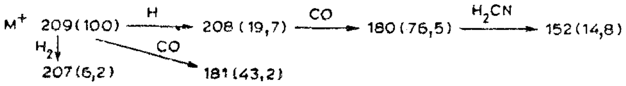
mp 209-210°C. IR spectrum (in mineral oil): 1680 (C=O) and 3400 cm^{-1} (NH); (in chloroform): 1710 (C=O) and 3460 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 227 (4.35) and 298 nm (4.31). Found: C 70.6; H 4.6; N 5.5%. $C_{15}H_{11}NO_3$. Calculated: C 71.1; H 4.3; N 5.5%.

5-Phenoxyindole (IX). A 2.5-g (0.01 mole) sample of VIII was heated at 240°C until CO_2 evolution ceased (7-10 min), after which the residue was purified with a column (elution with benzene) to give 0.8 g (40%) of a product with mp 110-111°C and Rf 0.66 (in chloroform). IR spectrum (in mineral oil): 3440 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 227 (4.37) and 277 nm (3.82). Found: C 80.7; H 5.0; N 7.0%; M^+ 209. $C_{14}H_{11}NO$. Calculated: C 80.4; H 5.2; N 6.7%; M 209.

Fragmentation scheme:



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INVESTIGATION OF THE STATE OF A SYMMETRICAL tert-BUTYL-SUBSTITUTED MACROHETEROCYCLIC COMPOUND IN SOLUTION BY PMR SPECTROSCOPY

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The PMR spectra of the macroheterocyclic compound obtained by the reaction of 5-tert-butyl-1,3-diiminoisoindoline with 1,3-phenylenediamine in refluxing butyl alcohol and purified by chromatography on aluminum oxide were recorded. It is shown that the compound does not contain a unified conjugated macroring system. The dependence of the chemical shift of the protons of the endocyclic imino groups on the nature of the solvent was investigated. It is shown that the formation of compound—solvent intermolecular hydrogen bonds is complicated by steric factors.

Macroheterocyclic compounds (MHC) that have structures similar to that of phthalocyanine, in which one or two isoindole fragments are replaced by residues of aromatic amines, find practical application as stabilizers and dyes for polymeric materials [1, 2]; this is responsible for the interest in the structures of these compounds and the peculiarities of the behavior of their molecules in solutions.

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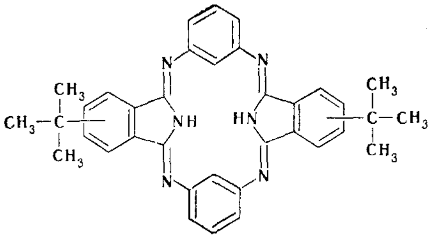
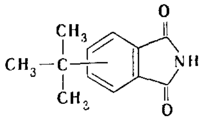
TABLE 1. Chemical Shifts of the Resonance Signals of I and II in Dimethyl Sulfoxide at 30°C

Compound	Chemical shifts, ppm, relative to hexamethyldisiloxane		
	NH	aromatic protons	aliphatic protons
I	10,21	7,99—6,51	1,37
II	11,11	7,83—7,60	1,33

The NMR spectra of metal-free macroheterocycles have not been previously studied, whereas the character of the electronic interactions in such molecules [3] makes them interesting subjects for structural studies. The introduction of tert-butyl groups in the phenyl rings of isoindole fragments of macroheterocyclic compounds imparts to them the solubility in organic solvent that is necessary for the use of PMR spectroscopy. We used 4-tert-butylphthalimide as the model compound and for the assignment of the signals in the spectra.


I


II

The PMR spectra of macroheterocycle I and 4-tert-butylphthalimide (II) include a singlet at strong field due to the protons of the tert-butyl groups and signals at 6-8 ppm due to the absorption of a strongly coupled spin system of aromatic protons. The broad signal at weak field, which vanishes when heavy water or base is added, can be assigned to the imine protons of I and II. The integral intensities of the resonance signals confirm the assignments made above. The parameters of the PMR spectra are presented in Table 1.

During a study of the PMR spectra of macroheterocycle I in dimethyl sulfoxide (DMSO) and acetone our attention was drawn to the fact that the signal of the endocyclic imine protons is found at very weak field (Table 1) as compared with the signal of tert-butyl-substituted phthalocyanine (—5.2 ppm relative to hexamethyldisiloxane in CCl_4) [4]. It is known that the presence of a resonance signal of phthalocyanine at such strong field is explained by shielding of the imine protons due to the presence of induced ring currents of a unified π-electron macroring system [5]. However, the appearance of an NH signal of macroheterocycle I at weak field constitutes evidence for the absence of a unified conjugated macroring π system of this compound, despite the fact that it formally obeys the Hückel rule (18 π electrons). This conclusion is confirmed by data from electronic spectroscopy [6] and the results of x-ray diffraction studies of such compounds [7].

Of particular interest is the dependence of the chemical shift of the signal of the imine protons of I and II on the nature of the solvent. It follows from the data presented in Table 2 that the greatest shift of this signal of 4-tert-butylphthalimide to weak field relative to CCl_4, which is characteristic for the formation of an intermolecular hydrogen bond [8], is observed in the case of the strongly solvating pyridine, whereas the NH signal of I in pyridine and p-dioxane is covered by the absorption of the aromatic protons ($\delta_{NH} < 8$ ppm). At the same time, acetone and DMSO, which have molecules with smaller volumes as compared with pyridine and p-dioxane, give rise to an appreciable shift of the NH resonance signal, which constitutes evidence for considerable intermolecular specific interactions.

This experimental fact evidently indicates that the formation of a hydrogen bond between the solvent molecules and the imine protons of macroheterocycle I is accompanied by appreciable steric hindrance due to steric shielding of the protons mentioned above. This conclusion is confirmed by the character of the dependence of the NH chemical shift of I on the mole fraction of DMSO in the p-dioxane—DMSO mixture presented in Fig. 1.

TABLE 2. Dependence of the NH Chemical Shift (ppm) of I and II on the Nature of the Solvent at 30°C

Compound	CCl_4	p-Dioxane	Pyridine	Acetone	DMSO
I	<8*	<8*	<8*	9,77	10,21
II	8,43	9,56	12,36	9,78	11,11

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*The NH resonance signal is covered by the absorption of the aromatic protons.

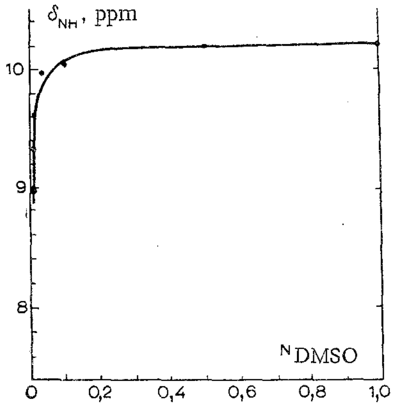

Fig. 1. Dependence of the NH chemical shift of I on the mole fraction of DMSO in the p-dioxane—DMSO mixture (the concentration of I was 0.18 mole/liter).

EXPERIMENTAL

Macroheterocyclic compound I was obtained by reaction of 5-tert-butyl-1,3-diiminoisoindoline [9] with 1,3-phenylenediamine in refluxing butyl alcohol and was purified by chromatography on aluminum oxide. 4-tert-Butylphthalimide was synthesized by the method described in [10]. The solvents were purified by the standard method [11].

The PMR spectra were recorded with an RYa-2305 spectrometer (60 MHz).

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