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Abstract

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THE TRI-*p*-AMINOTRIPHENYLOXONIUM CATION AS A STRUCTURAL ANALOG OF PARAFUCHSIN

In a previous paper ([1]) we described the nitration of a series of onium compounds, including salts of triphenyloxonium obtained by us earlier ([2]). In contrast to other aromatic onium compounds, which have a quite definite meta orientation in electrophilic substitution, triphenyloxonium salts are nitrated exclusively in the para position.

In the present article we describe the reduction of tri-*p*-nitrotriphenyloxonium borofluoride to the corresponding amino derivative and some of the properties of the latter. The reduction was carried out under the usual conditions with tin and hydrochloric acid. The tri-*p*-aminotriphenyloxonium chloride obtained in this reaction was converted by double-exchange reactions into other salts of this cation—the iodide, the double salt of the iodide with mercuric iodide, and the chloroplatinate. None of these salts has a sharp melting point; on heating they gradually char, without melting, at 150–200°.

Under the influence of oxonium oxygen, the basic properties of the amino groups in tri-*p*-aminotriphenyloxonium salts are appreciably weakened. These amino groups undergo diazotization only under the conditions used for diazotizing weakly basic amines, for example under the action of nitrosylsulfuric acid. The diazo compound obtained couples with β-naphthol, and, on treatment with a solution of sodium iodide, replaces the diazo groups by iodine.

On diazotization under the usual conditions, salts of tri-*p*-aminotriphenyloxonium are destroyed by an excess of sodium nitrite solution.

The tri-*p*-aminotriphenyloxonium cation, by its structure, is a formal analog of the parafuchsin cation; however, unlike the latter, it is colorless. It is of interest to compare the following series of compounds:

(I)
tri-*p*-dimethylaminotriphenylboron cation

(II)
pararosaniline-type carbonium cation with $N(CH_3)_2$ groups

pa

(IV)
tri-*p*-aminotriphenyloxonium cation

(V)
tri-*p*-dimethylaminotriphenylsulfonium cation

Fig. 1. Ultraviolet absorption spectrum of tri-*n*-aminotriphenyloxonium iodide (A) and tris-(*n*-dimethylaminophenyl)-sulfonium chloride (B)

Figure 1: Fig. 1. Ultraviolet absorption spectrum of tri-*n*-aminotriphenyloxonium iodide (A) and tris-(*n*-dimethylaminophenyl)-sulfonium chloride (B)

Of these, only parafuchsin and crystal violet possess an intense coloration. The remaining compounds absorb only in the ultraviolet part of the spectrum: $[n\text{-}(CH_3)_2NC_6H_4]_3C^+$ has λ_{max}589 mμ ($\lg \varepsilon_{max} = 4.92$) (3), $[n\text{-}NH_2C_6H_4]_3C^+$ has λ_{max}551 mμ ($\lg \varepsilon_{max} = 4.97$) (3), $[n\text{-}(CH_3)_2NC_6H_4]_3B$ absorbs in the ultraviolet region (4), $[n\text{-}(CH_3)_2NC_6H_4]_3S^+$ has λ_{max}315 mμ ($\lg \varepsilon_{max} = 4.72$), $[n\text{-}NH_2C_6H_4]_3O^+$ *has* λ_{max}263 mμ ($\lg \varepsilon_{max} = 4.56$) and 292 m$\mu$ ($\lg \varepsilon_{max} = 3.85$).

Fig. 1. Ultraviolet absorption spectrum of tri-*n*-aminotriphenyloxonium iodide (A) and tris-(*n*-dimethylaminophenyl)-sulfonium chloride (B)

Thus, for the intense absorption of light in the visible region characteristic of dyes in structures of the type:

$$\left(A - \underset{\text{benzene ring}}{C_6H_4} - E \right)_3,$$

where A is an auxochromic group, and E is an atom of one of the elements from B to O (and sulfur), two conditions are necessary.

First, E must possess an electron vacancy, as B and C do (a deficiency of an electron pair to complete the octet). In this case, the possibility of octet expansion, which sulfur has, does not replace the presence of a vacancy.

Second, E must possess the positive charge of a cation, which is delocalized between E and the auxochromic groups.

Either condition taken separately is insufficient for the appearance of color; a combination of both is necessary.

