# SYNTHESIS OF POLYMORPHIC α-(2-BENZOTHIAZOLYL)-α-PHENYL-β-PICRYLHYDRAZINES AND INVESTIGATION OF THEIR PROPERTIES IN THE CRYSTALLINE STATE AND IN SOLUTIONS

L. A. Petrov, O. B. Donskikh,
V. D. Galyaminskikh, B. P. Manannikov,
R. O. Matevosyan, and A. K. Chirkov

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Polymorphic modifications of α-(2-benzothiazolyl)-α-phenyl-β-picrylhydrazine were obtained. The structures of the crystals of the polymorphic modifications were investigated by x-ray diffraction and IR and UV spectroscopy, by a study of the electrical conductivities in nonaqueous media, and by microcalorimetric determination of the heats of solution. It is shown that the physical and chemical properties of the compounds obtained depend on their macromolecular structures in the crystalline state and in solutions.

In [1] it was shown that, depending on the temperature conditions of the reaction of α-(N-methyl-2-benzimidazolyl)-α-phenylhydrazine with trinitroanisole, one obtains two products with the same elementary composition corresponding to α-(N-methyl-2-benzimidazolyl)-α-phenyl-β-picrylhydrazine (I). The low-temperature synthesis of I yields picrylhydrazine Ia, which is readily oxidized in solution with lead dioxide to give the corresponding radical. The preparation of I in refluxing alcohol, benzene, and dioxane gives colored product Ib, which is also readily oxidized in solution by lead dioxide, but, in contrast to Ia, the oxidation yields a nonparamagnetic colored compound. Compound Ia was irreversibly converted to Ib on heating both in solution and in the crystalline state. α-(N-Benzyl-2-benzimidazolyl)-α-phenyl-β-picrylhydrazine and (at a somewhat lower rate) α-(N-phenyl-2-benzimidazolyl)-α-phenyl-β-picrylhydrazine undergo similar transformations.

To further study this interesting phenomenon, we undertook the preparation of the products of the conversion of α-(2-benzothiazolyl)-α-phenyl-β-picrylhydrazine (II) [2], the heteroring of which is of lower basicity than that of the heterorings of benzimidazole analogs of diphenylpicrylhydrazine (DPPH) [3].

Depending on the temperature conditions and the reagent concentration, the picrylation of α-(2-benzothiazolyl)-α-phenylhydrazine in alcohol, benzene, and dichloroethane gives two different (with respect to appearance and melting point) products with identical elementary composition corresponding to II. An investigation of the conductivities of IIa and IIb in benzene, their heats of dissolving in dioxane, and

TABLE 1. Characteristics of the Compounds Obtained

| Compound | mp, °C | Crystal color | Heat of dissolving in dioxane, kcal/mole | Crystallographic parameters | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Å | Å | Å | α° | β° | γ° | space group |
| IIa | 176 | Orange | +0,2 | 14,51 | 17,87 | 8,64 | — | 112,5 | — | $P2_1/a$ |
| IIb | 222 | Yellow | +6,0 | 11,10 | 12,05 | 7,68 | 92,7 | 102,1 | 101,7 | $P\bar{1}$ |

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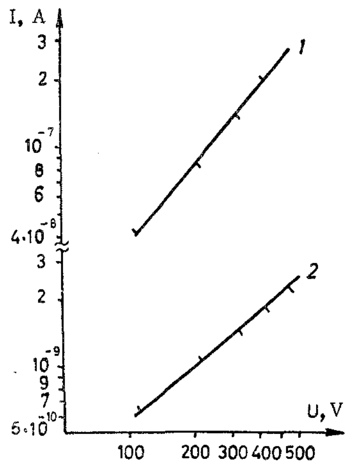

Fig. 1. Electrical conductivities of benzene solutions of the hydrazines: 1) hydrazine IIb; 2) hydrazine IIa.

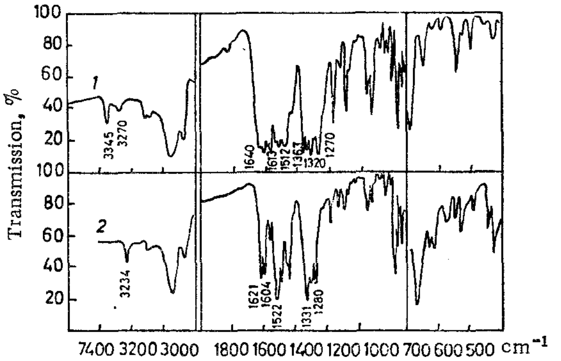

Fig. 2. IR spectra of polymorphic picrylhydrazines IIa and IIb.

