# Synthesis of Perfluoroalkylene Polyesters of Hypervalent Iodine Compounds and Interpreation of Their Structure

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ABSTRACT: Reaction of iodobenzene diacetate with $HOOC(CF_2)_nCOOH$, where $n = 2$ or 4, forms polymeric perfluoroalkylene esters. These have the same insolubility in all nonreactive solvents that characterized the alkylene esters made previously. Infrared spectroscopy provides a basis for structural interpretation. Iodobenzene bis(trifluoroacetate), which resembles the polymers in the carbonyl features of its vibration spectrum, was used extensively as a model compound. The fundamental carbonyl frequencies are shifted to higher wave number by fluorine substitution and to lower frequency by the $>I-C_6H_5$ group. The C=O stretching frequency is intermediate between that of the ester and that of the salt. The consistent occurrence of doublets in the stretching vibrations for the carbonyl groups of these esters indicates that a novel 1,5-dicarbonyl frequency interaction exists in these compounds. A linear polymer structure, rather than a cyclic structure, is preferred for these new compounds.

Although the hypervalent organic iodine compounds (compounds with a nominal iodine valence of three) have been known since 1886,[1] the nature of the bonding in these compounds remains a subject of discussion. As can be seen by reference to the 1943 review by Sandin,[2] these compounds were virtually ignored for some years after the Lewis octet rule became a dominant factor in chemical thought. Around 1930, the publication of work dealing with such compounds resumed. Sandin concluded that the octet rule could be applied to iodonium compounds in the classic way, but he found no clear evidence leading to an electronic structure for iodoxybenzene or for iodosobenzene or its salts. A more recent review by Banks[3] makes use of X-ray diffraction data available since the Sandin review but does not attempt any definitive interpretation of the relationship between bonding and structure.

A new problem of interest to structural chemists appeared when the statement that ring compounds were formed by reaction of iodosobenzene with a dicarboxylic acid or of iodosobenzene derivatives with salts of dicarboxylic acid[4] was followed shortly by the description of polymers formed by quite similar reactions.[5] It was obviously desirable to determine if the ring compounds were really polymers or if the supposed polymers were really cyclic. We can now report the synthesis of new polymers that offer a partial solution to some of the structural problems mentioned above.

## Experimental Section

The starting materials for synthesis were iodobenzene and diphenyliodonium chloride from Aldrich, perfluoroadipic acid and perfluorosuccinic acid from 3M Corp., and standard reagents. Iodobenzene diacetate and iodosobenzene were prepared by the method of Saltzman and Sharefkin.[6,7] Iodobenzene bis(trifluoroacetate) was first made by Alcock and Waddington[8] by two different methods. We used one of these, the reaction of iodosobenzene with trifluoroactic acid. Diphenyliodonium acetate was made by the method of Beringer, Galton, and Huang.[9]

**Synthesis of the Polyesters.** Livingston, Sullivan, and Musher[5] gave three methods for preparing polymers with iodine as a chain atom, one of which is ideally suited to our purposes. This is ester interchange between iodobenzene diacetate and a dicarboxylic acid. While in the earlier work the polymer made by this method was impure and unstable, the method has worked very well for us under the following conditions. $HOOC(CF_2)_nCOOH$, with $n = 2$ or 4, was mixed dry with iodobenzene diacetate (1 mol of acid per mole of iodine compound) in a 25-ml flask and heated on a glycerol bath at 105° under vacuum until no further acetic acid could be removed. Hot acetone and chloroform were used successively to extract unreacted acid and iodobenzene diacetate. The polymer was vacuum dried at 40°. $C_{10}H_5O_4F_4$ and $C_{12}H_5O_4F_8$ were produced, mp 171° dec and 184° dec, respectively. *Anal.* Calcd for $C_{10}H_5O_4F_4$: C, 30.76; I, 32.4. Found: C, 30.61; I, 32.2; 67% yield. Calcd for $C_{12}H_5O_4F_8$: C, 29.26; I, 25.8. Found: C, 29.49; I, 25.7; 61% yield. Infrared spectra were obtained with a Perkin-Elmer 621 grating spectrometer with samples prepared by the Nujol mull technique or, where appropriate, tableting with KBr.

