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The Crystal Structure of Two Modifications of Tetraethylammonium Triiodide, (C₂H₅)₄NI₃

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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 super structure 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 (λ (Cu $K\alpha$) = 1·5418, λ (Cu $K\alpha_1$) = 1·54051, λ (Cu $K\alpha_2$) = 1·54433 Å). The cell dimensions are

$$a = 14·207, \ b = 15·220, \ c = 14·061 \text{ Å,}$$

e.s.d. 0·05% for modification I ,

$$a = 14·552, \ b = 13·893, \ c = 15·156 \text{ Å,}$$

e.s.d. 0·05% for modification II .

There are 8 molecules per cell. The systematic absences indicate as possible space groups *Cmca* and *C2ca* for modification I, and *Pnma* and *Pn2₁a* 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, θ–2θ 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*).

	x	y	z	B
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) Å²
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* (Å²) *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* (C₂H₅)₄NI₃ (I)

The values listed are $10F_o$ and $10F_c$.

The table is a multi-column listing of structure factors. Each block has columns: H, K, L, FO, FC.

H	K	L	FO	FC
0	4	0	5544	5904
0	6	0	5263	5627
0	10	0	1954	2040
0	12	0	487	358
0	4	1	-1218	-1143
0	6	1	-2788	-2873
0	8	1	-2000	-2074
0	10	1	-1412	-1420
0	12	1	-1020	-1033
0	2	2	-574	-527
0	4	2	1063	1076
0	6	2	2921	2927
0	10	2	2723	2748
0	12	2	1309	1391
0	14	2	919	928

planes of the crystals were determined as accurately as possible. The dimensions of the crystals used were approximately $0.22 \times 0.22 \times 0.14$ mm^3.

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*).

	x	y	z	B
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* (Å^2) *for the iodine atoms in* $(C_2H_5)_4NI_3$ (II)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{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 $10F_c$.

Table 6 (cont.)

