Structure and Bonding in Linear Polyiodine Compounds.
A Theoretical Investigation

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Ab initio effective core potential calculations at the restricted Hartree-Fock level have been performed on the linear polyiodide ions I₃⁻, I₂⁻ and I⁻. For comparison, calculations on I₂ and linear I₃ and I₄⁻ have also been carried out. Relative to isolated units of I and I⁻, the stabilization energies of I₃⁻ and I₂⁻ were found to be -104.4 and -130.4 kJ mol⁻¹, respectively. The total energy for I₄⁻, however, is dominated by the electrostatic repulsion of the terminal atoms, and only a local minimum at 60.7 kJ mol⁻¹ above threshold was found. No stabilization was detected for I₃ and I₂⁻. The calculated bond lengths at minimum energy were all found to be longer than the optimized single bond length of I₂. This is in agreement with experimental findings. The bonding in I₃⁻, I₂⁻ and I⁻ is shown to be almost exclusively of pₓ character and is described in terms of multi-centered α-bonds involving all atoms. The results for I₁⁻, I₂⁻ and I₃⁻ are compared with those for systems containing linear arrays of 3, 4 and 5 sulfur atoms. Our calculated results are found to be in qualitative agreement with the sulfur-sulfur bonding in these compounds.

Dedicated to Professor Olav Foss on his 70th birthday

The linear triiodide ion, I₃⁻, has been extensively studied. A number of crystal structure investigations have shown that the I-I bonds are longer than that of the I₂ molecule in the vapour-phase, and that the ion may be symmetrical or unsymmetrical depending on the counter ion and the crystallographic environment. The existence of linear, discrete I₂⁻ ions was established by X-ray structure determinations on [Co(NH₃)₄I₂]⁺ and [Cu(NH₃)₃I₂]. The central I-I distance in I₂⁻ is somewhat longer than a single bond, the outer distances being appreciably shorter. Similar linear four-atom sequences have been observed previously, e.g. in CsI₄, where I₂⁻ units may be distinguished as made up of interacting I₂ molecules and I⁻ ions at right angles to each other. In no case, however, has a neutral linear I₄ molecule been encountered. The first I₄⁻ ion observed was bent, but approximately linear I₅⁻ units have subsequently been distinguished in channel-inclusion complexes of, e.g., trimesic acid and α-cyclo-
dextrin. Although the crystal structures of the latter are disordered, it is clear that the bonds are longer than a single bond.

The bonding in the polyiodides has been interpreted mainly along three different lines. Using triiodide as an example, one approach has been to regard the bonding as an electrostatic interaction between an I₂ molecule and an I⁻ ion. However, the existence of symmetrical I₃⁻ ions does not favour this model. Another approach has been to describe the bonding in terms of localized covalent bonds, using sp²d hybrid orbitals on the central atom for bonding. However, the promotion of an electron to a d-orbital requires a considerable amount of energy, and in order to make sp²d hybridization probable, the d-orbitals have to be perturbed so as to decrease their size relative to the size in an isolated atom. The third alternative has been to use the concept of delocalized α-bonding to describe the bonding in these ions. In this approach it is not necessary
to invoke promotion to d-orbitals; instead, molecular orbitals made up of atomic p-orbitals are considered used for σ-bonding.

Theoretical calculations on polyiodide ions are few, and have primarily been of the semi-empirical type owing to the large number of electrons involved.\(^{12-16}\) However, effective core potential calculations, treating only the valence electrons explicitly, are now accepted as a realistic alternative to the full ab initio procedure. The approach greatly simplifies numerical calculations on molecules and ions containing heavy elements, and new regions of the periodic table are thus accessible to accurate calculations.\(^{15-16}\) One study of I\(_5^-\) and I\(_7^-\) employing such an approach has already been published,\(^{17}\) and the authors conclude that both of the isolated ions are symmetrical and linear, and that counterion environment influences the structures.

Many questions concerning the bonding and stability of linear polyhalides are still unresolved. In the present paper the ab initio effective core potential approach is applied to linear systems of three, four and five iodine atoms. The calculations include frozen outer-core orbitals and a polarization d-function which was omitted in Ref. 17. In each case, the geometry has been optimized in order to check how well the experimentally observed bond distances are reproduced. The nature of the bonding in these systems is discussed.

