extracted with ether, and the extract was dried with sodium sulfate and distilled to remove the ether. Benzene (10 ml), 1 g of pyridine, and 0.6 g of acetyl chloride were added to the residue, and the mixture was refluxed for 30 min. The usual workup gave 0.46 g (11%) of N-acetyl-2-isopropylaminobenzophenone with mp 138-139°C (from benzene with petroleum ether). Found: C 76.8; H 7.0; N 4.9%. $C_{18}H_{19}NO_2$. Calculated: C 76.8; H 6.8; N 5.0%. No melting point depression was observed for a mixture of this product with the substance obtained by acetylation of 2-isopropylaminobenzophenone. The IR spectra of the two samples were identical.

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2-N-IMIDAZOLYL- AND 2-N-PYRAZOLYL-1,3-INDANDIONES

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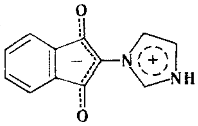
It was shown by spectroscopic methods that 2-N-imidazolyl-, 2-N-(N-methylimidazolyl)-, and 2-N-(N-methylpyrazolyl)-1,3-indandiones exist in the form of inner salts, whereas 2-N-pyrazolyl-1,3-indandione exists in the form of an enol with an intramolecular hydrogen bond.

The reaction of 2-dicyanomethylene-1,3-indandione oxide with six-membered heteroaromatic compounds is a good method for the preparation of onium betaines of 1,3-indandione [1, 2], which are of interest as components for the preparation of charge-transfer complexes (CTC) [3] and as subjects for the study of the electrophysical properties of the solid state (the semiconductor properties and photosensitivities) [4].

2-N-Imidazolyl-1,3-indandione (I) and 2-N-pyrazolyl-1,3-indandione (II) are readily formed in the reaction of 2-dicyanomethylene-1,3-indandione oxide with imidazole and pyrazole.

In order to establish their structures and to characterize their reactivities we studied the salt formation and alkylation, recorded the electronic, IR absorption, and PMR spectra, and determined the acidity constants (pK_a) and ionization potentials (IP).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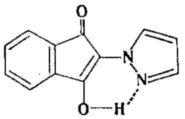
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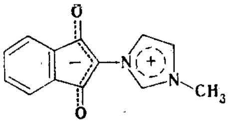
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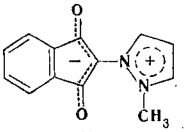
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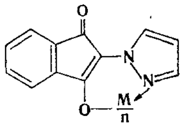
Va-d

V a M=Cu, b Co, c Ni, d Mn

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TABLE 1. PMR Spectra of I-IV

Compound	Solvent	Chemical shifts, ppm					
		phthaloyl protons	heteroring protons				N-CH_3 protons
			2'-H	3'-H	4'-H	5'-H	
I	DMSO	7,29—7,33	9,46	—	7,66	8,25	—
	$CDCl_3$	7,34	9,55	—	7,14	8,62	—
III	DMSO	7,31—7,35	9,57	—	7,70	8,30	3,89
	$CDCl_3$	7,34—7,36	9,64	—	7,03	8,71	3,89
II	$CDCl_3$	7,30	—	7,62	7,38	8,42	—
IV	DMSO	7,39—7,43	—	8,35	6,90	8,55	3,90
	$CDCl_3$	7,44—7,47	—	7,77	6,68	7,87	4,03

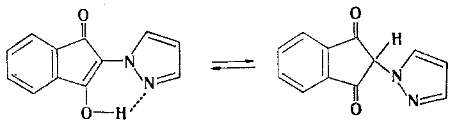
TABLE 2. IR Spectra of I-IV (1400-1800 cm^{-1})

Compound	ν, cm^{-1} (absorption, %), mineral oil
I	1661 (17), 1622 (36), 1584 (44), 1534 (50)
II	1708 (60), 1658 (62), 1606 (54), 1512 (41)
III	1658 (20), 1620 (62), 1585 (75), 1555 (77)
IV	1660 (8), 1623 (34), 1578 (34), 1516 (11)

The alkylation of I and II with dimethyl sulfate leads to the formation of 2-N-(N-methylimidazolia)- and 2-N-(N-methylpyrazolia)-1,3-indandione betaines (III and IV). Betaine III was also obtained by the reaction of 2-dicyanomethylene-1,3-indandione oxide with N-methylimidazole. The reaction of 2-dicyanomethylene-1,3-indandione oxide with N-methylpyrazole does not occur, evidently because of steric hindrance. The PMR spectra of I-IV are presented in Table 1.

