exists. Moreover, differences that do occur can be reasonably attributed to factors inherent in the continuum model or to approximations made in the present formalism and conveniently point the way to possible future improvements. In general, the MNDO results seem to be slightly superior to those obtained using AM1, which is probably a result of the better description of the electron distribution afforded by the older method. In this respect, AM1 fares rather poorly for neutral aromatic systems in which the predicted hydration energies are too negative.

Remarkably, the hydration energies of protonated amines are adequately treated by the present continuum method without the explicit inclusion of water molecules coordinated to the polar N–H bonds. This is not wholly true, however, for the hydration of the even more polarized conjugate acids of the oxygen bases.

Where comparisons were possible, the computed hydration energies were quite similar to those obtained using Rinaldi's multipolar expansion technique for a solute within an optimized ellipsoidal cavity. However, in contrast to the latter method, which critically depends on the ability to fit the solute within a cavity of specified shape, the present method is applicable to molecules, ions, and reacting systems of arbitrary shape.

Acknowledgment. We thank the Robert A. Welch Foundation for financial support of this work through grant N-1080.

Macrocyclic, Square Planar, Tetraalkynyl Tetraiodonium Salts: Structures, Stabilities, and Vibrational Frequencies via ab Initio Calculations

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Abstract: The geometries and stabilities of HCCH, ICCH, ICCl, IF_3, IF_2CCH, $IF(CCH)_2$, $I(CCH)_3$, $I_4(CC)_4^{4+}$, and four isomers of $I_4(CC)_4F_4$ were calculated at the ab initio HF/LANL1DZ level. Final geometries were used for electron correlation calculations at the MP4/LANL1DZ level. The results of the calculations demonstrate considerable stability and suggest square planar structures for the macrocyclic tetraalkynyl tetraiodonium compounds. The tetracation $I_4C_8^{4+}$ is predicted to exist as a single isomer due to a pseudotetrahedral 8-I-2 configuration and to have a structure with only negligible deviations from a perfect square. In contrast, the neutral $I_4C_8F_4$ species can exist as four different isomers as a consequence of the trigonal bipyramidal 10-I-3 configuration. These isomers have distinctly different geometries and energies due to the relative positions of the axial and equatorial C–I bonds. Macrocycles **16–19** have ring strain energy due to the existence of four unfavorable axial I–C bonds in each of the isomers. However, the calculated ring strain energy for the most stable isomer **16** is only 27 kcal/mol.

Introduction

There is considerable current interest in multicoordinate, polyvalent (hypervalent) main-group species.[1] Among the oldest, most interesting, and most extensively investigated polyvalent main-group compounds are those of iodine.[2] Multicoordinated iodine compounds with at least one organic ligand have been known since the discovery of $PhICl_2$ by Willgerodt in 1886.[3] In the intervening 100 years, thousands of polycoordinated iodine compounds have been reported, the most common class being the diaryliodonium salts. The latest members of this family, the alkynyl(phenyl)iodonium species,[4] have become valuable reagents for the ready preparation of diverse functionalized acetylenes[5] and other useful transformations.[6,7] Recently several new structural types of alkynyliodonium salts have been synthesized, such as bis(phenyliodonium)acetylene **1**,[7a] dialkynyliodonium salts **2**,[8] and *p*-phenylenebis(alkynyliodonium) triflate **3**.[9] However, iodonium salts with three or more iodonium and alkynyl or aryl moieties in the molecule are still unknown.

The unique T-shaped geometry of iodine(III) compounds described as 10-I-3 (for neutral) or 8-I-2 (for monocationic) species

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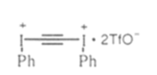

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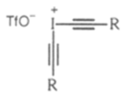

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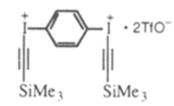

3

in the Martin–Arduengo formalism[10] predicts the possible formation of unusual square planar macrocyclic tetraiodonium salts, as illustrated by species **4–6**.

4

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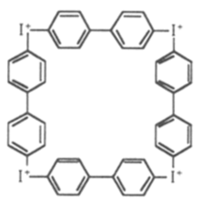

6

Such charged molecular squares or boxes are inherently interesting and also represent possible unique hosts for anionic species. In this paper we wish to report ab initio calculations for the cyclic tetraalkynyl iodonium tetracation **4** and the corresponding neutral molecules, the simplest members of this novel family of cyclic tetra I(III) species.

