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Structure and Stability of Quaternary Ammonium Interhalides: Experimental and Quantum-Chemical Study

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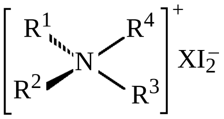
Abstract—The electronic structure of a series of ammonium interhalides $[R^1R^2R^3R^4N]XI_2$, where R^1 = CH_3, C_2H_5, C_3H_7, F, H; $R^2 = R^3 = R^4 = CH_3$, H; X = Cl, Br, I, was studied by *ab initio* calculations (RHF/3-21G, RHF/HW, MP2/HW). The thermodynamic stability of these compounds correlates with the strength of the hydrogen bond N–H···X and three-center interhalide bond X–I–I. Calculations confirmed that, in polar solvents, these compounds preferably decompose to $[R^1R^2R^3R^4N]^+$ and XI_2^- (with subsequent decomposition of the anion), and in nonpolar solvents, to the neutral species $[R^1R^2R^3R^4N]X$ and I_2. The calculation results were compared to the experimental data obtained by single crystal X-ray diffraction, ^{1}H NMR spectroscopy, and spectrophotometry.

The high biological activity of compounds incorporating molecular iodine accounts for the growing interest in these compounds whose structure is unusual for drugs. Organic (in particular, nitrogen-containing) triiodides exhibit antiphlogistic and analgetic effects; they promote fast epithelization of tissues. An important advantage of triiodides over antibiotics, sulfanilamides, and nitrofurans is that they have prolonged effect, are nontoxic, and exhibit no cumulative and side effects [1].

When developing new nitrogen-containing agents based on available iodine, it is necessary to find a correlation between the molecular structure of the organic halide and its capability for coordination with molecular iodine, and also to reveal trends in variation of the stability of these compounds in solution and in the solid phase. The synthesis of a systematic series of polyiodohalides of nitrogen-containing organic cations with different capability for release of molecular iodine can be efficiently preceded by a quantum-chemical analysis of the electron distribution and steric effects of substituents in these systems.

Interactions between halide anions and neutral halogen molecules in the systems of type $KtXY_2$ (X, Y = Cl, Br, I) in the gas phase and in media with various dielectric permittivities were recently studied by *ab initio* [2] and semiempirical [3] calculations. Extensive experimental data are available on the structure and properties of polyhalides of organic nitrogen bases, including single crystal X-ray diffraction data, stability constants of polyhalides, thermodynamic characteristics, data on decomposition kinetics in various media, and thermodynamic characteristics of complexes of molecular iodine with various solvents [4–6].

This work is the first theoretical study of some aspects of structural and thermodynamic stability of polyhalides of quaternary ammonium bases:



R^1 = CH_3, C_2H_5, C_3H_7, F, H; R^2, R^3, R^4 = CH_3, H;
X = Cl, Br, I.

Also, we studied by ^{1}H NMR trimethylbenzylammonium and triethylbenzylammonium diiodochlorides (**I** and **II**, respectively) and chlorides (**III** and **IV**, respectively).

Finally, we determined by UV spectroscopy the stability constants of **I** and **II**, and also of tetramethylammonium and tetrabutylammonium diiodobromides (**V** and **VI**, respectively) in chloroform.

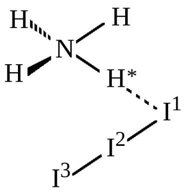
Apparently, the biological activity of $KtXI_2$ is determined by the pathway of their decomposition into fragments, which, in turn, depends on the structure of the complexes.

