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The Crystal Structure of Two Modifications of Tetraethylammonium Triiodide, $(C_2H_5)_4NI_3$

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(Received 13 May 1967)

The crystal structures of two modifications, I and II, of $(C_2H_5)_4NI_3$ have been determined by three-dimensional X-ray methods. Modification I crystallizes in space group *Cmca* with $a=14\cdot207$, $b=15\cdot220$, $c=14\cdot061$ Å, e.s.d. 0·05 %, $Z=8$; II crystallizes in space group *Pnma* with $a=14\cdot552$, $b=13\cdot893$, $c=15\cdot156$ Å, e.s.d. 0·05 %, $Z=8$. Anisotropic least-squares refinement was carried out with 909 independent reflexions for I ($R=0\cdot045$) and with 1094 reflexions for II ($R=0\cdot042$). In I, there are two independent I_3^- ions at special positions with symmetry $2/m$; the bond lengths in the two symmetrical I_3^- ions are 2·928 and 2·943 Å, e.s.d. 0·0025 Å. In II there are two independent I_3^- ions; the ions are nearly linear, but asymmetric with bond lengths of 2·912, 2·961 and 2·892, 2·981 Å, e.s.d. 0·0035 Å. A VESCF molecular orbital study of the electronic structure of the triiodide ions, including the effect of the crystal field, was made. A bond order *versus* bond length curve could be obtained.

Introduction

The nearly linear triiodide ion varies in structure with its environment in the crystal. Symmetric ions with equal bond lengths have, for instance, been observed in $(C_6H_5)_4AsI_3$ (Mooney Slater, 1959) whereas in crystals of CsI_3 (Tasman & Boswijk, 1955), the ions are asymmetric with a difference in I-I bond length of approximately 0·2 Å. From the data available at that time, Rundle (1961) concluded that the asymmetry and the total length of the ions increase with decreasing size of the surrounding cations. Hach & Rundle (1951) as well as Havinga & Wiebenga (1959) ascribe the variations in bond length to the influence of the (electrostatic) crystal field. Their qualitative conclusions

have recently been supported by Brown & Nunn (1966) for the triiodide ions in $(C_6H_5)_4AsI_3$ and in CsI_3 by theoretical variable electronegativity self-consistent field (VESCF) molecular orbital calculations in which the crystal field was taken into account. Mooney Slater (1959) and Slater (1959), on the other hand, have suggested that in certain crystals 'pressure' may force the I_3^- ions to become shorter and more symmetric.

Examination of the structural data on which these discussions are based shows that most of the data used do not give reliable information on the lengths of the I-I bonds in I_3^- ions. In $(CH_3)_4NI_5$, $(C_2H_5)_4NI_7$ and Cs_2I_8 , the I_3^- ions show strong interaction either with each other or with iodine molecules so that complexes with I_5^- , I_7^- and I_8^{2-} ions respectively occur in these

crystals (Hach & Rundle, 1951; Broekema, Havinga & Wiebenga, 1957; Havinga & Wiebenga, 1958; Havinga, Boswijk & Wiebenga, 1954). 'Separate' I_3^- ions have been studied in NH_4I_3 (Mooney, 1935), CsI_3 (Tasman & Boswijk, 1955) and in $(C_6H_5)_4AsI_3$ (Mooney Slater, 1959). The results of the early crystal analysis of NH_4I_3 could not be considered as accurate, however. Structure determinations of triiodide compounds having cations of sizes in between the small Cs^+ and large $[(C_6H_5)_4As]^+$ ions had not been reported. We started the structure determinations of some triiodide compounds with moderately large cations. $(CH_3)_4NI_3$ was studied first. Accurate I-I bond lengths could not be obtained, however, because of the occurrence of a superstructure and also because of noticeable changes in the intensities of the weak reflexions during the X-ray exposures. The compound $(C_2H_5)_4NI_3$ appeared to be more suitable for a detailed structure determination. We were able to show that there are two crystalline modifications of this compound, one with symmetric and another with asymmetric I_3^- ions. This invalidates the close connexion between cation size and structure of I_3^- ion as suggested earlier (Rundle, 1961).

Experimental

Sample preparation

$(C_2H_5)_4NI_3$ was obtained as a fine powder by adding iodine to an equivalent amount of $(C_2H_5)_4NI$ dissolved in alcohol. Large red-brown crystals were grown from a solution in methanol by slow evaporation of the solute. The crop appeared to contain two different crystalline modifications. Preliminary X-ray work was done first on modification I (space group $Cmca$). The presence of modification II (space group $Pnma$) was noticed later. As the crystals do not differ in shape or colour, the symmetry of the crystals used for the struc-

ture determination was checked by making Weissenberg photographs.

Unit cell and space group

The cell dimensions of the orthorhombic crystals were obtained from Weissenberg photographs taken with Ni-filtered Cu radiation; the zero-level pictures were superimposed with NaCl reflexion spots for calibration purposes. The lengths of the axes were obtained by least-squares adjustment of the $\sin^2\theta$ values of a large number of zero-level reflexions ($\lambda(Cu K\alpha)=1.5418$, $\lambda(Cu K\alpha_1)=1.54051$, $\lambda(Cu K\alpha_2)=1.54433 \text{ \AA}$). The cell dimensions are

$$\begin{aligned} a &= 14.207, b = 15.220, c = 14.061 \text{ \AA}, \\ &\quad \text{e.s.d. } 0.05\% \text{ for modification I,} \\ a &= 14.552, b = 13.893, c = 15.156 \text{ \AA}, \\ &\quad \text{e.s.d. } 0.05\% \text{ for modification II.} \end{aligned}$$

There are 8 molecules per cell. The systematic absences indicate as possible space groups $Cmca$ and $C2ca$ for modification I, and $Pnma$ and $Pn2_1a$ for II. The centrosymmetric space groups $Cmca$ and $Pnma$ were adopted during the structure determination; the successful refinement of the structure confirmed this choice.

Intensity data

Three-dimensional intensity data were collected with an automatic single-crystal Nonius diffractometer (Zr-filtered Mo radiation, $\theta-2\theta$ scan method). Reliable intensities were obtained for 909 reflexions of modification I and 1094 of modification II. Corrections for absorption ($\mu=62.0$ and 61.5 cm^{-1} respectively) were calculated with a program according to the Busing & Levy (1957) scheme. The dimensions of the bounding

Table 1. Final fractional coordinates and isotropic thermal parameters for $(C_2H_5)_4NI_3$ (I)*
The standard deviations are given in parentheses†. For numbering of atoms see Fig. 1(a).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
I(1)	0	0	0	
I(2)	0	0.19096 (12)	0.02518 (12)	
I(3)	0.5	0	0	
I(4)	0.5	0.02878 (9)	0.20699 (9)	
N	0.25	0.2915 (9)	0.25	3.6 (2) \AA^2
C(1)	0.2825 (14)	0.1723 (12)	0.1274 (13)	7.2 (4)
C(2)	0.3228 (10)	0.2343 (9)	0.2023 (10)	5.0 (3)
C(3)	0.1965 (9)	0.3481 (9)	0.1794 (9)	4.5 (2)
C(4)	0.2571 (11)	0.4122 (10)	0.1229 (10)	5.5 (3)

* The very inaccurate parameters of the hydrogen atoms are not given. Introduction of these atoms in the structure factor calculation hardly affects the F_c values.