**Solubility of the Polyesters.** One of the first things noted about the alkylene polyesters of hypervalent iodine compounds was their insolubility in both polar and nonpolar solvents.[5] After much experimentation, two conclusions were reached. (1) Most solvents that, when added to these polyesters, form homogeneous liquid phases, do so not by dissolving the polymers but by reacting with the polymers by virtue of the strong oxidizing effect of these hypervalent iodine compounds. Dimethyl sulfoxide is the "solvent" that has been studied most extensively. It in fact reacts with the polymers or with low molecular weight analogs such as iodobenzene diacetate. (2) The best evidence for solubility (as opposed to reaction) of a hypervalent iodine compound is a redox indicator test. The blue to violet color change with diphenylamine as the indicator[10] is an excellent test that will be positive for solutions containing trivalent iodine.

These studies have been extended to the perfluoroalkylene polyesters, with similar results. There is no evidence that aqueous, aromatic, or chlorinated solvents dissolve the polymers at all. Even a 1:1 (by volume) mixture of chloroform and acetic acid, which might be expected to alter the polymers by ester interchange, had no effect. Addition of dimethyl sulfoxide made the solid polymer

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(1) C. Willgerodt, *J. Prakt. Chem.*, **33**, 154 (1886).

(2) R. B. Sandin, *Chem. Rev.*, **32**, 249 (1943).

(3) D. F. Banks, *ibid.*, **66**, 243 (1966).

(4) G. P. Baker, F. G. Mann, N. Sheppard, and A. J. Tetlow, *J. Chem. Soc.*, 3721 (1965).

(5) H. K. Livingston, J. W. Sullivan, and J. I. Musher, *J. Polym. Sci., Part C*, **No. 22**, 195 (1968).

(6) H. Saltzman and J. G. Sharefkin, *Org. Syn.*, **43**, 60 (1963).

(7) J. G. Sharefkin and H. Saltzman, *ibid.*, **43**, 62 (1963).

(8) N. W. Alcock and T. C. Waddington, *J. Chem. Soc.*, 4103 (1963).

(9) F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Amer. Chem. Soc.*, **84**, 2819 (1962).

(10) J. Knop, *ibid.*, **46**, 263 (1924).

TABLE I

FUNDAMENTAL FREQUENCIES OF VIBRATIONS IN THE AROMATIC RING (BASED ON WHIFFEN'S DESIGNATION[a] OF THE FUNDAMENTALS)

| Whiffen symbol | Frequency in iodobenzene, $cm^{-1}$ | Frequency in hypervalent compds,[b] $cm^{-1}$ |
|---|---|---|
| a | 1178 | 1175–1178[c] |
| b | 1015 | 1010–1015 |
| c | 1159 | 1154–1160[c] |
| e | 1261 | 1260–1263[c] |
| f | 730 | 730–740 |
| g | 835 | 833–835 |
| h | 963 | 965–970 |
| i | 904 | 902–912 |
| j | 987 | 985–990 |
| k | 1575 | 1572–1580 |
| m | 1473 | 1470–1475 |
| n | 1437 | 1437–1445[c] |
| o | 1321 | 1322–1325 |
| p | 998 | 990–998 |
| q | 1060 | 1060–1065 |
| r | 654 | 648–654 |
| s | 613 | 612–620 |
| v | 684 | 673–688 |
| y | 448 | 451–455 |
| $z_1$ | 3064 | 3060–3065 |

[a] See ref 14. [b] The hypervalent compounds for which spectra were determined were iodosobenzene, iodobenzene diacetate, iodobenzene bis(trifluoroacetate), diphenyliodonium chloride, diphenyliodonium acetate, and the two polymers made from $HOOC(CF_2)_nCOOH$ as described in the Experimental Section. [c] For some of the compounds, this frequency coincides with frequencies corresponding to vibrations in nonaromatic parts of the molecule.

