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# STABILITY AND SPECTRAL CHARACTERISTICS OF 3-METHYL-3-PHENYL-1-ARYLPHTHALYL IONS

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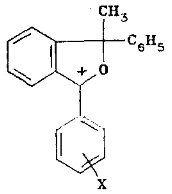
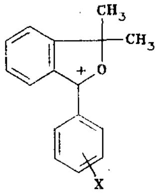
3-Methyl-3-phenyl-1-aryphthalyl ions are more stable than 3,3-diphenyl ions, but less stable than 3,3-dimethyl-1-arylphthalyl ions. The effect of substituents at $C_{(3)}$ and $C_{(1)}$ on stability and spectral characteristics of the ions is discussed.

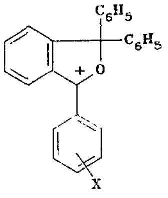
In the preceding work [1] on the acid–base conversions of 3,3-disubstituted 1-arylphthalyl ions we established that substituents at the 3-position, structurally distant from the reactive center, affect the stability of the ions substantially because of an inductive effect. Although the ions previously studied differed from one another in the electronic and steric structures of the substituents at $C_{(3)}$, nevertheless in each compound the two substituents were the same. To obtain more detailed information about the effect of the substituents at the 3-position, it was of interest to us to study the stability and spectral characteristics of a series of phthalyl ions containing two different substituents, e.g., methyl and phenyl, at $C_{(3)}$, and to compare the results with those described for the model series IIa-g and IIIa-g.



I a-g



II a-g



III a-g

I—III a X=H; b X=$p$-$CH_3$; c X=$m$-$CH_3$; d X=$p$-$CH_3O$; e X=$p$-Cl, f X=$p$-$(CH_3)_2N$; g X=$p$-$(C_2H_5)_2N$

For this purpose, by the reaction of 3-methyl-3-phenylphthalide with arylmagnesium halide followed by treatment with perchloric acid we obtained the respective perchlorates I'a-g, which contain the 3-methyl-3-phenyl-1-arylphthalyl cations Ia-g.

The cyclic structure of Ia-g and the presence of a carbenium-oxonium group were confirmed by electron spectroscopy; the absorption curves resemble those of the cations IIa-g

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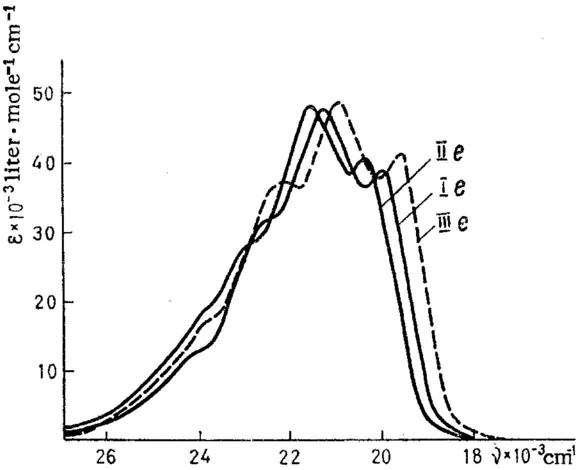


Fig. 1. Absorption spectra of cations in $CH_3COOH$.

TABLE 1. Acid–Base Conversion Constants of Cations Ia-g–IIIa-g

| Cation | $\lambda_{max}$, nm (lg ε) | $pK_{R^+}$ ($pK_a$) | Cation | $pK_{R^+}$ ($pK_a$) | Cation | $pK_{R^+}$ ($pK_a$) |
|---|---|---|---|---|---|---|
| Ia | 344 (4,45) | −2,85±0,05 | II$^a$ | −1,77 [5] | IIIa | −3,74 [8] |
| Ib | 368 (4,50) | −1,91±0,04 | IIb | −0,76 [6] | IIIb | −2,74 [3] |
| Ic | 346 (4,44) | −2,58±0,06 | IIc | −1,48 [6] | IIIc | −3,21 [3] |
| Id | 403 (4,66) | −0,60±0,03 | IId | +0,56 [5] | IIId | −1,06 [3] |
| Ie | 363 (4,53) | −3,47±0,04 | IIe | −2,18 [7] | IIIe | −4,12 [3] |
| If | 500 (4,58) | +3,58±0,02<br>(+3,67±0,10) | IIf | +4,94 [2]<br>(+4,50) | IIIf | +2,98 [9]<br>(+3,17) |
| Ig | 502 (4,67) | +3,99±0,01<br>(+4,59±0,01) | IIg | +5,14 [2]<br>(+5,74) | IIIg | +3,33 [9]<br>(+4,40) |

