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Crystal and Molecular Structure of Diphenyliodonium Diiodobromide

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Abstract—A new salt, diphenyliodonium diiodobromide $[C_{12}H_{10}I^+][BrI_2^-]$, was synthesized, isolated as brown crystals, and studied by XRD. The structure of the diphenyliodonium diiodobromide consists of separate, nearly linear anions BrI_2^-, and cations $C_{12}H_{10}I^+$. In the crystal of the salt there are strong intermolecular anion-anion ($BrI_2^-\cdots I_2Br^-$) and anion-cation ($I_2Br^-\cdots I^+$) interactions. The complexation in the system of organic cation bromide–elemental iodine was studied spectrophotometrically.

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New reagents based on hypervalent iodine compounds play an increasing role in preparative organic chemistry and are used in the synthesis both as oxidizing and electrophilic agents [1–3]. Diphenyliodonium iodide and chloride are used in the synthesis of polymers as photoinitiators of cationic polymerization [4].

It was noted in the literature that various iodonium salts show pharmacological activity, for example, diphenyliodonium and diphenyleneiodonium chlorides are hypoglycemic agents [5]. The effectiveness of diphenyliodonium salts in the treatment of hypertension was demonstrated in [6]. It was found experimentally that chlorine derivatives of diphenyliodonium salt catalyzed the chloride exchange through the inner membrane of mitochondria [7].

Structural studies of the iodohalides of N-, P-, S-, and As-containing organic cations widely figure in the modern scientific literature [8, 9].

The search for unique properties that open new areas of implementation of complex iodine compounds of various nature stimulates the predefined synthesis of iodonium salts containing an additional molecule of iodine in the complex diiodobromide anion of the composition $\{R_2I^+\cdot HlgI_2^-\}$, their comprehensive experimental and theoretical study, including revealing their structure by XRD investigation [10].

This work is aimed at the synthesis of diphenyliodinium diiodobromide ($C_{12}H_{12}BrI_3$), study of its molecular and crystal structure and its ability to retain molecular iodine in solution.

We investigated spectrophotometrically the equilibrium in the system of organic bromide–molecular iodine in chloroform (Fig. 1). While the diphenyliodonium bromide concentration was maintained constant, the iodine concentration was varied from isomolar (*1*) to 15-fold excess (*6*). The determination of the number of iodine molecules coordinated by diphenyliodinium bromide and of the stability constants was performed using the function of average iodine number n_{I2} described earlier [11].

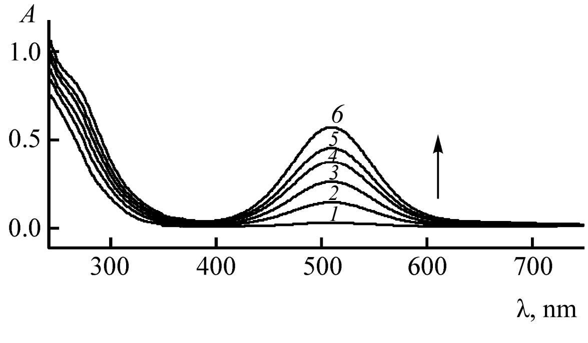

Fig. 1. Electronic absorption spectra of diphenyliodonium bromide (5.0×10^{-5} M) with molecular iodine in chloroform. $[D]/[I_2]$ = (*1*) 1:1, (*2*) 1:4, (*3*) 1:7, (*4*) 1:10, (*5*) 1:12, and (*6*) 1:15.

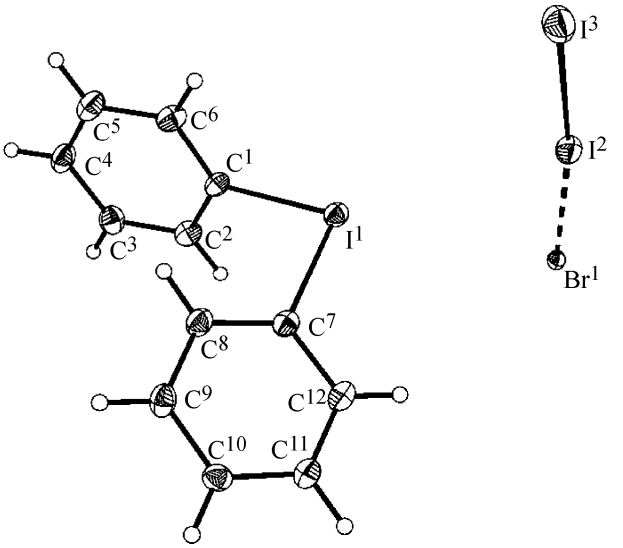

Fig. 2. Molecular structure of $C_{12}H_{10}BrI_3$ salt.

