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ELECTRON-ACCEPTOR PROPERTIES OF N,N'-ARYLENEBISPHTHALIMIDES

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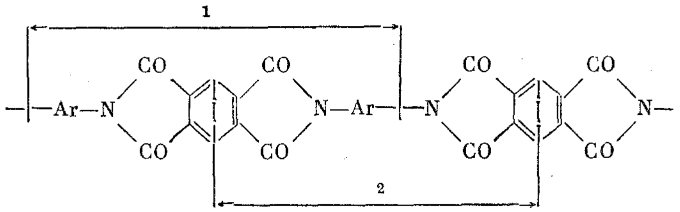
UDC 541.138:541.27:547.584

Aromatic polyimides are one of the classes of polyheteroarylenes that are of the greatest practical importance. The polymer chains of polyimides obtained from dianhydrides of aromatic tetracarboxylic acids and aromatic diamines consist of regularly alternating structural elements that differ in electronic nature. Correspondingly, in the polyimide chain, we can formally distinguish two mutually overlapping sections: an N,N'-diaryldiimide section (1) and an N,N'-arylenebisphthalimide section (2).



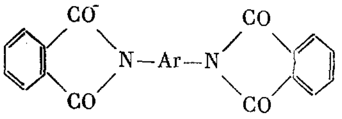
The electron-acceptor properties of polyimides with an arylene grouping Ar with a "cardo" [1], are completely determined by the N,N'-diaryldiimide section and are independent of the structure of the arylenebisphthalimide section of the polyimide chain. In these polymers, however, the conjugation chain is interrupted by the cardo grouping; and the possibility of extending this conclusion to other polyimides with an arylene fragment of a diamine having a system of conjugated bonds does require further examination. Polyamides of this type are, as a rule, insoluble, so that they are difficult to investigate by direct methods. Therefore, it becomes important to investigate the electron-acceptor properties of compounds that model the arylenebisphthalimide section of the polyamide chain. In this connection, we have carried out a polarographic study of the electron-acceptor properties of N,N'-arylenebisphthalimides having various arylene groups with the system of conjugated bonds.

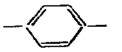
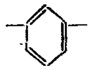
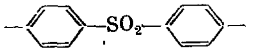
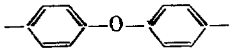
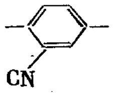
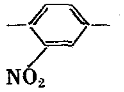
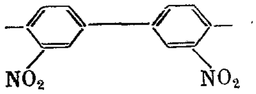
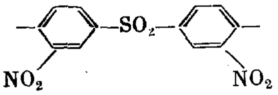
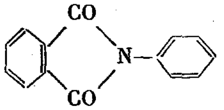
As objects of investigation we selected arylenebisphthalimides with substantial differences among themselves in the character of conjugation of the phthalimide fragments and in the degree of electron-acceptor capability of the arylene fragments of the diamines. From the results of this study, which are presented in Table 1, it follows that the electron affinity of the arylenebisphthalimides with unsubstituted arylene fragments is very little different from the electron affinity of N-phenylphthalimide (EA = 1.01 eV), and is at most ∼0.06 eV greater. When the nitrile group, a weak acceptor, is introduced into the arylene fragment, the electron affinity becomes 0.13 eV greater than that of phenylphthalimide; this increase, however, is substantially less than the effect of a nitrile group substituent when it participates in the overall conjugation system of the molecule [2]. A significant strengthening of the electron-acceptor properties is observed only in the case of the arylenebisphthalimides containing arylene fragments with nitro groups, which are strong acceptors; here, the electron affinity is 0.4-0.5 eV greater than that of phenylphthalimide.

L. Ya. Karpov Physical Chemistry Institute, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 313-315, February, 1983. Original article submitted April 15, 1982.

