

Solid-State Chemistry of Organic Polyvalent Iodine Compounds. VII. The Relationships between Crystal Packing Modes, Solid-State Intermolecular Interactions, and Infrared Spectra of Benzoxiodole Compounds*

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The importance of intermolecular interactions in determining crystal structures has been investigated for a series of 3-oxo-3H,2,1-benzoxiodol-1-substituted compounds. These compounds all contain a trivalent iodine atom which is involved in a stereospecific coordination interaction with an electronegative atom (oxygen or halogen) of a neighboring molecule. It has been found that only four basic packing modes occur for these compounds, formally characterized by the nature of the functional group which is coordinated to iodine. Infrared analysis of solution and solid-state samples of these compounds shows that the structurally identifiable intermolecular coordination modes which occur between I^(III) and carbonyl groups do in fact involve chemically stabilizing interactions. Shifts of about 10 cm⁻¹ to lower wavenumber are observed for the carbonyl stretching band of an *uncoordinated* carbonyl group in solid-state samples, as compared to its frequency in solution samples. The carbonyl stretching frequency of a *coordinated* carbonyl group is lowered from 20–80 cm⁻¹ (these bands occur at 1614–1678 cm⁻¹ in the solid state). Some of the compounds exist in molecular conformations in the solid state in which a possible *intramolecular* interaction between I^(III) and a carbonyl also may be contributing to the observed frequency shifts.

Introduction

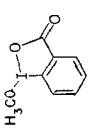
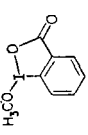
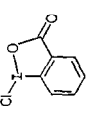
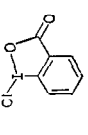
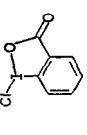
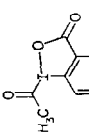
The most significant feature of the crystal structures of 3-oxo-3H,2,1-benzoxiodol-1-substituted compounds (hereafter called benzoxiodole compounds) is an intermolecular coordination interaction which occurs between trivalent iodine and an electronegative group, usually oxygen or a monovalent halogen. It has been shown for several benzoxiodoles that the coordination geometry about iodine is remarkably constant regardless of the nature of the coordinating groups or the symmetry relationships between the coordinated molecules (2). Upon investigation

of 20 benzoxiodole crystal structures it has become clear that in addition to the stereospecific coordination interaction, there are four basic packing modes which occur for benzoxiodole molecules, each one characterized by the type of group which is coordinated to trivalent iodine. Compounds which have no carbonyl groups other than the lactone carbonyl of the benzoxiodole ring (compounds Ia–Ie, Table I) crystallize such that an intermolecular coordination occurs between trivalent iodine and the lactone carbonyl of a screw-related molecule. The structure of the resulting chain of coordinated molecules is shown in Fig. 1a. When the benzoxiodole compound has a benzyloxy substituent covalently bonded to trivalent iodine, the lactone carbonyl no longer coordinates to trivalent iodine. Two new coordination modes are observed for these compounds (Figs. 1b and 1c). The most

* Partially based on a Ph.D. Thesis by the author, December 1974, University of Minnesota (1).

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TABLE I
UNIT CELL PARAMETERS AND INFRARED CARBONYL BAND ASSIGNMENTS FOR BENZOIODOLE COMPOUNDS

Compound	S. S. conformation ^a	Infrared assignments									
		KBr					CHCl ₃				
		a (Å)	b (Å)	c (Å)	β (degrees)	S.G. ^b	Z	O(1) ^c (cm ⁻¹)	O(2) ^d (cm ⁻¹)	Reference	
Ia		15.43	8.10	13.53	—	<i>Pbca</i>	8	1635	—	1637	(6)
b		8.10	10.06	12.60	118.3	<i>P2₁/a</i>	4	1648	—	1673	(6)
c		8.56	6.31	14.93	94.2	<i>P2₁/c</i>	4	1673	—	1698	(20)
d		5.96	8.40	15.95	96.8	<i>P2₁/n</i>	4	1660	—	1698	(20)
e		4.11	30.30	13.15	92.7	<i>P2₁/c</i>	8	1678	—	1698	(20)
f		16.191	7.762	7.705	82.0	<i>P2₁/a</i>	4	1668	1668	1692	(2)