† In the Tables the e.s.d.'s in the atomic parameters are given in units of the last decimal place.

Table 2. Anisotropic thermal parameters (\AA^2) for the iodine atoms in $(C_2H_5)_4NI_3$ (I)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
I(1)	0.0460 (8)	0.1037 (15)	0.0491 (10)	0	-0.0037 (10)	0
I(2)	0.0579 (8)	0.0986 (12)	0.0955 (11)	0	-0.0135 (10)	0
I(3)	0.0389 (7)	0.0537 (9)	0.0678 (11)	0	-0.0054 (8)	0
I(4)	0.0501 (6)	0.0661 (7)	0.0639 (8)	0	-0.0068 (6)	0

Table 3. Observed and calculated structure factors for $(C_2H_5)_4Ni_3$ (I)
The values listed are $10F_o$ and $10F_c$.

M	K	L	F _O	F _C	M	K	L	F _O	F _C	M	K	L	F _O	F _C	M	K	L	F _O	F _C	M	K	L	F _O	F _C							
0	4	0	5544	5904	1	1	8	1707	1820	3	1	5	1849	1803	5	3	2	-913	-879	7	1	5	-1414	-1433	9	1	4	907	940		
0	6	0	5263	5627	1	5	8	715	688	3	3	5	3835	3757	5	5	2	-1440	-1439	7	7	1	964	957	9	3	4	521	557		
0	10	0	1972	2040	1	7	8	1927	1861	3	7	5	1295	1256	5	7	2	-467	-443	7	7	1	954	949	9	3	4	512	530		
0	12	0	187	158	1	8	8	1181	1181	3	11	5	1181	1181	5	9	2	-446	-443	7	11	1	954	949	9	7	4	156	1591		
0	4	1	-1218	-1163	1	13	8	414	492	3	15	2	-416	-344	5	11	2	-444	-401	7	13	1	525	462	9	9	4	372	394		
0	6	1	-2788	-1173	1	13	8	494	913	3	15	6	-2291	-3216	5	1	3	-127	-312	7	1	2	513	509	9	11	4	715	730		
0	10	1	-2000	-2074	1	13	9	964	939	3	5	6	-1640	-1579	5	3	3	-205	-1990	7	3	2	796	824	9	1	5	1146	1156		
0	12	1	-1020	-1033	1	10	9	440	440	3	5	6	-1926	-1868	5	7	3	-354	-375	7	7	2	-420	-342	9	7	5	723	815		
0	2	2	-574	-527	1	13	10	-717	-691	3	11	6	-624	-588	5	9	3	570	597	7	9	2	-1065	-1082	9	1	6	828	894		
0	4	2	1063	1076	1	5	10	-594	-532	3	15	6	-471	-359	5	13	3	870	879	7	15	2	-465	-2186	9	3	6	1063	1122		
0	6	2	2979	27	1	9	10	-849	-817	3	1	7	-234	-2312	5	13	3	870	879	7	1	5	-248	-2186	9	10	3	533	539		
0	12	2	21	2748	1	12	9	-817	-817	3	1	7	-234	-2312	5	13	3	870	879	7	1	5	-1965	-1965	9	6	1	175	470		
0	12	2	1309	1391	1	12	4	481	524	3	5	7	-1792	-1653	5	1	4	1240	1113	7	7	3	616	649	9	11	6	-434	-439		
0	14	2	919	928	1	13	13	-568	-502	3	13	7	754	769	5	3	4	407	322	7	13	1	869	955	9	7	3	-1586	-1352		
0	16	2	1091	1142	1	5	14	267	267	3	7	4	424	375	5	5	4	1561	1662	7	1	4	1550	1521	9	3	7	-681	-708		
0	16	2	347	414	1	15	14	420	405	3	5	6	-1604	-1526	5	2	4	208	2197	7	5	4	891	775	9	8	2	10	1616		
0	8	3	-495	-497	1	15	14	337	337	3	5	6	-449	-434	5	11	6	1845	1844	7	7	4	1847	1872	9	8	3	368	348		
0	6	3	711	752	2	2	0	565	5860	3	11	8	911	916	5	13	4	620	558	7	9	4	555	628	9	7	8	1117	1091		
0	10	3	103	1151	1	13	12	0	565	584	3	13	8	558	412	4	15	1	1818	1844	7	11	4	545	544	12	4	6	1089	1025	
0	12	3	1070	1224	1	12	8	562	562	3	13	9	564	564	5	13	3	870	879	7	1	5	1965	1965	12	6	5	500	886		
0	14	3	574	592	2	8	0	687	706	3	3	9	873	878	5	9	5	1190	1273	7	1	5	1360	1401	9	3	9	424	553		
0	C	C	6588	6568	2	10	0	2053	2124	3	5	9	491	492	5	11	6	1459	1428	7	3	5	2602	2602	9	5	9	333	292		
0	2	4	2378	2441	2	2	2	-2594	-2452	3	7	9	574	579	5	1	6	1173	1107	7	7	5	927	904	9	7	3	414	340		
0	2	6	1709	1754	2	12	2	1295	1257	3	7	14	434	430	5	5	6	1323	1315	7	12	4	1287	1287	12	4	9	414	387		
0	6	6	2473	2524	1	11	12	1157	1157	3	5	6	1245	1245	5	1	6	1323	1315	7	12	4	1331	1331	12	4	9	409	343		
0	6	8	879	879	2	8	1	-1752	-1833	3	5	10	-713	-669	5	9	6	1744	1730	7	1	6	581	601	10	0	0	4760	5055		
0	10	1	1913	1974	2	10	1	-1299	-1308	3	7	10	368	233	5	11	6	-582	-500	7	3	6	1335	1373	12	0	2	2121	2173		
0	12	5	1550	1575	2	12	1	-950	-991	3	9	10	-709	-703	5	12	5	-2075	-2090	7	5	6	1382	1359	12	4	8	2632	2731		
0	14	6	1129	1129	2	12	7	-2747	-2653	3	5	12	-384	-384	5	13	6	-1084	-1084	7	1	5	-1445	-1445	12	4	8	2725	2879		
0	16	6	-1129	-1129	2	12	8	1000	1000	3	5	12	-266	-273	5	13	6	-1400	-1400	7	1	5	-1000	-1000	12	4	8	507	457		
0	12	5	-505	-505	2	6	2	265	2604	3	3	12	-390	-373	5	13	7	596	507	7	1	7	-1727	-1727	12	0	8	832	875		
0	C	C	4384	4287	2	10	2	2550	2605	3	3	13	-525	-573	5	1	6	1546	1606	7	3	7	-665	-653	12	10	8	610	589		
0	2	6	1709	1754	2	12	2	1295	1257	3	7	14	434	430	5	5	6	1546	1606	7	5	7	-1226	-1287	12	4	9	695	634		
0	6	6	2070	2095	2	12	2	1295	1257	3	7	14	434	430	5	5	6	1546	1606	7	5	7	-1331	-1378	12	4	9	372	343		
0	10	6	2473	2524	2	12	2	1295	1257	3	7	14	434	430	5	5	6	1546	1606	7	5	7	-1331	-1378	12	4	9	1093			
0	6	8	879	879	2	18	2	551	433	4	2	8	3667	4047	5	13	8	408	384	6	9	5	544	534	10	1	7	711	785		
0	12	6	6113	1189	2	4	3	1701	1701	4	4	6	453	492	5	13	9	681	730	7	7	8	1333	1361	10	0	2	1840	1830		
0	12	6	669	682	2	6	3	1047	970	4	6	6	465	486	5	13	9	700	780	7	7	8	624	663	12	6	13	578	598		
0	14	6	454	454	2	12	7	1445	1445	4	12	9	-1115	-1080	5	13	9	384	384	7	1	5	-1445	-1445	12	6	13	544	552		
0	2	7	-1315	-1308	2	2	0	2443	2320	6	0	2	0	2559	2964	8	6	2	0	2559	2964	12	11	4	420	420	12	11	4	549	552
0	4	7	748	769	2	2	4	3190	3116	4	6	1	-2038	-2026	5	10	3	510	510	7	5	9	414	424	12	11	4	1022	1069		
0	6	8	154	154	2	12	7	-1515	-1515	4	6	1	-2078	-2135	5	10	3	510	510	7	5	9	414	424	12	11	4	1022	1069		
0	8	9	354	354	2	12	7	2000	2373	4	8	4	477	404	5	13	8	778	778	7	1	5	-864	-879	12	8	9	442	403		
0	4	9	4	9	354	354	2	12	7	320	220	4	8	7	719	743	5	13	8	990	990	7	12	1	960	1032					
0	6	10	4	10	2211	72	4	12	7	402	-444	4	10	4	-1790	1776	5	12	2	2265	2263	8	12	1	665	685					
0	10	11	448	405	2	12	7	-402	-444	4	10	4	-1790	1776	5	12	2	2265	2263	8	12	1	665	685							
0	12	11	-772	-922	2	8	10	1101	1128	4	16	4	446	341	5	12	2	2265	2263	8	12	1	665	685							
0	14	11	-145	-145	2	12	7	309	296	4	6	8	-1016	-1016	5	12	2	2265	2263	8	12	1	665	685							
0	12	11	-527	-539	2	10	2	2792	2801	4	10	4	1195	1195	5	12	2	2265	2263	8	12	1	665	685							
0	C	C	901	947	2	10	2	210	2564	4	12	7	625	575	5	12	2	705	705	8	4	549	493	10	1	3	1071	1073			
0	12	17	171	171	2	12	7	2028	2235	4	16	4	13	384	5	12	2	1455	1500	8	6	5	-760	-800	14	2	2	1242	1242		
0	14	12	1032	1032	2	12	7	12	592	592	4	12	8	1261	747	5	12	2	1170	1170	8	6	5	-421							

