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Crystal and Molecular Structure of Tetraphenylarsonium Diiodobromide

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Abstract—Complex formation of tetraphenylarsonium bromide with molecular iodine in a chloroform solution was studied. Spectrophotometry with the use of the medium iodine number function was used to estimate the limiting number of iodine molecule coordinated with the bromide ion in the solution and the stability complex of the complex. According to X-ray diffraction data, the cation and anion of $[(C_6H_5)_4As]^+I_2Br^-$ in crystal reside in a special position on the C_2 axis, and a superposition of the I_3^- and Br_2I^- anions is observed, with ratios of 0.526 and 0.474, respectively. The resulting salt is isostructural to reported tetraphenylphosphonium interhalides.

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Structural studies of iodohalides of N-, P-, S-, and As-containing organic cations are intensively reported in contemporary scientific periodicals [1, 2]. A number of publications concern the synthesis and thermodynamic stability of interhalides of N-contain-ing heteroaromatic cations [3, 4]. For directed synthesis of interhalides one should take into account the structures of the cation and anion and the nature of the solvents [5]. Many recent research works focused on the effect of solvating medium of the composition, configuration, and thermodynamic stability of the organic polyhalide [6–10].

Kazheva et al. [11, 12] have studied the complex formation of phosphorus-containing organic cations, specifically (3-carboxypropyl)triphenylphosphonium and tetraphenylphosphonium, with elemental iodine. Quantum-chemical calculations revealed a correlation between stability of the complex anion and structural features of the cation. Based on X-ray diffraction data and correlations with quantum-chemical results, the referees established the solid-phase molecular structures and features of coordination of the anion by the P-containing cation. The $[Ph_3P(CH_2)_3COOH]^+$ cation coordinates the I_2Br^- anion by the terminal electronegative bromine atom, and the $[Ph_4P]^+$ cation, by terminal halogen atoms with equal probability.

Cotton and Kibala [13] have reported an X-ray diffraction study of the reaction products of triphenylphosphine and triphenylarsine with molecular iodine in various solvents (dichloroethane, toluene). Disproportionation of the coordinated iodine molecule forms the salts $[(PPh_3I)_2I_3]I_3$ and $[(PPh_3I)]I_3$. The length of the bond between the iodonium atom and the terminal atom of the unsymmetrical linear (α 177.23°) triiodide chain in $[(PPh_3I)]I_3$ is 3.551 A. The reaction of triphenylarsonium with iodine in dichloroethane gives rise to the salt $[(AsPh_3I)_2I_3]I_3$ which is isostructural to its phosphorus-containing analog.

Runsink et al. [14] have performed an X-ray structural study of [(Ph)4As]I_3 to find that the triiodide ion is almost ideally symmetrical and resembles a "free" triiodide ion [d(I–I) 2.90 Å and α 176.4°]. According to the Cambridge Structural Database [15], the mean statistical interatomic distance in the triiodide ion is 2.92 Å.

For directed synthesis of a series of diiodobromides of N-containing heterocyclic cations [5] Lykova et al. have studied the effect of iodine-coordinating solvents on the composition and crystal structure of such cations, since disproportionation of unsymmetrical anions (I_2Br^-, I_2Cl^-) gives rise to compounds of various compositions. The disproportionation of iodohalides involves the following stages: cleavage of the Br(Cl)···I bond in the complex and conversion of molecular iodine into the triiodide anion

via intermediate formation of the molecular complex $S \cdot I_2$ (S is solvent) [16].

The aim of the present work was to synthesize tetraphenylarsonium diiodobromide and assess its molecular and crystal structure and stability in a chloroform solution.

The target salt $C_{24}H_{20}AsI_2Br$ was synthesized for the first time by iodination of tetraphenylarsonium bromide with equimolar amount of iodine. The number of iodine molecules coordinated by the arsenic-containing cation and the stability constant of the corresponding iodohalide were determined by using the medium iodine number function $\bar{n}_{I_2}$, we described previously in [17]. To this end, we studied by spectrophotometry the equilibrium in the organic bromide–molecular iodine system in chloroform.