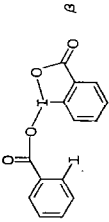
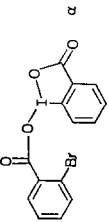
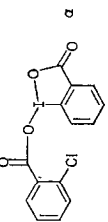
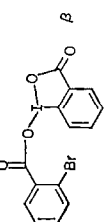
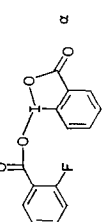
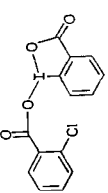
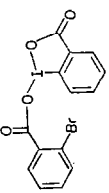
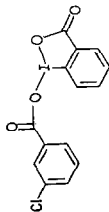
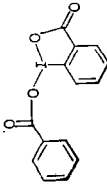
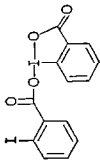
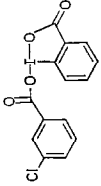
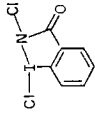
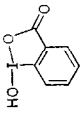
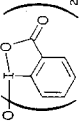
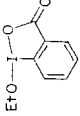
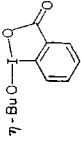
IIa		8.03	12.58	13.74	92.6	<i>P2₁/c</i>	4	1698	1622	1697	(21)
b		3.99	26.553	26.008	—	<i>Pbc2₁(?)</i>	8	1696	1619	1696	(22)
c		7.474	13.994	13.152	102.4	<i>P2₁/a</i>	4	1695	1614	1697	(22)
d		7.403	13.995	13.116	102.1	<i>P2₁/a</i>	4	1696	1616	1697	(22)
e		4.07	12.00	26.27	90.5	<i>P2₁/c</i>	4	1697	1630	1697	(23)

TABLE I—Continued

Compound	S. S. conformation ^a	Infrared assignments									
		a (Å)	b (Å)	c (Å)	β (degrees)	S.G. ^b	Z	KBr			Reference
								O(I) ^c (cm ⁻¹)	(O2) ^d (cm ⁻¹)	CHCl ₃ (cm ⁻¹)	
IIf		13.633	~4	13.523	—	P1	2	—	—	—	(22)
g		13.96	~4	13.96	—	P1	2	—	—	—	(22)
h		6.376	10.547	20.066	92.0	P2 _{1/n}	4	1689	1618	1696	(11)
i		6.56	9.94	20.61	94.1	P2 _{1/n}	4	1698	1631	1698	(11)

IIIa		α	4.21	30.86	22.52	93.3	Cc	8	1688	1645	1697	(6)
b		β	5.057	13.035	10.339	99.5	Pc	2	1689	1638	1697	(11)
c			5.78	6.49	12.88	103.1	P2 ₁	2	1660	—	1673	(4)
IVa			12.89	4.10	14.05	96.7	P2 ₁ /c	4	1610	—	(insoluble)	(5)
b			29.33	3.97	14.26	123.5	C2/c(?)	4	1670	—	(insoluble)	(6)
V			14.0	7.7	9.3	92.4	P2 ₁ /a	4	1642	—	1667	(6)
VI			8.9	8.2	15.4	96.0	P2 ₁ /c	4	1640	—	1666	(6)

^a The molecular conformation as determined by crystal structure analysis.

^b S.G. = space group.

^c O(1) is the lactone carbonyl.

^d O(2) is the exocyclic carbonyl.

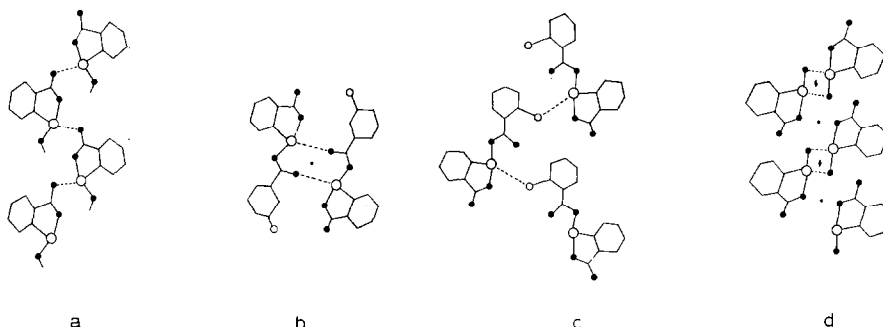


FIG. 1. Four modes of trivalent iodine coordination. (a) Lactone carbonyl to iodine (IIb); (b) exocyclic carbonyl to iodine (IIIh); (c) chlorine to iodine (IIIb); (d) etheral oxygen to iodine (IVa). \bigcirc = trivalent iodine, \circ = monovalent halogen, \bullet = oxygen.

