considerations. It is interesting that distortions in these cases have led to larger average volumes for the ions.

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References

DUNITZ, J. D. & ORGEL, L. E. (1957). *J. Phys. Chem. Solids*, **3**, 20.

EDWARDS, A. J. & PEACOCK, R. D. (1959). *J. Chem. Soc.* p. 4126.

GELLER, S. (1956). *J. Chem. Phys.* **24**, 1236.

GELLER, S. (1957). *Acta Cryst.* **10**, 243.

GELLER, S. & BALA, V. B. (1956). *Acta Cryst.* **9**, 1019.

GELLER, S. & WOOD, E. A. (1956). *Acta Cryst.* **9**, 563.

GILLEO, M. A. (1957). *Acta Cryst.* **10**, 161.

GUGGENHEIM, H. (1960). *J. Phys. Chem.* **64**, 938.

HOPPE, R. (1959). *Angew. Chem.* **71**, 457.

HUSH, N. S. (1958). *Disc. Faraday Soc.* **26**, 145.

HUSH, N. S. & PRYCE, M. H. L. (1957). *J. Chem. Phys.* **26**, 143.

HUSH, N. S. & PRYCE, M. H. L. (1958). *J. Chem. Phys.* **28**, 244.

JAHN, H. A. (1938). *Proc. Roy. Soc.* A, **164**, 117.

JAHN, H. A. & TELLER, E. (1937). *Proc. Roy. Soc.* A, **161**, 220.

MARTIN, R. L., NYHOLM, R. S. & STEPHENSON, N. C. (1956). *Chem. and Ind.*, p. 83.

MCCLURE, D. S. (1959). *Solid State Physics*, **9**, 400.

MOFFITT, W. & BALLHAUSEN, C. J. (1956). *Ann. Rev. Phys. Chem.* **7**, 107.

OKAZAKI, A. (1960). *J. Phys. Soc. Japan.* (To be published.)

OKAZAKI, A., SUENUME, Y. & FUCHIKAMI, T. (1959). *J. Phys. Soc., Japan*, **14**, 1823.

OPIK, U. & PRYCE, M. H. L. (1957). *Proc. Roy. Soc.* A, **238**, 425.

PALMER, W. G. (1954). *Experimental Inorganic Chemistry*, p. 556. Cambridge: University Press.

SANTEN, J. H. VAN, & WIERINGEN, J. S. VAN (1952). *Rec. Trav. Chim. Pays-Bas*, **71**, 420.

VLECK, J. H. VAN (1958). *Disc. Faraday Soc.* **26**, 96.

WEINSTOCK, B. & CLAASSEN, H. W. (1959). *J. Chem. Phys.* **31**, 262.

WELLS, A. F. (1950). *Structural Inorganic Chemistry*, 2nd ed., p. 375. Oxford: University Press.

Acta Cryst. (1961). **14**, 585

On the Polyhalide Ions*

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Experimental evidence is cited to show that cation size is responsible for variation of the structure of the triiodide ion, I_3^-, and that in an isolated state the ion is probably linear and symmetrical with an over-all length, D, similar to the shortest distances found in crystals. The applicability of a simple molecular orbital description of the bonding without the use of outer d-orbitals is shown to be in keeping with most of the observed facts for polyhalides and polyhalogens. Where modification is necessary it is shown that a contribution of outer d-orbitals to σ-bonding, and to π-bonding can be added naturally to the MO description. These contributions can, in an MO description, be made large or small to minimize the energy of the system, and seem preferable to the valence bond, hybrid orbital description in its usual form since the latter description seems to require an arbitrarily high contribution of outer d-orbitals.

Introduction

The nearly linear triiodide ion, I_3^-, varies in structure with its environment, and an increase in asymmetry of the bonds accompanies an increase in the total length, D, of the ion (Table 1) (R. Slater, 1959). This behavior parallels the theoretically predicted behavior for H_3 (Hirschfelder, Diamond & Eyring, 1937), and using this analogy J. Slater (1959) has suggested that in its lowest state the isolated I_3^- ion may have a length, D, comparable with the largest D observed in crystals, but in certain crystals 'pressure' may force the ion to have a shorter length until at some critical D the ion may become symmetrical.