The equilibrium concentration of iodine $[I_2]$ was calculated from the optical density at the absorption maximum of elemental iodine, using Eq. (1):

$$[I_2] = A_{max}/l\varepsilon_{I_2} . \quad (1)$$

The $\bar{n}_{I_2}$ value corresponding to each equilibrium concentration of iodine was calculated by Eq. (2).

$$\bar{n}_{I_2} = (c_{I_2} - [I_2])/c_{CatX}. \quad (2)$$

Here c_{CatX} is the analytical concentration of organic bromide and c_{I_2}, analytical concentration of molecular iodine.

The stability constant β of the complex ($0 < \bar{n}_{I_2} < 1$) was calculated by the least-squares method (log β 3.99), using Eq. (3) in the logarithmic form.

$$\log[\bar{n}_{I_2}/(1 - \bar{n}_{I_2})] = \log [I_2] + \log \beta. \quad (3)$$

Comparing the stability constants for triphenylarsonium diiodobromide (log β 3.99) and triiodide (log β 5.45) we can see that the stability of the complex anion increases in going from diiodobromide to triiodide. This tendency is quite expectable, since, according to the calculations in [18], in going from diiodochlorides to diiodobromides and further triiodides of organic cations, simultaneous weakening of the electrostatic interaction $Cat^+\cdots XI_2^-$ and strengthening of the $X^-\cdots I_2$ bond takes place, which stabilizes the anion and hinders release of molecular iodine from the $CatXI_2$ complex (X = Cl, Br, I).

The crystal structure of compound **I** is formed by cations (Ph_4As^+) and anions (I_3^-/IBr_2^-) (Fig. 1). The principal geometric parameters of the cation, specifically As–C bond lengths of 1.901(2)–1.907(2) Å, scarcely differ from those in the analogous salts (Ph_4As^+)Br_3^- [19] and (Ph_4As^+)I_3^- [14]. The CAsC bond angles vary in the range 104.95(12)°–112.11(9)°.

In compound **I** represented in Fig. 2 as the cation–anion couple (Ph_4As^+)(I_3^-/IBr_2^-), the counter ions reside in a special position on the C_2 axis. Due to the interaction of (Ph_4As^+)(I_3^-/IBr_2^-) couple in crystal due to H-bond formation between the central iodine atom with the phenyl H^4 atom, a superposition of the I_3^- and Br_2I^- anions is observed, with ratios of 0.526 and 0.474, respectively. The formation of the I_3^- and Br_2I^- ions via disproportionation of I_2Br^- under the action of the solvating solvent on crystallization can be represented by the following equation:

$$2\,CatBrI_2 + S = CatBr_2I_{(s)} + CatI_{3(s)}.$$

Thus, the salt in hand is isostructural (space group $P2/n$, Z 2) to previously described salts (Ph_4P^+)Br_3^- [20], (Ph_4P^+)I_3^- [21], (Ph_4As^+)Br_3^- [19], (Ph_4As^+)I_3^- [14], (Ph_4P^+)IBr_2^- [22], (Ph_4P^+)ICl_2^- [23], and (Ph_4Sb+)I_3^- [24].

In view of the statistical disorder in the crystal of salt **I**, the geometric parameters of the anions involve systematic errors. However, it should be mentioned that our obtained I^1–X (Br/I) bond length of 2.8349(3) Å is, in fact, equal to the arithmetic mean (2.807 Å) of the I_3^- bond lengths (2.919 Å) in (Ph_4As^+)I_3^- [14] and Br_2I^- (2.695 Å) в (Ph_4P^+)IBr_2^- [22]. The XI^1X bond angle, where X = Br/I, is 175.82(1)°.