common coordination mode involves formation of dimeric units of molecules mutually coordinated by intermolecular trivalent iodine coordination with the exocyclic carbonyl group (Group II compounds). This mode is of particular importance since it is the only packing mode which has been observed for the crystalline benzoxiodole products formed during single crystal rearrangements of their parent peroxides. In fact, II f and II g are apparently stable *only* when formed in the solid state in the presence of the peroxide lattice (3). In addition to this coordination mode, benzoyloxy-substituted benzoxiodoles can crystallize such that a monovalent halogen is coordinated to trivalent iodine (IIIa, b). As shown in Fig. 1c, this packing mode gives rise to chains of coordinated molecules, rather than molecular dimers, and neither of the carbonyl groups are involved in intermolecular coordination interactions (although there may be an *intramolecular* association between trivalent iodine and the exocyclic carbonyl group). IIIc, an unusual lactam structure, is the only other example of trivalent iodine to monovalent halogen coordination (4). IVa and b are significant because the only carbonyl groups present are the lactone carbonyls (and also, there are no monovalent halogen atoms), but they are *not* utilized as coordinating groups for trivalent iodine. For IVa the lactone carbonyl is hydrogen-bonded and trivalent iodine coordinates to the hydroxyl oxygen of a screw-related molecule (Fig. 1d, 5). The molecular geometry of IVb

prohibits formation of chains of coordinated screw-related molecules such as those found for Group I compounds. As a result, trivalent iodine coordinates to the cyclic etheral oxygen of a pseudo-inversion-related molecule (6).

Polymorphism is frequently observed for benzoxiodole compounds and in many cases infrared spectra can be used to identify the different polymorphs uniquely, particularly when their trivalent iodine coordination modes are different. In addition, shifts in the carbonyl stretching frequencies between solution and solid phase samples may be used to identify specific coordination interactions occurring in the solid state. By correlating the coordination modes (as determined by X-ray structural analysis) with carbonyl frequency differences between solution and solid-state samples, we were able to make group frequency assignments for both the endo- and exocyclic carbonyl groups in the solid state. (In solution, these bands are at essentially the same frequency.) Shifts of about 10 cm^{-1} to lower wavenumber for the carbonyl stretching band are observed in the solid-state samples (as compared to solution samples) when the carbonyl group is *not* coordinated to a trivalent iodine atom. Contact distances of less than 3.3 \AA between a lactone carbonyl group and the trivalent iodine of a neighboring molecule cause lowering of the carbonyl stretching frequency by $20\text{--}40\text{ cm}^{-1}$ to the observed frequencies of $1635\text{--}1678\text{ cm}^{-1}$. Close contacts, less than 3.05 \AA , between an

exocyclic carbonyl and trivalent iodine lower this carbonyl frequency by 50–80 cm^{-1} , so this band is observed at 1614–1645 cm^{-1} . This shift may in part be due to an intramolecular trivalent iodine coordination to the benzyloxy carbonyl (this intramolecular I—O contact distance is 2.8 Å), which independently results in a carbonyl frequency shift of 50–60 cm^{-1} to the observed values of 1638–1645 cm^{-1} . All of the carbonyl frequency shifts occurring in solid-state samples were to lower wavenumber as compared to their value in solution samples, indicating a stabilizing interaction resulting from coordination with trivalent iodine.

Experimental

X-ray structural data were obtained from the references cited in Table I. Structures IIb, f, g, and IIIb were solved in projection only. The structures of IIc, g, and i were derived from their isostructural analogs, IIc, f, and h, respectively. All the other structures were independently determined and are known in three dimensions.

