazole ring during melting and crystallization, is, so far as we know, observed for the first time.

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CITED LITERATURE

1. V. Ya. Pochinok, S. D. Zaitseva, R. G. El' gort, *Ukr. Khim. Zhurn.*, **17**, 509 (1951); V. Ya. Pochinok, S. D. Zaitseva, *Ukr. Khim. Zhurn.*, **16**, (3), 350 (1960).
2. G. A. Reynolds, J. A. v. Allan, J. F. Tinker, *J. Org. Chem.*, **24**, 1209 (1959).
3. G. A. Reynolds, J. A. v. Allan, *J. Org. Chem.*, **24**, 1478 (1959).
4. J. H. Boyer, E. J. Miller, *J. Am. Chem. Soc.*, **81**, 4671 (1959).

5. J. H. Boyer, M. S. Chang, R. F. Reinisch, *J. Org. Chem.*, **25**, 286 (1960).

6. J. H. Boyer, H. W. Hyde, *J. Org. Chem.*, **25**, 458 (1960).

7. N. P. Bednyagina, I. Ya. Postovskii, *ZhOKh*, **30**, 1431 (1960).

8. Yu. N. Sheinker, Ya. K. Syrkin, *Izv. AN SSSR, Ser. Fiz.*, **14**, 484 (1950).

9. E. Lieber, D. R. Levering, L. J. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

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