Computational Details

The geometries of HCCH, ICCH, ICCI, IF$_3$, IF$_2$CCH, IF(CCH)$_2$, I(CCH)$_3$, I$_4$(CC)$_4^{4+}$, and four isomers of I$_4$(CC)$_4$F$_4$ (**4**, **7–19**, Figures 1–3) were optimized employing analytical gradient methods[11] using the Los Alamos pseudopotential, including a valence double-ζ basis set for iodine[12] and valence double-ζ basis sets for all others atoms (SCF/LANDL1DZ).[13] The fundamental vibrational frequencies, normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods at the SCF/LANL1DZ level. The equilibrium geometries were used to evaluate electron correlation energies at the full fourth-order Møller–Plesset perturbation theory[14] for the noncyclic systems and at second-order for the cyclic species with the frozen-core approximation. The Gaussian 90 program suite[15] was used to perform all of the calculations whose results are discussed here.

Results and Discussion

To our knowledge, to date there are no literature data on ab initio studies for alkynyliodonium derivatives. However, experimental X-ray structural data are available for five alkynyliodonium species: ethynyl(phenyl)iodonium triflate,[16a] phenylethynyl(phenyl)iodonium tosylate,[16b] *tert*-butylethynyl(phenyl)iodonium periodate,[16c] dialkynyliodonium triflate **2**,[8] and *p*-phenylenebis(alkynyliodonium) triflate **3**.[9] To obtain the basic structural and energy data for the macrocyclic tetraiodonium molecules, the simple molecules HCCH, ICCH, ICCI, IF$_3$, IF$_2$CCH, IF(CCH)$_2$, and I(CCH)$_3$ (Figure 1) were studied first, and the results are compared with the available experimental structural data.

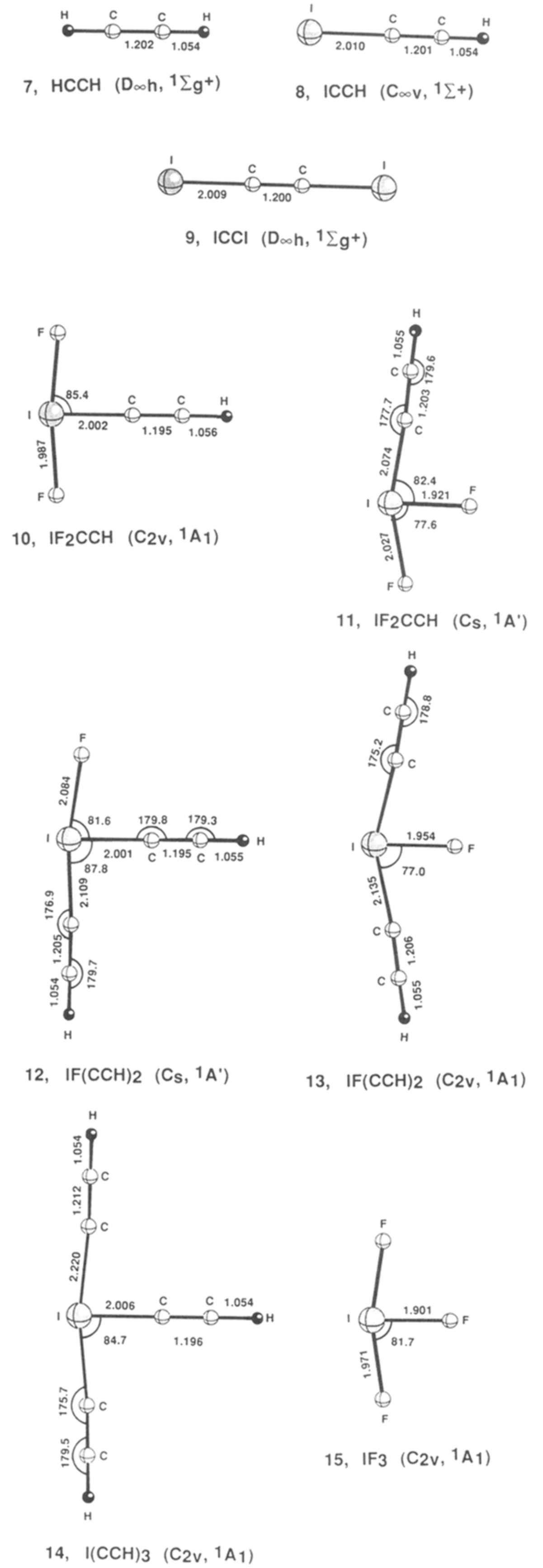

Figure 1. Calculated geometries (bond lengths in angstroms, angles in degrees) of alkynyl iodides **7–15**.