TABLE II

THE EFFECT OF GROUPS WITH DIFFERENT ELECTRONEGATIVITY ON THE CARBONYL (C=O) STRETCHING VIBRATION ($CM^{-1}$) IN ACETATES

| X in $CH_3COOX$ | $\nu$(C=O) | X in $CH_3COOX$ | $\nu$(C=O) |
|---|---|---|---|
| $-NO_2$ | 1798[a] | $-HgC_6F_5$ | 1603 |
| $-CH{=}CH_2$ | 1776 | $-HgC_6H_5$ | 1580[a] |
| -Et | 1740 | $>SnBu_2$ | 1580[a] |
| $-Si(CH_3)_3$ | 1715[a] | Salts[b] | 1522–1583 |
| $>I{-}C_6H_5$ | 1640, 1625 | | |

[a] J. P. Freeman, *J. Amer. Chem. Soc.*, **80,** 5954 (1958). [b] Salts of mono-, di-, or trivalent metals.

slowly disappear, but there was every indication that in this case, as in the experiments mixing dimethyl sulfoxide with iodobenzene diacetate or iodobenzene bis(trifluoroacetate), it was chemical reaction that was being observed, not solution.

### Statement of the Structural Problem

Where substances are insoluble, X-ray diffraction or vibrational spectroscopy provides the best methods for structure determination. Since we have not formed any single crystals of the polymers, we have turned to spectroscopy to obtain the necessary information. Ready reference to tables or previous studies of vibrational assignments cannot be used to solve structural problems involving hypervalent iodine compounds. Some of the difficulties are the following.

(1) Hypervalent iodine compounds are typically stable only for a few days or weeks at room temperature. The possibility that partially decomposed samples were being used for spectroscopy was not appreciated in the earliest work. Bell and Morgan[11] have criticized the work of Furlani and Sartori[12] on these grounds.

(2) Hypervalent iodine compounds are such strong oxidizing agents that they can form $Br_2$ by oxidation when pressed with KBr into tablets,[13] or $I_2$ by oxidation when placed on CsI plates for low-frequency spectroscopy. This was not recognized in some of the earlier infrared investigations.

(3) Most studies have been carried out with compounds containing phenyl or substituted phenyl groups, alkyl groups, and the O=C—O—I group. Since the last named group has never had satisfactory assignments made, it is not possible to make good assignments for the frequencies observed simply by referring to the literature.

(4) The most-used assignments for benzene derivatives are those of Whiffen, who assigned letters a-$z_5$ to the 30 fundamental vibrations of monosubstituted benzenes.[14] While most of his assignments can be accepted verbatim, Varsanyi[15] has questioned the q and r assignments and introduced a distinction between light and heavy substituents that leads to reinterpretation of Whiffen's i, t, u, and x vibrations. The end result is that there is not complete agreement on the nature of several of the substituent-sensitive vibrations in iodobenzene, and therefore no good basis for interpreting the spectra of its derivatives. For compounds containing -I-O bonds, there are no accepted assignments.

(5) The carbonyl vibration fundamentals in the esters can be recognized as such, but their positions are shifted and they exhibit shoulders or doublet peaks that are not readily explained.

In summary, the vibrational spectra of the hypervalent organic compounds cannot be given definitive assignments based on prior spectroscopic studies. Even the trifluoroacetoxy derivative, which is a model compound for the new compounds that we have synthesized, has merely had its infrared peak frequencies reported without assignment.[8]

Our approach to the development of suitable assignments has been to make measurements on fluoroaliphatic derivatives of iodobenzene and use this information to determine the most probable structure of the new compounds. First, we can confirm Lillien's conclusion[16] that substituents on the iodine atom have little effect on the vibration fundamentals that can be assigned to the C–C and C–H of the benzene ring. In Table I we present this information, keyed to the Whiffen assignments.[14]

Secondly, any possible difficulties resulting from overlap of aliphatic C–H fundamentals with others of interest can be circumvented by studying compounds in which the aliphatic moiety is fully fluorinated. As far as we can determine, the effect of the hypervalent iodine on alkyl, alkylene, perfluoroalkyl, or perfluoroalkylene fundamentals is slight.

