valence isomerization was discovered and studied (via the UV and IR spectra) for the first time on the example of these compounds.

2. The existence of a dynamic equilibrium between both valence isomers was established. The equilibrium is shifted toward the δ-aminodienones with increase in the temperature, and also the dielectric constant of the solvent and its capacity for specific solvation. An especially strong change occurs when the amount of water in organic solvents is increased.

3. The dienic δ-amino-γ-methyl(phenyl)carbonyl compounds exhibit a clearly expressed solvatochromism, the nature of which depends on the valence isomerization.

4. The aggregate state can exert an effect on the existence of the δ-aminodienones as either valence isomer; 6-dimethylamino-3-carbomethoxy-5-methyl-3,5-hexadien-2-one in the crystalline state represents the dienone, while in the molten state it represents the 2H-pyran.

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REACTION OF PHTHALODINITRILE WITH o-PHENYLENEDIAMINE AND 1,2,4-TRIAMINOBENZENE

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In a previous communication [1] we discussed in detail the condensation of phthalodinitrile (I) with aromatic o-cyanoamines and, in particular, with 3,3'-dicyano-4,4'-diaminodiphenylmethane, as a result of which a macroheterocyclic compound, containing condensed isoindole and quinazoline rings in its composition, is formed in high yield.

It seems very interesting to obtain macroheterocycles from (I) that also contain other condensed rings in their composition. The present paper is devoted to the synthesis of macroheterocyclic compounds, containing condensed isoindole and benzimidazole rings, from (I) and bis(o-phenylenediamines).

The possibility of forming the following system of condensed rings was first studied on the example of the model reaction of (I) with o-phenylenediamine (III):

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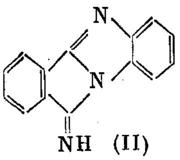
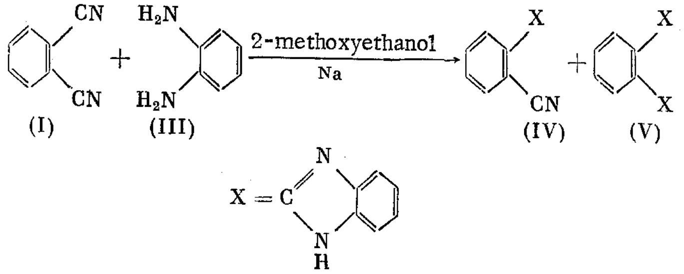


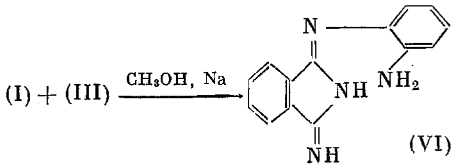
(II)

Previously [2] it was shown that the reaction products of (I) with (III) in refluxing 2-methoxyethanol, in the presence of sodium 2-methoxyethoxide, is not (II), but instead a mixture of (IV) and (V):



It is possible that the (II), formed under these reaction conditions, is rapidly isomerized to (IV) or else reacts with (III) to give (V).

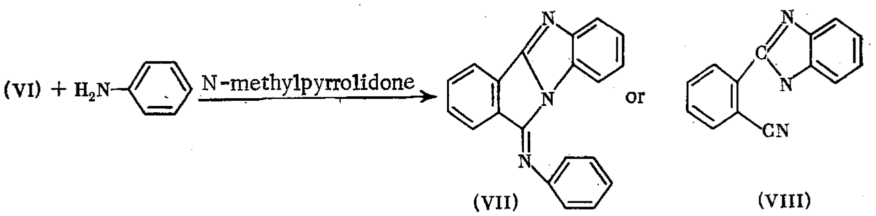
To verify this assumption we condensed (I) with (III) in methanol, in the presence of MeONa, at 20°C [1, 3], which led to (VI):



The structure of (VI) is confirmed by the elemental analysis and IR spectral data. The IR spectrum of (VI) has the absorption bands (ν, cm^{-1}): 3440, 3330 (NH_2), 3200 (NH), 1660 (C=N).

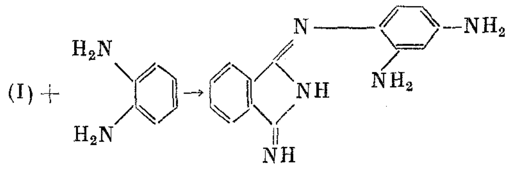
Based on the TLC and IR spectral data, when (VI) is heated at 220-250° in an argon stream it is converted to a mixture of (II) and (IV), and when reacted with (III) in N-methylpyrrolidone at 200° it is converted to (V). These data confirm the assumption that (II) is isomerized to (IV) and that (V) is formed when (II) is reacted with (III).

