Structure and Bonding in Linear Polyiodine Compounds. A Theoretical Investigation

Leif J. Sæthre,[a] Odd Gropen[a] and Jorunn Sletten[b]

[a]Department of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, N-9001 Tromsø and [b]Department of Chemistry, University of Bergen, Allégt. 41, N-5007 Bergen, Norway

Ab initio effective core potential calculations at the restricted Hartree-Fock level have been performed on the linear polyiodide ions I_3^-, I_4^{2-} and I_5^-. For comparison, calculations on I_2 and linear I_4 and I_4^{2+} have also been carried out. Relative to isolated units of I_2 and I^- the stabilization energies of I_3^- and I_5^- were found to be -104.4 and -130.4 kJ mol^{-1}, respectively. The total energy for I_4^{2-}, 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 I_4 and I_4^{2+}. The calculated bond lengths at minimum energy were all found to be longer than the optimized single bond length of I_2. This is in agreement with experimental findings. The bonding in I_3^-, I_4^{2-} and I_5^- is shown to be almost exclusively of p_σ character and is described in terms of multi-centered σ-bonds involving all atoms. The results for I_3^-, I_4, I_4^{2-} and I_5^- are also 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, I_3^-, has been extensively studied. A number of crystal structure investigations have shown that the I–I bonds are longer than that of the I_2 molecule in the vapour-phase, and that the ion may be symmetrical or unsymmetrical depending on the counter ion and the crystallographic environment.[1-4] The existence of linear, discrete I_4^{2-} ions was established by X-ray structure determinations on [Co(NH$_3$)$_4$I$_3$I$_4$][5] and [Cu(NH$_3$)$_4$I$_4$].[6] The central I–I distance in I_4^{2-} is somewhat longer than a single bond, the outer distances being appreciably longer. Similar linear four-atom sequences have been observed previously, e.g. in CsI$_4$, where I_8^{2-} units may be distinguished as made up of interacting I_2 molecules and I_3^- ions at right angles to each other.[7] In no case, however, has a neutral linear I_4 molecule been encountered. The first I_5^- ion observed was bent,[8] but approximately linear I_5^- units have subsequently been distinguished in channel-inclusion complexes of, e.g., trimesic acid[9] and α-cyclo-

dextrin.[10] 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.[11] Using triiodide as an example, one approach has been to regard the bonding as an electrostatic interaction between an I_2 molecule and an I^- ion. However, the existence of symmetrical I_3^- ions does not favour this model. Another approach has been to describe the bonding in terms of localized covalent bonds, using sp^3d 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 sp^3d 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 σ-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.[12-14] 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_3^- and I_5^- 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_3^-. 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_3^- 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_3^- ion in $[(C_6H_5)_4AsI_3]$,[3] and is consistent with our calculated value for I_2. Experimental bond lengths for unsymmetrical triiodides are in the 2.79–3.11 Å range.[5] The calculated stabilization energy for the reaction $I_2 + I^- \rightarrow I_3^-$ is -104.4 kJ mol^{-1}, and

Table 1. Orbital energies and gross atomic populations of the valence molecular orbitals of the I_3^- ion. The values correspond to a linear symmetric ion ($D_{\infty h}$) at the optimized geometry (3.04 Å). I_1 denotes the central atom of the sequence.

Orbital ($D_{\infty h}$)	Energy /au	Atomic population	
		I_1	I_2
$3\sigma_g$	$-.1711$	0.120	0.940
$2\pi_u$	$-.1881$	0.897	1.552
$1\pi_g$	$-.2094$	0.017	1.992
$1\pi_u$	$-.2647$	3.094	0.453
$2\sigma_u$	$-.3009$	0.756	0.622
$2\sigma_g$	$-.6091$	0.522	0.739
$1\sigma_u$	$-.6478$	0.079	0.961
$1\sigma_g$	$-.7133$	1.428	0.286

(a) I_3^- :

$$\begin{array}{ccc} -.54 & 0.09 & -.54 \\ \text{I} ----- & \text{I} ----- & \text{I} \\ & (3.04)\ (3.04) & \end{array}$$

s	1.98	2.00	1.98	Σs : 5.96
p_σ	1.56	0.84	1.56	Σp_σ: 3.96
d_σ	0.01	0.07	0.01	Σd_σ: 0.09