planes of the crystals were determined as accurately as possible. The dimensions of the crystals used were approximately $0.22 \times 0.22 \times 0.14$ mm³.

Structure determination and refinement

$(C_2H_5)_4NI_3$ (I)

From the strong intensities of the reflexions $h00$ ($h=2n$) and geometrical considerations it could be concluded that the I_3^- ions lie on the mirror planes $(0, y, z)$ and $(\frac{1}{2}, y, z)$. The y and z coordinates were deduced from a [100] Patterson projection. The Patterson map could be interpreted by assuming that the structure contains two independent I_3^- ions at special positions with symmetry $2/m$. A structure factor calculation showed the trial model to be essentially correct.

The eight $(C_2H_5)_4N^+$ groups could be placed in holes formed by eight I_3^- ions at the eightfold special position $8(e)$ in space group $Cmca$. The coordinates of the nitrogen and carbon atoms could be obtained from a three-dimensional F_o synthesis. Isotropic least-squares refinement with all observed reflexions hkl gave $R = 0.104$. During the following refinement cycles with anisotropic thermal parameters for the iodine atoms alone, R dropped to 0.045. The weighting scheme was

$$w = [1 + (|F_o| - 125)^2/4339]^{-1}.$$

Positive regions indicating positions of the hydrogen atoms could be seen in the final difference map including only those reflexions with $(\sin \theta)/\lambda < 0.4$ Å⁻¹; their parameters were not refined. The least-squares calculations were done on a TR4 computer with a program written by Palm and Peterse according to Cruick-

shank's (1961) scheme. The scattering factors were represented by analytical functions according to Moore (1963).

The final coordinates and thermal parameters with their e.s.d.'s as calculated from the least-squares residuals are given in Tables 1 and 2. The calculated structure factors based on these parameters are compared with the observed values in Table 3.

$(C_2H_5)_4NI_3$ (II)

In the space group $Pnma$ adopted for the structure determination, the mirror planes are perpendicular to the y direction. The strong intensities of the reflexions $0k0$ ($k=2n$) indicate that the I_3^- groups are located on these mirror planes, which implies that there are two independent I_3^- groups in the cell. Because of overlap in the [010] projection the sections $y=0$ and $y=0.5$ of a three-dimensional Patterson synthesis were calculated to determine the positions of the iodine atoms. After having found the positions of the iodine atoms, we obtained the coordinates of the $(C_2H_5)_4N^+$ groups (at eightfold general positions) from a three-dimensional F_o map. Refinement of the structure was carried out in the same way as described for modification I. The indices R were 0.090 after isotropic refinement, and 0.042 after anisotropic refinement (anisotropic thermal parameters for iodine atoms only). The weighting scheme was

$$w = [1 + (|F_o| - 137)^2/11250]^{-1}.$$

The final positional and thermal parameters with their e.s.d.'s are listed in Tables 4 and 5. The calculated structure factors based on these parameters are compared with the observed values in Table 6.