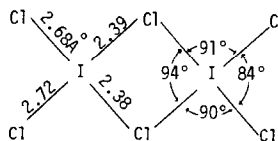
Most of the infrared spectra were run on a Perkin-Elmer Model 521 Grating Spectrophotometer (some were run on a Perkin-Elmer Model 257 Grating Infracord). Solid-state samples were routinely run as KBr discs. Nujol and Fluorolube mulls were run in addition for compounds Ia, b, f, IIa, IVa, and b for which the carbonyl stretching frequencies were found to be identical with the KBr samples. Solution samples were prepared as 0.01 *M* chloroform solutions and were run in a 1-mm NaCl liquid cell. Dilution studies on Ic were run on samples varying from 0.025 *M* to 16.0×10^{-4} *M*. The carbonyl band centered at 1673 cm^{-1} was split by 16 cm^{-1} and the relative intensities as well as the positions of the two bands were unchanged by dilution. An estimated precision for the reported carbonyl frequencies is ± 5 cm^{-1} .

Many of the samples used were kindly supplied by Professor J. Z. Gougoutas. Perdeutero-3-oxo-3H,2,1-benzoxiodol-1-chlorine was prepared and supplied by Dr. Douglas Naee, formerly of this laboratory. IVa was purchased from K & K Chemicals and recrystallized several times from boiling

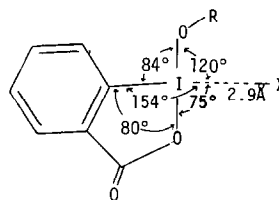
water (mp 225°*d*; reported, 231–232°*d* (4)). Other compounds were prepared as described in the references; see Table I.

Molecular Packing Modes

The importance of intermolecular interactions in determining crystal structures is particularly evident for trivalent iodine compounds in which stereospecific intermolecular interactions between electropositive trivalent iodine and electronegative groups are established. Dichloriodobenzene and diphenyliodonium halides crystallize such that the trivalent iodine atoms are associated with chlorine atoms of a neighboring molecule by short contacts of 3.20–3.40 Å (7, 8).¹ In these structures, the three substituents covalently bonded to trivalent iodine, and the atom coordinated to trivalent iodine form a square planar structure strikingly similar to the molecular structure of $(\text{ICl}_3)_2$ in which a fourth substituent is bonded to iodine (9).



More recently, it has been shown that for many different benzoxiodole compounds, an oxygen or halogen atom coordinates to trivalent iodine (2), also forming an approximately square planar structure with a constant geometry, as shown below:²



¹ It has been suggested that a good value for the van der Waals' radius of trivalent iodine is 1.6 Å (3). Since the van der Waals' radius of chlorine is 1.7 Å (24), an $\text{I}^{(\text{III})}$ —Cl intermolecular separation of 3.4 Å or less may be indicative of a coordination interaction.

² The interatomic distances and angles given are average values from several of the best determined benzoxiodole structures. The I—X distance given is for X = oxygen.

These stereospecific restrictions on the geometry of intermolecular interactions fix only the position of one atom, X , relative to the first molecule. The overall intermolecular packing geometry is also determined by the particular steric requirements associated with coordination between trivalent iodine and different functional groups and, in addition, by the symmetry relationships of the coordinated molecules. Despite the wide range of substituents on trivalent iodine in the series of compounds studied here and the many different space groups observed for these compounds, we have observed only four basic packing modes for benzoxiodole structures, characterized formally by the nature of the functional group to which iodine is coordinated.

Intermolecular coordination between trivalent iodine and the benzoxiodole lactone carbonyl group occurs in Group I compounds. Except for **Ie**, this coordination is established between screw-related molecules, giving rise to chains of coordinated molecules (Fig. 1a). We have found that the configuration of the chain of coordinated molecules is variable and can be related to \vec{b} , the screw axis length. A \vec{b} -axis length of ~ 10 – 11 Å, such as for **Ib**, is indicative of a nearly planar chain, in which the dihedral angle between the mean planes of the aromatic nuclei of the coordinated molecules is close to 180° . Shorter axes result from a more twisted chain configuration. Thus, **Ic** with $\vec{b} = 6.31$ Å has an intermolecular dihedral angle of $\sim 100^\circ$ between coordinated molecules. **Ie** is an anomaly with respect to the length of its \vec{b} -axis (30.30 Å), since it can be shown that the maximum \vec{b} -axis length consistent with the geometry of the stereospecific interaction for Group I compounds is ~ 11.5 Å.³ In this structure there are two molecules in an asymmetric unit and there are two *different* $I^{(III)}$ to lactone carbonyl interactions, each occurring between symmetry *independent* molecules. For this unusual structure, chains of coordinated molecules involving both types of interactions are formed parallel to the \vec{c} -glide direction.