Computational method

The calculations were carried out at the Restricted Hartree-Fock (RHF) level using the Effective Core Potential (ECP) approach described in detail in Refs. 18 and 19. This method involves the parameterization of the inner parts of the core in terms of a projection operator and a totally symmetric screening potential, and the freezing of the outer-core orbitals. The method has been compared with full ab initio calculations and has proven accurate for SCF, CAS SCF and CI calculations.\(^{18}\) In the present calculations the 1s–3s, 2p–3p and 3d atomic orbitals were parameterized, the 4s, 4p and 4d orbitals were kept frozen, and only the 5s and 5p valence electrons were allowed to participate in the bonding.

The basis set used included six s-type, six p-type and three d-type basis functions. The three d-type functions were contracted into one. This should allow a reasonable description of the M shell and give rise to fairly small truncation errors.\(^{16-19}\) Basis set parameters were taken from Ref. 20 and augmented with a d-function with exponent 0.25. This exponent was obtained from energy optimization of I\(_2^-\) at the experimental bond distance. The frozen orbitals were obtained through truncation and renormalization of the optimal AO's. The model potentials were generated by fitting orbital energies and outer orbital shapes to the full atomic Hartree-Fock orbitals.

Results and discussion

Calculations on I\(_2^-\) and I\(_7^-\). The optimized bond length for I\(_2^-\) is 2.741 Å. This is close to the value of 2.735 Å obtained from a comparable all-electron calculation,\(^{15}\) but somewhat larger than the experimental values of 2.667 Å and 2.715 Å for gaseous\(^{21}\) and solid\(^{22}\) I\(_2^-\), respectively. The elongation in the solid state is attributed to intermolecular interactions.

For the I\(_7^-\) ion, our calculation correctly predicts an appreciable lengthening of the I–I bond. The calculated equilibrium bond distance of 3.044 Å is about 4% larger than the value of 2.919 Å observed for the isolated I\(_7^-\) ion in [(C\(_6\)H\(_5\))\(_2\)AsI\(_4\)].\(^{3}\) and is consistent with our calculated value for I\(_7^-\). Experimental bond lengths for unsymmetrical triiodides are in the 2.79–3.11 Å range.\(^{5}\) The calculated stabilization energy for the reaction I\(_2^-\) + I\(_-\) → I\(_7^-\) is −104.4 kJ mol\(^{-1}\), and

<table>
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<th>Orbital</th>
<th>Energy (D(_{av})) /au</th>
<th>Atomic population</th>
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<td>0.940</td>
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<td>I(_2^-)</td>
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<td>1.552</td>
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<td>I(_4^-)</td>
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<td>I(_5^-)</td>
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<td>I(_6^-)</td>
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<tr>
<td>I(_7^-)</td>
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<tr>
<td>I(_8^-)</td>
<td>1.428</td>
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clearly favours the formation of an isolated $I_3^-$ ion.

Orbital energies and results of Mulliken population analysis of the valence orbitals of $I_3^-$ are given in Table 1. All valence MO's of $\pi$-symmetry are located between the $2\sigma_u$ level and the highest occupied $3\sigma_g$ level. The gross atomic population of the $1\pi_u$ pair of MO's is dominated by the lone pairs of the central atom, while the terminal pairs are found in the two $1\pi_g$ orbitals. The $2\pi_u$ pair possesses antibonding combinations of the $p_u$ atomic orbitals.

Fig. 1a shows the calculated atomic charges as well as the atomic $s$, $p_u$, and $d_u$ populations of the valence shell for $I_3^-$. As expected for $I_3^-$, the negative charge is distributed between the terminal atoms, while the central atom has a small positive charge. This charge distribution is attributed to the population of the $p_u$ orbitals in accordance with a delocalized three-centre four-electron (3c-4e) bond as originally proposed by Pimentel,23 and by Hach and Rundle.24 The $d_u$-orbital population is small and confirms the role of the $d$-orbitals as polarization functions. The importance of the valence $p_u$-orbitals for the bonding in $I_3^-$ may be seen from Fig. 2a. The four electrons occupy one delocalized bonding and one nonbonding molecular orbital of essentially $p_u$ character. The results for $I_3^{2-}$ and $I_3^-$ are discussed below.