Table 4. Final fractional coordinates and isotropic thermal parameters for $(C_2H_5)_4NI_3$ (II)

The standard deviations are given in parentheses. For numbering of the atoms see Fig. 1 (b).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
I(1)	0.03341 (16)	0.25	0.16504 (14)	
I(2)	0.01230 (13)	0.25	-0.03060 (12)	
I(3)	-0.00035 (16)	0.25	-0.22102 (14)	
I(4)	0.29817 (14)	0.25	0.02374 (13)	
I(5)	0.49541 (14)	0.25	-0.00875 (10)	
I(6)	0.69561 (14)	0.25	-0.04362 (11)	
N	0.2590 (9)	0.4911 (10)	0.2936 (8)	4.2 (3) Å ²
C(1)	0.1568 (15)	0.5254 (17)	0.1624 (13)	7.4 (6)
C(2)	0.2171 (13)	0.5646 (14)	0.2335 (12)	6.0 (5)
C(3)	0.1846 (13)	0.4346 (14)	0.3414 (11)	5.7 (4)
C(4)	0.1262 (14)	0.4948 (17)	0.4024 (13)	6.9 (5)
C(5)	0.3920 (15)	0.4606 (19)	0.1852 (15)	8.1 (6)
C(6)	0.3136 (13)	0.4179 (15)	0.2414 (12)	6.2 (5)
C(7)	0.3215 (13)	0.5470 (15)	0.3581 (12)	6.0 (5)
C(8)	0.3716 (14)	0.4818 (16)	0.4216 (14)	7.0 (5)

Table 5. Anisotropic thermal parameters (Å²) for the iodine atoms in $(C_2H_5)_4NI_3$ (II)

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₂₃	<i>U</i> ₁₃
I(1)	0.0999 (17)	0.0723 (13)	0.0943 (14)	0	0	-0.0121 (12)
I(2)	0.0658 (12)	0.0522 (9)	0.0973 (13)	0	0	-0.0047 (12)
I(3)	0.0995 (16)	0.0714 (12)	0.0949 (14)	0	0	-0.0117 (13)
I(4)	0.0777 (13)	0.0617 (11)	0.0887 (13)	0	0	-0.0024 (12)
I(5)	0.0846 (12)	0.0479 (8)	0.0564 (9)	0	0	-0.0013 (10)
I(6)	0.0837 (13)	0.0632 (11)	0.0632 (11)	0	0	0.0107 (11)

Discussion

Arrangement of the ions

The crystal structures of the two modifications of $(C_2H_5)_4Ni_3$ are shown in Fig. 1. The bond lengths and angles are given in Tables 7 and 8. The standard deviations in these Tables are calculated from the standard

deviations as estimated for the atomic coordinates from the least-squares residuals, with the errors in the cell dimensions also taken into account.

Both crystals have two independent I_3^- groups in the unit cell which lie on mirror planes. The Figure clearly shows that the arrangement of the I_3^- groups within a layer is remarkably similar in the two compounds. The

Table 6. Observed and calculated structure factors for $(C_2H_5)_4Ni_3$ (II)

The values listed are $10F_O$ and $10F_C$.

