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On the Crystal Structures of the Low-dimensional Clover Phases: Low Temperature Structure of (Benzophenone)$_4$ (LiI_5) and Comparison with (Benzophenone)$_9$ $(KI)_2I_7CHCl_3$

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The complex of benzophenone-lithium pentaiodide crystallizes in space group $P\bar{1}$ ($Z = 2$). The unit cell dimensions at 100 K are $a = 9.605(5)$, $b = 14.911(3)$, $c = 18.248(4)$ Å, $\alpha = 102.35(2)$, $\beta = 103.45(3)$ and $\gamma = 91.32(3)°$. The crystal structure consists of infinite columns of I_5^- molecules each of which is bent at the central iodine atom with an I—I—I angle of 105°. The pentaiodides are stacked such that one branch of each molecule participates in the column formation, while the second branch forms a two-atom side chain. Neighboring columns of pentaiodides are anti-parallel to each other. The columns of pentaiodide molecules are surrounded by the host benzophenone molecules. Each lithium cation is tetrahedrally coordinated to four oxygens of the benzophenone molecules. A refinement of the occupancy of the iodine atoms gives an iodine deficiency of 7%, equally distributed over all iodine positions. The result is supported by the elemental analysis and the measurements of the density of the crystals. The structure reported here differs from the benzophenone polyiodide complexes of potassium and ammonium in which the cation is six-coordinate and the polyiodide columns are not branched.

INTRODUCTION

The first of the complexes of iodide, iodine and benzophenone, (benzophenone)$_9$ $(KI)_2I_7CHCl_3$, hereafter referred to as BIKI, was reported by Clover in 1904. Several of the compounds have been found to possess a high, frequency dependent, ionic conductivity which is extremely anisotropic.[2,3] Since knowledge of the crystal structures is essential for an understanding of the physical

properties of these solids, we have started a number of crystallographic studies to elucidate the relation between structure and conductivity. The first complexes investigated were those of potassium and ammonium which both consist of column-like polyiodide chains surrounded by the hydrophobic side of the organic host molecules and columns of cations coordinated by the benzophenone oxygen atoms.[4] Many of the complexes suffer extensive disorder of the iodine species. The structure of the lithium iodide complex (BILI) reported here is the first completely commensurate structure known among this family of compounds and the first for which a full structure determination has been completed. An extensive Raman-spectroscopic study on these complexes is described in a companion paper.[5]

EXPERIMENTAL

BILI was synthesized by mixing stoichiometric amounts of benzophenone and lithium iodide with large excess iodine in chloroform at room temperature. Evaporation of the solvent to dryness yielded needle-like cyrstals which are metallic green when observed in reflected light.

Low temperature (100 K) intensity data were collected ($2\theta_{max} = 50°$) on a NONIUS CAD-4 diffractometer using graphite monochromated MoKα radiation ($\bar{\lambda} = 0.71070$ Å). The dimensions of the unit cell (Table I) and the lack of systematic absences indicated the crystals to be triclinic. The centrosymmetric space group $P\bar{1}$ was confirmed by the results of the structure analysis, in which the iodine atoms were located from a Patterson map while the remain-

TABLE I

Crystallographic Data of BILI

Molecular Mass	2738.8	
Space Group	$P\bar{1}$	$P\bar{1}$
Z	2	2
Temperature	100K	298K
a	9.605(5) Å	9.721(4) Å
b	14.911(3) Å	14.935(6) Å
c	18.248(4) Å	18.810(7) Å
α	102.35(2)°	102.26(3)°
β	103.45(3)°	104.32(2)°
γ	91.32(3)°	91.79(3)°
Volume	2475.7 Å^3	2575.5 Å^3
ρ_{calc} (100% I occupancy)	1.84 gm cm^{-3}	1.77 gm cm^{-3}
ρ_{calc} (93% I occupancy)	—	1.71 gm cm^{-3}
ρ_{exp}	—	1.66 gm cm^{-3}[a]
		1.70 gm cm^{-3}[b]

[a] from flotation in a chloroform-bromoform mixture.
[b] from flotation in aqueous $ZnCl_2$ solutions.

ing non-hydrogen atoms were found in Fourier maps calculated with the iodine phases. Least squares refinement of the positional and thermal parameters (anisotropic for I, isotropic for C, O and Li) of the non-hydrogen atoms, including all reflections with $F_0 < 3\sigma\ (F_0)$, gave final agreement factors: $R(F) = 0.0542$ and $R_w(F) = 0.0850$, where the weighting factor is derived from $w = 1/\sigma^2(F)$ and $\sigma(F^2) = 2F\sigma(F) = [\sigma^2(F^2)_{count} + (0.04\ F^2)^2]^{1/2}$. The number of observations and variables are 7346 and 274 respectively. Though several hydrogen atoms can be distinguished clearly in the final difference maps no attempts were made to introduce the 40 hydrogen atoms in the refinement process. Selected bond lengths and angles are presented in Table III.