0568-5230/83/3202-0279$07.50

TABLE 1. Electron-Acceptor Properties of N,N'-Arylenebisphthalimides



—Ar—	$E_{1/2}$, V	$\Delta E/\lg \frac{i_d}{\Delta i}$, mV	EA, eV
	1,85	95	1,00
	1,84	100	1,01
	1,78	61	1,07
	1,84	66	1,01
	1,71	42	1,14
	1,40	60	1,45
	1,36	56	1,49
	1,29	112	1,56
	1,84	53	1,01

In [1, 3, 4], it was shown theoretically and experimentally that phthalimide groups and N-aryl substituents can enter into a weak interaction through a mechanism of π-conjugation with each other, leading to a small increase in the electron affinity of N-arylphthalimides in comparison with unsubstituted phthalimides [1]. From the results that have been obtained, it follows that in arylenebisphthalimides with arylene fragments that do not have any strong electron acceptor (of the type of the nitro group) as a substituent, effective π-conjugation between the phthalimide groups through the π-system of the arylene fragment is essentially absent, and their electron-acceptor properties are actually determined by the n-arylphthalimide fragment alone. This effect may be related to the significant noncoplanarity of these molecules [5, 6], which leads to a sharp limitation of the effectiveness of π-conjugation, and also to quantum-chemical effects. In particular, our calculation of the molecules of N-phenylphthalimide and N,N'-p-phenylenebisphthalimide in the HMO approximation has shown that the energies of the LUMOs of these molecules coincide in magnitude, and hence their electron affinities must also be equal.

The increase in electron affinity of N,N'-arylenebisphthalimides with arylene fragments containing nitro groups, in comparison with N-phenylphthalimide, is probably unrelated to interaction of the phthalimide rings with the arylene fragment and the formation of a single system of π-conjugation (first of all with the formation of a single LUMO), but rather is related to the high electron-acceptor capability of the nitro-substituted arylene fragments, which in this particular case determine the electron-acceptor properties of these molecules.

EXPERIMENTAL

The majority of the N,N'-arylenebisphthalimides were obtained by the standard procedure (7) from phthalic anhydride and the corresponding aromatic diamines in dry, argon-saturated N-methylpyrrolidone with the total concentration of reactants approximately 10%. By these methods, the following were obtained: N,N'-p-phenylenebisphthalimide, mp 366-367°C; N,N'-n-phenylbisphthalimide, mp 319-321°C; N,N'-4,4'-diphenylenoxidebisphthalimide, mp 291°C; N,N-4,4'-diphenylenesulfonebisphthalimide, mp 321°C; N,N'-2-nitro-p-phenylenebisphthalimide, mp

260-260.5°C; N,N'-2-cyano-p-phenylenebisphthalimide, mp 308°C. The compounds were purified by recrystallization and were identified on the basis of their IR spectra. The N,N'-2,2'-dinitro-4,4'-diphenylenesulfonebisphthalimide and the N,N'-2,2'-dinitro-4,4'-diphenylenebisphthalimide were synthesized from potassium phthalimide with 3,3'-dinitro-4,4'-dichlorodiphenylenesulfone and 3,3'-dinitro-4,4'-dichlorodiphenylene, respectively, in DMSO, at respective temperatures of 120° and 180°C. The first of these compounds was recrystallized from CH_3COOH and then from dimethylacetamide with water, mp 235°C; the second was recrystallized from nitrobenzene with activated carbon, mp 360°C.

The electron-acceptor properties of these compounds were studied polarographically. The first half-wave reduction potentials were determined, and these potentials were used to evaluate the electron affinity in relation to p-chloranil, which was selected as the standard acceptor for comparison (EA = 2.45 eV [8]). The N,N'-arylenebisphthalimides were studied by the classical polarographic method, using an LP-7 polarograph, in a thermostatted cell at 25°C in a medium of anhydrous DMFA from which the atmospheric oxygen has first been removed by bubbling with dry Ar for a period of 1 h. The polarograms were recorded at a potential sweep rate of 0.2 or 0.1 V/min. The dropping period of the capillary with a potential of 1.5 V was 2.67 sec, and the rate of mercury discharge was 0.153 g/min. The potentials were measured by a pX-meter electrometer relative to a silver perchlorate comparison electrode (0.1 N Ag^+, acetonitrile/Ag); support salt 0.1 M tetrabutylammonium perchlorate.

CONCLUSIONS

The electron-acceptor properties of N,N'-arylenebisphthalimides and hence those of aromatic polyimides are determined solely by the arylphthalimide fragment and are practically independent of the structure of the arylene fragments except when they contain the strongly electron-accepting nitro group.

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