H	K	L	F _O	F _C	H	K	L	F _O	F _C	H	K	L	F _O	F _C	H	K	L	F _O	F _C	H	K	L	F _O	F _C	
2	0	0	2474	2414	7	0	11	1081	1018	6	2	0	-4700	-4653	12	3	0	520	487	10	4	2	1476	1700	
6	0	0	9781	9561	9	0	11	250	2472	9	2	0	-770	-745	12	3	0	1280	1255	11	4	2	-355	-3163	
6	0	0	9124	9215	2	0	11	923	1023	10	2	0	-2471	-2495	12	3	0	1295	1295	11	4	3	-124	-3205	
8	0	0	959	1012	10	0	12	336	240	14	2	0	-544	-571	2	3	1	657	660	2	4	3	-1113	-1057	
10	0	0	2727	2682	3	0	13	700	743	14	2	0	-1390	-3944	3	3	1	813	-828	4	4	3	1393	1357	
14	0	0	390	412	7	0	13	927	536	4	2	0	-1642	-1661	4	3	1	698	713	10	5	5	-576	-616	
3	0	0	-3432	-3597	8	0	14	515	515	5	2	0	-2383	-2400	1	3	1	1372	-1378	11	4	3	-1204	-1295	
4	0	0	1422	1423	1	0	15	543	543	7	2	0	-1162	-1178	7	3	1	443	-447	3	5	6	-1580	-1451	
5	0	0	1	2068	2064	3	0	15	942	888	8	2	0	-659	-666	8	3	1	820	856	10	4	3	-532	-565
9	0	0	-1852	-1919	7	0	15	524	493	1	2	0	-385	-493	1	4	1	-1049	-1049	5	5	6	-441	-484	
8	0	0	858	905	1	0	16	332	275	21	2	0	-488	-502	11	3	1	-780	-826	12	4	4	-1391	-1423	
9	0	0	497	522	2	1	0	779	793	0	2	0	-5465	-5540	12	3	1	514	609	3	4	4	-2454	-2471	
10	0	0	441	370	4	1	0	1466	1468	2	2	0	-2404	-2470	1	3	2	980	993	4	4	4	-3442	-3291	
7	0	0	-1876	-1876	6	1	0	149	149	3	2	0	-2455	-2455	3	3	2	245	245	5	4	3	-1557	-1557	
15	0	0	-446	-450	8	0	15	154	1508	3	2	0	-250	-151	6	4	4	-850	-840	2	4	4	-2424	-2228	
19	0	0	494	506	10	1	0	352	510	2	2	0	-2179	-2226	9	3	2	265	268	8	4	4	-938	1002	
0	0	0	2768	2699	12	1	0	649	616	5	2	0	-610	-655	6	3	2	-569	-579	10	4	3	-1468	-1639	
2	0	0	-510	-510	0	1	0	838	730	4	2	0	-1569	-1583	7	3	2	614	-599	11	4	3	-1780	-1700	
3	0	0	-387	-387	5	1	0	644	644	10	2	0	-1569	-1583	12	4	4	-686	-680	12	4	4	-1291	-1355	
3	0	0	-265	-265	1	2	0	659	702	8	2	0	-514	-495	9	3	2	-674	-682	13	4	4	-375	-404	
4	0	0	1378	1418	3	1	1	893	875	10	2	0	-174	-1765	13	2	3	-477	-429	14	4	4	-696	548	
5	0	0	-526	-526	1	1	0	1135	1135	1	2	0	-3840	-3778	5	3	2	563	536	10	4	4	-1040	-1040	
5	0	0	-874	-874	0	1	0	1135	1135	1	2	0	-3840	-3778	11	3	2	-563	-536	10	4	4	-1040	-1040	
5	0	0	-583	-583	1	1	0	1135	1135	1	2	0	-3840	-3778	12	3	2	-563	-536	10	4	4	-1040	-1040	
7	0	0	-1866	-1866	6	1	0	169	1240	3	2	0	-1404	-1474	3	3	2	396	396	13	4	4	-1544	-1544	
7	0	0	-402	-395	7	1	1	1072	1088	4	2	0	-1391	-1367	8	3	3	-364	-253	14	4	4	-1588	-1424	
8	0	0	1774	1788	8	1	1	946	980	5	2	0	-3196	-3208	11	3	3	-473	-420	5	4	4	-364	352	
11	0	0	-490	-455	9	1	1	1085	1045	6	2	0	-3187	-3187	12	3	3	-402	-342	1	4	4	-1042	-952	
11	0	0	-490	-455	9	1	1	1085	1045	6	2	0	-3187	-3187	13	3	3	-402	-342	1	4	4	-1042	-952	
12	0	0	3780	3823	11	1	1	693	693	4	2	0	-644	-692	12	3	3	-529	-568	12	4	4	-676	-636	
12	0	0	-1107	-1076	12	1	1	616	617	11	2	0	-443	-379	12	3	3	-366	-366	14	4	4	-2935	-2856	
13	0	0	291	184	13	1	1	325	357	12	2	0	-574	525	9	3	3	-300	-318	6	4	4	-1580	-1585	
13	0	0	-395	-395	15	1	1	325	357	12	2	0	-5529	-5624	11	3	3	-496	-424	13	4	4	-1040	-1040	
9	0	0	4011	3761	15	1	1	325	357	12	2	0	-5529	-5624	13	3	3	-496	-424	14	4	4	-1040	-1040	
6	0	0	-1458	-1497	7	1	2	529	572	2	2	0	-1533	-1552	13	3	3	-559	-599	14	4	4	-1800	1849	
7	0	0	-395	-475	9	1	2	594	660	12	2	0	-1421	-1284	14	3	3	-515	-566	15	4	4	-2017	-1984	
9	0	0	522	526	0	1	3	334	327	4	2	0	-2711	-2688	4	3	3	-525	-563	12	4	4	-2239	-2239	
15	0	0	-343	-294	1	1	3	251	251	5	2	0	-2711	-2688	6	3	3	-525	-563	13	4	4	-2239	-2239	
15	0	0	-343	-294	1	1	3	251	251	5	2	0	-2711	-2688	7	3	3	-525	-563	14	4	4	-2239	-2239	
15	0	0	-4955	-4934	3	1	3	378	667	2	2	0	-300	-330	7	3	3	-1002	-994	10	4	4	-394	481	
12	0	0	516	484	11	1	4	516	532	4	2	0	-775	-730	8	3	3	-933	-948	9	4	4	-1049	977	
12	0	0	533	427	0	1	5	420	429	5	2	0	-1019	-1022	12	3	3	-500	-535	9	4	4	-1049	-1049	
14	0	0	441	455	1	1	5	450	932	6	2	0	-1725	-1761	8	3	3	-567	-597	10	4	4	-1832	-1811	
15	0	0	349	349	1	1	5	450	932	6	2	0	-1725	-1761	10	4	4	-567	-597	11	4	4	-1832	-1811	
1	0	0	-551	-493	4	1	5	2701	2719	8	2	0	-512	-475	1	3	3	-1485	-1506	4	4	4	-1764	1795	
2	0	0	-2609	-2609	9	1	5	751	725	12	2	0	-651	-578	6	3	3	-1621	-1643	13	4	4	-2095	-2124	
2	0	0	-2023	-1984	6	1	5	201	2024	12	2	0	-775	766	7	3	3	-923	-949	8	4	4	-1390	-1316	
4	0	0	513	1373	7	1	6	395	909	10	2	0	-1738	-1389	11	3	3	-947	-597	12	4	4	-1390	-1353	
7	0	0	-1017	-956	9	1	6	373	403	12	2	0	-1724	-1724	13	3	3	-947	-597	14	4	4	-1010	-1010	
7	0	0	-529	-483	10	1	5	666	663	12	2	0	-1777	-1735	14	3	3	-574	-608	15	4	4	-1670	-1707	
10	0	0	-355	-355	21	1	6	388	388	13	2	0	-1737	-1737	21	3	3	-473	-473	21	4	4	-1670	-1707	
11	0	0	355	220	21	1	6	388	343	4	3	8	-407	416	21	3	3	-1445	-381	8	4	4	-1670	-1707	
14	0	0	-379	-379	15	1	6	388	203	10	2	0	-1010	-1010	15	3	3	-565	-565	16	4	4	-1670	-1707	
14	0	0	-379	-379	15	1	6	388	203	10	2	0	-1010	-1010	16	3	3	-565	-565	17	4	4	-1670	-1707	
10	0	0	-605	-516	6	1	7	516	516	7	2	0	-623	-607	9	3	3	-621	593	9	4	4	-1049	1023	
13	0	0	-643	-450	7	1	7	516	516	9	2	0	-912	-880	10	3	3	-621	593	9	4	4	-1106	1084	
13	0	0	-1377	-1377	10	1	7	516	516	9	2	0	-912	-880	11	3	3	-621	593	10	4	4	-1106	1084	
13	0	0	-1377	-1377	10	1	7	516	516	9	2	0	-912	-880	11	3	3	-621	593	10	4	4	-1106	1084	
12	0	0	-407	-381	7	1	8	516	516	9	2	0	-1015	-1013	12	3	3	-708	693	13	4	4	-1377	1377	
7	0	0																							

Table 6 (cont.)

