ELECTRONIC EFFECTS IN DIANION RADICALS OF NITRO DERIVATIVES OF 2-PHENYLBENZIMIDAZOLE

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The EPR spectra of the dianion radicals of 5(6)-nitro-2-(4-aminophenyl)benzimidazole (I), 5(6)-nitro-2-phenylbenzimidazole (II), 5(6)-nitro-2-(4-nitrophenyl)benzimidazole (III), 5(6)-nitro-2-(3-nitrophenyl)benzimidazole (IV), and 2-(4-nitrophenyl)benzimidazole (V), obtained by electrochemical reduction in dimethylformamide (DMF) in a Bu_4NClO_4-base electrolyte in the presence of Bu_4NOH (VI), were studied. Under the influence of VI, these compounds split out a proton from the imidazole ring and give anions I-V, which are capable of adding an electron reversibly. It was shown that the unpaired electron in I and II is localized in the benzimidazole system and that the splitting of the nitrogen atom of the nitro group does not depend significantly on the substituent in the phenyl ring. The introduction of a nitro group in the phenyl ring (III-V) leads to localization of the unpaired electron on it. The nature of the substituent in the benzimidazole system has a significant effect on the splitting constant for the nitrogen atom of the nitro group.

2-Phenylbenzimidazoles and particularly their nitro derivatives contain an "acidic" hydrogen atom attached to the nitrogen atom of the imidazole ring and readily form the corresponding anions [1]. The electrochemical reduction of these anions in dimethylformamide (DMF) proceeds with the reversible transfer of one electron and leads to the formation of dianion radicals [2]. A study of the distribution of the spin density of the unpaired electron in such radicals seems of interest in order to establish the reactivities of the indicated compounds and the effect of substituents.

The electrochemical reduction of nitro-substituted phenylbenzimidazoles in the resonator of an EPR spectrometer in the presence of an alkaline agent showed that in all of the investigated cases one observes an intense and sufficiently resolved EPR signal (the spectrum of the dianion radical of I is presented in Fig. 1 as an example), the character of which is determined primarily by the position of the substituent (the nitro group). In the spectrum of the dianion radical of II the hfs constant for the nitrogen atom of the nitro group (a_5 = 14.4 Oe) has a very high value; this is evidently associated with the quinoid structure formed due to the negative charge of the benzimidazole system. A similar increase in the constant is observed, for example, for p-nitrophenoxides [3]. The introduction into the phenyl ring of a donor substituent such as NH_2 (I) leads only to a slight increase in the constant for the nitrogen atom. At the same time, splitting from the hydrogen atoms of the phenyl ring cannot be isolated in the spectra. This constitutes evidence for the absence of direct conjugation in the I and II molecules. Replacement of the amino group by a nitro

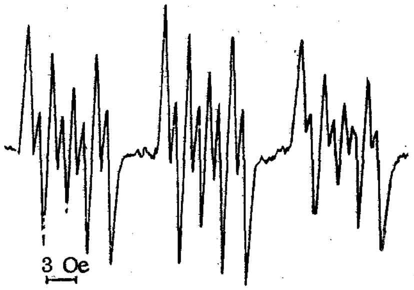

Fig. 1. EPR spectrum of the dianion radical of 5(6)-nitro-2-(4-aminophenyl)benzimidazole in dimethylformamide.

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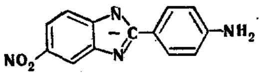
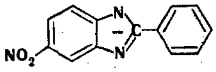
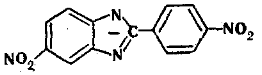
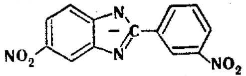
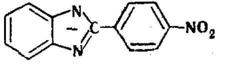
TABLE 1. Splitting Constants in the EPR Spectra of Nitro Derivatives of 2-Phenylbenzimidazole Obtained by Electrochemical Reduction in Dimethylformamide in the Presence of Tetra-n-butylammonium Hydroxide

№	Compound	Splitting constants, Oe								
		a_4	a_5	a_6	a_7	a_2'	a_3'	a_4'	a_5'	a_6'
I		2,7	14,7	4,9	1,3	—*	—	—	—	—
II		2,3	14,4	5,2	1,3	—	—	—	—	—
III		—	—	—	—	0,7	3,5	10,0	3,5	0,7
IV		—	—	—	—	4,0	12,3	4,0	1,3	4,7
V		—	—	—	—	1,1	4,0	11,5	4,0	1,1

*The constants are less than 0.3 Oe.

group (III) leads to pronounced redistribution of the density of the unpaired electron in the radical; the density is localized primarily in the phenyl part of the molecule (Table 1). In addition to this, the splitting constant for the nitrogen atom of the nitro group of the phenyl ring (III) is smaller than the corresponding constant in nitrobenzene [4] (a_N = 10.6 Oe), despite the donor properties of the benzimidazole anion. In contrast to III, in the case of IV, in which the nitro group is located in the meta position, the splitting for the nitrogen atom is considerably larger (Table 1). It may therefore be assumed that in this case (for III) there is conjugation between the nitro groups.