(b) I_4^{2-} :

$$\begin{array}{cccc} -.94 & -.06 & -.06 & -.94 \\ \text{I} ----- & \text{I} —— & \text{I} ----- & \text{I} \\ & (3.99)\ (2.81)\ (3.99) & & \end{array}$$

s	2.00	1.98	1.98	2.00	Σs : 5.96
p_σ	1.94	1.04	1.04	1.94	Σp_σ : 5.96
d_σ	0.00	0.04	0.04	0.00	Σd_σ : 0.08

(c) I_5^- :

$$\begin{array}{ccccc} -.27 & 0.10 & -.66 & 0.10 & -.27 \\ \text{I} —— & \text{I} ----- & \text{I} ----- & \text{I} —— & \text{I} \\ & (2.84)\ (3.40)\ (3.40)\ (2.84) & & & \end{array}$$

s	1.97	1.99	1.98	1.99	1.97	Σs : 9.90
p_σ	1.28	0.86	1.68	0.86	1.28	Σp_σ : 5.96
d_σ	0.01	0.06	0.00	0.06	0.01	Σd_σ : 0.14

Fig. 1. Atomic charges, optimized bond distances (Å) (in parentheses), and atomic s, p_σ and d_σ populations.

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 π-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_π atomic orbitals.

Fig. 1a shows the calculated atomic charges as well as the atomic s, p_σ and d_σ 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_σ 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_σ-orbital population is small and confirms the role of the d-orbitals as polarization functions. The importance of the valence p_σ-orbitals for the bonding in I_3^- may be seen from Fig. 2a. The four electrons occupy one delocalized bonding and one non-bonding molecular orbital of essentially p_σ character. The results for I_4^{2-} and I_5^- 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_2 single bond. The symmetrical triiodide has also been regarded as the limiting case of an electrostatic ion-dipole interaction between an

18

iodide ion and a polarized iodine molecule.[25] 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^{2-}. Linear or nearly linear tetraiodide ions have been observed in the solid state either as molecular ions, as in $[Co(NH_3)_6I_3I_4]$,[5] or coordinatively bonded, as in $Cu(NH_3)_4I_4$.[6] However, similar linear four-atom sequences have also been found in a number of other aggregates of polyiodides[26] and in solid iodine.[22] 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.[27]