H	K	L	F ₀	F _C	H	K	L	F ₀	F _C	H	K	L	F ₀	F _C	H	K	L	F ₀	F _C	H	K	L	F ₀	F _C			
1	6	5	-379	-325	3	8	9	728	678	7	9	5	482	465	4	10	2	-1019	-1026	7	1C	7	-509	-433	2	11	9
2	6	5	+1167	-1181	4	8	9	539	531	1	9	6	721	770	6	10	2	-766	-834	9	1C	7	-437	-470	1	11	10
3	6	5	-878	-840	6	8	9	-601	-1027	3	9	6	-781	-839	6	10	2	-781	-839	8	1C	8	-387	-328	0	11	11
4	6	5	507	-524	1	8	10	-357	-404	5	9	6	-782	-840	1	10	2	-1166	-1386	1	1C	8	-488	-413	2	11	11
5	6	5	-235	-378	8	8	10	488	502	5	9	6	-782	-840	3	10	3	-549	-573	4	1C	8	-413	-413	0	10	10
6	6	5	-1543	-1498	8	8	10	413	486	7	9	6	-405	-461	4	10	3	-672	-643	4	1C	8	-445	-435	2	12	0
7	6	5	-606	-526	9	6	10	490	513	0	9	7	-375	-370	5	10	3	-1433	-1455	1	1C	9	-379	-352	4	12	0
0	6	6	1747	1736	1	8	11	593	546	1	9	7	664	672	6	10	3	-581	-575	3	1C	9	-644	-347	6	12	0
1	6	6	-880	-859	3	8	11	1010	1000	2	9	7	-565	-533	3	10	3	-2688	-2084	3	1C	9	-567	-631	0	12	0
2	6	6	-722	-722	4	8	11	600	594	2	9	7	-479	-479	1	10	4	-659	-699	3	1C	9	-634	-634	6	12	0
3	6	6	708	691	7	8	11	715	660	7	9	7	-456	-492	2	10	4	-751	-756	2	1C	10	-243	-496	4	12	1
4	6	6	1321	1339	2	8	12	640	620	1	9	8	-507	-530	3	10	4	-786	-770	3	1C	10	-439	-468	5	12	1
5	6	6	390	367	2	9	0	-383	-305	3	9	8	-420	-494	4	10	4	-1361	-1374	1	1C	11	-514	-447	7	12	1
6	6	6	676	669	4	9	0	-684	-644	6	9	8	-595	-595	5	10	4	-1203	-1198	3	1C	11	-723	-712	0	12	2
7	6	6	-254	-254	6	9	0	-446	-737	0	9	9	-672	-676	6	10	4	-589	-578	1	1C	11	-505	-478	4	12	2
9	6	6	811	836	8	9	0	-741	-700	2	9	9	-565	-613	9	10	4	-820	-835	2	1C	12	-415	-369	6	12	2
1	6	7	816	824	9	9	1	-430	-421	4	9	9	-439	-455	9	10	4	-820	-835	0	11	0	-447	-410	7	12	0
2	6	7	-640	-642	3	9	1	289	194	1	9	0	-538	-507	10	10	4	-740	-750	8	11	0	-394	-394	1	12	0
3	6	7	751	751	3	9	1	303	303	9	9	0	-451	-451	10	10	4	-740	-750	8	11	0	-394	-394	1	12	0
4	6	7	1184	1182	3	9	1	719	784	5	9	10	-372	-401	8	10	5	-699	-684	3	11	0	-394	-375	3	12	0
5	6	7	794	816	6	9	1	-775	-791	6	10	5	-531	-532	6	10	5	-989	-1074	3	11	1	-327	-309	5	12	3
6	6	7	-642	-640	7	9	1	593	615	0	9	11	-445	-482	7	10	5	-420	-364	4	11	1	-449	-388	0	12	4
7	6	7	713	588	9	9	1	597	487	2	9	11	-445	-438	8	10	5	-153	-153	4	11	1	-511	-513	1	12	4
8	6	7	379	379	9	9	1	-490	-493	0	10	5	-435	-438	6	10	6	-1002	-987	9	11	1	-581	-582	4	12	4
9	6	7	612	625	10	9	1	499	493	2	10	0	-1744	-1713	2	10	6	-734	-759	10	11	1	-458	-458	4	12	4
1	6	7	-1563	-1280	9	9	3	-291	-200	4	10	0	-2979	-2616	3	10	6	-713	-719	3	11	4	-464	-412	4	12	4
2	6	7	681	733	9	9	3	-330	-326	6	10	0	-2140	-2135	4	10	6	-761	-761	0	11	5	-1507	-1519	6	12	4
3	6	8	484	520	9	9	3	-681	-681	10	10	0	-1161	-1161	5	10	6	-511	-626	2	11	5	-327	-296	5	12	4
4	6	8	-425	-425	3	9	5	-600	-600	3	10	0	-1381	-1320	9	10	6	-593	-610	1	11	5	-327	-296	5	12	4
5	6	8	315	324	9	9	5	413	426	4	10	1	-439	-485	1	10	7	-572	-604	4	11	5	-818	-818	2	12	5
7	6	8	-342	-403	2	9	5	-1518	-1512	5	10	1	-929	-933	2	10	7	-383	-414	6	11	5	-758	-778	3	12	5
8	6	8	548	462	3	9	5	298	165	7	10	1	-777	-725	3	10	7	-567	-601	1	11	6	-542	-559	6	12	5
9	6	8	514	493	4	9	5	-1248	-1284	0	10	2	-192	-1899	4	10	7	-744	-744	3	11	6	-514	-628	0	12	6
1	6	9	610	565	5	9	5	304	321	1	10	2	-191	-191	1	10	7	-717	-825	6	11	7	-419	-319	1	12	6
2	6	9	-432	-473	6	9	5	-995	-1024	2	10	2	-437	-397	6	10	7	-482	-509	6	11	8	-379	-398	2	12	6

stacking of the layers is different, however. In modification II successive layers are nearly on top of each other. On the other hand, successive layers are shifted by $\frac{1}{2}$ in the y direction in modification I. It can easily be seen from Tables 7 and 8, where all the $I \cdots I$ distances shorter than 4.5 Å are given, that there are no strong intermolecular interactions. In both modifications the $(C_2H_5)_4N^+$ groups lie in holes formed by eight I_3^- ions.

The $(C_2H_5)_4N^+$ ions

In modification I, the nitrogen atoms lie at twofold axes along the y directions whereas in II the groups are placed at general positions. The C-C distances, 1.53 Å on the average, are not significantly different from the accepted value for a single $C(sp^3)-C(sp^3)$ bond. It may be noticed, however, that the average value for the C-N bonds, 1.51 Å, is somewhat larger than the value of 1.47 Å found in $(CH_3)_4NICl_2$ (Visser & Vos, 1964) and in $(CH_3)_4NClO_4$ (McCullough, 1964). The C-C-N angles in the $(C_2H_5)_4N^+$ ions, about 114° , are comparable with the C-C-C angles in paraffin chains, 112 – 113° .

The I_3^- ions

In $(C_2H_5)_4NI_3$ (I) the I_3^- groups lie at special positions with symmetry $2/m$ and are thus symmetric. The lengths of the I-I bonds in the two independent symmetrical I_3^- groups are 2.928 and 2.943 Å, e.s.d. 0.0025 Å. We believe that the difference of 0.015 Å (s.d. 0.0035 Å) between these bond lengths cannot be significant, although it is four times its estimated standard deviation. It is generally known that standard deviations as calculated from the least-squares residuals give an underestimate of the experimental errors, especially for structure determinations where good agreement between F_o and F_c is achieved.

The I_3^- ions in II appear to be asymmetric in contradistinction to the geometry of the ions in modification I. The bond lengths are 2.912, 2.961 Å and 2.892, 2.981 Å, e.s.d. 0.0035 Å. The differences between the

bond lengths within the ions are 18 and 15 times its estimated standard deviation respectively.

In Table 9 the bond lengths observed for the I_3^- ions in different triiodide compounds are compared. The variation in geometry mentioned in the introduction is clearly shown. It is remarkable that in the two modifications of $(C_2H_5)_4NI_3$, ions of different shape have been found with I-I bond lengths ranging from 2.892 to 2.981 Å. In spite of variations in the geometry, the total lengths of the I_3^- ions in the two modifications are not significantly different. For the symmetric ions this length is 5.871 Å on the average and the corresponding value for the asymmetric ions amounts to 5.873 Å. Consequently it is not certain that the total length varies with the asymmetry of the ions, as suggested earlier from the difference in total length observed for the ions in CSl_3 and $(C_6H_5)_4AsI_3$. On the contrary, both for CSl_3 and $(C_6H_5)_4AsI_3$ the total length of the ions is equal to the length observed for the ions in $(C_2H_5)_4NI_3$ (I and II) within experimental error.