IF$_3$, IF$_2$CCH, IF(CCH)$_2$, and I(CCH)$_3$. In the compounds of iodine(III), the geometry about the iodine can be described as distorted trigonal pseudobipyramid (T-shaped structure).[2a] The central iodine atom is surrounded by three ligands and has ten total electrons in its valence shell. The equatorial positions are occupied by electropositive ligands and two sets of lone-pair electrons; the axial positions are taken up by electronegative

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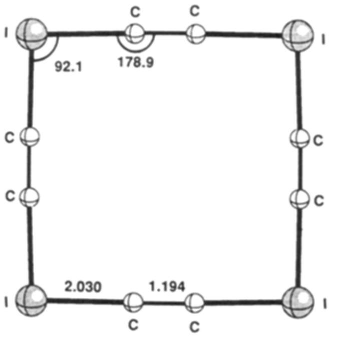


4, $I_4C_8^{4+}$ (D_{4h}, $^1A_{1g}$)

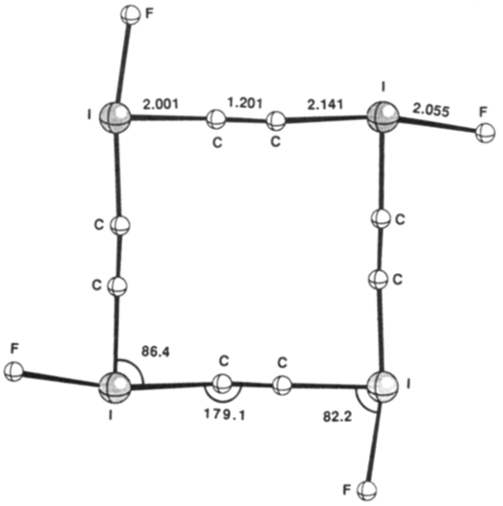
Figure 2. Calculated geometries (bond lengths in angstroms, angles in degrees) of square planar tetracation **4**.

Table I. Calculated Substitution Reactions Energies

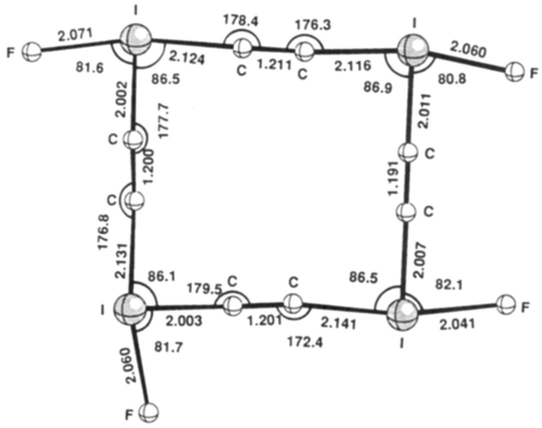
reaction	method	ΔE, kcal/mol
1. $IF_3 + HCCH \rightarrow IF_2CCH + HF$	SCF/LANL1DZ	−18
	MP2/LANL1DZ	−14
	MP3/LANL1DZ	−15
	MP4/LANL1DZ	−14
	MP4/LANL1DZ + ZPE[a]	−15
2. $IF_3 + 2HCCH \rightarrow IF(CCH)_2 + 2HF$	SCF/LANL1DZ	−8
	MP2/LANL1DZ	−4
	MP3/LANL1DZ	−6
	MP4/LANL1DZ	−4
	MP4/LANL1DZ + ZPE[a]	−5
3. $IF_3 + 3HCCH \rightarrow I(CCH)_3 + 3HF$	SCF/LANL1DZ	+16
	MP2/LANL1DZ	+17
	MP3/LANL1DZ	+16
	MP4/LANL1DZ	+18
	MP4/LANL1DZ + ZPE[a]	+15

[a] ZPE corrections calculated with HF/LANL1DZ frequencies scaled by 0.9.