Most significantly, the effect of the electronegativity of substituents on the carbonyl C=O stretching vibrations, summarized by Bellamy[17] but apparently first noted by Kagarise,[18] provides a positive identification for the C=O stretch. As Kagarise showed, this frequency is linearly proportional to the electronegativity on the Gordy scale, with

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(11) R. Bell and K. J. Morgan, *J. Chem. Soc.*, 1209 (1960).

(12) C. Furlani and G. Sartori, *Ann. Chim. (Rome)*, 47, 124 (1957).

(13) W. Wolf, personal communication.

(14) D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).

(15) G. Varsanyi, "Vibration Spectra of Benzene Derivatives," Academic Press, New York, N. Y., 1969.

(16) I. Lillien, *J. Chem. Soc.*, 4498 (1962).

(17) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, pp 141 ff.

(18) R. E. Kagarise, *J. Amer. Chem. Soc.*, **77,** 1377 (1955).

TABLE III

VIBRATION FUNDAMENTALS (CM$^{-1}$) ASSOCIATED WITH CARBON–OXYGEN IN THE SERIES ACID–HYPERVALENT IODINE COMPOUND–SALT

| Assignment for acid | $CF_3COOH$[a] | $C_6H_5I(OOCCF_3)_2$ | $NaOOCCF_3$ | $NaOOCCH_2Cl$[e] | $NaOOCCH_3$ | Assignment for salt |
|---|---|---|---|---|---|---|
| C=O stretch | 1843 (monomer)<br>1776 (dimer) | 1740<br>1703 | 1689[b]<br>1681[c]<br>1676[d] | 1595 | 1583[b] | $(CO_2)_{as}$ |
| (C—O) stretch | 1417 (monomer)<br>1456 (dimer) | 1385<br>1360 | 1446[b]<br>1441[d]<br>1435[c] | 1425 | 1421[b]<br>1421 | $(CO_2)_s$ |
| $CO_2$ def | 675 | 722 | 729[c]<br>728[d]<br>726[b] | 670 | 650[b] | $(CO_2)$ def |
| $CO_2$ rock | 449 | | | 576 | 622[d] | $CO_2$ rock |
| $CO_2$ rock | 435 | 422 | 410[c,d] | 429 | 470[d] | |

[a] J. R. Barcelo and C. Otero, *Spectrochim. Acta*, **18,** 1231(1962); infrared data are for the pure liquid except for monomer fundamentals, which are for the vapor. [b] E. Spinner, *J. Chem. Soc.*, 4217 (1964); infrared data from KBr disks. [c] R. E. Robinson and R. C. Taylor, *Spectrochim. Acta*, **18,** 1093 (1962); Raman data for aqueous solutions. [d] E. Spinner, footnote *b;* Raman data for aqueous solutions. [e] K. Nakamura, *Nippon Kagaku Zasshi*, **79,** 1420 (1958); infrared data from KBr disks.

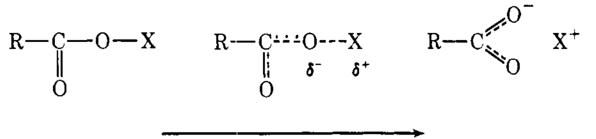
TABLE IV

COMPARISON OF CARBONYL STRETCHING FUNDAMENTAL VIBRATIONS (CM$^{-1}$) OF PERFLUOROCARBOXYLATE POLYMERS WITH THOSE OF MODEL COMPOUNDS

| Type of Compound | Assignment | X | | |
|---|---|---|---|---|
| | | $(OOCCF_3)_2$ | $OOCCF_2CF_2COO-$ | $OOC(CF_2)_4COO-$ |
| $C_6H_5IX$ | $\nu(C=O)$ | 1740, 1703 | 1735, 1710 | 1735, 1713 |
| | $\nu(C—O)$ | 1385, 1360 | 1340, 1290 | 1335, 1315 |
| K salt of X | $\nu(CO_2)_{as}$ | 1660 | 1680 | 1687 |
| | $\nu(CO_2)_s$ | 1435 | 1390 | 1390 |

$CF_3$ giving the highest frequency and $CH_3$ the lowest of any of the organic X groups studied by Kagarise. Our own results (Table II), augmented with selected literature data, show that it is possible to assign the C=O stretch for quite a range of acetates, and the results do correlate with the electronegativity of X.