In the first stage, we compared the energy characteristics and geometries of compounds **VII** with suc-

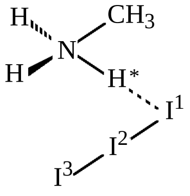
Table 1. Geometries and energy characteristics of compounds **VII**, calculated *ab initio*

Parameter	**VIIa**			**VIIb**			**VIIc**			**VIId**		
	3-21G	HW		3-21G	HW		3-21G	HW		3-21G	HW	
	RHF	RHF	MP2	RHF	RHF	MP2	RHF	RHF	MP2	RHF	RHF	MP2
r(N–H*), Å	1.064	1.077	1.102	1.048	1.061	1.085	1.042	1.053	1.079	1.039	1.050	1.079
r(H*–I^1), Å	2.358	2.325	2.301	2.425	2.386	2.354	2.428	2.401	2.359	2.432	2.410	2.345
$\angle$(NH*I^1), deg	170.1	172.2	171.0	165.5	169.2	166.9	172.0	175.5	170.8	178.2	179.8	179.7
r(I^1–I^2), Å	3.398	3.400	3.337	3.359	3.366	3.315	3.360	3.356	3.311	3.355	3.349	3.309
r(I^2–I^3), Å	2.953	2.909	3.007	2.964	2.921	3.021	2.965	2.925	3.023	2.965	2.293	3.014
$\angle$(I^{1}I^{2}I^3), deg	172.1	172.7	172.2	172.5	173.0	172.4	172.9	173.2	172.7	174.1	174.6	174.3
$\Delta q(I_3^-)$	–0.183	–0.216	–0.251	–0.156	–0.186	–0.231	–0.148	–0.175	–0.225	–0.145	–0.171	–0.228
E_{CT}, kcal mol^{-1}	–9.00	–8.22	–8.94	–7.97	–6.84	–7.70	–7.59	–6.27	–7.18	–7.15	–5.87	–6.86
ΔE_1, au	–0.1340	–0.1306	–0.1364	–0.1280	–0.1247	–0.1320	–0.1240	–0.1204	–0.1284	–0.1210	–0.1173	–0.1251
ΔE_{1m}, au	–0.1410	–0.1388	–0.1360	–0.1350	–0.1316	–0.1287	–0.1330	–0.1269	–0.1237	–0.1260	–0.1234	–0.1203
ΔE_2, au	–0.0144	–0.0119	–0.0168	–0.0161	–0.0134	–0.0191	–0.0162	–0.0138	–0.0195	–0.0165	–0.0139	–0.0191
ΔE_{2m}, au	–0.0170	–0.0143	–0.0210	–0.0192	–0.0162	–0.0241	–0.0198	–0.0169	–0.0246	–0.0191	–0.0165	–0.0228

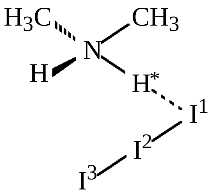
cessively increasing number of electron-donor methyl groups in the cationoid moiety (Table 1):



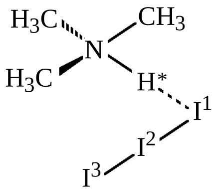
VIIa



VIIb



VIIc



VIId

According to the calculation results, all the complexes KtXI$_2$ (X = I) containing at least one hydrogen atom at nitrogen in the cationoid moiety are stabilized both by the N–H···X hydrogen bond and by the interhalogen bond in the XI$_2^-$ fragment (Fig. 1a, Table 1).

In the series of compounds **VIIa**–**VIId**, the N–H* bond length decreases, the H*–I^1 distance increases, and the NHI angle is close to 180° in all the cases. The I^1–I^2 bond length decreases, and the I^2–I^3 bond length slightly increases. These data suggest a decrease in the strength of the H–X bond, probably due to decreased charge transfer from the XI$_2^-$ moiety to the Kt$^+$ moiety (Table 3).

In compounds **VII**, the energy of the cation–anion interaction (stabilization energy of the complexes ΔE_1, ΔE_{1m}) and the energy of the interhalogen bond (ΔE_2, ΔE_{2m}), apparently, include as major components the electrostatic (E_{ES}) and charge-transfer (E_{CT}) components [8] (Table 3).

$$\Delta E_1(\Delta E_{1m}) = E(\mathrm{KtXI_2}) - E(\mathrm{Kt^+}) - E(\mathrm{XI_2^-}), \quad (1)$$

$$\Delta E_2(\Delta E_{2m}) = E(\mathrm{KtXI_2}) - E(\mathrm{KtX}) - E(\mathrm{I_2}). \quad (2)$$

Here, ΔE_1 and ΔE_2 are the stabilization energies calculated within the framework of the "supermolecular approach" (see calculation procedure), and ΔE_{1m} and ΔE_{m2} are those calculated by the Morokuma scheme, without optimizing the geometries of separate components of KtXI$_2$ [8].