The differences in shape of the I_3^- ions in the two modifications of $(C_2H_5)_4NI_3$ indicate that the shape of I_3^- ions in crystals is not dependent only on the size of the surrounding cations, as has been concluded from earlier structure determinations. The results of the present work suggest that there is a close connexion between the shape of the I_3^- ions and the way these ions are surrounded both by positive and negative ions in the crystal. Therefore we are led to ascribe the variations in bond lengths to (electrostatic) crystal field effects. Hence theoretical VESCF molecular orbital calculations were performed by us in the way described by Brown & Nunn (1966) to get a better estimate of the influence of the crystal field.

Theoretical calculations

The method used for the theoretical calculations has essentially been described by Brown & Nunn (hereafter B and N). To perform the semi-empirical calculations, however, a suitable choice of different parameters should be made, and it is in this respect that our

approach is different from that of B and N. In Table 10 the two sets of parameters are compared.

In both cases, the Coulomb repulsion integral $\gamma_{\mu\nu}$ is $I - A$ for $R=0$, and $14.4/R$ for large values of R . At moderate distances our value for $\gamma_{\mu\nu}$ is larger than that

of B and N. This larger value was taken, as in triiodide ions the valence p orbitals are directed along the bonds to neighbouring cores (see Havinga & Wiebenga, 1959), as against the case of organic compounds, where the valence p orbitals are perpendicular to the bonds. The

Table 7. Distances and angles in $(C_2H_5)_4NI_3$ (I) with e.s.d.'s in parentheses

I(1)–I(2)	2.928 (0.0025) Å	C(1)–C(2)–N	114 (1)°
I(3)–I(4)	2.943 (0.0025)	C(4)–C(3)–N	115
C(1)–C(2)	1.53 (0.02)	C(2)–N—C(3)	112
C(3)–C(4)	1.53 (0.02)	C(2)–N—C(3')	106
N—C(2)	1.51 (0.02)	C(2)–N—C(2')	110
N—C(3)	1.52 (0.02)	C(3)–N—C(3')	111
I(1)…I(4')	4.14		
I(2)…I(4')	4.50		

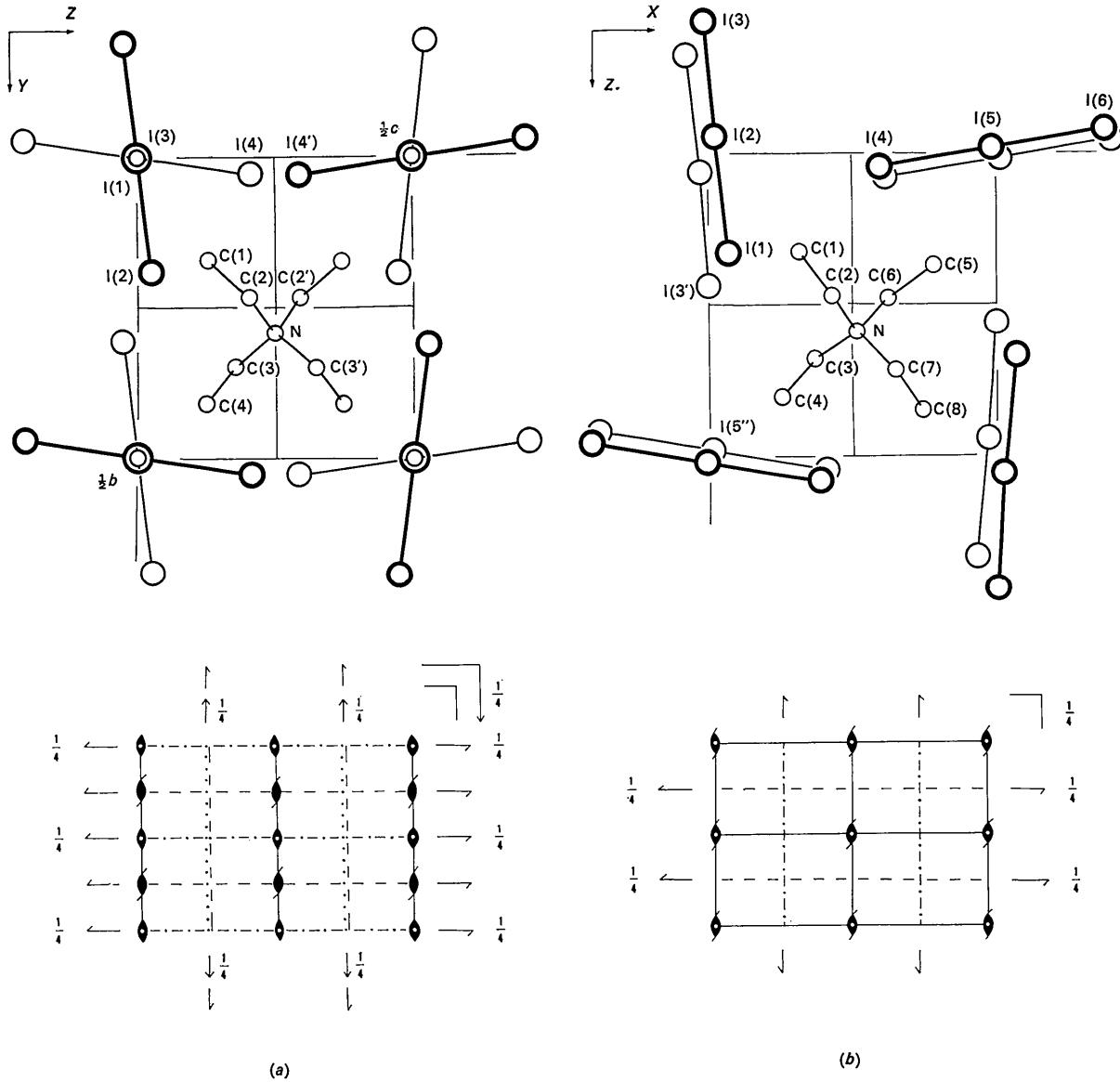


Fig. 1. Structures of the two modifications of $(C_2H_5)_4NI_3$. (a) $(C_2H_5)_4NI_3$ (I) viewed along [100]. The iodine atoms at heights 0 and $c/2$ are represented as heavy and light circles respectively. (b) $(C_2H_5)_4NI_3$ (II) viewed along [010]. The iodine atoms at heights $b/4$ and $3b/4$ are represented as heavy and light circles respectively.