The nature of the triiodide ion and its variation with environment is an interesting question related to the more general question of the nature of polyhalide ions. A number of suggestions have been made, and these have been evaluated by Havinga (1957). In this paper a wider range of experimental information is used as

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evidence that variation of the I_3^- ion with environment is probably related not to crystal pressure, but to cation influence as suggested earlier (Hach & Rundle, 1951), and that the ground state of the isolated ion is more probably symmetrical with a distance, D, comparable with the shortest D observed in crystals. The conclusions reached here, and previously, are based on an attempt to interpret the available experimental facts, which, alas, cannot prove the interpretation. This procedure seems safer, none-the-less, than interpreting an approximate theoretical treatment of the crudely analogous H_3 system, and more reliable than the rough theoretical work which has been attempted (Hach & Rundle, 1951; Pimentel, 1951; Havinga, 1957). Finally, some implications of this interpretation to polyhalides and polyhalogens in general are examined.

Polyhalides

The following observations were made by Sidgwick (1950) in reviewing the polyhalides some years ago:

(1) There are no crystalline triiodide salts of really small cations.

(2) There are almost no polyhalides of bivalent cations. (He lists none whose existence is established.)

(3) The stability of the triiodide salts to dissociation into iodides and I_2 increases with increasing size of the cation.

(4) The polyiodides, where more than one I_2 is coordinated to I^-, are limited to *very* large cations.

(5) In stability salts of $I_3^- > Br_3^- > Cl_3^-$; Br_3^- and Cl_3^- are known only in salts of very large cations.

(6) In mixed polyhalides the more electronegative (lighter) halogens are always coordinated about a less electronegative (heavier) halogen at the center of the ion.

Since Sidgwick's review more extensive structural information has become available. The following features of these structures seem to be consistent and pertinent:

(1) Interatomic distances are always greater than the sum of the covalent radii, though this is far more pronounced in homo-polyhalides than in mixed polyhalides.

(2) In all polyhalides angles of $\sim 180°$ and $\sim 90°$ predominate.

(3) In I_3^-, the individual bond distances vary in a systematic way with over-all length D, as noted by R. Slater (1959).

(4) The over-all length, D, for I_3^- decreases as cation size increases, as shown in Table 1.

As to compression of D by crystal pressure, in Slater's proposal this must increase as the cation becomes larger, even when the cation becomes a large organic cation (Table 1) and the crystal becomes soft. In the particular case of $(C_6H_5)_4As^+$, this ion is known to change configuration with environment (Mooney, 1940; Zaslow & Rundle, 1957). In the circumstances, the pressure proposal seems unlikely.

The above, of course, has nothing to do with the configuration of an isolated I_3^- ion constrained to have an abnormally large D. Here Slater's argument for a double well for the central iodine atom must be correct, since I^- plus I_2 is more stable than I^- and separated iodine atoms.

In agreement with Slater, Hach & Rundle (1951) assumed that at large distances the I_2–I^- ion interaction is that of an ion and a polarizable molecule, but that at shorter distances, orbital overlap and covalent bonding become important in decreasing interatomic distances. But cause and effect are not easily separated in the case of asymmetric I_3^- ions in salts with unsymmetrical coulomb fields, since minimization of the energy of the system as a whole determined the structure of the I_3^- ion in such salts. Hence the maximum distance, D, at which isolated I_3^- would have a double well for the central atom is not settled by the data in Table 1.