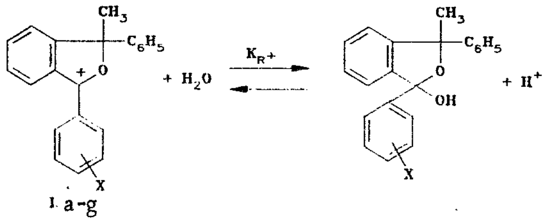
[2] and IIIa-g [3] (Fig. 1). The long wave maxima in the Ia-g spectra are shifted bathochromically with respect to the maxima of the 3,3-dimethyl- cations, and hypsochromically with respect to the maxima of the 3,3-diphenyl-1-arylphthalyl cations with the same substituents at $C_{(1)}$, and have $\lambda_{max}$ close to the calculated arithmetic mean of the values for IIa-g and IIIa-g.

For cations having an electron donor substituent at the 1-position, there is the following correlation between the wave number at $\lambda_{max}$ and the Braun–Okamoto $\sigma^+$-constant (n = 5, r = 0.995):

$$\tilde{\nu}=4.88(\pm 0.28)\times 10^3\sigma^+ + 2.88(\pm 0.05)\times 10^4.$$

Comparison of the slope of the straight line for this series of cations with the analogous values for IIa-g (tan α = $4.86\cdot 10^3$) and IIIa-g (tan α = $4.85\cdot 10^3$) [3] shows that in this case the effect of the substituent at $C_{(1)}$ on the location of the long wave band due to phthalyl cation absorption is independent of the nature of the substituent at $C_{(3)}$.

As in previous work, for the criterion of the relative stability of 3-methyl-3-phenyl-1-arylphthalyl cations we used $pK_{R^+}$, which characterizes the location of the acid–base equilibrium:



The $pK_{R^+}$ values of Ia-g determined spectrophotometrically [4], are shown in Table 1, where the same values for IIa-g and IIIa-g are shown for comparison.

The data show that $Pk_{R^+}$ of Ia-g depends significantly on the nature of the substituent at the 1-position; the more active substituents are those that contain electron donor groups that favor conjugation with the reactive center (p-$CH_3O$, p-$(CH_3)_2N$, p-$(C_2H_5)_2N$). Cations Id, f, g have higher $pK_{R^+}$ values, and consequently are more stable, than Ia.

TABLE 2. Properties of Perchlorates I'a-g

| Compound | mp, °C | Found, % |  |  | Empirical formula | Calculated, % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
|  |  | C | H | Cl |  | C | H | Cl |  |
| Ia | 145—147 | 65,8 | 4,5 | 9,3 | $C_{21}H_{17}ClO_5$ | 65,5 | 4,5 | 9,2 | 54 |
| Ib | 155—157 | 65,9 | 5,0 | 9,2 | $C_{22}H_{19}ClO_5$ | 66,2 | 4,8 | 8,9 | 76 |
| Ic | 141—143 | 65,9 | 5,0 | 9,1 | $C_{22}H_{19}ClO_5$ | 66,2 | 4,8 | 8,9 | 67 |
| Id | 172—174 | 63,4 | 4,9 | 8,3 | $C_{22}H_{19}ClO_6$ | 63,7 | 4,6 | 8,5 | 68 |
| Ie | 139—141 | 59,8 | 4,2 | 16,8 | $C_{21}H_{16}Cl_2O_5$ | 60,1 | 3,8 | 16,9 | 31 |
| If | 224—226 | 64,3 | 5,2 | 8,0 | $C_{23}H_{22}ClNO_5$ | 64,5 | 5,2 | 8,3 | 71 |
| Ig | 151—153 | 65,5 | 5,9 | 7,5 | $C_{25}H_{26}ClNO_5$ | 65,8 | 5,8 | 7,8 | 55 |

As was to be expected, 3-methly-3-phenyl-1-arylphthalyl cations are more stable than 3,3-diphenyl-, but less stable than 3,3-dimethyl-1-arylphthalyl cations. But in all cases the experimental $pK_{R^+}$ values show excessive deviations from the arithmetic means of $pK_{R^+}$ for cations IIa-g and IIIa-g. The nonobservance of additivity may be related to solvation effects, because for IIa-e $pK_{R^+}$ was determined in hydrochloric acid, whereas for Ia-e and IIIa-e it was determined in formic acid, due to the poor solubility of these compounds in hydrochloric acid. The dependence of carbenium ion stability on medium was also noted by the authors of [10] for substituted triarylcarbenium ions, which are like the phthalyl cations of the present work in their polarization mechanism.