H	K	L	FO	FC		H	K	L	FO	FC		H	K	L	FO	FC		H	K	L	FO	FC		H	K	L	FO	FC		H	K	L	FO	FC		H	K	L	FO	FC
1	8	5	-379	-325		3	8	9	728	678		7	9	5	482	465		4	10	2	-1019	-1026		7	10	7	-509	-433		2	11	9	524	542		3	12	6	319	411
2	8	5	-1167	-1181		4	8	9	539	531		1	9	6	721	770		6	10	2	-766	-834		9	10	7	-437	-470		1	11	10	-435	-434		4	12	6	670	708
3	8	5	-878	-840		6	8	9	-601	-642		3	9	6	1027	981		10	10	2	-783	-819		0	1C	8	-387	-328		0	11	11	531	479		4	12	7	464	469
4	8	5	507	494		1	8	10	-357	-381		5	9	6	-764	-769		1	10	3	-1426	-1386		1	1C	8	488	573		2	11	11	563	636		4	12	7	542	552
5	8	5	295	326		3	8	10	488	477		5	9	6	392	440		2	10	3	565	573		3	1C	8	-381	-413		0	12	0	3155	3137		5	12	7	486	477
6	8	5	-1543	-1498		8	8	10	413	486		7	9	6	405	461		4	10	3	-672	-649		5	1C	8	-415	-435		2	12	0	1149	1080		1	12	8	-606	-545
7	8	6	-606	-526		9	8	10	490	513		0	9	7	-375	-370		5	10	3	-1436	-1455		1	1C	9	-379	-352		4	12	0	1901	1914		5	13	1	407	400
0	8	6	1747	1736		1	8	11	593	546		1	9	7	664	675		6	10	3	681	665		2	1C	9	464	347		6	12	0	1334	1412		0	13	5	-816	-859
1	8	6	-880	-899		3	8	11	1012	1007		4	9	7	-362	-273		0	10	4	2078	2084		3	1C	9	-567	-633		10	12	0	775	868		2	13	5	-713	-755
2	8	6	1015	992		6	8	11	-499	-490		6	9	7	-494	-479		1	10	4	659	699		6	1C	9	514	512		3	12	1	-1015	-949		4	13	5	-599	-625
3	8	6	708	691		7	8	11	715	666		7	9	7	456	492		2	10	4	-751	-756		2	1C	10	-435	-496		4	12	1	387	403		3	13	6	373	441
4	8	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	621	688		0	14	0	-1881	-1946
5	8	6	390	367		2	9	0	-383	-305		3	9	8	-420	-498		4	10	4	-1361	-1412		1	1C	11	-514	-447		7	12	1	-368	-466		2	14	0	-916	-866
6	8	6	676	669		4	9	0	-608	-534		6	9	8	479	459		5	10	4	-616	-660		3	1C	11	-721	-717		0	12	2	1312	1332		4	14	0	-1177	-1188
7	8	6	-336	-254		6	9	0	-646	-737		0	9	9	-672	-676		6	10	4	-1203	-1198		4	1C	11	432	341		1	12	2	-390	-373		6	14	0	-957	-1002
9	8	6	811	836		8	9	0	-741	-700		2	9	9	-565	-613		4	10	4	-589	-578		5	1C	11	-505	-478		4	12	2	533	628		3	14	1	529	538
1	8	7	816	824		0	9	1	-430	-421		4	9	9	-439	-455		9	10	4	-820	-835		7	1C	11	-589	-369		6	12	2	707	680		0	14	2	-1049	-1031
2	8	7	-640	-642		1	9	1	289	194		1	9	10	638	607		10	10	4	-899	-960		2	1C	12	-415	-369		10	12	2	642	648		4	14	2	-557	-581
3	8	7	826	761		3	9	1	308	343		2	9	10	454	401		2	10	5	760	750		4	11	0	447	410		1	12	3	957	927		1	14	3	-604	-673
4	8	7	1184	1182		5	9	1	719	784		5	9	10	372	480		3	10	5	696	684		8	11	0	394	549		5	12	3	327	329		5	14	3	-747	-684
5	8	7	794	816		1	9	1	-775	-791		0	9	10	531	532		6	10	5	989	1075		0	11	1	394	375		5	12	3	884	950		0	14	4	-1036	-1006
6	8	7	-642	-640		7	9	1	593	615		0	9	11	-445	-482		7	10	5	420	367		1	11	1	449	388		0	12	4	1642	1612		2	14	4	-557	-417
7	8	7	713	588		9	9	1	567	489		2	9	11	-955	-988		0	10	6	-1511	-1513		3	11	1	-520	-513		1	12	4	-550	-535		4	14	4	-711	-686
8	8	7	394	398		10	9	1	-490	-483		0	10	0	-4315	-4338		1	10	6	1002	982		8	11	1	383	422		2	12	4	411	450		6	14	4	-608	-676
9	8	7	612	625		11	9	1	499	493		2	10	0	-1744	-1713		2	10	6	-734	-752		9	11	1	-477	-458		3	12	4	706	607		0	14	6	-741	-714
1	8	8	1363	1280		0	9	3	-291	-200		4	10	0	-2579	-2618		3	10	6	-713	-719		3	11	4	-464	-412		4	12	4	1104	1080		1	14	6	443	396
2	8	8	681	733		3	9	3	-330	-326		6	10	0	-2140	-2135		4	10	6	-764	-813		5	11	5	1507	1519		6	12	4	912	921		0	15	5	634	637
3	8	8	484	520		3	9	3	638	618		10	10	0	-1274	-1311		6	10	6	-621	-624		1	11	5	-327	-298		9	12	4	550	541						
4	8	8	405	425		0	9	5	-1800	-1843		3	10	1	1381	1320		9	10	6	-553	-610		2	11	5	697	707		10	12	4	719	695						
6	8	8	315	328		1	9	5	413	426		4	10	1	-439	-485		1	10	7	-572	-604		4	11	5	818	899		2	12	5	-625	-632						
7	8	8	-342	-403		2	9	5	-1518	-1512		5	10	1	-929	-933		2	10	7	383	414		1	11	6	758	778		3	12	5	-441	-380						
8	8	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	-760	-793						
9	8	8	514	493		4	9	5	-1248	-1284		0	10	2	-1920	-1899		4	10	7	-820	-824		3	11	6	-514	-628		0	12	6	865	887						
1	8	9	410	565		5	9	5	304	321		1	10	2	-719	671		5	10	7	-717	-625		6	11	7	417	319		1	12	6	-479	-531						
2	8	9	-432	-473		6	9	5	-995	-1024		2	10	2	437	397		6	10	7	482	509		1	11	8	379	398		2	12	6	604	598						

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 CsI_3 and $(C_6H_5)_4AsI_3$. On the contrary, both for CsI_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 $14\cdot4/R$ 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