We interpret the data of Table 1 and the points above, as meaning that for these salts the coulombic interaction between cation and anion favors an asymmetric ion with a well defined I^- ion, while chemical bonding favors a symmetrical I_3^- ion. It is to be noted that if I_2 is to coordinate to I^- in a crystal it must displace cations. For very small cations, the coulombic interaction between M^+ and I^- is interpreted as being so important that no I_3^- ions form; for cations of intermediate size the change in structure of the I_3^- ion with cation size is in just the expected direction with the coulombic influence decreasing with ion size,

Table 1. *Distances in salts*, MI_3, I_1–I_2–I_3 (Å)

Salt	D	d_{12}	d_{23}	M–I_1	M–I_3	References
NH_4I_3	5·91	2·82	3·10	3·8†	3·6†	(Mooney, 1935)
CsI_3	5·86	2·83	3·04	3·94–4·25	3·70–3·88	(Tasman & Boswijk, 1955)
Cs_2I_8*	5·85	2·85	3·00	3·85–3·96	3·97–4·02	(Havinga, Boswijk & Wiebenga, 1954)
$(C_2H_5)_4NI_7$*	5·80	2·90	2·90	5·51, 5·61	5·51, 5·61	(Havinga & Wiebenga, 1958)
$(C_6H_5)_4AsI_3$	5·80	2·90	2·90	5·03, 6·46	5·03, 6·46	(R. Slater, 1959)

* Here I_3^- ions are also linked, though weakly, to I_2 and this, as well as cation influence may alter the I_3^- configuration, especially in the case of Cs_2I_8 where the interaction is much like that in I_5. See text.

† Calculated assuming that the parameters for the cation are equal to those of isomorphous CsI_3. Since this is rough, only an average distance is given.

Table 2. *Bond distances in polyhalide ions* (Å)

	d	Σr	Δ_o	Δ_c*	References
I_3^- (sym.)	2·90	2·68	0·22	0·19	(R. Slater, 1959)
Br_3^-	2·53, 2·54	2·28	0·26	0·19	(Romers & Keulemans, 1958)
ICl_2^-	2·34	2·33	0·01	0·19	(Mooney, 1939)
Cl–I–Br⁻	2·38, 2·50	2·33, 2·48	0·05, 0·02	0·19	(Mooney, 1937*a*)
ICl_4^-	2·33, 2·35	2·33	0·01	0·19	(Mooney, 1937*b*)

* Assuming one-electron pair in the two bonds, and Pauling's rule relating bond distance to bond number.

leading naturally to the type of systematic distance relations noted by R. Slater (1959); for very large cations, the structure is dominated by bonding considerations. Surely of the compounds in Table 1 the most nearly isolated I_3^- ion is that in $(C_6H_5)_4AsI_3$, and without appealing to any detailed model of the bonding, the experimental evidence favors a symmetrical I_3^- ion in the isolated state.

Pimentel (1951) and Hach & Rundle (1951) proposed independently a molecular orbital (MO) scheme for the bonding in I_3^- which makes use of only the p_z orbitals of the iodine atoms, and the latter authors showed how this could be extended to aid in the understanding of the I_5^- ion. Indeed, the model was based almost wholely on inferences from the limited structural data then available. Since then, the detailed structures of $(C_2H_5)_4NI_7$, (Havinga & Wiebenga, 1958), Cs_2I_8 (Havinga, Boswijk & Wiebenga, 1954) and $(CH_3)_4NI_9$ (James, Hach, French & Rundle, 1955) have been found to have interesting and peculiar structures which are more in keeping with this proposal than any other which has yet been made. Points in favor of the proposal are: (1) The suggested MO's account in a reasonable way for the predominance of bond angles of $\sim 90°$ and $\sim 180°$; (2) Only one MO in the trihalides is bonding, and hence there is only one bonding electron pair for two bonds, which is in keeping with distances in the homotrihalides; (3) The non-bonding MO is confined to the terminal halogens in the trihalides, and would place a higher electron density on them, and this should favorterminal positions for the more electronegative halogens in mixed polyhalides; (4) In the V-shaped I_5^- ion, the corner halogen receives contribution from two such non-bonding electron pairs, and should be the iodine most like an I^- ion, in keeping with the structure; (5) Besides these experimental points Havinga (1957) has shown that crude MO treatments, based on this proposal, indicate that the observed configurations of the polyhalide ions are more stable than other conceivable configurations. For example, he shows that these calculations favor the V-shaped X_5^- ion as found in the I_5^- ion when equal coulomb integrals are assumed for the halogens, but favor the planar, square $X(X')_4$, as found in ICl_4, when coulomb integrals are changed in accordance with the electronegativity difference between iodine and chlorine.