A decrease in the strength of the H···X bond in the series of compounds **VIIa**–**VIId** facilitates the heterolytic pathway of decomposition of KtXI$_2$ in polar media:

$$\mathrm{KtXI_2} \longrightarrow \mathrm{Kt^+} + \mathrm{XI_2^-}. \quad (3)$$

Indeed, in the trimethyl-substituted complex **VIIg** with the lowest in this series stabilization energy ΔE_1, the bond lengths in the interhalide moiety are close to those in the free I$_3^-$ anion, and the I^{1}I^{2}I^3 angle in the series of compounds **VIIa**–**VIId** tends to 180° (the NH*I angle differs from 180° by 1.2°).

In this work we also analyzed the electronic structure and trends in variation of the thermodynamic stability of mixed halides KtXI$_2$ (X = Cl, Br). The

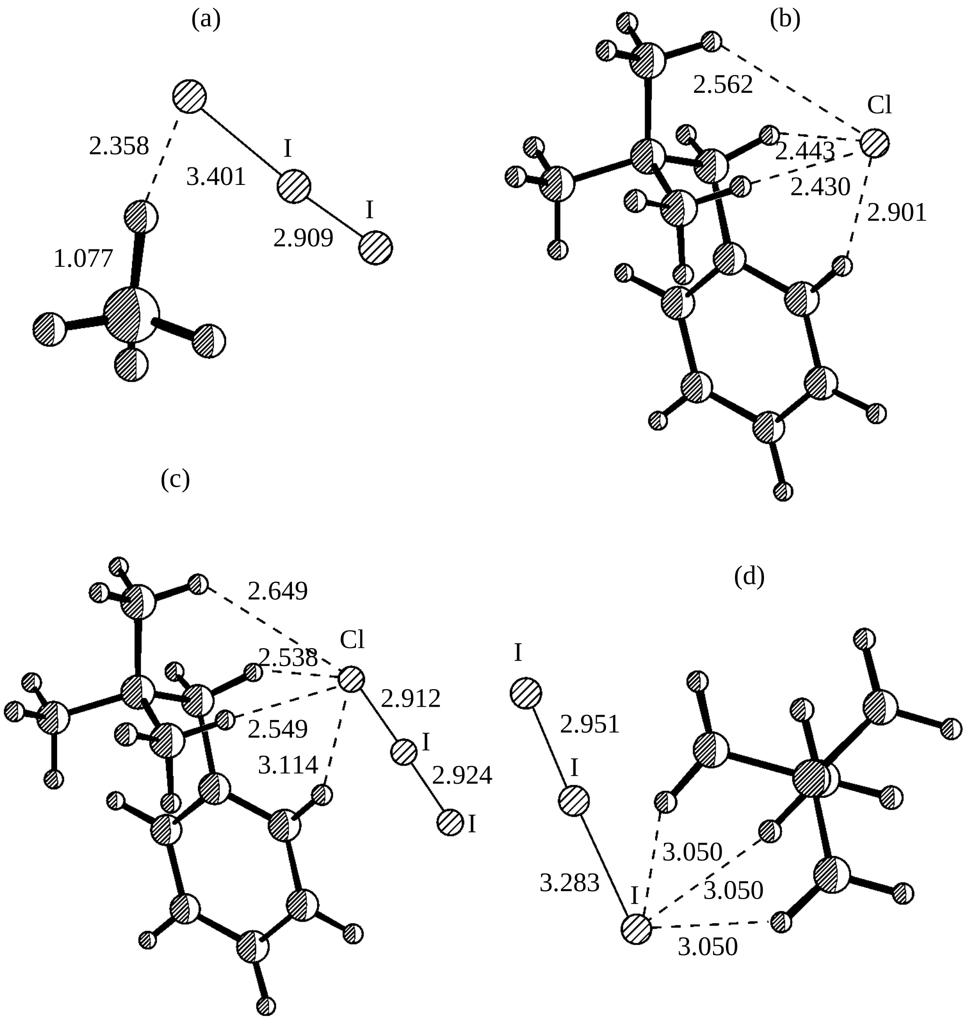


Fig. 1. Principal geometric parameters of halides (HW calculations): (a) **VIIa**, (b) **VIIb**, (c) **I**, and (d) **VIIIa**. The bond lengths are given in Å, and bond angles, in degrees (Tables 1, 2).

results qualitatively coincide with those obtained for X = I.

We also calculated the energies ΔE_1 and ΔE_2 for the complex NH_4I_3 in aqueous solution (3-21G basis, polarizable continuum model [9]). Indeed, as expected, decomposition by scheme (3) is energetically preferable in a polar medium ($\Delta E_1 > 0$), whereas the energy of stabilization of the anionic moiety ΔE_2 in a polar medium is somewhat higher than in a nonpolar medium [the stabilization energy, taking into account the solvation correction, is as follows (au): $\Delta E_1(H_2O)$ 0.061 and $\Delta E_2(H_2O)$ −0.0160].

The solvent effect on the associative processes in solutions of organic halides and interhalides **I**–**IV** was studied by ^{1}H NMR spectroscopy.