To examine the crystal packing the I^1–Br_2 distance was normalized at 2.695 Å [22] and the C–H distance, at 1.08 Å (by electron diffraction data). Like in earlier described salts, the crystal contains a number of weak C–H···Br and C–H···I contacts. The central atom I1 has the shortest contacts (C^4–$H^{4A}\cdots I^1$, $H^{4A}\cdots I^1$ 3.03 Å, $C^4H^{4A}I^1$ 137°), the Br···H contacts of the terminal bromine atoms are longer (3.13–3.26 Å) than the sum of the van der Waals radii (3.02 Å) [25]. The stacks of translationally identical cations are parallel to the a axis of the elementary crystal cell, the cations are bound pairwise via H bonds of equal length with the medium iodine atom, $H^4\cdots I^1$ 3.03 Å, and the H^3 and H^5 atoms of both cations are at the same distance of 3.23 Å from the medium iodine atom. Considering the nature of cation–anion interactions in salt **I** and also the fact that the difference in the van der Waals radii of Br and I (0.17 Å) [25] compares with the difference of

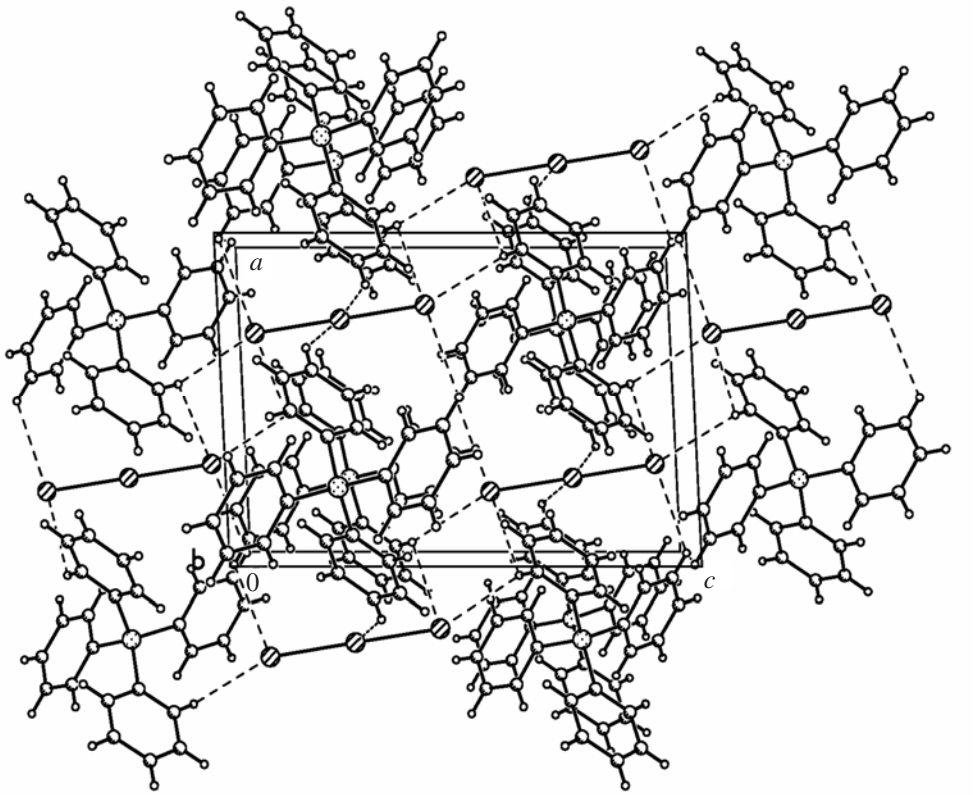

Fig. 1. Fragment of the crystal structure of $(Ph_4As^+)(I_3^-/IBr_2^-)$ as viewed along the *b* axis.

the I–Br and I–I bond lengths (0.22 Å) in the anions, one can understand why the latter cocrystallize.

Thus, over the series of related compounds, (3-carboxypropyl)triphenylphosphonium, tetraphenylphosphonium, and tetraphenylarsonium diiodobromides, we observe gradual transition from the electrostatic cation–anion interaction (unique coordination of diiodobromide through bromine with (3-carboxypropyl) triphenylphosphonium [11]), to alternative bonding of tetraphenylphosphonium with diiodobromide by the terminal atoms of the latter [12], and, finally, to interaction of the $(Ph_4As^+)(I_3^-/IBr_2^-)$ pair in the crystal of **I** due to formation of a strong H bond of the central iodine atom of the anion with the phenyl H^{4A} atom.

EXPERIMENTAL

Synthesis of compound I. A solution of iodine (1.2690 g) in chloroform was added to a stirred chloroform solution of tetraphenylarsonium bromide (2.3163 g). The solvent was removed at room temperature. Recrystallization was accomplished by slowly saturating a solution of diiodobromide **I** in dichloromethane by petroleum ether vapors. Compound **I** looks like brown crystals melting at 232–236°C.