³ The quantitative aspects of this geometrical analysis will be presented in a future paper in this series.

3-Oxo-3H,2,1-benzoxiodol-1-yl-acetate (If) is the only Group I compound which has two carbonyl groups. The exocyclic carbonyl does not appear to be involved in any intermolecular coordination interaction with trivalent iodine (the shortest intermolecular $I^{(III)}$ to exocyclic carbonyl distance is greater than 4 Å). This is in marked contrast to the extensively studied benzoyloxy substituted benzoxiodole compounds which also have two carbonyl groups but for these compounds *only* the exocyclic carbonyl is involved in intermolecular coordination. The geometry of the highly characteristic dimeric units involving two $I^{(III)}$ to benzoyl carbonyl interactions between inversion or pseudo-inversion related molecules is shown in Fig. 1b. For **Ia-g**, which have 2'-halophenyl groups, a transoid conformation is adopted in which this halogen atom cannot sterically hinder formation of the coordinated dimers. For bulky halogen substituents, the molecules are significantly nonplanar (e.g., **Ia**, **c**, and **d** have dihedral angles of 37° , 18° , and 14° , respectively, between the two phenyl rings). Essentially planar dimeric units, on the other hand, are observed for **Ie**, **h**, and **i** which have the smaller *ortho*-fluoro or *ortho*-hydrogen groups. For all these structures, the lactone carbonyl groups are greater than 3.7 Å from the closest intermolecular trivalent iodine atom.

For this coordination mode there is no single unit cell dimension which can generally be expressed as a function of the packing geometry, as was the case for Group I compounds, primarily because the symmetry element relating the Group II coordinated molecules is nondirectional. There is, however, a second intermolecular contact between inversion-related monovalent halogen atoms which occurs for all *o*-halogen substituted derivatives of Group II compounds, and results in the formation of chains of dimer units as shown in Fig. 2. The interhalogen distances are equal to or somewhat greater than the sum of the van der Waals radii of the halogens. This clustering effect for monovalent halogen atoms also has been observed for the three polymorphs of 3-oxo-3H,2,1-benzoxiodol-1-chlorine (**Ic-e**) and for

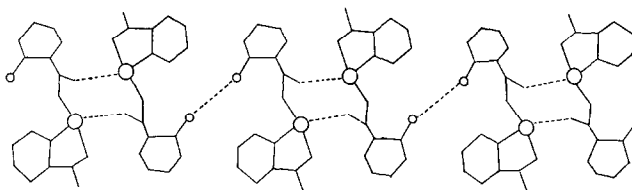


FIG. 2. The packing of centrosymmetric dimers of IIc into chains via monovalent halogen contacts. \bigcirc = trivalent iodine; \circ = monovalent halogen.

IIIc (*vide infra*). A recent report by Paul, Curtin, and Miller has illustrated the importance of halogen contacts in the crystal structures of several *p*-halobenzoic acids, *p*-halobenzamides, and *p*-halobenzoic acid anhydrides (10). Similarly, *m*-chlorobenzoic acid (11), and *o*-halobenzoic acids also have similar interhalogen contacts (12*a, b*).

The structure of IIa involves an intermolecular contact of the same geometry, relative to monovalent halogen, as found for interhalogen contacts but in this case a lactone carbonyl group is associated with monovalent iodine (I—O distance = 3.4 Å). The meta-chlorine substituent of IIh is the only monovalent halogen atom in the series which has no close neighboring halogen or electronegative group. In fact, IIh is isostructural with the nonhalogenated compound, IIIi.

The meta-chlorine substituent is important in IIIb, a polymorphic modification of IIh, where it is the atom which is coordinated to trivalent iodine (Fig. 1c). The coordinated molecules are glide related and are associated into a chain parallel to the glide direction. A similar coordination mode is observed for IIIa, a polymorph of IIa, where the monovalent iodine and a trivalent iodine of a screw-related molecule are coordinated (the I—I distance 3.7 Å). Neither the lactone nor benzoyloxy carbonyl groups are close to any intermolecular halogen atoms in these compounds.