A comparison of the ^{1}H NMR spectra of trialkylbenzylammonium chloride and diiodochloride (alkyl = methyl, ethyl), recorded in $CDCl_3$, reveals the following changes in the proton signal positions (Table 2): The split multiplet of the aromatic ring (2H, 3H) (Fig. 1b) upon binding of the anion in a complex (Fig. 1c) transforms into a multiplet of five magnetically equivalent protons (5H), and the methylene singlet is shifted upfield by 0.2 ppm. This may be due to a decrease in the charge transfer in going from the halide to interhalide [$\Delta q_M(Cl^-)$ −0.196 and $\Delta q_M(ClI_2^-)$ −0.115 (HW basis set) for **III** and **I**, respectively]. The splitting of the benzene proton signals in the spectra of trialkylbenzylammonium chlorides is quite understandable, taking into account additional interaction of Cl^- with the hydrogen atom of the aromatic moiety[1] (Fig. 1b). The position of the alkyl proton

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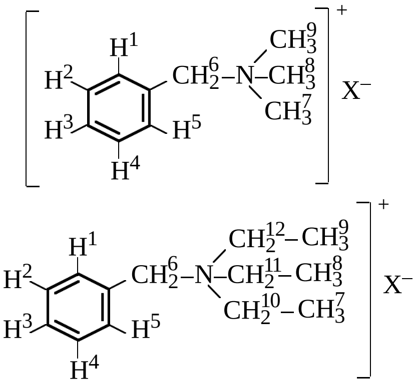
[1] This is indirectly confirmed by the lack of symmetric coordination of the chloride ion with $N(CH_3)_3$.

Table 2. Positions of the proton signals in the ^{1}H NMR spectra of trimethylbenzylammonium diiodochloride **I**, triethylbenzylammonium diiodochloride **II**, trimethylbenzylammonium chloride **III**, and triethylbenzylammonium chloride **IV** (δ, ppm relative to TMS)



Comp. no.	H^1,H^5	H^2, H^3, H^4	H^6	H^7, H^8, H^9	H^{10}, H^{11}, H^{12}
			$CDCl_3$		
I	7.55	7.55	4.7	3.30	–
II	7.55	7.55	4.5	1.5	3.35
III	7.6	7.35	4.95	3.35	–
IV	7.45	7.35	4.70	1.35	3.35
			CD_3OD		
I	7.6	7.6	4.6	3.15	–
II	7.6	7.6	4.5	1.5	3.35

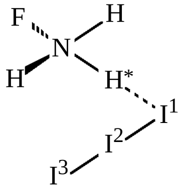
signals does not change upon complexation. At the same time, diiodochlorides have fully identical ^{1}H NMR spectra in $CDCl_3$ and in CD_3OD in which solvation-separated ion pairs are present.