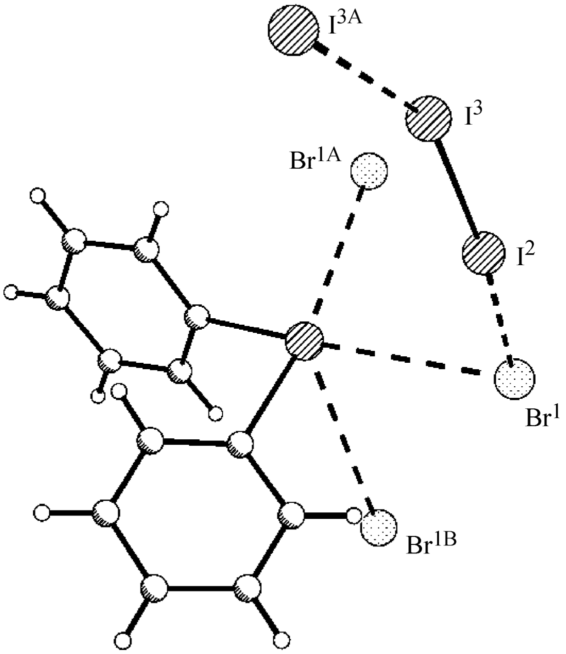

Fig. 3. Short intermolecular contacts of iodonium cations with bromine atoms of the anions.

The iodine equilibrium concentration was calculated from the value of optical density at the maximum of the individual absorption band of elemental iodine (λ = 510 nm) with the equation $[I_2] = A/(l\varepsilon)$.

The diphenyliodonium bromide, like *N*-(1-adamantyl)pyridinium bromide, can coordinate in solution two iodine molecules to form highly stable complexes [12]. The stability characteristics of the polyhalides in the range $0 < n_{I2} < 2$ are estimated from the equation that relates the values of average iodine number n_{I2} and the equilibrium concentration of iodine $[I_2]$ in the solution.

$$\frac{\bar{n}_{I2}}{(1-\bar{n}_{I2})[I_2]} = \beta_1 + \beta_2\frac{(2-\bar{n}_{I2})}{(1-\bar{n}_{I2})}[I_2],$$

$$\log\beta_1 = 3.78,\ \log\beta_2 = 7.09.$$

In chloroform, the formation of diphenyliodonium diiodobromide at the isomolar ratio of reacting components can be represented by the equilibrium: $R_2I^+ Br^- + I_2 \leftrightarrow R_2I^+BrI_2^-$. Upon slow evaporation of the solvent brown crystals of diphenyliodonium diiodobromide are formed.

The molecular and crystal structure of the salt obtained was studied by XRD. The structure consists of diphenyliodonium diiodobromide with almost linear anions BrI_2^-, and the cations $C_{12}H_{10}I^+$ (Fig. 2).

The I–I–Br angle is 173.63(2)°, and the distances Br^1–I^2 and I^2–I^3 are 2.9805(7) and 2.7906(6) Å, respectively. The bond angle $C^1I^1C^7$ in the iodonium cation is 91.6(2)°, torsion angles $I^1C^7C^8C^9$ and $I^1C^1C^6C^5$ in the diphenyliodonium diiodobromide molecule are178.1(5)° and 173.4(5)°, respectively.

The lengths of C^1–I^1 and C^7–I^1 bonds in the cationic component are slightly different: 2.104(6) and 2.140(7) Å, respectively. The average length of the C–C bonds in the phenyl rings is close to the standard value [13], and the carbon atoms are located in the ring plane almost completely.

The iodine atoms of the iodonium cations form short intermolecular contacts with three bromine atoms of the anions: I^1–Br^{1A} 3.3836(7) Å, I^1–Br^1 3.5245(7) Å, I^1–Br^{1B} 3.9685(7) Å (Fig. 3).

Due to the $I^3\cdots I^{3A}$ interaction [3.7948(9) Å] isolated dimeric anions $BrI_2\cdots I_2Br$ are formed in the structure (Fig. 4). Between the dimeric anions and the stacks of cations extended along the *a* axis there are only weak I···H contacts with phenyl rings ($I^3\cdots H^{5A}$ 3.17 Å and $I^4\cdots H^{3A}$ 3.26 Å), close by the length to the sum of the van der Waals radii [14].