The calculations on I_4^{2-} were performed in steps in which the central I_2 bond length was optimized for successive fixed terminal bond distances. In all cases, linear $D_{\infty h}$ 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
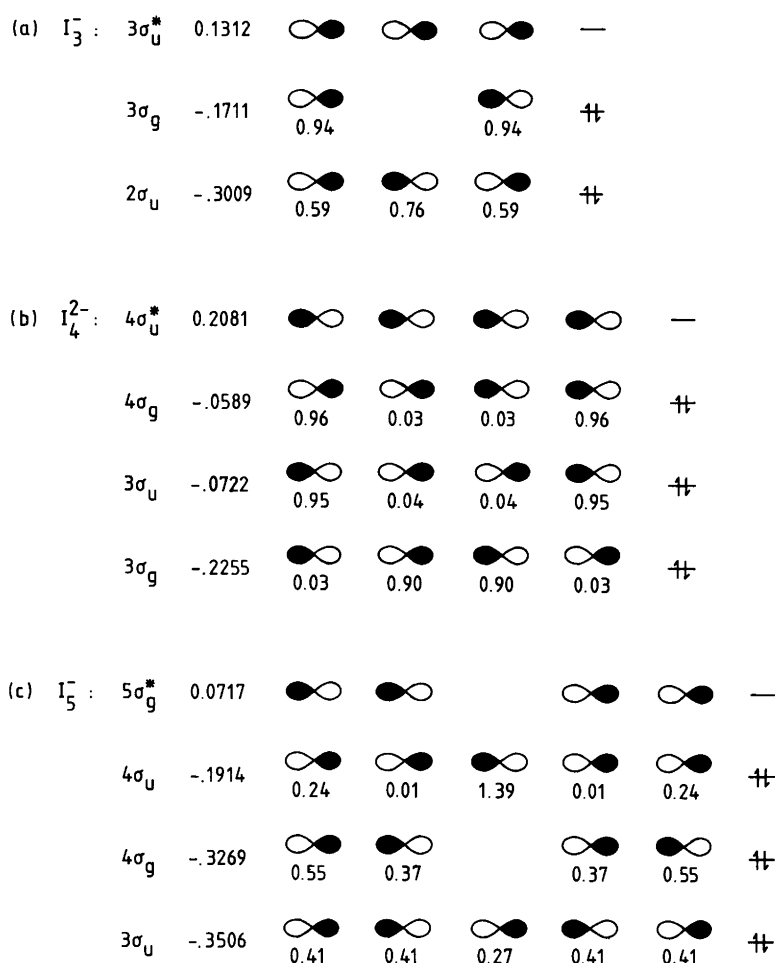
Fig. 2. Schematic illustration of the highest occupied and the lowest unoccupied molecular orbitals of σ symmetry. Energy (au) and atomic p_σ orbital populations are indicated for each molecular orbital.
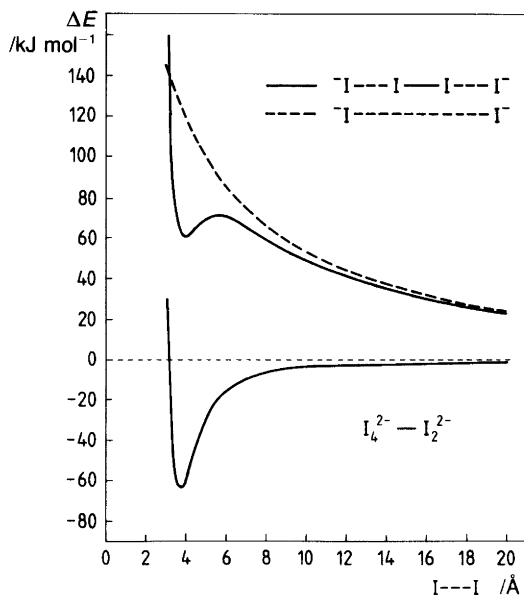
Fig. 3. Calculated energy of I_4^{2-} as a function of the terminal bond distances (upper full line). The dashed line shows the repulsive interaction energy for two I^- ions corresponding to the distances in the I_4^{2-} molecule. The effect of subtracting this energy from the I_4^{2-} energy curve is also shown (lower full line). All values are given relative to I_2 and I^- at infinite separation.

a local minimum corresponding to distances of 3.991 Å and 2.807 Å for the terminal and central bond, respectively. This minimum is located 60.7 kJ mol^{-1} above the threshold energy, with a local barrier of 10.6 kJ mol^{-1}. The energy of formation of I_4^{2-} from I^- and I_3^- is 165.1 kJ mol^{-1}, and this process is thus considerably less favourable.

Fig. 3 also shows the repulsive energy interaction for two I^- ions at distances corresponding to those in the I_4^{2-} molecule. It is seen that the total energy of the I_4^{2-} ion is dominated by the electrostatic repulsion of the terminal ions. At shorter interaction distances, however, the contribution to molecular bonding becomes apparent. The lower full line of Fig. 3 shows the effect of subtracting the repulsive I_2^{2-} energy from the I_4^{2-} energy. This curve thus roughly represents the net bonding interaction in I_4^{2-}. The energy minimum for the curve is located -62.8 kJ mol^{-1} below the threshold energy. The corresponding bond lengths are 3.761 Å and 2.811 Å for the terminal and central bonds, respectively.

According to our calculations, the formation of an isolated I_4^{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_4^{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_4^{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_3^- and I_5^- owing to the presence of fewer electrons per centre in these molecules. Hence, electron correlation may modify the interaction curve for I_4^{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 2. Orbital energies and gross atomic populations of the valence molecular orbitals of the I_4^{2-} ion. The values correspond to a linear symmetric ion $(D_{\infty h})$ at the optimized geometry $(I_1-I_1' = 2.81$ Å, $I_1-I_2 = 3.99$ Å). I_1 and I_2 denote the central and terminal atoms, respectively.