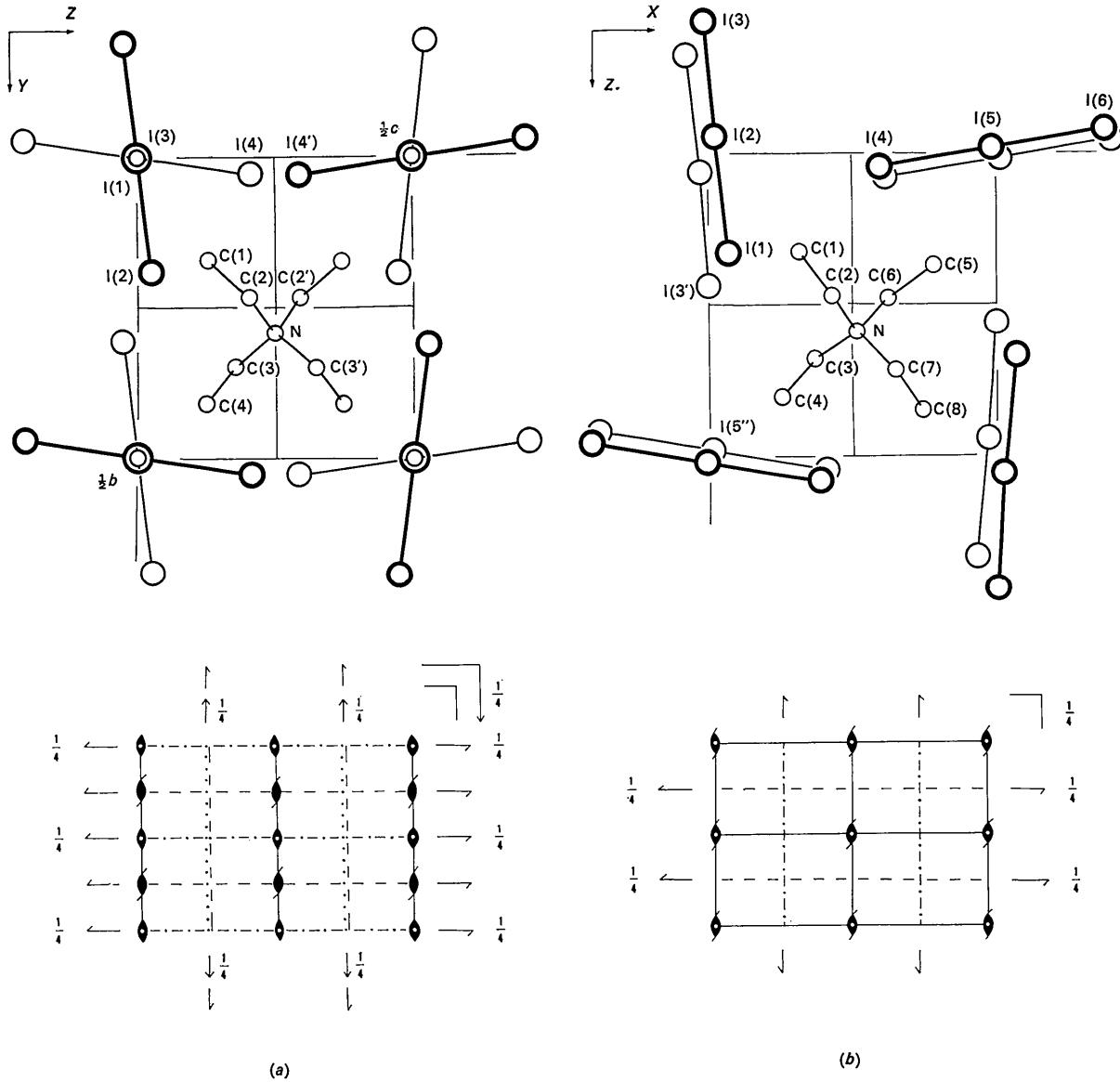|	
I(1)···I(4′)	4·14
I(2)···I(4′)	4·50

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)		
I(5) –I(6)	2·961 (0·0035)	C(1)–C(2)–N	115 (1)
		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: $\gamma_{\mu\nu}=14\cdot4/R$ for $R\geq3\cdot7$ Å $\gamma_{\mu\nu}=-0\cdot843R+I-A$, linear interpolation between $\gamma_{\mu\nu}=14\cdot4/R$ for $R=3\cdot7$ Å and $\gamma_{\mu\nu}=I-A=7\cdot01$ eV for $R=0$.
$R=$ distance of core centres.
$I=$ ionization energy, $A=$ electron affinity.
B and N: $\gamma_{\mu\nu}=14\cdot4/(a+R)$ with $14\cdot4/a=I-A$, the Mataga–Nishimoto formula introduced for organic compounds.

Core resonance integral
Present work: $\beta_{\mu\nu}=1\cdot89R-7\cdot53$, from spectra, linear interpolation between $\beta_{\mu\nu}=-2\cdot48$ for $R=2\cdot67$ Å (I_2 gas) and $\beta_{\mu\nu}=-1\cdot99$ for $R=2\cdot93$ (I_3^- ion).
B and N: $\beta_{\mu\nu}\simeq1\cdot24R-4\cdot58$ (for $R>2\cdot81$ 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.
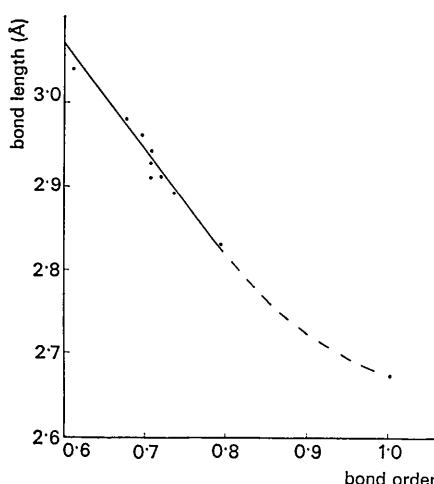
Fig.2. Bond length – bond order curve for I_3^- ions.

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 tri-iodide 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.

critical value of R (3·7 Å) 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 tri-iodide 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 tri-iodine 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

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