$\mathbf{COORDINATION} \ \mathbf{COMPOUNDS} =$

Crystal and Molecular Structure of Diphenyliodonium Triiodide

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Abstract—A new salt diphenyliodonium triiodide ($C_{12}H_{10}I_4$) was obtained. The [$C_{12}H_{10}I^+$][I_3^-] compound was isolated as red brown crystals and studied by single-crystal X-ray diffraction. The structure of diphenyliodonium triiodide consists of separate, virtually linear I_3^- anions and $C_{12}H_{10}I^+$ cations. Strong intermolecular anion—anion ($I_3^- \cdots I_3^-$) and anion—cation ($I_3^- \cdots I^+$) interactions in the crystal structure leads to a change in the symmetry of triiodide ions. The complex formation in the system organic cation iodide—elementary iodine was studied by spectrophotometry. The complex composition was found (1 : 1), and the stability constant of the complex in chloroform was determined ($\log \beta = 3.91$).

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Among large amount of iodine-containing organic compounds, iodonium salts receive attention in the literature. In these salts, I⁺ ions are bound to carbon atoms of aryl (hetaryl) groups (R) or coordinated to heteroaromatic thioamides. Compounds of the first type exhibit antibacterial activity against anaerobic microorganisms [1]. Last 20 years, new reagents based on polyvalent iodine compounds play an increasing role in preparative organic chemistry; they are used in organic synthesis as oxidants and electrophilic agents [2, 3]. A limited number of iodonium salts of the second type are known. These compounds are produced by reactions of heteroaromatic thioamides with molecular iodine following by formation of cationic dimers of thioamide with bridging iodine atom and triiodide counterion [4-6].

Iodonium salts of the first type have closely associated anionic parts of the molecules and form pseudotrigonal bipyramids with the RIR angles close to 90°.

Search of unique properties opening new application fields of iodine complexes of different nature stimulates target synthesis of iodonium salts containing additional iodine molecule in complex triiodide ion of the composition $\{R_2I^+I_3^-\}$ and their experimental and theoretical studies including X-ray crystallography. Evaluation of bioactivity and other properties directly dependent on the iodine form is impossible without studying structural features and stabilities of iodine-containing compounds.

The new salt diphenyliodonium triiodide $(C_{12}H_{10}I_4, 1)$ was synthesized by mixing chloroform solutions of diphenyliodonium iodide and molecular iodine; compound 1 was isolated in the form of red brown crystals.

EXPERIMENTAL

Synthesis. Diphenyliodonium triiodide was obtained by iodination of diphenyliodonium iodide with molecular iodine. A weighed portion (0.0350 g, 8.58×10^{-5} mol) of diphenyliodonium iodide (98%, Alfa Aesar) was dissolved in a methanol-chloroform mixture (1 : 2), and iodine (0.0218 g, 8.58×10^{-5} mol) was dissolved in chloroform. After mixing the solutions, the solvent was removed by slow evaporation at room temperature. The C₁₂H₁₀I₄ compound synthesized is a crystalline substance of red brown color; $T_{\rm m} = 125 - 128^{\circ}$ C.

¹H NMR spectra were recorded in $CDCl_3$ on a Bruker DPX 600 diffractometer.

¹H NMR of diphenyliodonium iodide (CDCl₃), δ , ppm: 7.40 (t, 4H, *m*-CH), 7.55 (t, 2H, *p*-CH), 7.96 (d, 4H, *o*-CH, $J_{\text{H, H}} = 7.56$).

¹H NMR of diphenyliodonium triiodide (1) (CDCl₃), δ , ppm: 7.11 (m, 2H, *m*-CH), 7.39 (m, 2H, *p*-CH₂; 2H, *m*-CH), 7.58 (m, 1H, *o*-CH), 7.71 (dd, 1H, *o*-CH, $J_1 = 8.19, J_2 = 1.11$), 7.96 (dd, 2H, *o*-CH, $J_1 = 8.22, J_2 = 1.00$).

Electronic absorption spectra of chloroform solutions with various ratios between concentrations of organic cation iodide and elementary iodine were recorded in a range of 250–800 nm in quartz cuvettes of path length l = 1 cm on a Varian Cary 50 spectrophotometer. A solution of diphenyliodonium iodide with the constant concentration of 2.0×10^{-5} mol/L was used as an initial solution. The ratio between diphenyliodonium iodide and elementary iodine in the reaction mixture was varied from 1:1 to 1:15.

X-ray crystallography. Crystals of **1** ($C_{12}H_{10}I_4$, FW = 661.80) are monoclinic, space group P21/c,



Fig. 1. Linear I_3^- anions and $C_{12}H_{10}I^+$ diphenyliodonium cations in crystal structure of $C_{12}H_{10}I_4$.