Also, the interhalide anion tends to disproportionate, which is predetermined by formation of stable σ complexes by solvent molecules with I_2 [6] and is described by the following scheme [4]:

$$2\mathrm{KtHalI_2} + \mathrm{S} \rightleftarrows \mathrm{KtHal}_{(S)} + \mathrm{KtI}_{3(S)} + \mathrm{HalI}_{(S)}. \quad (4)$$

Indeed, according to 3-21G calculations (polarizable continuum model), the solvation energy of the systems under consideration is comparable with their stabilization energies (e.g., for NH_4I_3, $\Delta E_{\mathrm{solv}} = -0.0159$ au). Thus, the role of the solvent in equilibrium (4) is significant.

We also examined the effect of electron-acceptor substituents in the cationoid fragment on the thermodynamic stability of complexes $KtXI_2$. For this purpose, we compared the calculation results for two model complexes: **VIIa** and **VIIe**. We found that introduction of fluorine results in strengthening of the N–H*···I^1 bond: r(N–H*) 1.091, r(H*–I^1) 2.253 Å; ∠(NH*I^1) 164.6°, ∠(NI^{1}I^2) 65.4°, r(I^1–I^2) 3.460, r(I^2–I^3) 2.936 Å; ∠(I^{1}I^{2}I^3) 171.30°.

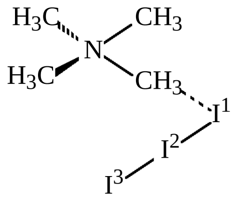


VIIe

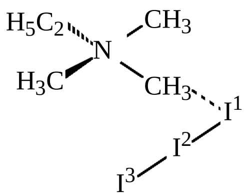
The same trend is observed on further introduction of electron-acceptor groups. The systems fully substituted with electron-acceptor groups tend to decompose by pathway (5) rather than by the formally heterolytic pathway considered above.

$$\mathrm{KtXI_2} \longrightarrow \mathrm{KtX} + \mathrm{I_2}. \quad (5)$$

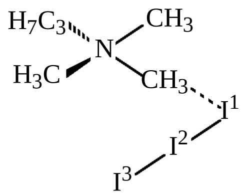
We also analyzed a series of compounds **VIIIa**–**VIIId** to examine how substituents having similar electronic properties but different size affect the stability of $KtXI_2$ (Table 4).



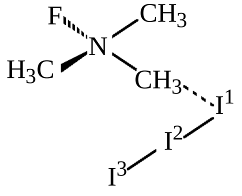
VIIIa



VIIIb



VIIIc



VIIId

The maximal $|\Delta E_1|$ in **VIIIa**–**VIIId** is attained in the case of coordination of I_3^- (via terminal iodine atom) with three hydrogen atoms of alkyl groups, i.e., at three weak interactions C–H···I [2, 10–13]. The stabilization energy ΔE_1 of complexes **VIII** is noticeably lower, and ΔE_2, higher in the absolute value, as compared to complexes **VII**.

Thus, in complexes **I** introduction of electron-donor substituents decreases the stability (the N–H*···I bonds become less strong), and in going to complexes **VIII** the destabilization is due to replacement of hydrogen bonding by very weak interactions C–H···I (Fig. 1d, Table 4). This fact is fully consistent with

Table 3. Components (kcal mol^{-1}) of interaction energies (ΔE_1) determined according to the Kitaura–Morokuma scheme [7] (3-21G basis)