IIIc is the only lactam structure which has been determined and is also the only compound in the series which has been found to crystallize in an optically active space group (*P2₁*). Of the three possible coordinating functions in this molecule (the lactone

carbonyl, the chlorine bonded to nitrogen (Cl-1), and the chlorine bonded to iodine (Cl-2)), only Cl-2 is coordinated by an unusually short contact (3.36 Å) to trivalent iodine and has the expected intermolecular coordination geometry. This chlorine is also only 4.0 Å from Cl-1 in the screw-related molecule and from Cl-1 in an \bar{a} -translation related molecule. The lactone carbonyl groups are flanked by phenyl rings, and have no close intermolecular contacts to halogens.

The two group IV molecules are characterized by intermolecular trivalent iodine coordination to either the ethereal oxygen of the benzoxiodole ring or the exocyclic ethereal oxygen (Fig. 1d). The lactone carbonyl oxygen would be expected to be a better electron donor than an ethereal oxygen, but for IVa this carbonyl is hydrogen-bonded to a glide-related molecule. In addition, trivalent iodine coordinates to the hydroxyl oxygen of a screw-related molecule. The I—O separation is 2.9 Å, and the coordination geometry is only slightly distorted from that of other benzoxidoles (2). It is interesting that despite the complex packing geometry observed for IVa, it is observed as an oriented *crystalline* phase during hydrolysis of single crystals of virtually every benzoxiodole compound.

IVb, the anhydride of IVa, crystallizes such that trivalent iodine is coordinated to the cyclic ethereal oxygen of an inversion-related molecule. Coordination between trivalent iodine and the lactone carbonyl, while possible for two or more molecules in an asymmetric unit, would be sterically highly unfavorable for symmetry-related molecules (particularly because of the short *intra*-molecular I—I contact of 4.2 Å).

Infrared Analysis of Coordination Modes

Differences in the infrared spectra of polymorphic modifications of organic compounds have long been recognized (13), but correlations between the infrared band shifts and specific differences in molecular packing modes and intermolecular interactions unique to the different polymorphs have not been explored. The use of infrared analysis for identifying intermolecular interactions in solution, however, has proven meaningful. Hassel has reported spectroscopic evidence of molecular charge-transfer complexes in solution for iodine·dioxane, iodoform·dioxane, and diiodoacetylene·1,4-cyclohexanedione, for which crystal structures of these complexes show monovalent iodine to oxygen contact distances of 2.81, 2.94, and 2.93 Å, respectively (14). Complexes of molecular iodine with carbonyl compounds in solution show shifts to lower wavenumber of 20–50 cm^{-1} in the carbonyl stretching bands as compared to the frequency of a free carbonyl group in solution. Similarly, shifts of 75–140 cm^{-1} are observed for carbonyl groups complexed in solution with highly electropositive metal halides such as AlCl_3 , SnCl_4 , or TiCl_4 (15). We have found that comparison of the infrared carbonyl frequencies of benzoxiodole compounds in solution with their frequencies in the solid state can serve as a qualitative technique for identifying particular solid-state coordination modes (otherwise known only from crystal structure analyses) and in addition gives important information about the chemical nature of these coordination interactions.

Benzoxiodole compounds generally exhibit only one carbonyl stretching band in solution (which may be a split band, as discussed below), centered at 1673 cm^{-1} for 1-alkoxy-substituted derivatives, and 1697 cm^{-1} for 1-halo-, acetoxy-, or benzyloxy-derivatives (Fig. 3a). These values are about 100 cm^{-1} lower in frequency than the carbonyl bands of corresponding carbocyclic compounds (1790–1777 cm^{-1} (16)) and are consistent with the carbonyl frequencies observed for several other polyvalent iodocarboxylates (17) as well as for compounds with other

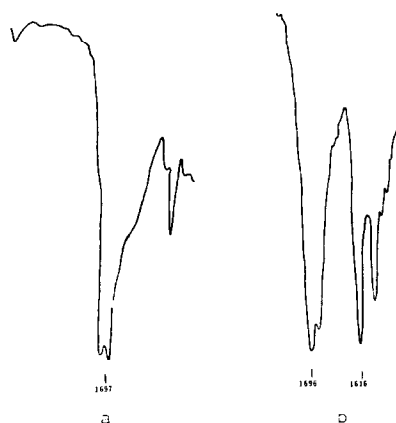


Fig. 3. Carbonyl stretching bands for IIId; (a) 0.01 *M* chloroform solution; (b) KBr disc.