Thus, using the the XRD method we for the first time investigated the molecular and crystal structure of diphenyliodonium diiodobromide. The diiodobromide ions form isolated dimers due to the short contacts

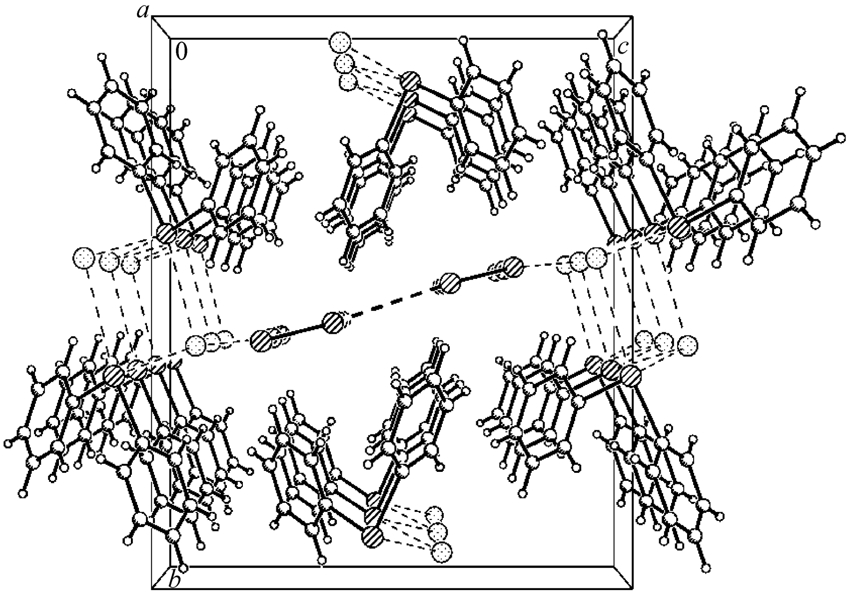

Fig. 4. Fragment of crystalline structure of $[C_{12}H_{10}I][BrI_2]$.

between the terminal iodine atoms (3.795 Å) and combine the stacks of cations through intermolecular interactions of the bromine atoms with the iodine atoms of iodonium cations. It is found that in the chloroform solution the symmetrical bulky iodonim cation promotes the formation of stable diphenyliodonium tetraiodobromide.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker DPX 250 instrument from solutions in $CDCl_3$.

Electron absorption spectra of chloroform solutions with different ratios of concentrations of organic cation and elemental iodide were recorded on a Cary 50 spectrophotometer (Varian) using quartz cells (l = 1.0 cm) in the wavelength range of 250–800 nm. The initial solution of diphenyliodonium bromide had a constant concentration of 5.0×10^{-5} M. In the reaction series the ratio of diphenyliodonium bro-mide:elemental iodine was changed from 1:1 to 1:15.

Diphenyliodonium diiodobromide was obtained by iodination of diphenyliodonium bromide with molecular iodine. A weighed sample 0.0700 g (0.194 mmol) of diphenyliodonium bromide (98%, Acros Organics) was dissolved in methanol, weighed sample 0.0492 g (0.194 mmol) of iodine was dissolved in chloroform. After mixing the solutions, the solvents were removed by slow evaporation at room temperature. The synthesized compound $C_{12}H_{10}BrI_3$ is a red-brown crystalline solid, mp 150–152°C.

The ^1H NMR spectrum (δ, ppm, J Hz): 7.42 t (4H, m-CH, J = 7.72), 7.56 t (2H, p-CH, J = 7.40), 7.98 d (4H, o-CH, J = 7.57).

X-Ray diffraction analysis. Crystals of diphenyliodonium diiodobromide, $C_{12}H_{10}BrI_3$ (M = 614.81 g mol^{-1}) are monoclinic, space group $P2_1/c$, at 100(2) K a = 5.8938(3), b = 17.4330(7), c = 14.6758(6) Å, α = 90°, β = 90.0140(10)°, γ = 90°, V = 1507.89(12) Å^3, Z = 4, d_{calc} = 2,708 g cm^{-3}. The experimental set of 17 620 reflections was obtained on a diffractometer Bruker SMART APEX2 CCD at 100(2) K (λMo–K_α radiation, $2\theta_{\max}$ = 58°), crystal size 0.40×0.33×0.15 mm. The correction for extinction (μ = 8.843 mm^{-1}) was introduced using the SADABS software [15] (the coefficients of transmission $T_{\max}$ and $T_{\min}$ are 0.350 and 0.126, respectively). After averaging equivalent reflections 3985 independent reflections were obtained (R_{int} = 0.0389), used in solving and refining the structure. The structure was solved by the direct method, all nonhydrogen atoms were refined with respect to F^2_{hkl} in anisotropic approximation. The final value of uncertainty factors: R_1 = 0.0352 (based on the F_{hkl} for 3985 reflections with $I > 2\sigma(I)$), wR_2 = 0.0969 (based on F^2_{hkl} for all independent reflections), $GOOF$ = 1.011, the number of refined parameters is 145, the maximum and minimum residual electron density peaks are 3.985 and –1.059 e Å^{-3} respectively. All calculations were performed with the software set SHELXTL PLUS 5 [16].

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