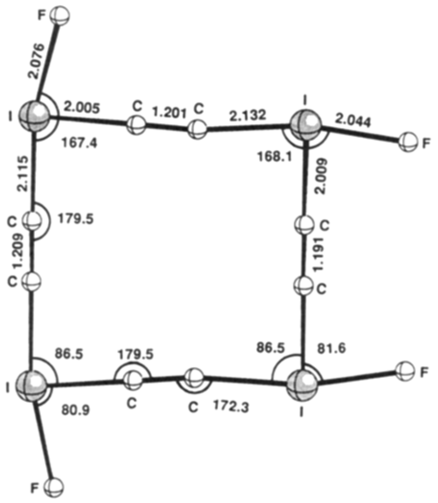
ligands. Molecules IF_3, IF_2CCH, $IF(CCH)_2$, and $I(CCH)_3$ have the expected distorted T-shaped structure (Figure 1), and all are local minima on the potential energy surface (i.e., they have no imaginary frequencies; table of vibrational frequencies in supplementary material). Two isomers are possible for IF_2CCH: structure **10** has an equatorial acetylenic group, and structure **11** has the acetylenic group in the axial position. Two isomers are also possible for $IF(CCH)_2$: isomer **12** has an acetylenic group in both an equatorial and an axial position, while isomer **13** has both acetylenic groups in axial positions. The IC≡C fragment in the structures of IF_2CCH, $IF(CCH)_2$, and $I(CCH)_3$ deviates from linearity, with a bond angle of 176–178°, which is consistent with the experimental X-ray data of 177°.[8,16a] The C≡C bond lengths in both axial and equatorial positions are close to 1.20 Å. Experimentally determined C≡C bond lengths in alkynyliodonium salts vary from 1.15 to 1.20 Å.[8,9,16] The I–C bond length is substantially different for the axial and the equatorial position.



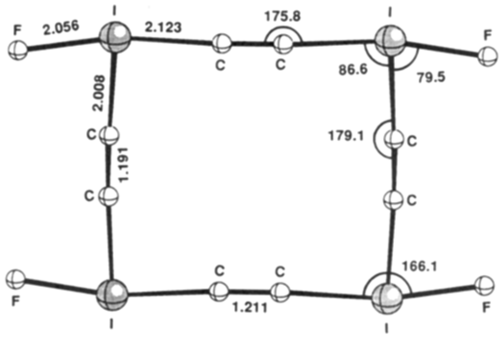
16, $I_4C_8F_4$ (C_{4h}, $^1A_1$)



17, $I_4C_8F_4$ (C_s, $^1A'$)



18, $I_4C_8F_4$ (C_{2v}, $^1A_1$)



19, $I_4C_8F_4$ (D_{2h}, ^1A_g)

Figure 3. Calculated geometries (bond lengths in angstroms, angles in degrees) of square tetraalkynyl tetraiodonium molecules **16–19**.

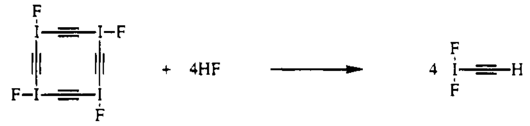
The minimal difference of 0.07 Å is found for the IF_2CCH isomers **10** and **11**, and the maximal difference 0.21 Å is for $I(CCH)_3$ (**14**). The valence C–I–C angles for $IF(CCH)_2$ (**12**) and $I(CCH)_3$ (**13**) are 87.8 and 84.7°, respectively. It is known that the equatorial position is the most favorable for the electropositive ligand in T-shaped molecules.[17] From the difference of total energies for isomers **10** and **11** (22.8 kcal/mol at HF/LANL1DZ; 19.7 kcal/mol at MP2/LANL1DZ; 20.3 kcal/mol at MP3/LANL1DZ; 19.6 kcal/mol at MP4/LANL1DZ) and for isomers **12** and **13** (28.5 kcal/mol at HF/LANL1DZ; 22.9 kcal/mol at MP2/LANL1DZ; 23.9 kcal/mol at MP3/LANL1DZ; 23.7 kcal/mol at MP4/LANL1DZ), the "strain" energy of the alkynyl group transfer from the equatorial to the axial position is estimated as 20–24 kcal/mol.

Table I shows calculated reaction energies for subsequent substitution of fluorine atoms by the acetylenic moiety in the IF_3 molecule. According to this calculation, the first substitution reaction leading to the equatorial acetylenic ligand (structure **11**) is essentially exothermic ($\Delta E = -15$ kcal/mol); substitution of two fluorine atoms (structure **12**) is only slightly exothermic ($\Delta E = -5$ kcal/mol); and the final substitution of all fluorine atoms (structure **14**) is endothermic ($\Delta E = +15$ kcal/mol; all data at MP4/LANL1DZ + ZPE). According to this calculation, one may expect that experimental preparation of trisalkynyliodine **14** is unlikely due to its thermodynamic instability.