According to the results of the structure determination the formula unit of BILI appeared to be (benzophenone)$_4$(LiI_5). However, as this composition does not agree very well with the chemical analysis (Table II), a careful experimental measurement of the density was undertaken. The results given in Table I again suggest an iodine deficiency when compared with the calculated value based on the cell dimensions and the stoichiometric formula.

The least squares refinement was therefore continued varying in addition to the parameters described above the occupancies of all iodine atoms. This refinement did not give any change in the positional parameters, but it did indicate an iodine deficiency of about 7.0% equally distributed over all iodine positions (Table IV). The final agreement factors are: $R(F) = 0.0541$, $R_w(F) = 0.0834$. The improvement in $R_w(F)$ by about 2% is highly significant at the 99.5% confidence level when subjected to the Hamilton R factor ratio test.[13] A much better agreement with the elemental analysis (Table II) and the calculated density (Table I) is obtained when a 7% iodine deficiency is taken into account.

DISCUSSION

The molecular geometry of I_5^- and the columnar arrangement of the molecules are presented in Figure 1.[6] To our knowledge there have been no earlier

TABLE II

Composition of BILI (weight percentages)

	%C	%H	%O	%Li	%I
Experimental	46.93	3.11	4.99	0.49	43.98
Theoretical (B_4LiI_5)	45.57	2.92	4.67	0.50	46.33
Theoretical 7.0% I deficiency	47.10	3.04	4.83	0.52	44.50

TABLE III

Selected Bond Lengths and Bond Angles

I(1)—I(2)	2.782(1)Å	
I(4)—I(5)	2.783(1)Å	
I(1)—I(3)	3.172(1)Å	
I(3)—I(4)	3.093(1)Å	
I(3)—I(2)	3.689(1)Å	
I(2)—I(4)	4.420(1)Å	
Li—O	1.93(1)Å[a]	
C—O	1.22(1)Å[a]	1.23Å[b]
C(carbonyl)—C(ring)	1.49(1)Å[a]	1.49Å[b]
C—C (ring)	1.40(1)Å[a]	1.39Å[b]
I(1)—I(3)—I(4)	105.09(2)°	
I(2)—I(1)—I(3)	174.70(1)°	
I(3)—I(4)—I(5)	179.63(3)°	
O—Li—O	109(7)°[a]	

[a] Bond lengths and angles are average values. Numbers in parentheses are standard deviations of the mean.
[b] Values are average bond lengths in pure benzophenone.[11]

observations of branched polyiodide columns consisting of bent I_5^- molecules, though a sheet structure of bent I_5^- molecules has been observed in Me_4NI_5.[7] The intramolecular I—I distances involving the central iodine atom I(3) (3.172(1) and 3.093(1) Å) are significantly longer than the terminal I—I distances which are 2.782(1) and 2.783(1) Å. Similar differences occur in linear pentaiodide species. In α-cyclodextrin $Cd_{1/2}I_5.26H_2O$, for example, the sequence of bond lengths is 2.97, 3.17, 3.14 and 2.96 Å,[8] while the corresponding values in the trimesic acid pentaiodide complex has been given as 2.74, 3.26, 3.26 and 2.74 Å.[9] The intermolecular distance along the chain is 3.689(1) Å which is considerably shorter than twice the iodine Van der Waals radius. This length is comparable to intermolecular I···I distances observed in many other crystals containing iodine species and indicates a weak but significant interaction along the chain direction.

The lithium ion (Li) is in a distorted tetrahedral environment of four benzo-

TABLE IV

Iodine Occupancies from Final Least Squares Refinement

I(1)	0.927(4)
I(2)	0.932(4)
I(3)	0.934(4)
I(4)	0.930(4)
I(5)	0.931(4)