In 1951, a disadvantage of this proposal was that it seemed incompatible with the structures of the polyhalogens. Since then the structures of $^-ClF_3$ (Smith, 1953; Burbank & Bensey, 1953; Magnuson, 1957) and BrF_5 (Burbank & Bensey, 1957; Magnuson, 1957) have become definite, and as Havinga (1957) has pointed out, these structures are now quite compatible with the same MO treatment based on p-orbitals only.

In mixed halides, however, the bond distances, Table 2, and stability (Sidgwick, 1950) suggest a qualitative difference in the nature of the bonding, and the discussion by Pauling (1939), in which he makes use of 5*d*-orbitals (outer *d*-orbitals) of the central iodine in, for example, ICl_2^- and ICl_4^- has been generally accepted for these ions, though even Pauling seems to have given up his proposal for I_3^- and I_5^- (Pauling, 1960). Havinga (1957) has discussed the chief objections to Pauling's formulation, and as long as equal weight is given to *ns*-, *np*- and *nd*-orbitals in forming hybrid orbitals, as in Pauling's unmodified proposal, such objections seem to be valid.

An extension of the original MO scheme can, of course, make use of outer *d*-orbitals, somewhat in the manner in which Pauling suggests; but in an MO scheme it is immediately obvious that the coefficients of the outer *d*-orbitals are variable, whereas in its simplest form the hybrid orbital valence bond scheme seems to require a large contribution of outer *d*-orbitals so as to achieve sp^3d^2-octahedral orbitals, etc. For example, in IX_4^- the non-bonding MO belonging to the representation b_{1g} will combine to some unknown extent with the $5d_{x^2-y^2}$ orbital of the central iodine

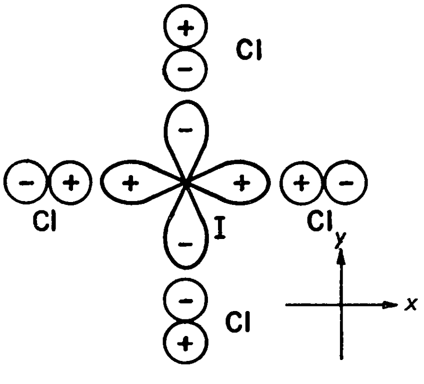

Fig. 1. Schematic drawing of σ-bonding MO of $5d_{x^2-y^2}$ (outer *d*-orbital) of iodine and linear combination of surrounding σp-orbital of chlorine. MO belongs to the irreducible representation b_{1g} of D_{4h}.

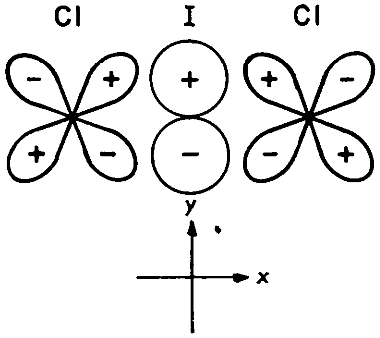

Fig. 2. Schematic drawing of π-bonding MO formed from linear combination of $3d_{yz}$-orbitals (outer d-orbitals) of chlorine and $5p_y$-orbital of iodine. In ICl_2^- this will be one of a degenerate pair of orbitals (other from d_{xz} and p_x) belonging to C_u. Similar π-bonding can obviously exist in ICl_4^-.

without the need for promoting other electrons to other outer d-orbitals (e.g., d_{z^2}) so as to achieve sp^3d^2 hybrids (Fig. 1).

Perhaps even more important, in all of these compounds a type of π-bonding can occur, through MOs (Fig. 2), which will allow some of the p-electrons of the central halogen to flow out to empty outer d-orbitals of the surrounding electronegative halogens. Where the exterior halogens are much more electronegative than the central halogen, as in ICl_2^-, ICl_4^-, etc. such redistribution of charge may become significant.