Orbital $(D_{\infty h})$	Energy /au	Atomic population	
		I_1	I_2
$4\sigma_g$	$-.0587$	0.038	0.962
$2\pi_g$	$-.0665$	0.012	1.988
$2\pi_u$	$-.0669$	0.002	1.998
$3\sigma_u$	$-.0722$	0.051	0.949
$1\pi_g$	$-.1405$	1.988	0.012
$1\pi_u$	$-.2076$	1.998	0.002
$3\sigma_g$	$-.2255$	0.966	0.034
$2\sigma_u$	$-.4897$	0.010	0.990
$2\sigma_g$	$-.4905$	0.004	0.996
$1\sigma_u$	$-.5607$	0.991	0.009
$1\sigma_g$	$-.6674$	0.999	0.001

20

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_2 and I^- fragments. This is more clearly revealed in Fig. 2b, where the populations of the most important valence σ-orbitals are shown. The bonding $3\sigma_g$ MO is mainly localized to the central I–I bond, whereas the $3\sigma_u$ 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 $3\sigma_u$ and $4\sigma_g$ 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_4^{2-} may be interpreted as charge-transfer complexes formed by two iodide donors and one acceptor iodine molecule.[28] 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_σ orbitals. The bonding in I_4^{2-} may therefore be described as a 4c–6e bond formed by the p_σ orbitals,[29] 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_4^{2-} is almost parallel and slightly displaced relative to the curve for I_5^-. 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_4 and I_4^{2+}. 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 $3\sigma_g$ and $4\sigma_g$ levels. Removal of two electrons from the $4\sigma_g$ level to produce neutral I_4 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_2 fragments, and no minimum is found. Instead, a strong repulsive interaction at
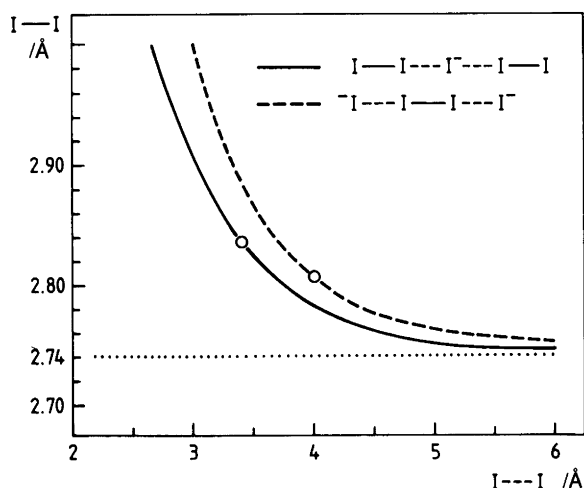

Fig. 4. The effect of close contacts between I^- and I_2 as calculated for I_4^{2-} (dashed line) and for I_5^- (full line). The optimized bond length for the I_2 single bond is dotted for comparison. The circles refer to optimized geometries at minimum energies.
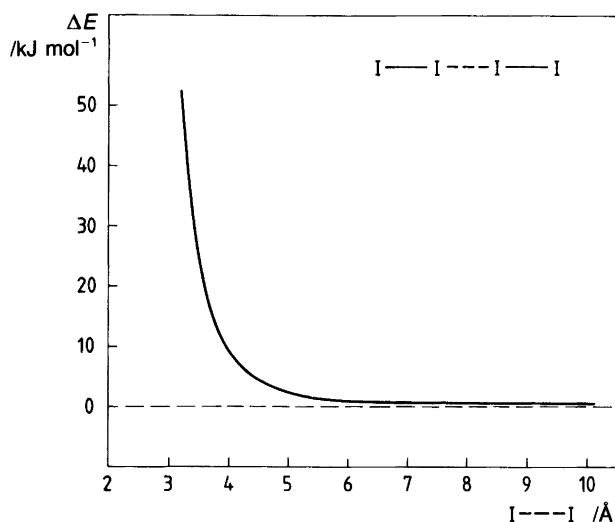
ΔE
/kJ mol⁻¹

I ——— I --- I ——— I

Fig. 5. Calculated energy of I_4 as a function of the intermolecular distance. The values are given relative to isolated I_2 molecules.