It is apparent from Table 1 that a change in the chemical shifts of the protons of the heteroring as a function of the solvent is observed for all of the investigated compounds. The 2'-H and 5'-H protons (I and III) experience weak-field shifts in $CDCl_3$ as compared with the spectra in d_6-DMSO; this can be explained by the formation of an intramolecular C—H···O hydrogen bond between the 2'-H and 5'-H protons and the oxygen atom of the anionic system in $CDCl_3$. In d_6-DMSO the solvation capacity of the solvent hinders the formation of intramolecular hydrogen bonds. The change in the chemical shift is just the opposite for the 4'-H proton when the solvent is replaced. Similar principles have also been observed in a study of 2-(N-pyridinia)-1,3-indandione betaine [5].

According to the data from the IR spectra, solid II exists in the enol form (Table 2). According to the data from the PMR spectra, the following equilibrium is observed in solution in $CDCl_3$:



IIa IIb

The detection in the spectrum of a signal at 5.31 ppm (Table 1), which corresponds to 2-H resonance, and a multiplet at 7.8-8.1 from the phthaloyl protons indicates the presence of diketo form IIb. The percentage of the IIb form is 25%.

In the case of IV all of the heteroring protons, including the 5'-H proton, experience a paramagnetic shift of the resonance signals in d_6-DMSO as compared with $CDCl_3$; this is due to the solvation capacity in d_6-DMSO. Intramolecular hydrogen bonds are absent in view of the evident noncoplanarity of the molecule.

Groups of bands that are characteristic for the anionic form of β-diketones are observed in the IR spectra of I, III, and IV (Table 2) [6]; this constitutes evidence for the inner-salt structure of I, III, and IV. The normal wave numbers of the vibrations of C=O and C=C bonds are observed in the IR spectrum of II; this indicates the enol structure of II with intramolecular hydrogen bonds (Table 2). The possibility of the formation of such bonds is confirmed by the production of complex metal salts Va-d.

TABLE 3. Electronic Absorption Spectra and Solvatochromism of I-IV

Compound	Solvent	λ_{max}, nm (ε)
I	Water	252 (23200), 330 (1160)i, 416—418 (1400)
	50% ethanol	253 (18000), 273 (14400), 280—284 (12000 i), 306 (3160), 317 (3000), 331 (2800), 420 (1400)
	Ethanol	253 (13200), 277 (17600), 286 (156), 307 (5000), 318 (6500), 332 (6720), 425 (1500)
	Chloroform	255 (13000), 282 (11360), 292 (11360), 310 (6400), 322 (8000), 336 (8000), 425 (2000)
II	50% ethanol	232 (27800), 252 (19000), 290 (5600), 326 (2450), 342 (2000), 402 (1000)
III	Water	251 (22400), 332 (1200) i,* 418 (1400)
	50% ethanol	252 (19000), 275 (14000), 283—287 (12000) i, 319 (4000), 333 (3400), 420 (1600)
	Ethanol	253 (13200), 279 (12000), 289 (11200), 309 (4400), 320 (5800), 334 (5600), 423 (1300)
	Chloroform	253 (15600), 287 (12800), 298 (13600), 312 (7500), 326 (11000), 340 (10800), 424 (1600)
IV	Water	242 (40000), 250 (36900), 275—280 (6500) i, 398 (1750)
	50% ethanol	244 (38000), 252 (35000), 280 (7400), 394 (1900)
	Ethanol	245 (34100), 252 (30900), 285 (7400), 392 (2000)

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*i = inflection.

TABLE 4. 2-N-Pyrazolyl-1,3-indandionates V

Compound	Crystal color	Crystallization solvent	N found, %	Empirical formula	N calc., %	Yield, %
Va	Brown	DMF	10,8	$C_{24}H_{12}CuN_4O_4$	11,5	50
Vb	Red	DMF + ethanol	11,1	$C_{24}H_{12}CoN_4O_4$	11,6	58
Vc	Dark-red	DMF + ethanol	11,0	$C_{24}H_{12}NiN_4O_4$	11,6	50
V	Dark-red	Same	11,5	$C_{24}H_{12}MnN_4O_4$	12,1	52

A low-intensity maximum at 390-430 nm, which is characteristic for the anion or enol of 1,3-indandione derivatives [7], and a number of intense maxima at 230-350 nm are observed in the electronic spectra of I-IV. In the case of inner salts I, III, and IV bands of intramolecular charge transfer from the anionic to the cationic part on the basis of solvatochromism were detected at, respectively, 277 and 286 nm for I, 279 and 289 nm for III, and 285 nm for IV (ethanol) (Table 3).

