BENZO[1,2-d : 3,4-d']DIIMIDAZOLE DERIVATIVES

IV.* STRUCTURE AND TAUTOMERISM OF 2-AMINO DERIVATIVES OF 3,6-DIMETHYL- AND 3,6,7-TRIMETHYLBENZO[1,2-d : 3,4-d']DIIMIDAZOLE

Yu. V. Koshchienko and A. M. Simonov

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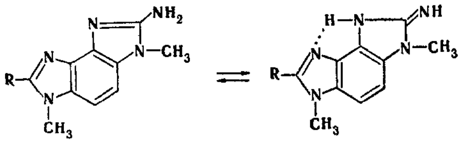
The structure and tautomerism of 2-amino-3,6-dimethyl-, and 2-amino-3,6,7-trimethylbenzo[1,2-d : 3,4-d']diimidazoles were studied by means of IR and UV spectroscopy. It was found that they exist in the amino form in the crystalline state and in methanol solution.

It is known that amino derivatives of imidazole systems for which tautomerism is possible exist practically entirely in the amino form in the crystalline state and in solution [2, 3]. It seemed of interest to study the phenomenon of tautomerism for 2-amino derivatives of benzo[1,2-d : 3,4-d']diimidazole (Ia, b) in connection with the possible stabilization of the imino form due to the hydrogen bond between the hydrogen atom of the cyclic NH group and the pyridine nitrogen atom of the other imidazole ring.



I a,b

I a R=H; b R=CH3

To elucidate the problem of the structure of Ia, b in the crystalline state, we used the method of comparison of the IR spectra of these compounds with the spectra of their N-deutero derivatives, as was previously done for other heterocyclic amines [2-4].

The IR spectra of amines Ia, b in the crystalline state contain absorption bands caused by the stretching and deformation vibrations of the NH_2 group. For Ia, ν_{NH_2} 3145, 3340 cm^{-1}, and δ_{NH_2} 1664 cm^{-1}; for Ib, ν_{NH_2} 3175, 3330 cm^{-1}, δ_{NH_2} 1678 cm^{-1} (Fig. 1). However, the bands of the stretching vibrations are shifted to the low-frequency region; this is possible due to the formation of intermolecular hydrogen bonds [5]. After partial deuteration of amines Ia, b, the δ_{NH_2} band at 1664 cm^{-1} for Ia and at 1678 cm^{-1} for Ib is markedly weakened, while bands related to the vibrations of N—D bonds appear at 2200-2400 cm^{-1}. If amines Ia, b exist in the imino form, the band at 1660-1680 cm^{-1} could have been assigned to the stretching vibration of the exocyclic C = N bond; but it should not have experienced pronounced shifts after deuteration since it depends relatively little on the mass of the atom attached to the nitrogen and should have remained unchanged (as is the case for 1,3-dimethylbenzimidazolone imine [2]).

On the basis of the material set forth above, it can be concluded that amino compounds Ia, b exist in the amino form in the crystalline state.

The use of IR spectroscopy for the elucidation of this problem in solution is impossible because of the insolubility of Ia, b in suitable organic solvents (they are soluble only in water and alcohol). These properties of the amines also hinder the use of UV spectroscopy for this purpose.

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*See [1] for communication III.

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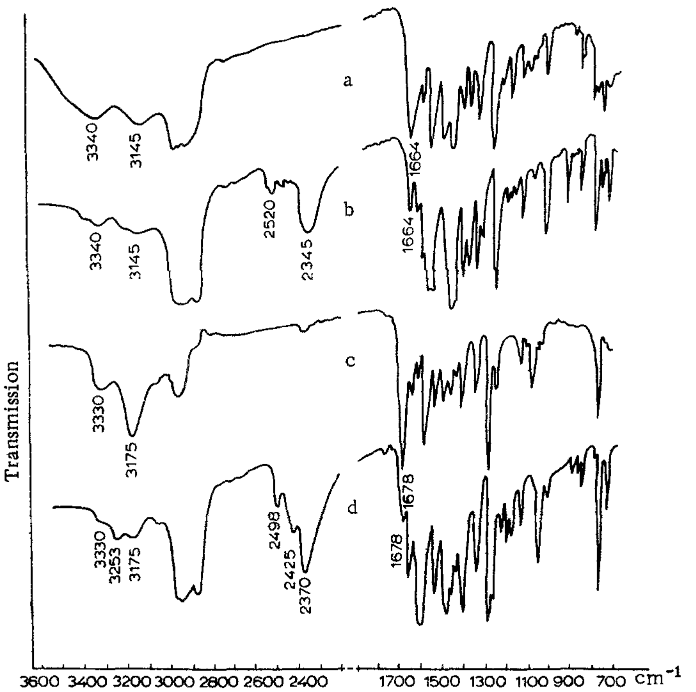
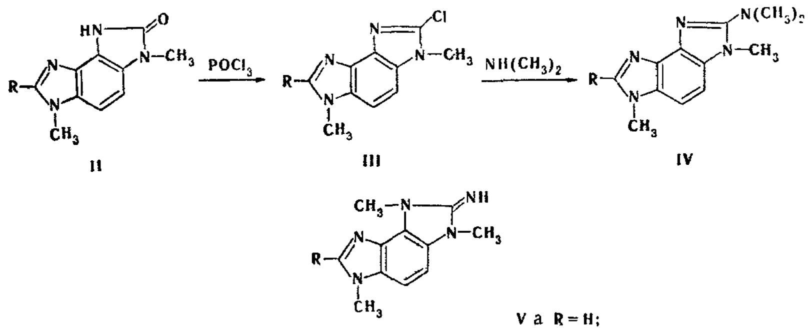


Fig. 1. IR spectra (in mineral oil): a) 2-amino-3,6-dimethylbenzo[1,2-d : 3,4-d']diimidazole; b) its N-deutero derivative; c) 2-amino-3,6,7-trimethylbenzo[1,2-d : 3,4-d']-diimidazole; d) its N-deutero derivative.