Experimental Part

Salts of tri-*n*-aminotriphenyloxonium. a) **Chloride.** A mixture of 2.74 g (6 mmol) of tri-*n*-nitrotriphenyloxonium borofluoride, 6.85 g (0.06 g-atom) of metallic tin, and 41 ml of conc. HCl was heated with a reflux condenser until the tin had completely dissolved, then diluted with 900 ml of water. Hydrogen sulfide was passed through the resulting solution, heated to 60°, until complete precipitation of tin sulfides. The precipitate was filtered off and washed with water, and the filtrate was evaporated to dryness. The residue—the hydrochloric acid salt of tri-*n*-aminotriphenyloxonium chloride—was reprecipitated with

absolute ether from methanol. Yield of the salt 2.1 g (78% of theory). It is a white powder, soluble in water and methanol, poorly soluble in acetone and ether. On heating, the salt chars without melting in the range 160–175°.

$C_{18}H_{21}N_3OCl_4$.	Found % :	N 8.58
	Calculated % :	N 8.64

When aqueous solutions of inorganic salts were added to an aqueous solution of tri-*n*-aminotriphenyloxonium chloride, other salts of this cation were obtained.

b) **Iodide.** A colorless, finely crystalline substance, moderately soluble in acetone, poorly soluble in cold water, insoluble

* The spectrum was recorded in the optics laboratory of the Institute of Organoelement Compounds of the Academy of Sciences of the USSR (see Fig. 1).

in ether. On heating it chars, without melting, in the range 180–200°. The salt was purified by recrystallization from water.

Found, %:	C 51.28; 51.13;	H 4.42; 4.29	
$C_{18}H_{18}N_3OJ$. Calculated, %:	C 51.58;	H 4.32	

c) **Double salt of the iodide with mercuric iodide.** A pale-yellow, finely crystalline substance, soluble in acetone, poorly soluble in water, insoluble in ether. On heating the salt chars, without melting, in the range 200–230°.

Found, %:	C 33.70;	H 2.93;	J 39.00
$C_{36}H_{36}N_6O_2HgJ_4$. Calculated, %:	C 33.42;	H 2.87;	J 39.24

d) **Chloroplatinate.** The salt is a cream-colored powder, poorly soluble in water, acetone, alcohol, and nitromethane, soluble in dilute hydrochloric acid. On heating it chars, without melting, in the range 200–250°.

Found, %:	N 5.76; 5.67
$C_{18}H_{19}N_3OPtCl_6$. Calculated, %:	N 5.99

Salts of tri-*n*-iodotriphenyloxonium. a) **Triiodide.** 0.3 g (0.66 mmol) of tri-*n*-aminotriphenyloxonium chloride was gradually added, with cooling, to a solution of 0.2 g (2.6 mmol) of $NaNO_2$ in 4 ml of conc. H_2SO_4 ($d = 1.84$). The resulting clear solution of the diazonium salt was poured into 15 ml of ice water, and then a conc. aqueous solution of NaJ was added to the same mixture until precipitation of tri-*n*-iodotriphenyloxonium triiodide was complete. Its yield was 0.6 g (87% of theory). After reprecipitation with abs. ether from acetone, the salt consists of dark-red crystals with decomposition point 180–181°, readily soluble in acetone, insoluble in water and ether.

Found, %:	C 21.61; 21.48;	H 1.18; 1.28;	Hal 74.58; 74.96	
$C_{18}H_{12}OJ_4$. Calculated, %:	C 21.50;	H 1.20;	Hal 75.71	

b) **Iodide.** Obtained from the triiodide by twofold reprecipitation of the latter with ether from acetone saturated with sulfur dioxide. The salt has decomposition point 163–164°; it is soluble in acetone, poorly soluble in cold water, insoluble in ether and hydrocarbons. It crystallizes with one molecule of water.

Found, %:	C 27.96; 28.45;	H 1.70; 1.94;	Hal 66.44; 66.40	
$C_{18}H_{14}O_2J_4$. Calculated, %:	C 28.08;	H 1.83;	Hal 65.93	

Reaction of tri-*n*-aminotriphenyloxonium chloride with $NaNO_2$ in hydrochloric acid. A solution of 1 g (2.3 mmol) of tri-*n*-aminotriphenyloxonium chloride in 10 ml of conc. HCl was treated with a saturated solution of 2 g (30 mmol) of $NaNO_2$ in water, and then with an excess of conc. sodium iodide solution. The precipitate that formed was extracted with ether; the ethereal solution was washed with an aqueous solution of Na_2SO_3 and dried over $CaCl_2$. The residue after evaporation of the ether was heated under a reflux condenser with 8 ml of conc. HCl and 1.6 g of metallic tin until the latter dissolved. The undissolved precipitate was filtered off, washed with water, and dried. It is n,n'-diiododiphenyl ether. Its yield was 0.45 g (67% of theory). M.p. 138–139° (after recrystallization from alcohol).

According to the literature data (5), the m.p. of n,n'-diiododiphenyl ether is 139°.

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named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.