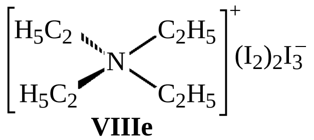
ΔE_{1m} component, kcal mol^{-1}	VIIa	VIIb	VIIc	VIId	VIIIa	VIIIb	VIIIc
Electrostatic interaction energy (E_{ES})	–87.37	–83.96	–80.52	–78.71	–66.30	–65.39	–64.77
Exchange repulsion energy (E_{EX})	17.12	15.39	14.85	14.54	9.16	9.06	8.89
Polarization energy (E_{PL})	–6.34	–5.81	–7.36	–5.61	–4.36	–4.24	–4.21
Charge-transfer energy (E_{CT})	–9.00	–7.97	–7.59	–7.14	–4.22	–4.14	–4.07
Higher-order components of total energy (E_{MIX})	–3.11	–2.27	–2.84	–2.38	–0.99	–0.98	–0.96
Total interaction energy (ΔE_{1m})	–88.70	–84.62	–83.46	–79.30	–66.71	–65.69	–65.12
Components of E_{CT}:							
Charge-transfer energy, anion	–8.82	–7.76	–7.34	–6.86	–4.01	–3.93	–3.86
Charge-transfer energy, cation	–0.18	–0.21	–0.25	–0.28	–0.21	–0.21	–0.21

Table 4. Geometries and energy characteristics of compounds **VIII**, calculated *ab initio*

Parameter	VIIIa		VIIIb		VIIIc		VIIId		
	3-21G	HW	3-21G	HW	3-21G	HW	3-21G	HW	
	RHF	RHF	RHF	RHF	RHF	RHF	RHF	RHF	MP2
$r(C–H^*)$, Å	1.075	1.083	1.080	1.084	1.081	1.083	1.070	1.085	1.100
$r(H^*–I^1)$, Å	3.005	3.050	3.020	3.081	3.020	3.079	2.950	3.020	2.996
$\angle(CH^*I^1)$, deg	155.2	155.2	156.0	156.2	156.5	156.7	149.6	148.1	147.3
$r(I^1–I^2)$, Å	3.304	3.283	3.299	3.258	3.293	3.256	3.349	3.324	3.285
$r(I^2–I^3)$, Å	2.983	2.951	2.987	2.966	2.989	2.968	2.963	2.934	3.028
$\angle(I^1I^2I^3)$, deg	175.3	175.0	174.8	173.3	174.5	173.3	174.5	174.0	173.5
$\Delta q(I_3^-)$	–0.0785	–0.0835	–0.0764	–0.0738	–0.0747	–0.0722	–0.0959	–0.0991	–0.1061
E_{CT}, kcal mol^{-1}	–4.22	–2.50	–4.14	–2.45	–4.07	–2.41	–5.26	–3.20	–3.48
ΔE_1, au	–0.1030	–0.0992	–0.1013	–0.0987	–0.1006	–0.0979	–0.1148	–0.1117	–0.1163
ΔE_{1m}, au	–0.1063	–0.1035	–0.1047	–0.1017	–0.1038	–0.1009	–0.1196	–0.1163	–0.1137
ΔE_2, au	–0.0191	–0.0177	–0.0196	–0.0192	–0.0198	–0.0194	–0.0157	–0.0152	–0.0210
ΔE_{2m}, au	–0.0223	–0.0215	–0.0230	–0.0238	–0.0233	–0.0242	–0.0182	–0.0182	–0.0253

the single crystal X-ray diffraction data for 1,10-phenanthrolinium diiodochloride: its crystal structure includes the N–H···Cl hydrogen bond and numerous weak interactions C–H···I playing an important role in the the lattice formation [2].

At the same time, in complex **VIIIe** studied by single crystal X-ray diffraction [8], the bond lengths in the triiodide moiety are equal: $r(I^1I^2) = r(I^2I^3) =$ 2.910 Å.