The delocalized covalent description of the bonding in $I_3^-$ given above is consistent with the existence of symmetrical $I_3^-$ ions with bonds longer than the $I_3$ single bond. The symmetrical triiodide has also been regarded as the limiting case of an electrostatic ion-dipole interaction between an
iodide ion and a polarized iodine molecule. The calculated charge distribution suggests that electrostatic attraction contributes to the bonding, but it does not support a purely ionic picture.

**Calculations on I_4^-.** Linear or nearly linear tetraiodide ions have been observed in the solid state either as molecular ions, as in [Co(NH_3)_6]I_4, or coordinatively bonded, as in [Cu(NH_3)_4]I_4. However, similar linear four-atom sequences have also been found in a number of other aggregates of polyiodides and in solid iodine. The long terminal bonds have lengths from 3.34 Å to 3.61 Å, with a central bond in the 2.68–2.81 Å range. As expected, the shortest terminal bonds correspond roughly to the longest central bond. An intermediate I_4^2-, formed from I^- and I_3^-, has been suggested to exist in solution.

The calculations on I_4^- were performed in steps in which the central I_2 bond length was optimized for successive fixed terminal bond distances. In all cases, linear D_4h symmetry was preserved. The upper full-line curve of Fig. 3 shows the total energy relative to isolated I_2 and I^- ions as a function of the terminal bond distance. Relative to infinite separation, no minimum was found. However, the energy curve has

![Image](image11x33to488x676)

(a) I_3^-: 3σ^u_0 0.1312

3σ_g -0.1711

2σ_u -0.3009

(b) I_4^2-: 4σ^u_0 0.2081

4σ_g -0.0589

3σ_u -0.0722

3σ_g -0.2255

(c) I_5^-: 5σ^g_0 0.0717

4σ_u -0.1914

4σ_g -0.3269

3σ_u -0.3506

Fig. 2. Schematic illustration of the highest occupied and the lowest unoccupied molecular orbitals of σ similarity. Energy (au) and atomic ρσ orbital populations are indicated for each molecular orbital.
According to our calculations, the formation of an isolated $I_2^-$ ion is not favoured. However, the observed systems have been studied in solution or in the crystalline state, where they are stabilized by solvation or lattice energies. It is therefore conceivable that environmental stabilization may account for the experimental observations. Fig. 3 indicates that if the energy of $I_2^-$ is calculated relative to $I^-$ ions at finite separation, the formation of the molecular ion might be favourable.

The results obtained above do not, however, completely rule out the possibility of formation of isolated and stable $I_2^-$ ions. Our calculations are performed within the RHF approximation, and electron correlation is not taken into account. It is expected that the inter-fragment correlation energy between $I^-$ and $I_2^-$ will increase in magnitude as the distance between the fragments decreases. This effect may be less important for $I_1$ and $I_2^-$ owing to the presence of fewer electrons per centre in these molecules. Hence, electron correlation may modify the interaction curve for $I_2^-$ in Fig. 3 (upper full line) and convert the local minimum at the RHF-level to a global minimum with approximately the same interatomic distances.

The calculated bond lengths at minimum energy correspond to an elongation of the central

<table>
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<th>Orbital $(D_{nn})$</th>
<th>Energy (au)</th>
<th>Atomic population $I_1$</th>
<th>$I_2$</th>
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<td>1.998</td>
</tr>
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<td>0.002</td>
<td>1.998</td>
</tr>
<tr>
<td>3$\sigma_u$</td>
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<tr>
<td>1$\pi_u$</td>
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<td>0.012</td>
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<td>1$\pi_v$</td>
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<td>0.002</td>
</tr>
<tr>
<td>3$\sigma_u$</td>
<td>-0.2255</td>
<td>0.966</td>
<td>0.034</td>
</tr>
<tr>
<td>2$\sigma_u$</td>
<td>-0.4897</td>
<td>0.010</td>
<td>0.990</td>
</tr>
<tr>
<td>2$\sigma_p$</td>
<td>-0.4905</td>
<td>0.004</td>
<td>0.996</td>
</tr>
<tr>
<td>1$\sigma_p$</td>
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</tr>
<tr>
<td>1$\sigma_d$</td>
<td>-0.6674</td>
<td>0.999</td>
<td>0.001</td>
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I–I bond, in agreement with the experimental observations. However, the terminal bond distances are appreciably longer than those observed in the solid state. Orbital energies and gross atomic populations at the local minimum geometry are given in Table 2. As expected for such long interaction distances, the bonds are almost localized into I$_3$ and I$^-$ fragments. This is more clearly revealed in Fig. 2b, where the populations of the most important valence $\sigma$-orbitals are shown. The bonding 3$\sigma_5$ MO is mainly localized to the central I–I bond, whereas the 3$\sigma_3$ MO represents the terminal bonds. However, the participation of the central atoms in the latter MO is too small to produce a strong interaction. It is seen that both the 3$\sigma_3$ and 4$\sigma_3$ orbitals mainly represent charge localized on the terminal atoms.

