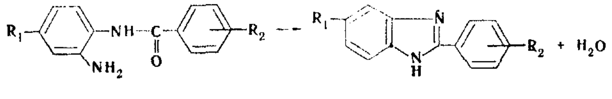
SYNTHESIS AND IR SPECTRA OF 2-PHENYLBENZIMIDAZOLE AND ITS AMINO DERIVATIVES

V. K. Shchel'tsyn, A. Ya. Kaminskii,
T. P. Shapirovskaya, I. L. Vaisman,
V. F. Andrianov, and S. S. Gitis

UDC 547.785.1.5.07:543.422.4

2-Phenylbenzimidazole and its mono and diamino derivatives were synthesized in yields up to 85% by cyclodehydration of o-aminobenzanilides in hydrochloric or sulfuric acid. The IR spectra of the compounds obtained were studied, the principal bands of the stretching and deformation vibrations of the NH and NH_2 groups were assigned, and the presence of associates with a hydrogen bond was established.

The known methods for the synthesis of phenylbenzimidazole and its amino derivatives are difficult to carry out, lead to low yields [1-3], or have received very little study [4, 5]. In this connection, we attempted to synthesize 2-phenylbenzimidazole and its amino derivatives by cyclodehydration of o-aminobenzanilines in hydrochloric or sulfuric acid. As demonstrated in the literature, the yields of the products of this reaction depend to a considerable extent on the structures of the starting compounds [6, 7].



I $R_1=R_2=H$; II $R_1=H$, $R_2=p\text{-}NH_2$; III $R_1=NH_2$, $R_2=H$; IV $R_1=NH_2$, $R_2=m\text{-}NH_2$

The synthesis of 5(6)-amino-2-(m-aminophenyl)benzimidazole (IV) has been studied in greatest detail. In preliminary experiments, it was established that the reaction rate has a high temperature coefficient. At ~100°C, the starting compound is completely converted after 10-30 min, and the yield of IV reaches 80% in both dilute and concentrated acids.

The hydrochloride of the resulting IV partially precipitates at the boiling point of the mixture and crystallizes practically completely at room temperature from 3-4 N (and higher) concentrations of acid. The solubility of the hydrochloride of IV in sulfuric acid increases as the concentration of the latter increases, and all of the salt can therefore be isolated only from 1-4 N acids.

2-Phenylbenzimidazole and its monoamino derivatives (I-III) were obtained in lower yields than IV by cyclodehydration in 4 N hydrochloric acid (see Table 1); this is apparently associated with the high rate of hydrolysis of mono- and diaminobenzanilides.

The principal bands in the IR spectra of the compounds obtained and their assignment in accordance with the data available in the literature [8, 9] are presented in Table 1. One should note that the δ N−H band of the benzimidazole ring is found at somewhat higher frequencies as compared with the band of unsubstituted benzimidazole (1620 cm^{-1} in CH_2Cl_2 [8]); this is due to the electron-donor character of the phenyl ring as well as the effect of a more polar solvent.

All-Union Scientific-Research and Design Institute of Monomers, Tula. Tula State Pedagogical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 115-116, January, 1973. Original article submitted November 30, 1971.

TABLE 1. Characteristics of the Investigated Compounds (IR Spectra in Acetonitrile)

Compound	mp, °C	Yield, %	ν_{C-N}	1600 cm^{-1} region			ν_{N-H}, cm^{-1}			$2\delta_{N-H}$
				δ_{NH}	δ_{NH_2}	$\nu_{C=C}$	ν_{as} NH$_2$	ν_s NH$_2$	ν_{N-H}	
I	299—300	65,5	1279*	1630	—	1605	—	—	3323	—
II	240—241	75,1	1278*	1626	1615 (1624*)	1590	3475	3380	3326	3241
III	296—296,5	60,3	1280* 1306*	1631	1688 (1639*)	1594 1607	3461	3369	3323	3240
IV	257—258	85,0	1281*	1635	1615 (1615*) 1633 (1638*)	1594	3458†	3370†	3330	3240

---

*In KBr pellets.

†The band is diffuse because of the superimposition of several bands.

For the spectra in the solid phase, one also observes a group of bands over a broad region (2600-3500 cm^{-1}), which are related to the vibrations of differently associated NH and NH$_2$ groups and were previously noted in the spectrum of unsubstituted benzimidazole in the solid state [8].

The formation of simple associates is also confirmed by the certain increase in the frequency of the NH$_2$ band in the solid phase as compared with a solution in acetonitrile. It is known that the shift of the NH$_2$ bands to higher frequencies due to the formation of hydrogen bonds is proportional to the basicity of the proton acceptor [10,11]. Since the amine is a stronger base than acetonitrile [12], the N–hydrogen bond becomes stronger on passing from the solution to the solid phase; this is reflected in the indicated shift of the NH$_2$ band.

EXPERIMENTAL

The starting o-aminobenzanilides were obtained by catalytic hydrogenation of the corresponding nitrobenzanilides in ethanol: 2'-aminobenzanilide had mp 149-150°, 2',4'-diaminobenzanilide had mp 199-200°, 2',4-diaminobenzanilide had mp 176.5-177.5°, and 2',4',3-triaminobenzanilide had mp 189-190°.

5(6)-Amino-2-(m-aminophenyl)benzimidazole (IV). A mixture of 24.2 g (0.1 mole) of 2',4',3-triaminobenzanilide and 250 ml of 4 N hydrochloric acid or 500 ml of 2 N sulfuric acid was heated to the boiling point and cooled after 30 min. The precipitated salt of IV was removed by filtration and neutralized to pH 8-8.5 with 4 N sodium hydroxide solution. The precipitated IV was washed with water and dried at 102-105° and then at 150° to remove the water of crystallization. This procedure gave 19 g (85%) of IV with mp 257-258° (from aqueous alcohol).

Compounds I-III were similarly obtained.

Samples of I-IV were recrystallized from aqueous alcohol to record the IR spectra. The IR spectra of KBr pellets and acetonitrile solutions were recorded with a UR-20 spectrophotometer.

LITERATURE CITED

1. M. A. Phillips, J. Chem. Soc., 2393 (1928).
2. B. A. Porai-Koshits and G. M. Kharkharova, Zh. Obshch. Khim., 25, 2138 (1955).
3. O. Kym, Ber., 32, 2178 (1899).
4. German Patent No. 70,862 (1892); Friedl., 3, 34 (1894).
5. Heterocyclic Compounds [Russian translation], Vol. 5, Inostr. Lit., Moscow (1961), p. 218.
6. K. J. Morgan and A. M. Turner, Tetrahedron, 25, 915 (1969).
7. V. Sterba, J. Arient, and J. Slosar, Coll. Czech. Chem. Commun., 31, 1093 (1966).
8. K. J. Morgan, J. Chem. Soc., 2343 (1961).
9. Yu. N. Sheinker, A. M. Simonov, Yu. M. Yutilov, V. N. Sheinker, and E. I. Perel'shtein, Zh. Organ. Khim., 2, 917 (1966).
10. J. Pimentel and A. McClellan, The Hydrogen Bond, W. H. Freeman (1960).
11. L. K. Dyall, Spectrochim. Acta, 25A, 1727 (1969).
12. L. K. Dyall and J. S. Kemp, Spectrochim. Acta, 22, 467 (1966).