$I_4C_8^{4+}$. The square planar tetracation **4** is a minimum on the potential energy surface (it has no imaginary frequencies). However, structure **4** is quite flexible with respect to out-of-plane deformations. The corresponding frequency $\nu_{15}(b_{1u})$ is only 11 cm^{-1}. The structure has only negligible deviations from an exact square. The valence angle C–I–C is 92.1° (Figure 2). This value can be compared to the experimental data for C–I–C with an angle of 92.6° in dialkynyliodonium triflate **2**.[8] All four C–I distances are the same (2.03 Å), which is consistent with the experimentally determined bond lengths of 2.01–2.02 Å.[8] The axial and equatorial positions in **4** cannot be distinguished because I^+ has the deformed tetrahedral 8-I-2 structure. The remaining bond lengths and angles for **4** are also typical of alkynyliodonium salts. This highly symmetrical tetracation **4** has only five active frequencies in the IR spectrum.

$I_4C_8F_4$. Neutral molecules **16–19** can be obtained from cation **4** by addition of four fluorine ligands. This operation transforms a pseudotetrahedral 8-I-2 species into the trigonal bipyramidal 10-I-3 configuration, leading to four different isomers (Figure 3). Calculated frequencies show that isomers **16–19** have either planar (structure **16**) or quasiplanar structures (**17–19**; each of these structures has one out-of-plane imaginary frequency about 10 cm^{-1} and therefore is slightly distorted from the plane). According to our calculations, isomer **16** is the most stable; isomers **17**, **18**, and **19** are higher in energy by 5.0, 5.2, and 9.7 kcal/mol (at MP2/LANL1DZ//HF/LANL1DZ), respectively. This energy hierarchy can be explained by the relative positions of axial and equatorial C–I bonds. All four I centers in **16–19** have one axial and one equatorial bond. The most energetically favorable is the $IC\equiv CI$ moiety, with one equatorial and one axial I–C bond. This sequence of bonds is fully realized in structure **16**. Each of the isomers **17** and **18** has two favorable $IC\equiv CI$ moieties, one $IC\equiv CI$ moiety with two equatorial I–C bonds and one with two axial I–C bonds. However, these isomers are slightly different in energy, because in **17** the strained fragments are linked to each other, while in **18** they are separated. The highest-energy isomer **19** has only unfavorable $IC\equiv CI$ moieties.

Macrocycles **16–19** contain ring strain energy due to the existence of four axial I–C bonds in each of the isomers. As we pointed out for the acylic molecules **10** and **11** and **12** and **13**, moving the acetylene moiety from the equatorial position to an axial position causes 20–24 kcal/mol of strain energy. The ring strain energy for the most stable isomer **16** can be calculated from the thermochemistry of eq 1. According to our calculations, the



(1)

ring strain energy for **16** is 27 kcal/mol (at the MP2/LANL1DZ + ZPE//SCF/LANL1DZ level).

Compared to the square tetracation **4**, the structures of neutral macrocycles **16–19** are significantly distorted. The valence C–I–C angles in all these species are less than 90° (86–87°), and the four I–C bonds no longer equal. The axial I–C bonds (2.12–2.14 Å) are substantially longer than the equatorial I–C bonds (2.00–2.01 Å). This discrepancy in geometry and vibrations may lead to considerable differences in physical and spectral properties of these isomers.

In conclusion, the results of our calculations demonstrate the stability and hence the possible existence of square planar structures for macrocyclic tetraethynyl tetraiodonium compounds. The tetracation $I_4C_8^{4+}$ exists as a single isomer due to a pseudotetrahedral 8-I-2 configuration and has a structure with only negligible deviations from an exact square. The neutral $I_4C_8F_4$ species can exist in four different isomers as a result of the trigonal bipyramidal 10-I-3 configuration. These isomers have distinctly different geometries and energies due to the relative positions of the axial and equatorial C–I bonds in the square. Macrocycles **16–19** contain a ring strain energy due to the existence of four unfavorable axial I–C bonds in each of the isomers. However, the ring strain energy for the most stable isomer **16** is only 27 kcal/mol. Experimental work is in progress to attempt to prepare such novel charged molecular squares or boxes.

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Supplementary Material Available: Table of calculated vibrational frequencies and IR intensities (9 pages). Ordering information is given on any current masthead page.

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