The obtained results permit the conclusion that the system of condensed isoindole and benzimidazole rings cannot be obtained when (I) is condensed with (III), and consequently also with bis(o-phenylenediamines). It is possible that the conversion of (II) to (IV) or (V) is caused by the presence of an exocyclic NH group in this compound [4]. Consequently, it seemed interesting to study the possibility of similar reactions when a substituted NH group is present in compound (II). For this purpose we condensed (VI) with aniline in N-methylpyrrolidone at 200°. The reaction products were studied employing elemental analysis, TLC, and IR and mass spectrometry. Based on the TLC data, only one product was obtained as a reaction result, having in its mass spectrum a molecular ion M^+ with m/e 295, which could correspond to either compound (VII) or (VIII).



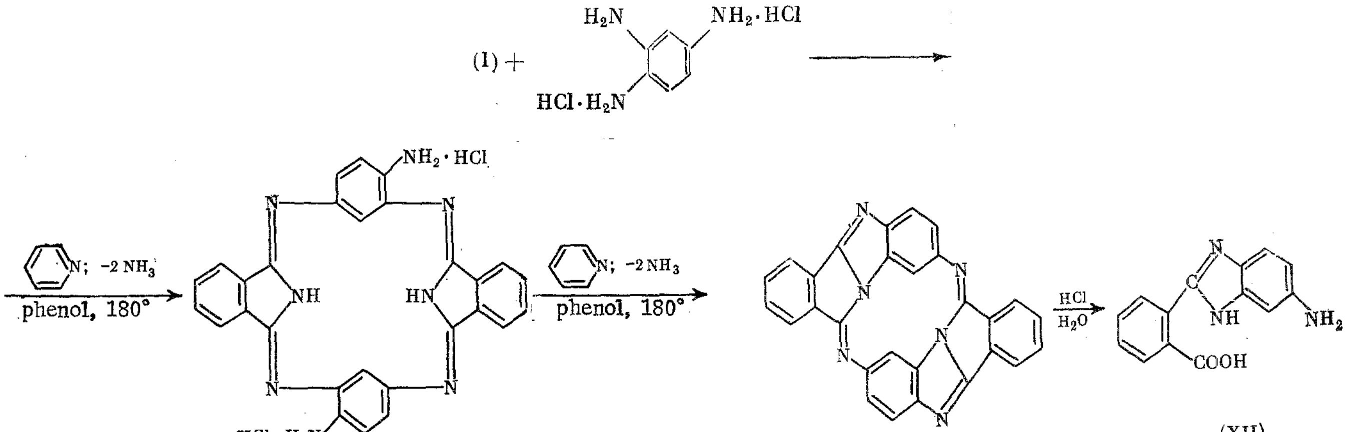
The absence of the 2200 cm^{-1} band (C≡N) in the IR spectrum makes it possible to unequivocally choose compound (VII). Based on the TLC and IR spectral data, new products are not formed when (VII) is heated under the conditions of isomerizing (II) to (IV), which indicates that (VII) is stable at 250°. We selected 1,2,4-triaminobenzene (TAB) as the starting compound for the synthesis of a macroheterocyclic compound.

Starting with the data on the basicity of the amino groups in aromatic multiatomic amines [5, 6], which for TAB probably decreases in the order 1 > 4 > 2, and the mechanism for the reaction of (I) with amines [7], it is possible for (IX) to be an intermediate reaction product which can be expected to undergo transformations similar to the transformations of



(IX)

(II) to (IV) and (V). In order to prevent this it is necessary that one of the o-phenylenediamine groups be unreactive when forming the macroheterocycle. Consequently, to synthesize the macroheterocycle we used the TAB as the 1,4-dihydrochloride. The HCl groups of TAB were neutralized during synthesis in two steps, on the assumption that the amino group in the 4 position is neutralized first [6]. On conclusion of forming the macroheterocycle [7] the amino group in the 1 position was neutralized, the reaction of which with the NH group of the isoindole ring, judging by the NH_3 liberation, led to the quantitative formation of the following system of condensed heterocycles:



(X) (XI) (XII)

The structure of (XI) is confirmed by the elemental analysis and IR spectral data. The absorption bands of the NH and NH_2 groups are completely absent in the IR spectrum of (XI), but bands at 1660 and 1620 cm^{-1} (C=N) are present. In addition, the structure of (XI) was confirmed by studying the products of its hydrolysis with 5% HCl solution: only one product was isolated by TLC, which has an M^+ with m/e 254 in its mass spectrum; its IR spectrum has bands at 3440, 3330 (NH_2), 3200 (NH), 1690 (C=O), and 1620 cm^{-1} (C=N), which makes it possible to assign it the structure of (XII). There is no doubt that (XII) can only be the hydrolysis product of (XI) [1, 8].

As a result, the reaction of (I) with 1,2,4-triaminobenzene dihydrochloride gave a macroheterocyclic compound that contains condensed isoindole and benzimidazole rings in its composition. It may be assumed that replacing (I) by the tetranitriles of aromatic tetracarboxylic acids in the reaction with TAB will make it possible to obtain polymers, the structure of whose unit link resembles that of (XI).

EXPERIMENTAL

The mass spectra were taken on the AEI MS-30 instrument; the direct insertion temperature was 100-380°, that of the ionization chamber was 350°, and the energy of the ionizing electrons was 70 eV. The IR spectra were taken on an IKS-22 instrument either as a hexachlorobutadiene or Nujol mull.

The starting (I), (III), and TAB were purified by known procedures. The employed (I) had mp 141° (cf. [9]), (III) had mp 103° (cf. [10]), and TAB had mp 100° (cf. [11]).

Condensation of Phthalodinitrile (I) with o-Phenylenediamine (III). A solution of 1.28 g (0.01 mole) of (I) and 1.08 g (0.01 mole) of (III) in 30 ml of abs. MeOH, containing 0.02 g of Na, was stirred for one day at 20°. The reaction mixture was poured into water, and the obtained precipitate was filtered and dried in vacuo over P_2O_5 to give 2.0 g (85%) of (VI), mp 155-157°. Found: C 70.81; H 5.39; N 23.19%. $C_{14}H_{12}N_4$. Calculated: C 71.19; H 5.08; N 23.73%.

Heating of (VI) in Argon. The compound was heated in an argon stream at 220-250° and the pyrolysis products were sublimed. Based on the TLC data (Silufol UV-254, eluant = benzene—acetone, 1:1 by volume), a mixture of (II) and (IV) was obtained.

Condensation of (VI) with Aniline. A solution of 2.36 g (0.01 mole) of (VI) and 0.94 g (0.01 mole) of aniline in 50 ml of abs. N-methylpyrrolidone was heated at 200° until the NH_3 evolution ceased. The (VI) conversion was 98%. The reaction mass was cooled and the reaction products were precipitated with water. Recrystallization from DMF gave 2.2 g (75%) of (VII), mp 314-315°. Found: C 81.11; H 4.65; N 14.02%. $C_{20}H_{13}N_4$. Calculated: C 81.36; H 4.41; N 14.24%.

Condensation of (I) with 1,2,4-Triaminobenzene (TAB) Dihydrochloride. A mixture of 1.28 g (0.01 mole) of (I), 1.96 g (0.01 mole) of TAB dihydrochloride, 0.79 g (0.01 mole) of pyridine, and 0.5 g of LiCl in 100 ml of phenol was heated at 180° until the NH_3 evolution ceased, after which another 0.79 g (0.01 mole) of pyridine was added and the heating was continued until the NH_3 evolution ceased. Based on the amount of evolved NH_3, the (I) conversion was 98%. The reaction mass was poured into MeOH, and the obtained precipitate was filtered and dried. The reaction product was chromatographed on a silica gel column (eluant = DMF) to give (XI) in 90% yield. Found: C 77.78; H 3.85; N 19.12%. $C_{28}H_{14}N_6$. Calculated: C 77.40; H 3.25; N 19.34%.

CONCLUSIONS

1. The condensation of phthalodinitrile with o-phenylenediamine and aniline gave a compound that contains condensed isoindole and benzimidazole rings.

2. The condensation of phthalodinitrile with 1,2,4-triaminobenzene dihydrochloride in phenol, in the presence of pyridine, gives in high yield a macroheterocyclic compound that contains condensed isoindole and benzimidazole rings in the macroheterocycle.

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