Furthermore, the carbonyl C–O stretching vibration can be considered to be affected by the electronegativity of substituents. This comes about in the following way. Robinson and Lister[19] have shown a linear relationship to exist between bond order and force constants in carbon–oxygen bonds. With decreasing negativity of the X group, the polarity of the bond increases, the order of the C—O bond increases, and the order of the C=O bond decreases



direction of increasing polarity

Kagarise[18] showed the effect of adding one, two, and three halogens to the acetate group of an ester. The effect is particularly striking when fluorines are used, as shown in Figure 1. It will be noted that the mono- and difluoroacetates exhibit doublets because of rotational isomerism, as explained by Brown.[20] The data for iodobenzene, organotin, and organomercury esters are entirely consistent with his for ethyl esters of substituted acetates.

The transition from acid to salt in the carbon–oxygen fundamentals is perhaps best illustrated by the data in Figure 1 and Table III. In the latter, data for iodobenzene bis(trifluoroacetate) are shown to lie intermediate between those for trifluoroacetic acid and those for sodium salts, all the trifluoroacetate carbonyl frequencies being quite readily distinguishable from the frequencies associated with chloroacetate and acetate salts.

With this background it is possible to interpret all the features of the carbon–oxygen fundamentals of the new iodine-containing polymers (Table IV). The doublets in the stretch-

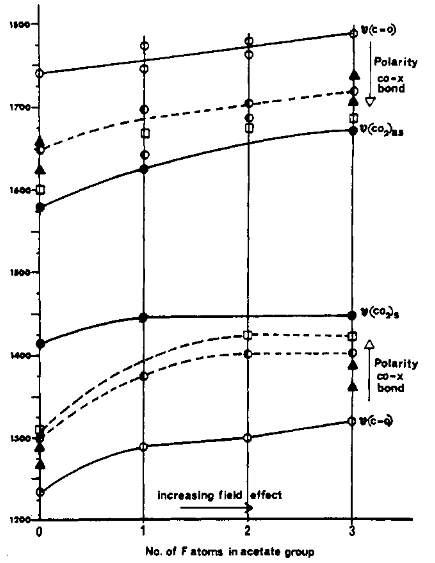


Figure 1. The effect of polarity of the CO–X bond and field effect on $\nu(C=O)$ and $\nu(C—O)$ vibrations: (○) $(CH_{3-m}F_mCOO)Et$, (▲) $(CH_{3-m}F_mCOO)_2IPh$, (◐) $(CH_{3-m}F_mCOO)SnBu_3$, (□) $(CH_{3-m}F_mCOO)HgPh$, (●) $(CH_{3-m}F_mCOO)^{\ominus}M^{\ominus}$. Data were taken from T. L. Brown, *Spectrochim. Acta*, **18,** 1615 (1962); M. Vilarem and J. C. Maire, *C. R. Acad. Sci., Ser. C*, **262,** 480 (1966); E. T. McBee and D. L. Christman, *J. Amer. Chem. Soc.*, **77,** 755 (1955); G. B. Deacon and F. B. Taylor, *Aust. J. Chem.*, **21,** 2675 (1968); K. Ito and N. J. Bernstein, *Can. J. Chem.*, **34,** 170 (1956); and E. Spinner, *J. Chem. Soc.*, 4217 (1964).

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(19) E. A. Robinson and M. W. Lister, *Can. J. Chem.*, **41,** 2988 (1963).