To study the tautomerism in solution it was necessary to obtain the fixed amino and imino forms, record their UV spectra, and compare these spectra with the spectra of the amines themselves.



To obtain amino form IV, 2-oxo-3,6,7-trimethyl-1,2-dihydrobenzo[1,2-d : 3,4-d']diimidazole (II) [6] was converted, by the action of phosphorus oxychloride, to 2-chloro derivative III, and heating of the latter in an autoclave with dimethylamine gives 2-dimethylamino-3,6,7-trimethylbenzo[1,2-d : 3,4-d']diimidazole (IV).

Attempts to synthesize fixed imino forms Va, b proved to be unsuccessful. Treatment of amines Ia, b with alkylating agents (methyl benzenesulfonate and methyl iodide) gave monoquaternary salts, which were converted, by the action of alkalis, to a mixture of products, from which imine V could not be isolated in pure form.

On the basis of the similarity in the UV spectra of fixed amino form IV and amines Ia, b themselves, which were recorded from methanol solutions (Fig. 2), one can arrive at the conclusion that these compounds probably exist in the amino form in methanol solution.

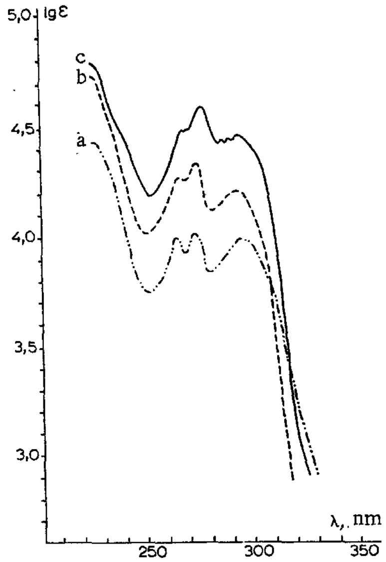


Fig. 2. UV spectra in methanol: a) 2-amino-3,6-dimethylbenzo-[1,2-d : 3,4-d']diimidazole (Ia); b) 2-amino-3,6,7-trimethylbenzo-[1,2-d : 3,4-d']diimidazole (Ib); c) 2-dimethylamino-3,6,7-trimethylbenzo[1,2-d : 3,4-d']diimidazole (IV).

EXPERIMENTAL

Deuteration of Ia, b was carried out by refluxing a solution of 0.1 g of the substance in 1.5 ml of C_2H_5OD for 2 h, after which the solvent was removed by distillation. The operation was repeated three times.

IR Spectra. The IR spectra of mineral oil suspensions of the substances were recorded with a UR-20 spectrometer. The UV spectra of methanol solutions were recorded with an SF-4A spectrophotometer.

2-Chloro-3,6,7-trimethylbenzo[1,2-d : 3,4-d']diimidazole (III). A 1.84-g (8.5 mmole) sample of II was refluxed with 10 ml of phosphorus oxychloride for 10 h, after which the excess phosphorus oxychloride was removed in vacuo with an aspirator. The residue was treated with 25 ml of water and neutralized with 22% ammonium hydroxide. The resulting precipitate was removed by filtration and washed with water to give 1.8 g (90%) of colorless crystals (from alcohol) with mp 300-301°. Found: C 56.2; H 4.7; Cl 14.9; N 23.7%. $C_{11}H_{11}ClN_4$. Calculated: C 56.3; H 4.7; Cl 15.1; N 23.9%.

2-Dimethylamino-3,6,7-trimethylbenzo[1,2-d : 3,4-d']diimidazole (IV). A mixture of 0.59 g (2.5 mmole) of III, 1.02 g (12.5 mmole) of dimethylamine hydrochloride, and 1.23 g (15 mmole) of anhydrous sodium acetate in 6 ml of ethanol was heated in an autoclave at 140° for 10 h, after which the mixture was cooled, and the precipitated inorganic substances were removed by filtration. The solvent was removed by distillation to give 0.45 g (75%) of yellowish hygroscopic crystals (from toluene–petroleum ether) with mp 145-146°. Found: C 64.0; H 7.3; N 28.5%. $C_{13}N_{17}N_5$. Calculated: C 64.2; H 7.0; N 28.8%.

LITERATURE CITED

1. A. M. Simonov, Yu. V. Koshchienko, and T. G. Belenko, Khim. Geterotsikl. Soedin., 107 (1973).
2. Yu. N. Sheinker, A. M. Simonov, Yu. M. Yutilov, V. N. Sheinker, and E. I. Perel'shtein, Zh. Organ. Khim., 2, 917 (1966).
3. A. F. Pozharskii, I. S. Kashparov, Yu. P. Andreichikov, A. I. Buryak, A. A. Konstantinchenko, and A. M. Simonov, Khim. Geterotsikl. Soedin., 807 (1971).
4. Yu. N. Sheinker and E. M. Peresleni, Zh. Fiz. Khim., 36, 1705 (1962).
5. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen (1958).
6. Yu. V. Koshchienko, A. M. Simonov, and A. F. Pozharskii, Khim. Geterotsikl. Soedin., 1132 (1971).