VIIIe

This apparently corresponds to the ion pair stabilized exclusively by nonspecific Coulombic interactions, A similar effect was observed in tetraphenylarsonium triiodide $AsPh_4I_3$ in which the bonds lengths in the interhalide are also equal: $r(I^1I^2) = r(I^2I^3) =$ 2.90 Å, whereas in the compounds with a strong charge transfer the bonds in the anion are nonequivalent [NH_4I_3: $r(I^1I^2)$ = 3.10, $r(I^2I^3)$ 2.82; CsI_3: $r(I^1I^2)$ 3.04, $r(I^2I^3)$ 2.83 Å] (Fig. 1a) [8, 14–17].

Generally, N-tetrasubstituted triiodide complexes in which the alkyl groups contain no less than two carbon centers should exist as ion pairs, with the charge transfer from the trihalide to ammonium moiety being close to zero.

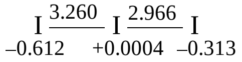
Thus, in the gas phase or in a nonpolar medium all the examined complexes KtI_3 can be ranked in the following order with respect to increase in the stabilization energy ΔE_1, ΔE_{1m} [the Morokuma charge-transfer energies (E_{CT}) and Mulliken charge transfer increase in this order]:

$$N(CH_3)_3C_3H_7I_3 < N(CH_3)_3C_2H_5I_3 < N(CH_3)_4I_3 < NF(CH_3)_3I_3 < NH(CH_3)_3I_3 < NH_2(CH_3)_2I_3 < NH_3CH_3I_3 < NH_4I_3 < NFH_3I_3. \quad (6)$$

The charge transfer is maximal when the three-centered bond N–H···I is formed in the system; if such a bond is absent, the symmetrical coordination of the triiodide ion with three hydrogen atoms of alkyl groups is optimal for weak specific interaction of the organic moiety with the triiodide ion. For example, in **VIIIb** the coordination with three CH_3 groups is by 0.0005 au less favorable that the coordination with two CH_3 groups and one CH_2 group. The data obtained (Table 3) also show that increase in the number of carbon atoms in one alkyl group at the nitrogen atom has virtually no effect on ΔE_1 and ΔE_{1m}.

Also, as follows from analysis of the energy of donor–acceptor interactions within the frameworks of both Mulliken [18] and Morokuma [7] schemes, the quantities Δq and E_{CT} in **VIIIa**–**VIIIc** vary insignificantly. In complex **VIIId** with one fluorine atom (π donor and σ acceptor), the three weak bonds C–H···I are stronger than in $N(CH_3)_4I_3$ (according to all our calculations, Table 4). Hence, replacement of the alkyl groups by acceptor substituents R increases the charge transfer in the optimal configuration of $NR(CH_3)_3I_3$.

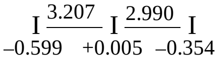
It can be readily seen from Tables 3 and 4 that, the stronger the interaction of the cation with the iodohalide terminal atom, the weaker the "iodine molecule" is retained in the anion (increase of ΔE_1 and decrease of ΔE_2 in the absolute value). Weakening of the $X^-\cdots I_2$ interaction is clearly seen when comparing the anions in $N(CH_3)_4XI_2$ and $N(C_2H_5)_4XI_2$ (HW basis):



$$\underset{-0.612}{I}\overset{3.260}{\text{———}}\underset{+0.0004}{I}\overset{2.966}{\text{———}}\underset{-0.313}{I}$$

I_3^- from $N(CH_3)_4I_3$

IXa



$$\underset{-0.599}{I}\overset{3.207}{\text{———}}\underset{+0.005}{I}\overset{2.990}{\text{———}}\underset{-0.354}{I}$$

I_3^- from $N(C_2H_5)_4I_3$

IXb

These calculation results explain the trends, revealed by UV spectroscopy, in variation of the stability of interhalide anions in combination with quaternary ammonium cations with different lengths of alkyl chains. We have studied spectrophotometrically the equilibrium in the system organic halide–molecular iodine in chloroform. The amount of coordinated iodine molecules was determned using the mean iodine number function n_{I_2} described previously [19]:

$PhCH_2N(CH_3)_3ClI_2 : \log \beta$ 3.18 $N(CH_3)_4BrI_2 : \log \beta$ 4.28

$PhCH_2N(C_2H_5)_3ClI_2$: $\log \beta$ 4.08 $N(C_4H_9)_4BrI_2 : \log \beta$ 4.73

The equilibria in solutions and the mean iodine number function are described as follows:

$$KtX + I_2 \rightleftarrows KtXI_2, \; \beta = [KtXI_2]/[KtX][I_2], \quad (7)$$

$$\bar{n}_{I_2} = \frac{C_{I_2} - [I_2]}{C_{KtX}}. \quad (8)$$

Here, C_{I_2} and C_{KtX} are the analytical concentrations of iodine and organic halide, respectively; $[I_2]$ is the equilibrium concentration of iodine.

The stability constants β of **I**, **II**, **V**, and **VI** were calculated by the least-squares method from Eq. (9) describing coordination of one iodine molecule with a molecule of organic halide:

$$\frac{\bar{n}_{I_2}}{1 - n_{I_2}} = \beta[I_2]. \quad (9)$$

The calculated structural data for **IXa** and **IXb**, together with the UV data, show that, as the length of the alkyl radical is increased, the $Kt\cdots XI_2$ interaction tends to weaken, and the geometric parameters of the anion approach those of isolated XI_2^-.

Thus, quantum-chemical calculations for the gas phase in combination with spectrochemical studies of solutions in a nonpolar solvent revealed specific interactions in interhalides of quaternary ammonium cations containing no more then two carbon atoms in the alkyl chain. Also, a direct correlation was revealed between the growth of the energy of the H···I bond and weakening of the interaction of KtX with I_2, characterizing the capability to release molecular iodine.

EXPERIMENTAL

The electronic absorption spectra of chloroform solutions with differtent ratios of organic halide and molecular iodine were recorded on an SF-46 spectrophotometer in cells with the path lengths of 1.0 (for the range 30 000–50 000 cm^{-1}) and 5.0 cm (for the range 14 000–30 000 cm^{-1}). The initial solutions were 1.0×10^{-3} M $PhCH_2N(CH_3)_3Cl$, $PhCH_2N(C_2H_5)_4Cl$, $N(CH_3)_4Br$, and $N(C_4H_9)_4Br$ in methanol–chloroform, 4 : 96, and 1.0×10^{-3} M I_2 in chloroform. In the reaction series, we varied the concentration of molecular iodine from its deficiency to a 4–6-fold excess, at a constant concentration (1.0×10^{-5} and 2.0×10^{-5} M) of the organic halide.

The ^1H NMR spectra (solutions in CD_3OD and $CDCl_3$) were recorded on a Bruker DPX-250 spectrometer.

Quantum-chemical calculation procedure. Since the donor–acceptor interactions (their wide variety is extensively studied in numerous recent calculation works [20–22]), apparently, play a decisive role in the gas-phase stabilization of the hypervalent systems in question, correct description of these interactions requires adequate level of quantum-chemical calculations [20, 23, 24]. Taking into account that the systems contain several heavy atoms, we chose the basis sets RHF/3-21G, RHF/HW, and MP2/HW [25–27]; calculations in these basis sets gave nicely consistent results for all the complexes.

All the calculations were performed with a Pentium III-550 computer using GAMESS software [28]. The initial geometry optimization was performed by the restricted Hartree–Fock method (RHF) in the 3-21G basis [25] and in the HW pseudopotential basis [25]. The RHF results were used as starting in the calculations taking into account the electron correlation according to the second-order Møller–Plesset perturbation theory (MP2). The geometries of molecular structures corresponding to stationary points on the potential energy surface were optimized to the gradient of 10^{-5} au/bohr. The matrices of force constants were calculated numerically using the GAMESS program.

All the energies of complexation (ΔE_1) and donor–acceptor $X\cdots I_2$ bonds (ΔE_2) were calculated without taking into account the superpositional error, as the differences between the total energies of the complexes and their isolated components. The total energies of the ions used for estimating the interaction energies in the complexes were found by the geometry optimization with the starting parameters corresponding to the conformations of the components in the associates.

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