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 I_2 fragments more properly, electron correlation must be included in the calculations. However, there is no experimental evidence for the existence of a linear I_4 molecule in the gas phase. Electron deflection studies of Cl_4 and Br_4 show that these molecules are polar;[30] this is consistent with an L-shaped structure for the most stable free dimer configuration, as found in their crystal structures.[31] Since the crystal structures of Cl_2 and Br_2 are isomorphous with that of I_2, this suggests a similar configuration for I_4 in the gas phase. *Ab initio* calculations on Cl_4, 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).[32]

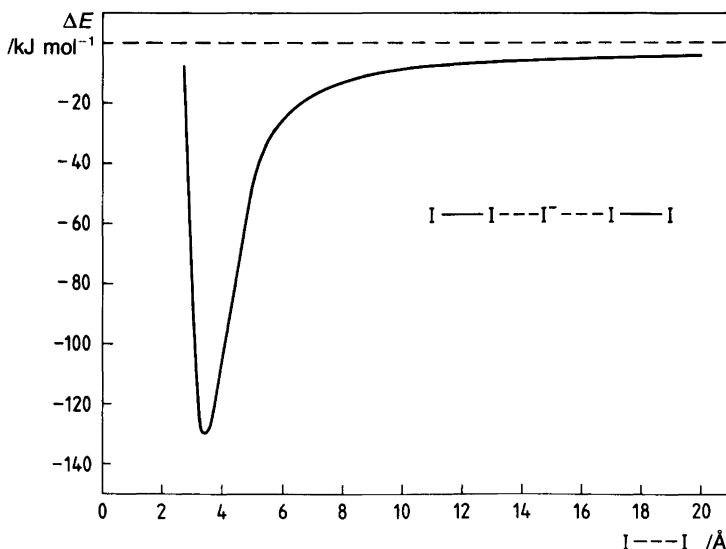From Fig. 2b it also follows that further remov-

Fig. 6. Calculated energy of I_5^- as a function of the distance between the central I^- and the approaching I_2 units.
The values are given relative to I_2 and I^- at infinite separation.

22

al of an electron pair from the $3\sigma_u$ level to produce linear I_4^{2+} would result in a molecule with a strengthened central bond. Our calculations on linear $(D_{\infty h})$ I_4^{2+} show that this prediction is correct, but that the molecule dissociates into I_2 and I^+ fragments with no minimum at the RHF-level. Crystal structure studies on I_4^{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_3/KI_5 complex of valinomycin,[34] or as interacting units, as in $N(CH_3)_4I_5$.[8] 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·$H_2O)_{10}$·HI_5 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 α-cyclodextrin (α-CD) contains chains of disordered I_5^- units.[10] The average central and terminal bond lengths in (α-CD)$_2$Cd$_{0.5}$I$_5$·27H$_2$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 $(D_{\infty h})$ structure. The I–I bond lengths were optimized for a series of fixed 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_4^{2-} 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 α-CD pentaiodides, disordered chains of both $(I_2-I^--I_2)_\infty$ and $(I_3^--I_2)_\infty$ 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 π molecular orbitals are located between the highest and next highest σ orbitals. The highest occupied π orbitals (the $3\pi_u$ pair of MO's) are dominated by the lone pairs of the central atom. The atomic charge distribution and population of the valence σ-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_4^{2-} (0.12 e). In both I_5^- and I_4^{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_4^{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_σ 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 σ-symmetry are illustrated

Table 3. Orbital energies and gross atomic populations of the valence molecular orbitals of the I_5^- ion. The values correspond to a linear symmetric ion at the optimized bond lengths ($I_1-I_2 = 3.40$ Å, $I_2-I_3 = 2.84$ Å). I_1 and I_3 denote the central and terminal atoms, respectively.

Orbital $(D_{\infty h})$	Energy /au	Atomic population		
		I_1	I_2	I_3
$4\sigma_u$	$-.1914$	1.388	0.062	0.243
$3\pi_u$	$-.1980$	3.650	0.136	0.039
$2\pi_g$	$-.2459$	0.002	0.908	1.091
$2\pi_u$	$-.2492$	0.293	0.760	1.093
$1\pi_g$	$-.3094$	0.001	1.090	0.909
$1\pi_u$	$-.3102$	0.047	1.108	0.868
$4\sigma_g$	$-.3269$	0.024	0.409	0.579
$3\sigma_u$	$-.3506$	0.273	0.421	0.442
$3\sigma_g$	$-.6276$	1.598	0.123	0.079
$2\sigma_u$	$-.6698$	0.012	0.466	0.528
$2\sigma_g$	$-.6768$	0.345	0.360	0.468
$1\sigma_u$	$-.7688$	0.003	0.528	0.471
$1\sigma_g$	$-.7695$	0.019	0.532	0.458

schematically. These are primarily of *p*-character. The $3\sigma_u$ MO is responsible for the delocalized bond involving all five atoms, while the $4\sigma_g$ 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^- 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_4^{2-} 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 σ-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.[36] On the basis of theoretical calculations, delocalized 3c–4e bonding has been suggested.[37]