The atomic charges and orbital populations are shown in Fig. 1b. According to Hassel, molecular ions like I$_2^{-}$ may be interpreted as charge-transfer complexes formed by two iodide donors and one acceptor iodine molecule. However, our calculations indicate that only a small amount of charge is transferred to the central iodine molecule. Fig. 1b also shows that the two negative charges are mainly localized to the $p_\sigma$ orbitals. The bonding in I$_2^{-}$ may therefore be described as a 4e–6e bond formed by the $p_\sigma$ orbitals, but at the optimized local minimum the delocalization is rather small. For shorter interaction distances delocalization becomes more pronounced, although the main features remain the same.

In the crystal structures the degree of proximity of the terminal ions is determined by counter ions and crystal packing, and experimentally the terminal distances are appreciably shorter than those calculated for the free molecular ion. The effect of two approaching I$^-$ ions on the I$_2$ bond length is shown in Fig. 4. The dashed curve shows that the I–I distance increases as the I----I separation decreases. Our calculations thus confirm the experimental trends mentioned above. At I----I = 3.40 Å the calculated I–I bond length is about 0.15 Å greater than that of a single bond, which is close to what is observed experimentally (~0.12 Å). When the I----I distances are decreased to 3.00 Å, the bond lengths eventually become equal. However, the energy of this configuration lies about 140 kJ mol$^{-1}$ above the local minimum value. The curve for I$_2^{2-}$ is almost parallel and slightly displaced relative to the curve for I$_2^-$. The displacement indicates that the effect of close interaction of one I$_2$ bond with two ions is larger than the effect of one ion on two I$_2$ bonds, as might have been expected.

Calculations on linear I$_3$ and I$_3^+$. From the schematic illustration in Fig. 2b it follows that the bonding of the central part of the molecule is due to population of the 3$\sigma_5$ and 4$\sigma_3$ levels. Removal of two electrons from the 4$\sigma_3$ level to produce neutral I$_n$ would weaken the central bond and strengthen the terminal bonds. Calculations on linear I$_4$ do indeed show that the molecule dissociates into two I$_3$ fragments, and no minimum is found. Instead, a strong repulsive interaction at

![Fig. 4. The effect of close contacts between I$^-$ and I$_2$ as calculated for I$_2^{2-}$ (dashed line) and for I$_2^-$ (full line). The optimized bond length for the I$_2$ single bond is dotted for comparison. The circles refer to optimized geometries at minimum energies.](image-url)
a distance less than the van der Waals distance is predicted, as shown in Fig. 5. In order to describe the dispersion interaction between the two I₂ fragments more properly, electron correlation must be included in the calculations. However, there is no experimental evidence for the existence of a linear I₄ molecule in the gas phase. Electron deflection studies of Cl₄ and Br₂ show that these molecules are polar, this is consistent with an L-shaped structure for the most stable free dimer configuration, as found in their crystal structures. Since the crystal structures of Cl₂ and Br₂ are isomorphous with that of I₂, this suggests a similar configuration for I₄ in the gas phase. *Ab initio* calculations on Cl₄, including dispersion energy, predict the existence of a stable linear molecule (−2.1 kJ mol⁻¹) which, however, is less favourable than an L-shaped configuration (−7.8 kJ mol⁻¹).