In fact, replacement of the nitro group in benzimidazole by a hydrogen atom (V) leads to an appreciable increase in the splitting for the nitrogen atom of the nitro group (a_4 = 11.5 Oe).

Thus the studies show that, depending on the position and number of nitro groups in the investigated dianion radicals (I-V), the unpaired electron may occupy a vacant orbital in both the imidazole system and in the phenyl ring. In conformity with this, the effect of a substituent in the benzimidazole system on the splitting constant for the nitrogen atom of the nitro group of the phenyl ring is greater than in the reverse case.

EXPERIMENTAL

Pure grade dimethylformamide (DMF) was purified by the method in [5] immediately prior to the preparation of the solutions. The 2-phenylbenzimidazoles* were crystallized twice from ethanol. The concentration of the investigated compounds was $5 \cdot 10^{-4}$ mole/liter, and the concentration of tetra-n-butylammonium hydroxide was $(1\text{-}1.5) \cdot 10^{-3}$ mole/liter.

The EPR spectra were recorded with a Rubin radiospectrometer at room temperature. The electrochemical generation of the dianion radicals was accomplished by the method in [6] in DMF in a 0.1 N tetra-n-butylammonium perchlorate base electrolyte. The EPR sectra were analyzed by the methods in [7, 8].

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DIPYRAZOLINYL-SUBSTITUTED 1,4-DISTYRYLBENZENES

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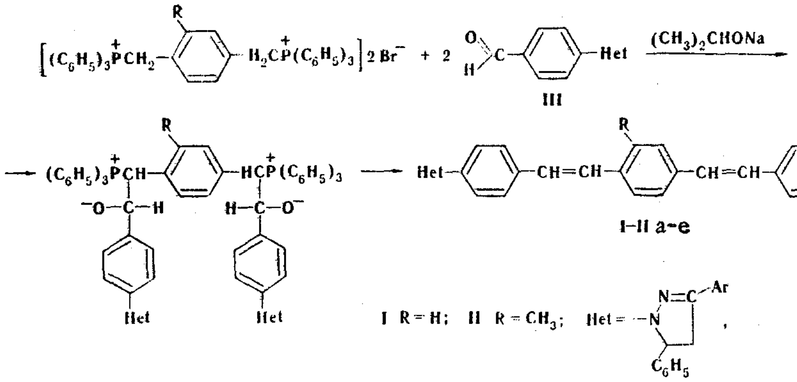
A number of dipyrazolinyl-substituted 1,4-distyryl- and 1,4-distyryl-2-methylbenzenes — new luminophores that have intense yellow-green luminescence — were obtained by the Wittig reaction by refluxing 1-(4-formylphenyl)-3-aryl-5-phenyl-2-pyrazolines and aromatic bisphosphonium salts in isopropyl alcohol in the presence of sodium isopropoxide. The low reactivities of the aldehydes used and the predominant formation of trans isomers in the Wittig reaction are noted. Data from the IR and electronic absorption spectra and the fluorescence spectra of the synthesized compounds are presented.

The introduction of a 3-aryl-2-pyrazolin-1-yl residue into 1,2-diarylethylenes or their heterocyclic-substituted derivatives makes it possible to obtain effective organic luminophores that have longer-wavelength luminescence than their structural fragments [1, 2]. In order to search for new luminophores with yellow-green luminescence it seemed expedient to synthesize a number of dipyrazolinyl-substituted derivatives of 1,4-distyrylbenzene (Ia-e).

It is known that a substantial deficiency of luminophores with molecules with linear structures that limits the possibilities of their practical application is their low solubility in organic media [3]. This deficiency can be eliminated to a certain extent in a number of 1,4-distyrylbenzenes by the incorporation of methyl groups in the central benzene ring [4]. In this connection, we synthesized II in addition to luminophores I.

Luminophores I and II were synthesized by the Wittig reaction starting from the corresponding phosphonium salts and 1-(4-formylphenyl)-3-aryl-5-phenyl-2-pyrazolines (III) via the scheme



See Table 1 for the Ar values.

Attempts to carry out the reaction under traditional conditions [5], i.e., in methanol at room temperature and with the use of sodium methoxide for the conversion of the phosphonium salt to the corresponding intermediate phosphorane [6], showed that aldehydes III do not

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