Cations If,g contain $N(Alk)_2$ groups, which favor salt formation. For such compounds, equilibrium is established at a definite pH not only between carbocation $R^+$ and carbinol base ROH, but also between base ROH and hydroxyammonium ion $HR^+OH$:

$$R^+ + H_2O \overset{K_{R^+}}{\rightleftarrows} ROH + H^+ \overset{K_a}{\rightleftarrows} HR^+OH.$$

In [11, 12] the acid—base conversions of aminotriarylcarbinols were studied in detail, and a procedure for determining $K_{R^+}$ and $K_a$ was proposed. The $pK_a$ values determined in the present work that characterize the basicity of the dialkylamino groups in If,g are also shown in Table 1.

The effect of substituents at $C_{(1)}$ on Ia-g stability can be estimated quantitatively from the following correlation ($n = 7$, $r = 0.998$):

$$\lg K_{R^+} = 3.68(\pm 0.14)\cdot\sigma^+ + 3.00(\pm 0.28).$$

In this series of compounds the reaction constant ρ is practically the same as the similar values for IIa-g ($\rho = 3.62$) and IIIa-g ($\rho = 3.74$) [3]. This is evidence that the sensitivity of this series of cations to substituents at $C_{(1)}$ is independent of the kind of substituent at the 3-position.

## EXPERIMENTAL

The spectral properties of the 3-methyl-3-phenyl-1-arylphthalyl perchlorates in 90% HCOOH (I'a-e) and in glacial $CH_3COOH$ (I'e, g) were obtained on a Specord UV-VIS spectrophotometer. The starting 3-methyl-3-phenylphthalide was obtained according to [13].

The properties of the synthesized perchlorates I'a-g are given in Table 2.

Synthesis of I'a-g Perchlorates (General Procedure). To a solution of arylmagnesium bromide (from 6.25 mmole of magnesium and 6.25 mmole of aryl bromide in 5 ml of anhydrous THF) was added dropwise a solution of 0.7 g (3.13 mmole) of 3-methyl-3-phenylphthalide in 10 ml of absolute ether. The reaction mixture was stirred for 0.5 h at room temperature, then for 1 h with heating on water bath. After cooling the mixture was poured on ice, decomposed with 1:4 dilute HCl (I'a-e) of 10% aqueous $(NH_4)_2SO_4$ (I'f, g), and treated with 50 ml of ether. The ether layer was separated, washed with water, and dried with $MgSO_4$. After removal of solvent the oily product was dissolved in 5 ml of hot glacial acetic acid (I'a-e) or 100 ml of ether (I'f, g), and 2 ml of 57% $HClO_4$ was added. After one day the crystalline precipitate was filtered off and crystallized from glacial $CH_3COOH$ (perchlorates I'a-f) or an acetic acid—ether mixture (perchlorate I'g).

Determination of $pK_{R^+}$. Perchlorates I'a-g were used. I'a-e were used in aqueous formic acid, prepared by diluting 99.7% HCOOH (analytical grade) with double-distilled water. The concentration was determined by titration with 0.1 N NaOH with 0.1% precision. I'f, g were used in 0.1 M citrate buffers at various pH values [14]. The concentration of working perchlorate solutions was $(2-3)\cdot 10^{-5}$ M. Optical density was determined at the analytical wavelength corresponding to $\lambda_{max}$ (Table 1). It was previously established that hydroxyphthalanes do not absorb in this region of the spectrum. The constants for the cations were calculated by the formulas:

$$pK_{R^+} = H_R + \lg D/(D_0 - D),$$

$$(c \cdot l \cdot \varepsilon - D)/D = K_{R^+}(1/a_{H^+}) + K_{R^+}/K_a,$$

Here $H_R$ is the acidity function of aqueous HCOOH [15]; D is the optical density of the solution at a given acidity or pH; $D_0$ is the optical density that remains constant when the acidity is increased further; C is the starting perchlorate concentration, M; *l* is the layer thickness, cm; ε is the molar absorption coefficient of I'f, g at $\lambda_{max}$ (Table 1) in glacial acetic acid; and $a_{H^+}$ is the hydrogen ion activity. The optical density of solutions of I'a-e was measured as soon as they were prepared; that of solutions of I'f, g, after one day. For each compound, 5-7 determinations were made at various acidities or pH. The experimental data were processed by the least squares method.

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