From Fig. 2b it also follows that further remov-
al of an electron pair from the $3\sigma_g$ level to produce linear $I_5^+$ would result in a molecule with a strengthened central bond. Our calculations on linear ($D_{ab}$) $I_5^+$ show that this prediction is correct, but that the molecule dissociates into $I_3$ and $I^+$ fragments with no minimum at the RHF-level. Crystal structure studies on $I_2^+$ reveal that the molecule is rectangular with two $I_2^+$ units joined together by two relatively weak bonds.\(^{33}\)

**Calculations on $I_5^-$.** V-shaped $I_5^-$ ions have been found experimentally either as isolated units, as in the KI/KI$_5$ complex of valinomycin,\(^{34}\) or as interacting units, as in N(CH$_3$)$_3$I$_5$.\(^{6}\) Both anions possess two long central bonds (3.08 and 3.17 Å) and two relatively short terminal bonds (2.76 and 2.82 Å). Linear or almost linear $I_5^-$ ions have been observed only as polymeric chains in various hosts, and are not well characterized. For (trimesic acid·H$_2$O)$_{10}$·3HI, the bond lengths 3.26 Å and 2.74 Å have been suggested for the central and terminal bonds, respectively.\(^{9}\) The central cavity of $\alpha$-cycloextrin ($\alpha$-CD) contains chains of disordered $I_5^-$ units.\(^{10}\) The average central and terminal bond lengths in ($\alpha$-CD)$_2$Cd$_{0.5}$I$_4$·2H$_2$O are 3.16 and 2.97 Å, respectively. The colour of the blue starch iodine complex has also been attributed to the presence of a linear $I_5^-$ chain on the basis of Raman and Mössbauer spectroscopy.\(^{35}\)

Our calculations on $I_5^-$ were confined to a linear symmetric ($D_{ab}$) structure. The I–I bond lengths were optimized for a series of fixed I–I–I central bonds. Fig. 6 shows the energy curve for interaction of the two $I_2$ units with a central $I^-$ ion. In contrast to $I_5^-$ the energy curve for $I_5^-$ is clearly bonding, with a minimum energy of $-130.4$ kJ mol$^{-1}$ relative to infinite separation of $I^-$ and two $I_2$ molecules. Relative to isolated units of $I_3^-$ and $I_2^-$, however, the stabilization is only $-26.0$ kJ mol$^{-1}$. In the $\alpha$-CD pentaiodides, disordered chains of both ($I_5^--I_2$)$_n$ and ($I_5^-I_3$)$_n$ are found to be present.\(^{10}\)

The optimized central and terminal bond lengths at minimum energy were found to be 3.399 Å and 2.835 Å, respectively. Both distances are considerably longer than the optimized single bond length in $I_2$, and are indicative of partial bonding in the ion. The results are in agreement with the experimental distances found for the more weakly interacting $I_5^-$ fragments of the trimesic acid complex.\(^{9}\)

Orbital energies and gross atomic populations at the minimum energy geometry are given in Table 3. As for $I_3^-$, all the $\pi$ molecular orbitals are located between the highest and next highest $\sigma$ orbitals. The highest occupied $\pi$ orbitals (the $3\pi_g$ pair of MO’s) are dominated by the lone pairs of the central atom. The atomic charge distribution and population of the valence $\sigma$-system is shown in Fig. 1c. As expected, charge is transferred from the central $I^-$ ion to the two $I_2$ molecules when the $I_5^-$ unit is formed. The transfer to each molecule is calculated to be 0.17 e, which is quite similar to that received by the central $I_2$ molecule in $I_5^{2-}$ (0.12 e). In both $I_5^-$ and $I_5^{2-}$ this results in multi-centered delocalized bonding. However, Fig. 1c shows that for $I_5^-$ the charge is transferred to the terminal atoms, and a favourable alternating charge distribution similar to that found for $I_3^-$ is established. For $I_5^{2-}$, additional electrostatic repulsion is expected because of the build-up of charge on both atoms of the central $I_2$ molecule.

Fig. 1c also shows that the charge transfer takes place essentially in the $p_o$ system, and that the bonding in $I_5^-$ may be discussed in terms of a delocalized $5c$-$6e$ bond. This is shown more clearly in Fig. 2c, in which the highest occupied molecular orbitals of $\sigma$-symmetry are illustrated.