This π-bonding cannot occur in fluorides, and two points are worth noting: (1) Few polyhalide ions involving fluorine are known. (2) In the T-shaped ClF_3 and BrF_3, and in the tetragonal pyramidal BrF_5 molecules the bonds in the nearly linear $F–X–F$ arms are longer than the unique bond, Table 3, as is to be expected if the main bonding in these arms is due to only one σ-bonding MO, as found in the trihalides.

Table 3.

	X–F ('Linear' arms)	X–F Unique	References
ClF_3	1·598 Å	1·698 Å	(Smith, 1953)
	1·62	1·52	(Burbank & Bensey, 1953)
BrF_3	1·721	1·81	(Magnuson, 1957)
	1·72	1·84, 1·85	(Burbank & Bensey, 1954)
BrF_5	1·75(2), 1·81, 1·82	1·68	(Burbank & Bensey, 1954)

In conclusion, it seems that a consistent first approximation to the bonding in all these polyhalogens and polyhalides is through MOs based mainly on p-orbitals of the halogens, with some lesser contribution of outer d-orbitals to σ-bonding much as Pauling has proposed, and some outer d-orbital π-bonding as suggested here. Either new experimental work or altogether more reliable theoretical work will be necessary to assess the relative importance of these latter two types of interactions, but they may well be responsible for the variable distances shown in these compounds, varying with the electronegativity difference of the halogens, and with the presence or absence of fluorine, as outlined above.

Finally, in neighboring parts of the periodic system it seems likely that σ- and π-MOs similar to those suggested here would allow the admixture of outer d-orbitals in a lesser, more realistic manner, than in an extreme, hybrid, valence bond description.

References

Burbank, R. D. & Bensey, F. N. (1953). *J. Chem. Phys.* **21**, 602.

Burbank, R. D. & Bensey, F. N. (1957). *J. Chem. Phys.* **27**, 983.

Hach, R. J. & Rundle, R. E. (1951). *J. Amer. Chem. Soc.* **73**, 4321.

Havinga, E. E. (1957). Bijdtrage Tot de Kennis van de Structur van Polyhalogeniden, Thesis, Univ. of Groningen.

Havinga, E. E., Boswijk, K. H. & Wiebenga, E. H. (1954). *Acta Cryst.* **7**, 487.

Havinga, E. E. & Wiebenga, E. H. (1958). *Acta Cryst.* **11**, 733.

Hirschfelder, J., Diamond, H. & Eyring, H. (1937). *J. Chem. Phys.* **5**, 695.

James, W. J., Hach, R. J., French, D. & Rundle, R. E. (1955). *Acta Cryst.* **8**, 814.

Magnuson, D. W. (1957). *J. Chem. Phys.* **27**, 223.

Mooney, R. C. L. (1937*a*). *Z. Kristallogr.* **98**, 324.

Mooney, R. C. L. (1937*b*). *Z. Kristallogr.* **98**, 377.

Mooney, R. C. L. (1939). *Z. Kristallogr.* **100**, 519.

Mooney, R. C. L. (1940). *J. Amer. Chem. Soc.* **62**, 2995.

Pauling, L. (1939). *Nature of the Chemical Bond*, pp. 103–4. Ithaca, New York: Cornell University Press.

Pauling, L. (1960). *Nature of the Chemical Bond*, 3rd ed., pp. 180–2. Ithaca, New York: Cornell University Press.

Pimentel, G. (1951). *J. Chem. Phys.* **19**, 446.

Romers, C. & Keulemans, E. W. M. (1958). *Proc. K. Ned. Akad. Wet.* B, **61**, 346.

Sidgwick, N. V. (1950). *Chemical Elements and Their Compounds*, vol. II, pp. 1190–1200. Oxford: University Press.

Slater, J. C. (1959). *Acta Cryst.* **12**, 197.

Slater, R. C. L. Mooney (1959). *Acta Cryst.* **12**, 187.

Smith, D. F. (1953). *J. Chem. Phys.* **21**, 609.

Tasman, H. A. & Boswijk, K. H. (1955). *Acta Cryst.* **8**, 59.

Zaslow, B. & Rundle, R. E. (1957). *J. Phys. Chem.* **61**, 490.