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 dithioles, 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.[38] In these five-sulfur sequences there are 6 σ-electrons available for bonding, and the MO-description of the σ-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 dithioles,
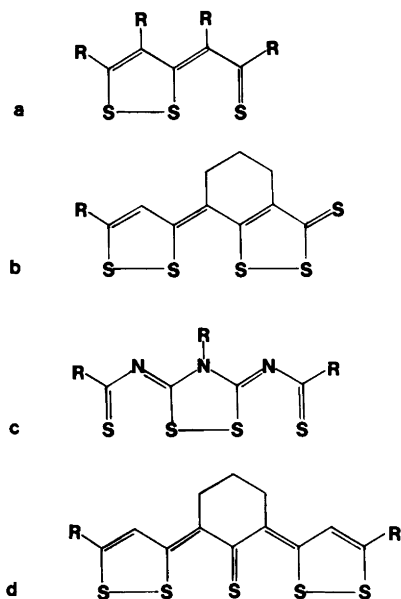

Fig. 7. Approximately linear arrays of 3, 4 and 5 sulfur atoms as they occur in (a) 1,6,6a-trithiapentalenes and (b–d) in extended sulfur analogues.

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 σ-bonding, as in the I_4^{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_4^{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_2 and the linear polyiodine species I_3^-, I_4^{2-}, I_4, I_4^{2+} and I_5^- assuming $D_{\infty h}$ symmetry. Relative to isolated units of I_2 and I^-, only I_3^- and I_5^- are found to be stable as free ions. For I_3^- 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_4^{2-} is also observed experimentally, but since the calculated energy for the I_4^{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_4^{2-} will cause the molecule to dissociate into two I_2 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_2 and I^+ fragments are formed and no minimum is encountered. The I_4^{2+} cation has so far only been observed as a rectangular unit.

The calculated bond lengths at minimum energy for I_3^-, I_4^{2-} and I_5^- are all greater than the optimized single bond length for I_2 (2.741 Å). For I_3^- the bonds are 3.044 Å, whereas for I_4^{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_3^-. The effect of close contacts between I^- and I_2 has been extensively studied for I_4^{2-} and I_5^-. 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_4^{2-} than for I_5^-.

Mulliken population analysis has been used to discuss the bonding in I_3^-, I_4^{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 σ-bonds involving all atoms. In the case of I_3^- and I_5^- this bonding is highly delocalized, whereas for I_4^{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_3^- and I_5^-, the bonding takes place as a charge transfer from I^- to I_2. The charge is transferred to the terminal atoms, resulting in a favourable alternating charge distribution for these ions. For I_4^{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_3^-, I_4, I_4^{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_σ bonding in the sulfur analogues.