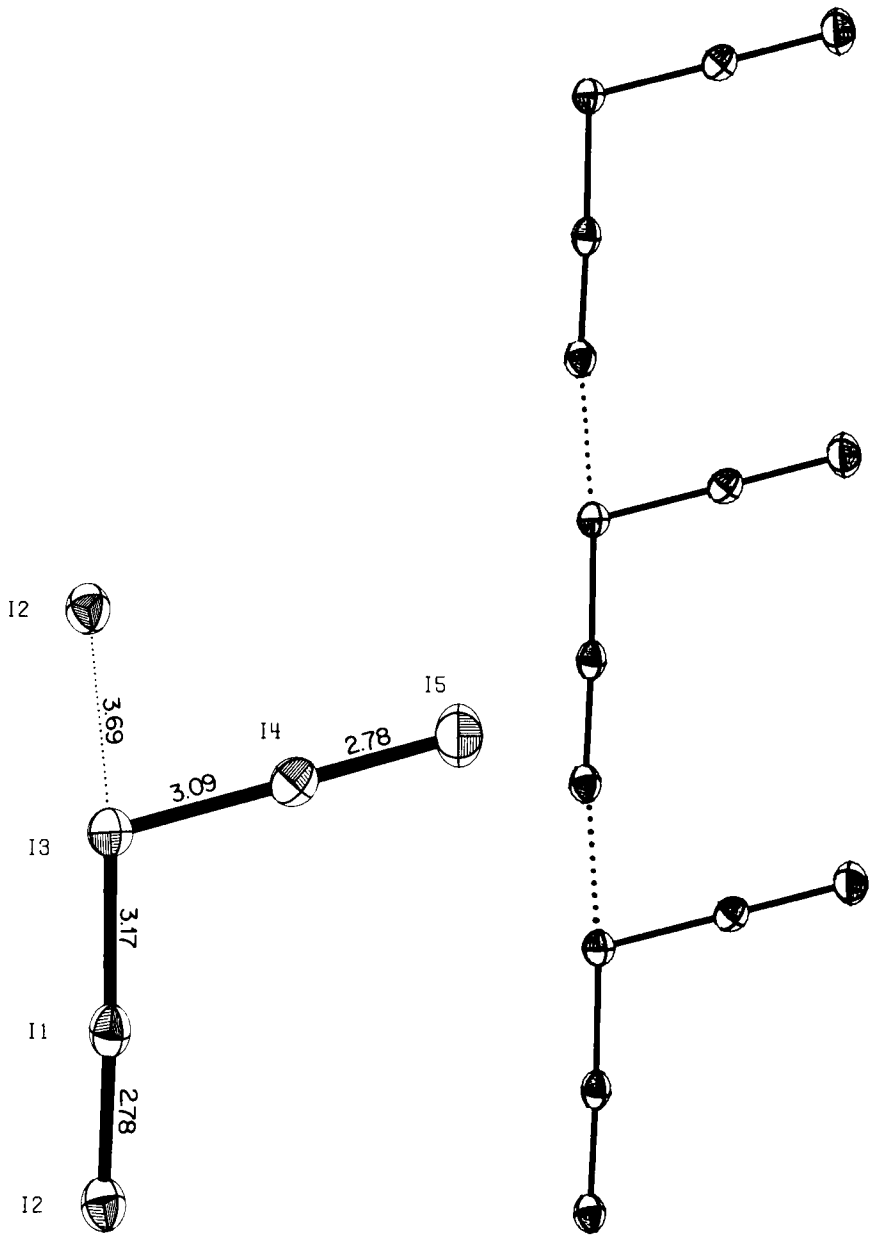

FIGURE 1 (a) Molecular geometry; (b) Packing of I_5^-. Ellipsoids are in 90% probability surfaces.

phenone oxygen atoms (Figure 2). The average Li-O distance (1.92(2) Å) is consistent with the sum of the respective ionic and Van der Waals radii ($r(Li^+) = 0.60$ Å and $r(O)_{vdw} = 1.40$ Å).[10] A survey of lithium coordination numbers by Griffin[11] has shown that four coordination of Li^+ is not exclusive, six coordination being almost as common. Nevertheless, the four coordination of the cation distinguishes this Clover-phase from the structure of the potassium and ammonium complexes, and leads to a different polyiodide structure and the exclusion of solvent molecules from the lattice. As noted before, the structure of the K^+ and NH_4^+ phases, (BIKI and BINI respectively) shown schematically in projection in Figure 3 contains columns of cations in antiprismatic six-fold coordination by benzophenone oxygen atoms and linear columns of disordered iodine atoms.[4,5]

The intermolecular bond lengths within the benzophenone molecules are comparable to those in pure benzophenone (Table III). As may be expected the torsion angles around the exocyclic C—C bond are much softer and show a considerable deviations from the average. Though most of the angles are within 3° of the average of 33°, one of the benzophenone molecules is much more distorted with torsional angles of 56.1(7) and 14.8(7)°. These differences are tentatively attributed to packing forces. The non-planarity of the bonds around the carbonyl carbon atoms may be explained in the same manner.

