

Supplementary Information for

Rethinking Polyiodides: The Role of Electron-Deficient Multicenter Bonds

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Details on CSD datasets for non-branched polyhalides

Polyiodides:

- I_3^- , I_5^- , I_8^{2-}

Dataset from ref. 26 of the manuscript.

- *Heptaiodide. I_7^- :*

19 entries from 15 CSD refcodes:

BABTIL; GOBFUY; JAPRUO; OFEDUY; ONOCOM; RECLAM; SOCWAK; WAQVUH; WERBUQ; XAGJUM; XEHQUW; YUPXOY; ZIVXUX; ONIRIP; XEKWET.

- *Tetraiodide dianion, I_4^{2-} :*

30 entries from 28 CSD refcodes:

BOPDUF; CENTEW; CENTIA; CENTOG; CENTUM; CEWMIA; FEBZOD; FECBEW; JOPKOQ; LAGFEG; LAGFOQ; NABWOD; NABWOD01; ONUNOB; OZEGEH; PUSYEI; SAZZEA; SIWYON; SOCVOX; TAVXOD; TIRBEB01; TOKZOK; XUBMEP; YEWKUG; YICJAX; YICJAX01; YIRLOA; YONKET;

Other polyhalides:

- *Homotrihalides*

- Trichloride, Cl_3^-

9 entries from 9 CSD refcodes:

CUPTIQ; CUPTIQ10; DEGLIK; FAHXIZ; FAHXOF; FAHXUL; PHASCL; UHUQAP; ZEHTIP

- Tribromide: Br_3^-

345 entries from 274 CSD refcodes:

PAJSEC; WAWQEU; AFAYAI; AKIMOX; ALAZIY; APTHCB; ARESOI; ARESUO; ARETAV; ARETEZ; ARETID; ARETOJ; ARETUP; AZAXAD; AZEKEW; AZEKEW01; BADBEQ; BAFTOT; BEFWAM; BEGJEF; BEGJEF01; BEGJII; BEGJOP; BEGJUV; BEGKEG; BEMLIO; BEMYAW; BEMYEA; BEPZEB; BEPZEB01; BIMPAO; BMOPHX; BUJBOZ; BULLOL; BULLUR; BZDZTB; CALSEN; CAZPUR; CITKOI; CITTEH; CITVAF; CIWYOW; COCGAF; COVSUB; COVSUB10; CUBDIP; CUBRAS; DAHGUO; DAHGUO01; DAKVUG; DEPNUJ; DEQXOP; DESNEX; DESNUN; DESPAV; DIXTIP; DIZDUL; DOSRUB; DUSGED; DUXKOW; DUXKUC; EKOPOL; EPERAV; EQIVEH; ETEVIL; ETEVUX; ETOXUI; ETOYET; FAJHUT; FASYAZ; FOGWON; FOGYAB; FOHDAH; FUNNEJ; FUNNIN; FURTOE; GOBCIM; GUVKEP; HADLII; HAGNIN; HANYAZ; HAZWEM; HEJNIT; HIFWIF; HIFWOL; HIFXAY; HIPVIM; HISZUE; HOJMAU; HUBGIX; ICOVIG; ICOVUS; ITUZON; IXOMOZ; IXUMUJ; IYEVAL; JAWBOY; JENGIV; JEPGUG; JEPGUG01; JEXZIY; JOKJUQ; JOXGIO; KACWER; KAHZAV; KOHQOQ; KOZVIH; KOZVON; KUKSEP; KUKSIT; LACTOC; LACTUI; LAGGEH; LAHCUW; LIFBEH; LIFZAC; LODJAR; LUXBAJ; MEGDAG; MIVJUW; MOHMIF;