unit cell parameters at 100(2) K are a = 5.9618(3) Å, b =17.6277(10) Å, c = 14.7481(8) Å, $\alpha = 90^{\circ}$, $\beta =$ 90.048(1)°, $\gamma = 90°$; V = 1549.92(14) Å³; Z = 4, $\rho_{calc} =$ 2.836 g/cm³. The experimental array of 16427 reflections was obtained on a Bruker SMART APEX2 CCD diffractometer at 100(2) K (λ Mo K_{α} radiation, graphite monochromator, $2\theta_{max} = 58^{\circ}$) from a single crystal with dimensions of $0.45 \times 0.25 \times 0.20$ mm. Correction for absorption ($\mu = 8.017 \text{ mm}^{-1}$) was applied with the use of the SADABS program [7] (transmission coefficients T_{max} and T_{min} are, respectively, 0.297 and 0.123). After averaging equivalent reflections, 3695 independent reflections (R(int) = 0.0393) were used to solve and refine the structure. The structure was solved by the direct method; all non-hydrogen atoms were refined on F_{hkl}^2 in anisotropic approximation. The final discrepancy factors were R1 = 0.0236 (calculated on F_{hkl} for 3568 reflections with $I > 2\sigma(I)$, wR2 =0.0547 (calculated on F_{hkl}^2 for all independent reflections), GOOF = 1.021, the number of the reflections refined was 145, the maximum and minimum values of the

Bond lengths (d) and bond angles (ω) for compound 1

Bond	$d, \mathrm{\AA}$	Angle	ω, deg
I(2)–I(3)	3.072	I(2)I(3)I(4)	174.20
I(3)–I(4)	2.814	C(1)I(2)C(7)	92.54
I(1)–C(1)	2.140	I(1)C(1)C(6)	118.02
I(1)–C(7)	2.103	I(1)C(1)C(2)	118.97
C(1)–C(2)	1.393	C(1)C(2)C(3)	118.04
C(2)–C(3)	1.389	C(2)C(3)C(4)	120.55
C(3)–C(4)	1.388	C(3)C(4)C(5)	120.55
C(4)–C(5)	1.387	C(4)C(5)C(6)	120.47
C(5)–C(6)	1.405	C(5)C(6)C(7)	117.66
C(6)–C(1)	1.381	C(6)C(1)C(2)	123.01

residual electron density were 0.912 and -1.282 e Å⁻³, respectively. All calculations were performed with the SHELXTL PLUS 5 program package [8].

RESULTS AND DISCUSSION

The equilibrium in the system organic halide– molecular iodine in chloroform was studied by spectrophotometry. The amount of iodine molecules coordinated to diphenyliodonium iodide and stability constants were determined with the use of the average iodine number \overline{n}_{l_2} , described elsewhere [9].

The equilibrium iodine concentration ([I₂]) was calculated from the absorbance at the maximum wavelength of the absorption band of elementary iodine (A_{max}) by equation [I₂] = $A_{\text{max}}/(l\epsilon_{12})$.

The stability constant β at $0 < \overline{n}_{I_2} < 1$ was calculated by the least squares method by equation

$$\overline{n}_{I_2}/(1-\overline{n}_{I_2}) = \beta[I_2], \quad \log\beta = 3.91 \pm 0.02.$$

The formation of diphenyliodonium triiodide in a chloroform solution can be represented by equilibrium $R_2I^+I^- + I_2 \implies R_2I^+I_3^-$. Red brown crystals were isolated on slow evaporation of the solvent.

The molecular and crystal structures of salt **1** were studied by X-ray crystallography. The structure of diphenyliodonium triiodide consists of separate, nearly linear I_3^- anions and $C_{12}H_{10}I^+$ cations (Fig. 1).

The angle III is 174.20° , and the I(2)–I(3) and I(3)–I(4) distances are equal to 3.072 Å and 2.814 Å, respectively.

Figure 2 shows the crystal packing of the layers parallel the x0z plane. Unusual Van-der-Waals interactions I···H exist between the layers; the shortest interatomic contacts between the layers are I(3)···H(5A) and I(4)···H(3A) (3.17 Å and 3.26 Å, respectively).

The structure consists of the layers formed due to dipole-dipole interactions of iodine atoms of iodonium



Fig. 2. Fragment of crystal structure of $[C_{12}H_{10}I^+][I_3^-]$.



Fig. 3. Structure of a layer formed by dipole–dipole interactions I···I (I(1)···I(2) 3.4686(3) Å (-x + 1, y + 1/2, -z + 3/2), 3.6212(4) Å (x, -y + 3/2, z + 1/2), 4.0328(3) Å (-x + 2, y + 1/2, -z + 3/2), I(4)···I(4') 3.7787(5) Å (-x, -y + 1, -z + 2)).

cations with those of triiodide anions (Fig. 3); only weak contacts I…H occur between the layers (Fig. 2).

The C–I bond lengths in the cationic moiety are somewhat different; the C(1)–I(1) distance (2.140 Å) nearly coincides with C–I that in alkyl iodides (Table).

The torsion angles I(1)C(2)C(3) and C(2)I(1)C(8)C(7) in the diphenyliodonium triiodide molecule are 178.3(3)° and 85.5(3)°, respectively.

The average C–C bond length in the phenyl rings is close to the standard value [10], and the carbon atoms do not deviate from the ring plane (the deviation is less than 1.14°).

Therefore, the molecular and crystal structure of diphenyliodonium triiodide was studied for the first time by X-ray crystallography. The C–I bond length in iodonium cation virtually coincides with the bond of the analogous bond in alkyl iodides. Triiodide ions are asymmetric due to different character of intermolecular interactions of their terminal atoms. The corresponding bond lengths with the central atoms of two iodonium cations are 3.469 Å and 3.621 Å, and those with the terminal iodine atom of the triiodide ion of an adjacent molecule are equal to 3.779 Å) (I–I chains of the (I⁺)₂…I₃⁻…I₃⁻…(I⁺)₂ type are formed). The evaluation of the capability of diphenyliodonium triiodide to

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keep molecular iodine in a chloroform solution was made.

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