(20) T. L. Brown, *Spectrochim. Acta*, **18,** 1615 (1962).

ing peaks require special comment. Bell and Morgan[11] first reported such doublets, which they observed for iodobenzene diacetate. In our own laboratories Krosec[21] repeatedly has found doublets in the carbonyl region for the polymers $-I(Ph)-OOC(CH_2)_nCOO-$. They are also prominent in the fluorine-containing analogs, as shown in Table IV. Doublets are not observed in ring compounds in which trivalent iodine is a heteroatom. Wolf, Chalekson, and Kobata[22] report single values for the C=O stretching frequency of 1632 $cm^{-1}$ for the 1,3-diacetoxy- and 1607 $cm^{-1}$ for the 1-acetoxy-3-hydroxy derivatives of 1,3-dihydro-1,3,2-benzodiiodoxole. The second acetoxy group in the diacetoxy is kept well away from the first, we believe, by virtue of the 1,3 position of the iodines in the five-membered ring. There is no frequency coupling and therefore no splitting in this symmetrical molecule.

We believe that the wide X–I–X bond angle in the hypervalent iodine compounds, which we have discussed previously,[5] makes for considerable stereochemical interaction between the two carbonyl groups of iodobenzene diacetate and the other esters. Bellamy[23] has summarized information relating to frequency coupling in 1,2-, 1,3-, and 1,4-dicarbonyl compounds. We may well have the first example of such coupling in 1,5-dicarbonyl compounds. In view of the probable collinearity of the O–I–O segment, it is quite plausible that these compounds should have as much stereochemical interaction between carbonyls as is normally observed in a 1,3-dicarbonyl compound.

This information suggests a resolution of the differences that exist between the work of Baker, Mann, Sheppard, and Tetlow[4] and our own syntheses of hypervalent iodobenzene derivatives made from dicarboxylic acids[5] and of the tellurium-containing polymers made by an analogous reaction between diphenyltellurium dichloride and salts of dicarboxylic acids.[21,24] We have uniformly assigned polymer structures to our products, whereas Baker, *et al.*, suggested that they had made cyclic compounds. The fact that the same types of doublets are seen in all of our dicarboxylates, with a range of chain lengths from two to eight carbon atoms and either $(CH_2)_n$ or $(CF_2)_n$ between the carbonyls, indicates that we have in every case made the same kind of molecules. We believe that these are acyclic molecules (*i.e.*, linear polymers), not ring compounds. The insolubility of our iodobenzene dicarboxylates also argues for a polymeric structure in which the bonding is of a character intermediate between covalent and ionic, as suggested by the data in Table III and by our earlier work with iodobenzene disulfonates.[25] According to this interpretation, the polymers do not dissolve in the aromatic or chlorinated solvents because they have too much polar character, and they do not dissolve in water or dioxane because they have too much nonpolar character.

## Summary

(1) New hypervalent iodine compounds with the formula $-I(C_6H_5)OOC(CF_2)_nCOO-$, with $n = 2$ or 4, have been prepared by an improvement of a synthesis previously reported for $-I(C_6H_5)OOC(CH_2)_nCOO-$ compounds.

(2) Infrared spectroscopy of these compounds and numerous model compounds show that the vibrations associated with the phenyl group are but little affected by the introduction of hypervalent iodine.

(3) In contrast, the hypervalent iodine atom and the other nonphenyl substituents have a very large effect on the carbonyl stretching vibrations.

(4) Interpretation of the carbonyl stretching vibrations in iodobenzene bis(trifluoroacetate) and the new polymers shows that the compounds are intermediate between covalent and ionic in bond character.

(5) Increasing fluorine substitution increases the frequency of the C=O and C—O stretching fundamentals, in keeping with observations that have been made for other types of esters.

(6) The C=O and C—O stretching vibrations exist as doublets, indicating that, even though these are 1,5-dicarbonyl compounds, the rigidity and large bond angle of the O–I–O group lead to splitting by virtue of frequency interactions between sterically interacting carbonyl groups.

(7) All the available data support the assignment of a linear polymer structure to the new compounds. Their insolubility in polar and nonpolar solvents is consistent with the bond character indicated by the carbonyl portion of the infrared spectra.

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(23) Reference 17, pp 128–32.

(24) H. K. Livingston and R. Krosec, *J. Polym. Sci., Part B*, **9**, 95 (1971).

(25) H. K. Livingston and J. Kresta, Abstracts, 23rd International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971, p 984.