The acidity constants for I and II and their protonated forms were determined spectrophotometrically in 50% aqueous ethanol solutions. 2-N-Imidazolia-1,3-indandione (I) is an NH acid with pK_a 7.0, while 2-N-pyrazolyl-1,3-indandione (II) is an OH acid with pK_a 4.0. In an acidic medium I and II are protonated at the carbon atom in the 2 position. The pK_a values are 0.4 and —0.4, respectively, for the protonated forms of I and II.

The ionization potentials were determined by the method of charge-transfer complexes (CTC) in solution and were 7.3 for I and III, 7.6 for II, and 7.8 eV for IV. As compared with 2-N-pyridinia-1,3-indandione betaine, the acceptor imidazolium and pyrazolium parts in I, III, and IV have lower electron affinities, and this gives rise to a hypsochromic shift of the intramolecular charge-transfer band and an increase in the overall electron-donor properties, except for IV in view of the noncoplanarity of this molecule.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with IKS-14A and Specord 75-IR spectrometers. The electronic spectra were recorded with a Specord UV-vis spectrophotometer. The PMR spectra were recorded with a WH 90/DS spectrometer with hexamethyldisiloxane as the internal standard. The acidity constants were determined by S. V. Kalnin'.

2-N-Imidazolia-1,3-indandione Betaine (I). A 0.34-g (0.005 mole) sample of imidazole was added to a solution of 1.12 g (0.005 mole) of 2-dicyanomethylene-1,3-indandione oxide in 20 ml of dioxane, and the mixture was heated on a boiling-water bath for 5 min. The orange precipitate was removed by filtration and treated with 6 ml of a 5% solution of sodium hydroxide. The mixture was filtered, and the filtrate was acidified to pH 3 with dilute (1:1) hydrochloric acid to give 5.8 h (55%) of orange crystals with mp 230°C (dec., from water). Found: C 67.6; H 3.8; N 12.9%. $C_{12}H_8N_2O_2$. Calculated: C 67.9; H 3.8; N 13.2%.

2-N-Pyrazolyl-1,3-indandione (II). A mixture of 1.06 g (0.005 mole) of 2-dicyanomethylene-1,3-indandione oxide and 0.34 g (0.005 mole) of pyrazole in 15 ml of dioxane was refluxed for 20 min. It was then cooled, and II was isolated in the form of dark-red crystals with mp 188°C (from ethanol) in a yield of 0.72 g (68%). Found: C 67.8; H 3.8; N 13.1%. $C_{12}H_8N_2O_2$. Calculated: C 67.9; H 3.8; N 13.2%.

2-N-(N-Methylimidazolia)-1,3-indandione Betaine (III). A) A 0.4-ml (0.005 mole) sample of N-methylimidazole was added to a solution of 1.12 g (0.005 mole) of 2-dicyanomethylene-1,3-indandione oxide in 20 ml of dioxane, and the mixture was heated for 5 min. Workup gave 0.85 g (75%) of betaine III in the form of orange crystals with mp 273-275°C (dec., from water). Found: C 64.2; H 4.4; N 12.1%. $C_{13}H_{10}N_2O_2$. Calculated: C 64.6; H 4.4; N 12.4%.

B) A 0.3-ml (3.2 mmole) sample of dimethyl sulfate and a 10% solution of potassium hydroxide were added to a mixture of 0.53 g (2.5 mmole) of betaine I, 0.14 (2.5 mmole) of potassium hydroxide, and 10 ml of water until the mixture was alkaline, after which betaine III was removed by filtration. The yield was 0.45 g (79%).

2-N-(N-Methylpyrazolia)-1,3-indandione Betaine (IV). A solution of 1.06 g (0.005 mole) of II in 7 ml of dimethyl sulfate was heated on a boiling-water bath for 2 h, after which the mixture was made alkaline with a 20% solution of sodium hydroxide (∿20 ml) and extracted with chloroform. The chloroform was removed to give 0.8 g (65%) of lemon-yellow crystals of betaine IV with mp 144°C (from benzene). Found: C 64.3; H 4.3; N 12.2%. $C_{13}H_{10}N_2O_2$. Calculated: C 64.6; H 4.4; N 12.4%.

2-N-Pyrazolyl-1,3-indandionates (Va-d). Salts Va-d were obtained by mixing ethanol solutions of II (2.5 mmole) with the following aqueous solutions: a) copper sulfate; b) cobalt chloride; c) nickel chloride; d) manganese sulfate (1.3 mmole). The characteristics of salts Va-d are presented in Table 4.

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