MOXFUD; MPYBAN; MUXVIK; NEGXII; NEGXOO; NEGXUU; NEGYAB; NEGYEF; NEGYIJ;
NEQTOU; NOFYUC; NUNYOK; ODAWIB; ODMNBR; OFOXUD; OFOYAK; OJORUB; OLIHID;
OQUYAB; PAKBAH; PAQRUX; PASOHB; PICSBB; PITLLEL; POPWEZ; POYXIN; POYXOT;
POYXUZ; PUKWUO; PUQNEW; QAKZOV; QALVEH; QELPAY; QIFDOB; QIVHIP; QIXCIK;
QORMAO; QORMIW; QORMOC; QQQALJ01; QULTOG; QULTOG01; QUMSBR; QUWBUG;
RAQGIB; RECMET; RECMIX; RECMOD; REJTUY; REKBEO; REKBIS; RIBWAC; RIHJEA; RIKZEQ;
ROTCOV; RUGGEI; RUKFEI; RUTLUQ; SAMDUF; SAMFAN; SAQVAI; SEGMOG; SEGMOG01;
SIVHAJ; SIVHEN; SIVHIR; SIVHOX; SIVHUD; SIVJAL; SIVJEP; SIVJIT; SUHJIO; SUPVOQ;
TAYTUJ; TEHRUT; TIWFIO; TIYRUP; TOYZOZ; TOZLAV; TOZLID; TPASTB; TPASTB01; TUFTRUK;
TUMHUE; UKACUF; UKADAM; UKAGOD; URESES; URUBIT; UWANOW; UWOVOT; UYUTEQ;
VAGNUN; VAVTES; VIKHON; VOJTAS; VUSFOE; WADJAJ; WADSIH; WARMIN; WARMOT;
WATHOR; WATJOS; WATJUY; WOBDID; WODWUK; WULDAJ; XAJZIT; XAXGUY; XAXHAF;
XEHJIE; XEWVEB; XIQTIB; XODKAC; XOWZIT; XURGEW; YAMJII; YAMJOP; YAMJUV; YAMKAC;
YESGUY; YIZCAL; YODZEW; YOFLUD; YOFMEO; YOJDAD; YOPDOY; YOTMOK01; YOZNIN;
YUVXUL; YUZDIJ; ZOZFIG; BAVYAC; XALFAV; BEQKIV; DEHVEV; MESPEJ; WETKUF.

- *Heterotrihalides:*

- FClF^-
1 entry from 1 CSD refcode: NUSGAM
- FBrF^-
1 entry from 1 CSD refcode: QAKZEL
- ClBrCl^-
8 entries from 8 CSD refcodes:
GOLKAV; MURREZ; MURRID; SAFGIT; SUPTON; TEACBR; TEACBR01; TEACBR02;
- ClBrBr^-
2 entries from 2 CSD refcodes: MURRUP; URUBUF

- *Tetrahalides*

- Tetrabromide dianion, Br_4^{2-}
3 entries from 3 CSD refcodes: FENBOQ; FIMDOU; TUMHOY

- *Pentahalides*

- *Pentabromide, Br_5^-*
6 entries from 6 CSD refcodes: CITTIL; HIFWUR; MURRUP; QAJJIY; RECMET; WEDDAO

- ClBrClBrCl⁻
3 entries from 3 reftypes: GABDOG; SAFGEP; SAFGIT

- *Hexahalides*

None.

The search actually returns the FIDBOM crystal structure, containing two head-to-tail “bonded” Br₃⁻ anions in the shape of an L. The “bond” (“bond” length 3.593(1), i.e. close to sum of VdW radii), however, does not appear tight enough to significantly differ from a mere van der Waals contact and has therefore been excluded.

- *Heptahalides*

None.

Some branched (pyramidal) species are found instead, CSD reftypes: DIDHUW ((ClBr)₃Cl⁻), ORUKUK ((FCl)₃F⁻), QIFDIV (Br₇⁻), QIFDUH (Br₇⁻), SAFFUE ((ClBr)₃Cl⁻).

- *Octahalides*

- Octachloride dianion, Cl₈²⁻:
1 entry from 1 CSD reftype: ESAYEE
- Octabromide dianion, Br₈²⁻:
2 entries from 2 CSD reftypes: PAQSAE; REKBAK