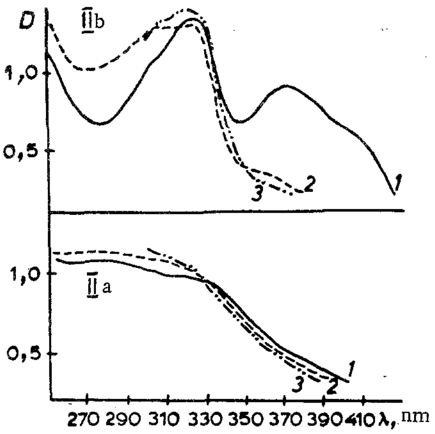

Fig. 3. UV spectra of picrylhydrazines IIa and IIb: 1) in alcohol; 2) in benzene; 3) in dichloroethane.

of the structures of the crystals by x-ray diffraction (Table 1 and Fig. 1) demonstrated that the isolated compounds are polymorphic.

Polymorphic IIa and IIb have different IR absorption in the region of the frequencies of the stretching vibrations of the NH groups (3230-3350 $\text{cm}^{-1}$), of the asymmetrical vibrations of the nitro groups (1520-1550 $\text{cm}^{-1}$), and of the symmetrical vibrations of the nitro groups and the C-N stretching vibrations (1280-1360 $\text{cm}^{-1}$) (Fig. 2).

We were unable to accomplish interconversions of IIa and IIb by prolonged refluxing in different solvents. If the process of dissolving of the compounds were to proceed up to the monomolecular solvated state, there would then be no hindrance to interconversions of polymorphic modifications IIa and IIb in one or another solvent. However, the stability of the modifications of II in solutions apparently indicates that the process of dissolving in this case terminates with a stable (in the solvents used) macromolecular formation.

Thus the formation of one or the other polymorphic compounds IIa or IIb is fixed in the very synthesis itself by the state of the reaction mass (solvent, temperature conditions, and reagent concentrations). The picrylation of α-(2-benzothiazolyl)-α-phenylhydrazine in dilute alcohol solutions at 30-35°C gives the IIa modification in 70% yield. An increase in the initial reagent concentrations lowers the yield of IIa due to the formation of IIb. Picrylhydrazine modification IIb is primarily formed in 70% yield in benzene and in 60% yield in dichloroethane when concentrated solutions of the reagents are refluxed for 2 h. It is interesting that prior refluxing of a concentrated solution of trinitroanisole in alcohol leads to an almost instantaneous occurrence of the above-described picrylation to give IIb in 80% yield. It is important to note that the trinitroanisole isolated after refluxing for 2 h in alcohol did not differ from the starting material either with respect to melting point or reactivity. Prolonged refluxing of the trinitroanisole in alcohol apparently changes its macromolecular structure in solution, which is stable only at the boiling point of the alcohol. The reaction in a similar manner of the structured solution of the trinitroanisole with α-(2-benzothiazolyl)-α-phenylhydrazine is directed to favor the formation of IIb.

A similar phenomenon was observed in [4]. Depending on the temperature conditions, complexes of these compounds that differ in structure and properties are formed in the reaction of trinitroanisole with sodium ethoxide.

Polymorphic IIa and IIb differ considerably with respect to their chemical properties. Thus IIa forms complexes with ammonia and aliphatic amines both in the crystalline state and in solutions. The stability constant of the complex of this compound with piperidine in benzene, which was calculated by the method in [5], is 45 liter/mole. Polymorph IIb does not form complexes with amines, and, in contrast to IIa, is readily hydrolyzed by aqueous ammonia in dioxane to give an almost quantitative yield of α-(2-benzothiazolyl)-α-phenylhydrazine and picric acid.

The oxidation of polymorphic IIa and IIb by lead dioxide in dioxane gives colored solutions of radicals. The hyperfine structure of the ESR spectra of an oxidized solution of IIa consists of four lines, while that of an oxidized solution of IIb consists of three considerably less intense lines.

Thus the chemical properties of polymorphic IIa and IIb are a function of their macromolecular structure in the crystalline state and in solutions.

Considering the effect of the nature of the solvent during the synthesis of IIa and IIb and also the dependence of the chemical and physical properties of solutions of these compounds on the crystallographic parameters of the solid-phase state, one might have proposed a different interaction of the solvent with the polymorphic modifications of II. In fact, in a study of the electronic absorption spectra of benzene, alcohol, and dichloroethane solutions of IIa and IIb, it was found that IIb, in contrast to IIa, displays a distinctly expressed solvatochromic effect (Fig. 3).