The iodine deficiency must be taken into account in any explanation of the conductivity of BILI as measured by Labes and coworkers (private communication). A mechanism of "iodine-hole" migration is possible, but would require a chemical rearrangement during the migration process, unless the I_5^- group moves as a unit.

Further studies are being undertaken to investigate the relation between the marked dependence of the structure on the nature of the cation, and the electrical properties of these phases.

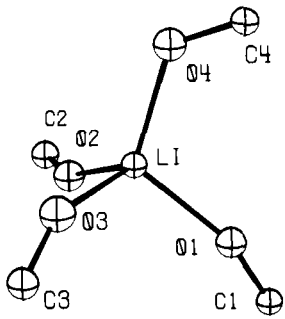

FIGURE 2 Coordination of Li^+ in the complex. Ellipsoids are 50% probability surfaces for isotropic thermal motion.

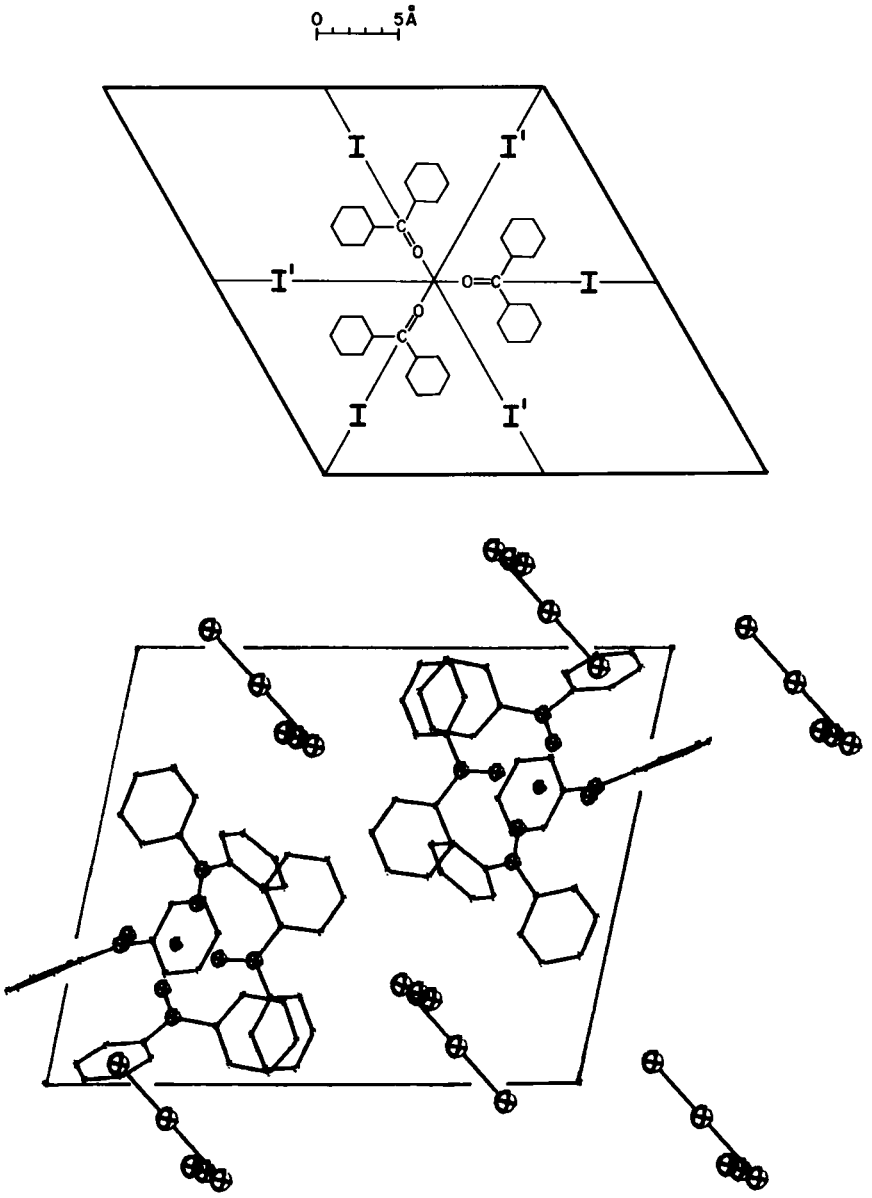

FIGURE 3 (a) The (001) projection of the structure of the potassium and ammonium benzophenone iodine complexes. The cations are in a column at the center of the benzophenone oxygen atoms. Benzophenone molecules in a second layer are in staggered positions and complete an anti-prismatic coordination of the cations. (b) ORTEP drawing of the projection of BILI looking down the a axis. The large spheres represent the iodine atoms. The unit cell is indicated.

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