electropositive elements, such as tin and mercury bonded to the oxygen of a carboxylic acid (18). Often, the carbonyl bands of benzoxiodole compounds in solution are split by 5–20 cm^{-1} , an effect also observed in the spectra of structurally similar α,β -unsaturated lactones (19). It seems reasonable that Fermi resonance is responsible for the splitting found in the benzoxiodole carbonyl bands since it occurs in the spectra of solutions of compounds with *only* one carbonyl group as well as in the spectra of some compounds with two different carbonyl groups. Compounds Ia–Ie, which have only one carbonyl group, exhibit split carbonyl bands in solution samples, which cannot be due to geometrical or conformational isomerism. The splitting which occurs for compounds Ic–e in solution, is independent of concentration so is probably not due to intermolecular association. Also the perdeutero analog of Ie shows no carbonyl splitting either in the solid state or in solution, a strong indication that Fermi resonance is responsible for the splitting in the perhydro compound. Thus, for compounds which have two carbonyl groups, no attempt was made to assign to them independent frequencies in the solution phase, even when a split carbonyl band was observed. There is no evidence from the spectra of these solution phase samples that any intermolecular trivalent iodine coordination with carbonyl groups is occurring. In fact, the insensitivity of the solution

phase carbonyl stretching band to the coordination mode which the carbonyl group exhibits in the crystalline phase, suggests that similar intermolecular associations are not occurring to any measureable extent in solution.⁴

In the solid state, however, for compounds with two different carbonyl groups, there are two different carbonyl stretching bands whose frequencies can be correlated with the molecular packing modes of the compounds in the crystalline phase. Of the four coordination modes characterizing benzoxiodole structures, intermolecular lactone carbonyl to trivalent iodine interactions occur only for Group I compounds, and intermolecular exocyclic carbonyl to trivalent iodine interactions occur only for Group II compounds. For Group I compounds, there is a shift in the carbonyl stretching band in solid-state samples of 20–40 cm^{-1} to lower wavenumber as compared to the frequency observed for solution samples, indicating a chemically stabilizing interaction. If is the only Group I compound which has two carbonyl groups. Even though the exocyclic carbonyl is *not* intermolecularly coordinated to iodine, both it and the coordinated lactone give rise to bands which are shifted about 25 cm^{-1} in the solid state, occurring together as a single broad band at 1668 cm^{-1} .⁵ It has been shown from the crystal structure of If, that the exocyclic carbonyl is only 2.9 Å from an *intramolecular* trivalent iodine. The possibility that an *intramolecular* interaction is stabilizing this molecular conformation in the

⁴ It is estimated that at least 10% of the total number of molecules present in solution would have to be associated by close trivalent iodine to carbonyl contacts in order to observe a shifted carbonyl band. We observe no shifted carbonyl band, but it is still possible that molecular association does occur in low concentration in solution.

⁵ Previous investigators had reported two bands in the carbonyl region at 1660 and 1615 cm^{-1} for If in the solid state, which they attributed to the two different carbonyl groups (17). We have found, however, that crystals of the acetate can be hydrolyzed at ambient temperatures and humidity to give IVa, which has a broad carbonyl band at 1610 cm^{-1} . When protected from hydrolysis, only one band is seen in both solution and solid-state samples of If.

solid state but *not* in solution is supported by the infrared spectra of IIIa and IIIb. These compounds also have two carbonyl groups, but neither are coordinated to iodine. In the solution phase, IIIa and IIIb have the characteristic single carbonyl band, but in the solid state, two bands are seen in the carbonyl region. One is shifted only 8 cm^{-1} to lower wavenumber as compared to the single carbonyl frequency in solution, and is probably due to the lactone carbonyl. The other band has been shifted 50–60 cm^{-1} to lower wavenumber and has been assigned to the exocyclic carbonyl group. The molecular conformation of IIIa and IIIb are the same as If with regard to the rotation of the exocyclic ester group relative to the benzoxiodole ring. Thus, IIIa and IIIb also have close intramolecular contacts (2.75 Å) between iodine and the exocyclic carbonyl, which may be responsible for the observed carbonyl frequency shifts.