Thus, like the properties considered above, the phenomenon of solvatochromism for the investigated compounds proved to be a function of the crystallographic parameters of the substance in the solid-phase state.

## EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrophotometer. A Specord UVVIS spectrophotometer was used to obtain the UV spectra of $5 \cdot 10^{-5}$ mole/liter solutions of the picrylhydrazines.

The conductivities of benzene solutions of IIa and IIb were measured with an apparatus similar to that described in [6]. The measurements were made under dry argon at 24 ± 0.1°. Chromatographically pure benzene was used to prepare the solutions. The hydrazines were conditioned in vacuo ($1 \cdot 10^{-5}$ mm) for 2 days. The solution concentration was $5 \cdot 10^{-4}$ mole/liter.

The heats of dissolving of the hydrazines in dioxane were determined in the microcalorimeter of a Calvet system with a sensitivity of 0.0334 cal/h • mm. The samples ($1.6 \cdot 10^{-5}$ mole) were dissolved in 8 ml of dioxane to give solutions with a concentration of $2 \cdot 10^{-3}$ mole/liter. The heat of dissolving was determined by graphical integration of the curve that reflects the trend of the change in temperature during dissolving.

The lattice constants were determined from scannings of the zero-layer lines of the x-ray diffraction patterns of rotation about the crystallographic axis with an accuracy of ~1%. The reciprocal lattice photographs of IIa indicated that the crystals are affilitated with a monoclinic system. Reflections with even h are present in the (hOl) zone, while reflections with even K are present among the (OKO) reflections. Thus the only possible space group is $P2_1/a$. The Laue diffraction pattern and the reciprocal lattice photographs of crystals of IIb indicate their affiliation with a triclinic system. The possible symmetry space groups may thus be P1 in the absence of a symmetry center or $P\bar{1}$ if a symmetry center is present. Analysis of the faceting of the crystals makes it possible to give preference to group $P\bar{1}$.

α-(2-Benzothiazolyl)-α-phenyl-β-picrylhydrazine Modification IIa. Solutions of 2 g of α-(2-benzothiazolyl)-α-phenylhydrazine in 80 ml of alcohol and 2 g of trinitroanisole in 80 ml of alcohol were mixed and heated at 30-35° for 2 h. The reaction mass was then allowed to stand for 24 h to give an orange-yellow precipitate, which was removed and washed with 40 ml of chloroform. The chloroform mother liquor was evaporated to half its original volume and diluted with an equal amount of hot alcohol. On cooling, the solution gave orange crystals of IIa (70%) with mp 176-178°. Found: C 50.6; H 2.8; N 18.4%. $C_{19}H_{12}N_6O_6S$. Calculated: C 50.4; H 2.6; N 18.6%. The chloroform-insoluble residue was recrystallized from dimethylformamide–ethanol (1 : 1) to give yellow crystals of IIb (15%) with mp 222-223°.

α-(2-Benzothiazolyl)-α-phenyl-β-picrylhydrazine Modification IIb. A) Concentrated boiling alcohol solutions of 2 g of α-(2-benzothiazolyl)-α-phenylhydrazine and 2 g of trinitroanisole were mixed and refluxed for 2 h. The mass was then allowed to stand for 24 h. The resulting yellow crystalline precipitate was washed with chloroform and recrystallized from dimethylformamide–alcohol (1 : 1) to give yellow crystals of IIb (70%) with mp 222-223°.

B) A solution of 2 g of trinitroanisole in 80 ml of alcohol was refluxed for 2 h, after which a hot solution of 2 g of α-(2-benzothiazolyl)-α-phenylhydrazine in 80 ml of alcohol was added, and IIb formed in 1-2 min. The IIb obtained by method B was identical to the IIb obtained via method A. Found: C 50.2; H 2.4; N 18.3%. $C_{19}H_{12}N_6O_6S$. Calculated: C 50.4; H 2.6; N 18.6%.

Hydrolysis of α-(2-Benzothiazolyl)-α-phenyl-β-picrylhydrazine Modification IIb. A total of 40 ml of 25% ammonium hydroxide was added to a dioxane solution of 2 g of IIb, and the mixture was heated at 50° for 15 min. The dioxane and water were then evaporated in vacuo, and the residue was washed with water slightly acidified with HCl. The wash water yielded 0.7 g of picric acid, while the solid was crystallized from alcohol to give 0.8 g of α-(2-benzothiazolyl)-α-phenylhydrazine.

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