Table 8. Distances and angles in $(C_2H_5)_4NI_3$ (II) with e.s.d.'s in parentheses

I(1) -I(2)	2.981 (0.0035) Å	I(1) -I(2) -I(3)	177.7 (0.1) °
I(2) -I(3)	2.892 (0.0035)	I(4) -I(5) -I(6)	179.5 (0.1)
I(4) -I(5)	2.912 (0.0035)	C(1)-C(2)-N	115 (1)
I(5) -I(6)	2.961 (0.0035)	C(4)-C(3)-N	114
C(1)-C(2)	1.49 (0.03)	C(5)-C(6)-N	115
C(3)-C(4)	1.51 (0.03)	C(8)-C(7)-N	113
C(5)-C(6)	1.54 (0.03)	C(2)-N—C(3)	111
C(7)-C(8)	1.54 (0.03)	C(2)-N—C(6)	111
N—C(2)	1.50 (0.03)	C(2)-N—C(7)	106
N—C(3)	1.52 (0.03)	C(3)-N—C(6)	106
N—C(6)	1.51 (0.03)	C(3)-N—C(7)	112
N—C(7)	1.54 (0.03)	C(6)-N—C(7)	111
I(3') ··· I(5'')	4.10		
I(1) ··· I(4)	4.41		
I(2) ··· I(4)	4.24		

Table 9. Bond lengths (Å) in I_3^- ions, with their e.s.d.'s

Compound	R_{12}	R_{23}	$R_{12} + R_{23}$
$(C_2H_5)_4NI_3$ (I)	2.928 (0.0025)	2.928 (0.0025)	5.856 (0.005)
	2.943 (0.0025)	2.943 (0.0025)	5.886 (0.005)
$(C_2H_5)_4NI_3$ (II)	2.961 (0.0035)	2.912 (0.0035)	5.873 (0.0035)
	2.981 (0.0035)	2.892 (0.0035)	5.873 (0.0035)
CsI_3	3.04 (0.015)	2.83 (0.015)	5.87 (0.015)
$(C_6H_5)_4AsI_3$	2.91 (0.015)	2.91 (0.015)	5.82 (0.03)*

* The values for $(C_6H_5)_4AsI_3$ are obtained from a recent least-squares refinement of this compound using $h0l$ and $hk0$ data presented by Mooney & Slater (1959).

Table 10. Choice of parameters (in eV) for the VESCF-MO calculations

Coulomb repulsion integral

Present work: $\gamma_{\mu\nu} = 14.4/R$ for $R \geq 3.7$ Å, $\gamma_{\mu\nu} = -0.843R + I - A$, linear interpolation between $\gamma_{\mu\nu} = 14.4/R$ for $R = 3.7$ Å and $\gamma_{\mu\nu} = I - A = 7.01$ eV for $R = 0$.

R =distance of core centres.

I =ionization energy, A =electron affinity.

B and N: $\gamma_{\mu\nu} = 14.4/(a + R)$ with $14.4/a = I - A$, the Mataga-Nishimoto formula introduced for organic compounds.

Core resonance integral

Present work: $\beta_{\mu\nu} = 1.89R - 7.53$, from spectra, linear interpolation between $\beta_{\mu\nu} = -2.48$ for $R = 2.67$ Å (I_2 gas) and $\beta_{\mu\nu} = -1.99$ for $R = 2.93$ (I_3^- ion).

B and N: $\beta_{\mu\nu} \approx 1.24R - 4.58$ (for $R > 2.81$ Å), from iodine dissociation curve.

Table 11. Results of the VESCF calculations on triiodide ions, $I_1-I_2-I_3$

Compound	Observed distances		Net charges			Bond orders		Potential difference*	
	R_{12} (Å)	R_{23} (Å)	Q_1	Q_2	Q_3	P_{12}	P_{23}	$V_1 - V_2$ (volt)	$V_3 - V_2$ (volt)
$(C_2H_5)_4NI_3$ (I)	2.928	2.928	-0.50	0	-0.50	0.707	0.707	0.321	0.321
	2.943	2.943	-0.49	-0.02	-0.49	0.707	0.707	0.013	0.013
$(C_2H_5)_4NI_3$ (II)	2.892	2.981	-0.45	-0.01	-0.54	0.736	0.677	0.022	0.379
	2.912	2.961	-0.47	-0.02	-0.51	0.719	0.695	0.072	0.174
CsI_3	2.83	3.04	-0.37	0	-0.63	0.792	0.611	-0.236	1.030
$(C_6H_5)_4AsI_3$	2.91	2.91	-0.48	-0.04	-0.48	0.706	0.706	-0.184	-0.185

* Potential difference caused by the external charges.

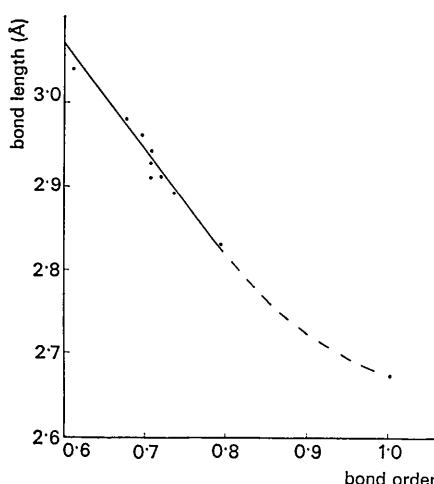


Fig. 2. Bond length - bond order curve for I_3^- ions.

critical value of R (3.7 \AA) in our expression for $\gamma_{\mu\nu}$ is the shortest non-bonded distance between neighbouring ions in the crystal, and beyond that distance no difference is thus made for the calculation of potentials due to charged groups within or outside the I_3^- ion considered.

We preferred an estimate of $\beta_{\mu\nu}$ from the spectra of iodine gas (Asundi & Venkateswarlu, 1947) and of triiodide ions in solution (Popov & Swensen, 1955) above the $\beta_{\mu\nu}$ values estimated by B and N from the iodine dissociation curve. In the latter estimate errors due to inner shell repulsions will occur; moreover the SCF wave functions are unsatisfactory for large atomic distances. In estimating $\beta_{\mu\nu}$ we used the $\gamma_{\mu\nu}$ values mentioned above. The spectra were analysed as described by Wiebenga (Wiebenga, 1965; Internal Report, available from the authors): the line of 6.1 eV in the spectrum of iodine gas was assigned to a transition from the bonding to the anti-bonding orbital in iodine, the average value of the bands at 4.28 and 3.44 eV in the I_3^- spectrum was taken as the transition energy from the non-bonding to the anti-bonding orbital in these ions.

The results of the VESCF calculations on the triiodide ions in the different crystals are listed in Table 11. A plot of the calculated bond orders versus the observed bond lengths is shown in Fig. 2. Within the range of the triiodide ions the relation between P and R can be approximated by a straight line. Only the

short and rather inaccurately determined I-I bond in $(C_6H_5)_4AsI_3$ shows a marked, though not significant, deviation from this line. It may thus be concluded that the variations in bond lengths observed for the triiodide compounds may be explained from crystal field effects.

To check whether the bond length in $(C_6H_5)_4AsI_3$ is really equal to those in the remaining symmetric I_3^- ions a three-dimensional refinement of the crystal structure of this compound will be undertaken shortly.

We are indebted to Prof. E. H. Wiebenga for many valuable discussions, to Drs. R. Olthof for programming the VESCF and potential calculations and to Drs. J. L. de Boer and Mr J. Heystek for their assistance during the experimental work. The calculations were done at the Groningen University Computing Centre. We gratefully acknowledge the support of the Netherlands Organization for the Advancement of Pure Research.

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