The ^1H NMR spectrum of compound **I** was measured on a Bruker DPX-250 spectrometer in deuterochloroform; δ, ppm: 7.65 d.d (8H, Ph, *J* 1 7.9 Hz, J_2 1.4 Hz), 7.73–7.90 m (12H, Ph).

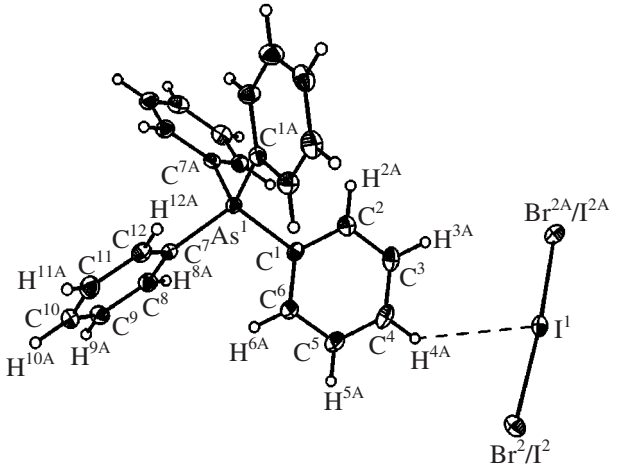

Fig. 2. General view of the $(Ph_4As^+)(I_3^-/IBr_2^-)$ cation–anion pair in the crystal of compound **I** as represented by thermal ellipsoids (*p* 50%).

The electronic absorption spectra of chloroform solutions with varied organic cation:elemental iodine concentration ratio were measured on a Specord UV VIS spectrophotometer, absorbing layer thickness 1.0 cm (30000–50000 cm^{-1}) and 5.0 cm (14000–30000 cm^{-1}). The initial concentrations of tetraphenylarsonium bromide and elemental iodine in chloroform were 1.0×10^{-3} M. In the reaction series, the concentration of organic bromide was constant (5.0×10^{-5} M), while that of iodine was varied from deficiency to a 5-fold excess.

X-ray diffraction analysis of crystals of complex **I** was performed on a Smart APEX CCD diffractometer. Intensities of 9995 reflections were measured at 100 K [$\lambda(MoK_\alpha)$ 0.71072 Å, ω-scanning at 0.5° steps, $2\theta < 58°$], and 3105 unique reflections were used in further refinement. Treatment and averaging of experimental data and inclusion of absorption were performed using the SAINT Plus and SADABS program suite.

The structure was solved by the direct method and consecutive electron density syntheses. Hydrogen atoms were located geometrically. The I^1–Br^1 bond length [2.8349(3) Å] suggests a superposition of the I_3^- and Br_2I^- anions in the crystal. The *R* factors for models with full occupancy of halogen in a general position in the case of bromine and iodine were estimated at 0.0529 and 0.0422. Taking into account that the distance between I and Br at such a superposition should be of about 0.2 Å, i.e. below the resolution at $2\theta_{max}$ of 58°, the contributions of iodine and bromine were refined in terms of equivalent coordinates (EXYZ) and anisotropic thermal parameters (EADP) for both atoms. The refinement was performed on F_{hkl}^2 anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms.

The final uncertainty factors for complex **I** for the I_2 and Br_2 occupancies of 0.526(1) and 0.474, were as follows: R^1 0.0214 [on F_{hkl} for 2816 reflections with $I > 2\sigma(I)$], wR^2 0.0531, and *GOOF* 1.008. The calculations were performed using the SHELXTL 5.10 programs [26]. Crystals of complex **I**, 100 K, monoclinic, space group *P*2/*n*, *a* 10.2592(9), *b* 7.6351(7), *c* 15.0455(13) Å; β 92.8824(61)°, *V* 1177.02(18) $Å^3$, *Z* 2 (0.5), d_{calc} 2.030 g cm^{-3}, $\mu(MoK_\alpha)$ 57.53 cm^{-1}, *F*(000) 678.

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