### Table 3. Orbital energies and gross atomic populations of the valence molecular orbitals of the $I_5^-$ ion.

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<tr>
<th>Orbital</th>
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<th>Atomic population</th>
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<tbody>
<tr>
<td>$I_1$</td>
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<td>$I_3$</td>
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<tr>
<td>40$_u$</td>
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<td>10$_g$</td>
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schematically. These are primarily of $p$-character. The $3\sigma_u$ MO is responsible for the delocalized bond involving all five atoms, while the $4\sigma_u$ MO strengthens the terminal bonds. The two electrons in the $4\sigma_u$ MO are mainly non-bonding, with charge localized to the central and terminal atoms. Fig. 2c explains qualitatively the partial bonding in this system; it also explains why the central bonds are longer than the terminal ones.

As mentioned above, the symmetrical $I_3-$ ion may be considered as the limiting structure of $I_2$ and an approaching $I^-$. The interaction weakens and lengthens the original $I$-$I$ bond, as is observed experimentally in crystals when an unsymmetrical environment prohibits formation of a centrosymmetric system. Similarly, $I_5^-$ may be considered as the limiting structure of $I^-I^-$ and two approaching $I_2$ molecules. The effect of the $I^-$ interaction on the $I_2$ bond lengths is shown in Fig. 4. As was found for the $I_5^-$ ion, the interaction is quite substantial and leads to a pronounced increase in the lengths of the $I_2$ bonds. This is in agreement with the bond lengths found for the two linear $I_5^-$ ions mentioned above. Although the ions are polymeric and not well characterized, the unit with the shortest central bonds possesses the longest terminal bonds and vice versa.

When the $I$-$I$ distance is reduced below the minimum value, all bonds eventually become equal in length. In this configuration the bond lengths are 2.93 Å, with a total energy of 55 kJ mol$^{-1}$ above the calculated minimum. This energy corresponds to the bond lengths 4.52 Å and 2.78 Å when the $I$-$I$ distance is increased above the minimum value. Thus, within 55 kJ mol$^{-1}$ the bond lengths may vary from 4.52/2.78 Å to 2.93/2.93 Å. This shows that the bonding in linear $I_5^-$ ions is weak and easily perturbed.

Comparison with systems containing linear sulfur sequences. Approximately linear arrays of 3, 4 and 5 sulfur atoms occur in the 1,6,6a-trithiapentalenes (Fig. 7a) and in the extended sulfur analogues (Figs. 7b–d). In these molecules, the carbon (or carbon-nitrogen) skeleton tends to keep the sulfur atoms linearly arranged, i.e. in positions which favour delocalized $n$-centre $\sigma$-bonding.

The 1,6,6a-trithiapentalenes have been extensively studied. The S–S bonds are always found to be longer than those of isolated cyclic 1,2-di-thioles; symmetrical as well as unsymmetrical sulfur sequences are encountered. On the basis of theoretical calculations, delocalized 3c–4e bonding has been suggested.

In the extended analogues containing five sulfur atoms (Fig. 7d), all the S–S bonds have been found to be longer than those in cyclic di-thioles, with the outer distances being the shorter ones. Unsymmetrical as well as symmetrical sequences are observed, indicating a five-centre system which is easily perturbed. CNDO/2 calculations on model five-sulfur compounds are in qualitative agreement with the experimental results as far as relative distances and perturbation of system are concerned. In these five-sulfur sequences there are 6 $\sigma$-electrons available for bonding, and the MO-description of the $\sigma$-bonding is analogous to that for $I_5^-$. Our calculations are thus in qualitative agreement with the experimental and theoretical results for the five-sulfur compounds.

The four-sulfur systems examined are of two different types. In one (Fig. 7b), the two outer bonds are found experimentally to be of the same length as S–S bonds in isolated cyclic di-thioles,
while the central distance is appreciably longer than the distances in $1,6,6a$-trithiapentalenes or the five-sulfur compounds. Even though the carbon skeleton puts a restraint on the total S–S distance, no lengthening effect on the outer bonds is observed. CNDO/2 calculations on a model four-sulfur compound$^{38}$ give distances in qualitative agreement with the experimental findings and with the results of our $I_4$ calculations. Both experimental and theoretical results thus suggest that an arrangement with essentially localized 2c–2e bonds is energetically more favourable than one with a delocalized 4c–4e bond.