For Group II compounds, *intramolecular* contacts between iodine and the exocyclic carbonyl are observed (with the same geometry as for If, IIIa and IIIb), but in these cases the exocyclic carbonyl is also involved in an *intermolecular* coordination to trivalent iodine. Infrared spectra of these solid-state compounds show two carbonyl stretching bands, one of which is only slightly shifted from the single frequency observed for solution samples, while the other is a sharp band shifted as much as 80 cm^{-1} to lower wavenumber (Fig. 3b).⁶ This latter band most likely is due to the doubly coordinated exocyclic carbonyl group, while the higher frequency band is due to the uncoordinated lactone carbonyl.

These are the largest carbonyl frequency shifts observed for any benzoxiodole compound. Still, one cannot unequivocally differentiate between Group II and Group III compounds solely on the basis of the infrared frequency shifts between solution and solid

⁶ Infrared data is not available for IIf and g since these are metastable polymorphs apparently formed only during single crystal transformations of the parent peroxide (3). They occur as unique *crystalline* phases during these transformations, but other chemical species are also present which interfere with direct infrared analysis of these polymorphs.

phase samples. The Group III compounds have shifts of 50–60 cm^{-1} for the exocyclic carbonyl, while Group II compounds show shifts of 67–83 cm^{-1} . Both of these shifts are greater than any shift observed as a result of lactone carbonyl coordination to trivalent iodine (20–38 cm^{-1}), as observed for Group I compounds.

It is interesting that IIIc, the only lactam in these series, has the same lactone carbonyl stretching frequency in solution as Ia and b. Consistent with the fact that IIIc has no lactone to iodine coordination in the solid state, only a small shift (13 cm^{-1}) to lower wavenumber is observed in spectra of solid phase samples of this compound.

Group IV compounds also have no carbonyl coordination to trivalent iodine in the solid state. IVa does have a hydrogen-bonded carbonyl group, giving rise to a very low stretching frequency of 1610 cm^{-1} . Unfortunately, this compound is insoluble in suitable infrared solvents. If one assumes that the uncoordinated lactone carbonyl group absorbs at 1697 cm^{-1} , as for most other benzoxiodole compounds, then the carbonyl frequency shift due to hydrogen-bonding is only slightly greater than the largest carbonyl frequency shifts observed for trivalent iodine coordination. IVb has no carbonyl coordination in the solid state, and shows a stretching frequency of 1670 cm^{-1} . (This compound is also insoluble in suitable infrared solvents.)

Other regions of the infrared spectra of these benzoxiodole compounds, besides the carbonyl region, were studied, but no other consistent spectral patterns reflecting the different crystal structures were evident.

Crystal Structure Predictions

The infrared spectra of 3-oxo-3H,2,1-benzoxiodol-1-ethoxy and 1-butoxy (V, VI) show that the carbonyl stretching frequencies are 25 cm^{-1} lower in the solid-state as compared to their frequencies in solution samples. Since there is only one molecule per asymmetric unit for both compounds and their \vec{b} -axis lengths do not exceed 11.5 Å (Table I), it is quite likely that both these compounds have I^(III) coordinating to the lactone carbonyl

of a neighboring screw-related molecule, as for the Group I compounds. The configurations of the screw-axis chains for V and VI may be similar to the twisted configuration of the orthorhombic methoxy derivative, Ia, since the \vec{b} -axis lengths are nearly the same for these three compounds. The effect of increasingly bulky aliphatic substituents on the unit cell parameters appears to be reflected in the length of the axes parallel to the glide directions. For the methoxy derivative, Ia, the \vec{c} -glide is perpendicular to the screw-axis and \vec{c} is 13.53 Å. For the ethoxy derivative (V), which has an \vec{a} -glide, \vec{a} is 14.0 Å; and for the butoxy derivative (VI) which has a \vec{c} -glide, \vec{c} is 15.4 Å. Even though V and VI have the same space group as the monoclinic polymorph of the methoxy derivative, Ib, comparison of both the length of the \vec{b} -axis and of the axes parallel to the glide directions (for Ib, \vec{a} is 8.1 Å) indicates that the molecular packing of V and VI is probably more similar to that of the orthorhombic polymorph, Ia.

One could also have predicted prior to the crystal structure determination of the orthorhombic structure Ia, that trivalent iodine was coordinated to the lactone carbonyl (by its infrared spectra) and that of the three possible screw-axis directions, *only* the \vec{b} -axis could have been the screw axis about which coordination was occurring, since the postulated maximum length of a coordination axis is exceeded by the other two screw axes.

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