References

1. Tasman, H. A. and Boswijk, K. H. *Acta Crystallogr. 8* (1955) 59.
2. Cheesman, G. H. and Finney, A. J. T. *Acta Crystallogr., Sect. B 26* (1970) 904.
3. Runsink, J., Swen-Walstra, S. and Migchelsen, T. *Acta Crystallogr., Sect. B 28* (1972) 1331.
4. Bats, J. W., de Boer, J. J. and Bright, D. *Inorg. Chim. Acta 5* (1971) 605.
5. Tebbe, K. F. In: Rheingold, A. L., Ed., *Homoatomic Rings, Chains and Macromolecules of Main Group Elements*, Elsevier, New York 1977, p. 551 and references therein.
6. Dubler, E. and Linowsky, L. *Helv. Chim. Acta 58* (1975) 2604.
7. Havinga, E. E., Boswijk, K. H. and Wiebenga, E. H. *Acta Crystallogr. 7* (1954) 487.
8. Broekema, J., Havinga, E. E. and Wiebenga, E. H. *Acta Crystallogr. 10* (1957) 596.
9. Herbstein, F. H. and Kapon, M. *Acta Crystallogr., Sect. A 28* (1972) S74.
10. Noltemeyer, M. and Saenger, W. *J. Am. Chem. Soc. 102* (1980) 2710.
11. Wiebenga, E. H., Havinga, E. E. and Boswijk, K. H. *Adv. Inorg. Chem. Radiochem. 3* (1961) 133.
12. Wiebenga, E. H. and Kracht, D. *Inorg. Chem. 8* (1969) 738.
13. (a) Gabes, W. and Nijman-Meester, M. A. M. *Inorg. Chem. 12* (1973) 589; (b) Gabes, W. and Stufkens, D. J. *Spectrochim. Acta, Part 30 A* (1974) 1835; (c) Hollingworth, R. W. and Hacobian, S. *Aust. J. Chem. 27* (1974) 1381.
14. Kertesz, M. and Vonderviszt, F. *J. Am. Chem. Soc. 104* (1982) 5889.
15. Strömberg, A., Gropen, O. and Wahlgren, U. *J. Chem. Phys. 80* (1984) 1593.
16. Gropen, O., Wahlgren, U. and Petterson, L. *Chem. Phys. 66* (1982) 66.
17. Datta, S. N., Ewig, C. S. and van Wazer, J. R. *J. Mol. Struct. 48* (1978) 407.
18. Petterson, L., Wahlgren, U. and Gropen, O. *Chem. Phys. 80* (1983) 7.
19. Gropen, O., Wahlgren, U. and Petterson, L. *Chem. Phys. 66* (1982) 459.
20. Strömberg, A., Gropen, O. and Wahlgren, U. *J. Comput. Chem. 4* (1983) 181.
21. Rank, D. H. *J. Opt. Soc. Am. 36* (1946) 239.
22. van Bolhuis, F., Koster, P. B. and Migchelsen, T. *Acta Crystallogr. 23* (1967) 90.
23. Pimentel, G. C. *J. Chem. Phys. 19* (1951) 446.
24. Hach, R. J. and Rundle, R. E. *J. Am. Chem. Soc. 73* (1951) 4321.
25. van Arkel, A. E. and de Boer, J. H. *Rec. Trav. Chim. Pays-Bas 47* (1928) 593.
26. (a) Belicchi, M. F., Fava, G. G. and Pelizzi, C. *Acta Crystallogr., Sect. B 37* (1981) 924; (b) Herbstein, F. H. and Schwotzer, W. *Angew. Chem. Int. Ed. Engl. 21* (1982) 219; (c) Kramer, J. A., Herbstein, F. H. and Hendrickson, D. H. *J. Am. Chem. Soc. 102* (1980) 2293; (d) Herbstein, F. H. and Kapon, M. *J. Chem. Soc., Chem. Commun.* (1975) 677; (e) Hassel, O. and Hope, H. *Acta. Chem. Scand. 15* (1961) 407.
27. Genser, E. E. and Connick, R. E. *J. Chem. Phys. 58* (1973) 990.
28. Hassel, O. *Mol. Phys. 1* (1958) 241.
29. (a) Carpenter, G. B. *J. Chem. Educ. 40* (1963) 385; (b) Müller, H. *Wiss. Z. Friedrich-Schiller-Univ. Jena, Mathem.-nat. R. 26* (1977) 611.
30. (a) Harris, S. J., Novick, S. E., Winn, J. S. and Klemperer, W. *J. Chem. Phys. 61* (1974) 3866; (b) Chance, K. V., Bowen, K. H., Winn, J. S. and Klemperer, W. *J. Chem. Phys. 72* (1980) 791.
31. Bersohn, R. *J. Chem. Phys. 16* (1962) 3445 and references therein.
32. Prissette, J. and Kochanski, E. *J. Am. Chem. Soc. 100* (1978) 6609.
33. Gillespie, R. J., Kapoor, R., Faggiani, R., Lock, C. J. L., Murchie, M. and Passmore, J. *J. Chem. Soc., Chem. Commun.* (1983) 8.
34. Neupert-Laves, K. and Dobler, M. *Helv. Chim. Acta 58* (1975) 432.
35. Teitelbaum, R. C., Ruby, S. L. and Marks, T. J. *J. Am. Chem. Soc. 102* (1980) 3322.
36. Hansen, L. K., Hordvik, A. and Sæthre, L. J. In: Sterling, C. J. M., Ed., *Organic Sulphur Chemistry*, Butterworths, London 1975, p. 1 and references therein.
37. Gleiter, R. and Hoffmann, R. *Tetrahedron 24* (1968) 5899.
38. Sletten, J. *Acta Chem. Scand., Ser. A 30* (1976) 397 and references therein.