In the other type of four-sulfur compounds (Fig. 7c) the central distance is the shorter one, the bond length being comparable to that of the shorter bond in unsymmetrical $1,6,6a$-trithiapentalenes. Clearly, the proximity of the outer S-atoms has brought about a lengthening of the central S–S bond relative to that of an isolated dithiole. In these four-sulfur systems there are 6 $p$-electrons available for $\sigma$-bonding, as in the $I_2^-$ ion.$^{38}$ Again, CNDO/2 calculations give distances in qualitative agreement with the observed ones.$^{38}$ The findings are thus in qualitative agreement with our calculation on $I_2^-$ which showed that close contacts with terminal atoms may lead to an appreciable lengthening of the central bond.

Summary and conclusions

*Ab initio* ECP calculations at the RHF-level have been performed on $I_1$ and the linear polyiodine species $I_1^-$, $I_4^-$, $I_4$, $I_4^+$ and $I_5^-$ assuming $D_{onh}$ symmetry. Relative to isolated units of $I_1$ and $I_1^-$, only $I_1^-$ and $I_5^-$ are found to be stable as free ions. For $I_1$ and $I_5^-$ the stabilization energies at the optimized geometries are found to be $-104.4$ and $-130.3$ kJ mol$^{-1}$, respectively. This result is consistent with the existence of these ions in solution and in the solid state.

The ion $I_2^-$ is also observed experimentally, but since the calculated energy for the $I_2^-$ ion is dominated by the electrostatic repulsion of the terminal ions, only a local minimum at 60.7 kJ mol$^{-1}$ above threshold was encountered. However, when the repulsive energy is subtracted the molecular bonding contribution is clearly revealed. It is thus conceivable that environmental stabilization may account for the experimental observations.

Calculations on $I_4$ show that removal of two electrons from $I_2^-$ will cause the molecule to dissociate into two $I_1$ fragments with no minimum at the RHF-level. There is, at present, no experimental evidence for the existence of a stable linear $I_4$ molecule, in agreement with the calculated results. Additional removal of two electrons to give linear $I_4^{2-}$ also leads to dissociation, but now $I_1$ and $I_1^+$ fragments are formed and no minimum is encountered. The $I_2^+$ cation has so far only been observed as a rectangular unit.

The calculated bond lengths at minimum energy for $I_1^-$, $I_2^-$ and $I_5^-$ are all greater than the optimized single bond length for $I_1$ (2.741 Å). For $I_1^-$ the bond is 3.044 Å, whereas for $I_2^-$ a short central bond (2.807 Å) and two relatively long terminal bonds (3.991 Å) were found at the local minimum. For $I_5^-$ the two central bonds (3.399 Å) and the two terminal bonds (2.835 Å) are more equal in length, with a mean value (3.12 Å) which is close to that found for $I_1^-$. The effect of close contacts between $I_1^-$ and $I_1$ has been extensively studied for $I_2^-$ and $I_2$. For both molecules an appreciable increase in the $I-I$ bond length is calculated for distances below the van der Waals distance, the effect being somewhat greater for $I_2^-$ than for $I_5^-$. Mulliken population analysis has been used to discuss the bonding in $I_1^-$, $I_2^-$ and $I_5^-$. The results gave no support to the description of the bonding in terms of localized covalent bonds formed through $sp^3d$ hybridization. For all anions, the $d$-functions are merely polarization functions. The bonding is, on the other hand, very nicely described in terms of multi-centered $\sigma$-bonds involving all atoms. In the case of $I_1^-$ and $I_2^-$ this bonding is highly delocalized, whereas for $I_2^-$ the bonding is more localized due to large interaction distances at the local minimum.

All of the anions can be considered as products between closed shell molecules and ions, and in this respect they may be interpreted as charge-transfer complexes formed by iodide donors and iodine acceptors. In the case of $I_1^-$ and $I_5^-$, the bonding takes place as a charge transfer from $I_1^-$ to $I_1$. The charge is transferred to the terminal atoms, resulting in a favourable alternating charge distribution for these ions. For $I_2^-$, the charge transfer takes place from the terminal atoms to the central $I_2$ molecule, which is a very unfavourable situation. This is consistent with only a weak interaction for this molecular ion.
The results for $I_1$, $I_4$, $I_5^{1/2}$ and $I_5$ have also been compared with those for the linear arrays of 3, 4 and 5 sulfur atoms that occur in 1,6,6a-trithiapentalenes and extended sulfur analogues. The sulfur-sulfur bonding in these compounds is found to be in qualitative agreement with the calculated results, thus emphasizing the importance of $p_s$ bonding in the sulfur analogues.

References


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