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Solution Structure of Some λ^3 Iodanes: An ^{17}O NMR and DFT Study

Francesca Mocci,* Gianluca Uccheddu, Angelo Frongia, and Giovanni Cerioni*

*Dipartimento di Scienze Chimiche, Università di Cagliari, Complesso Universitario, S.S. 554,
Bivio per Sestu, I-09042 Monserrato (CA), Italy*

cerioni@unica.it; francy@dsc.unica.it

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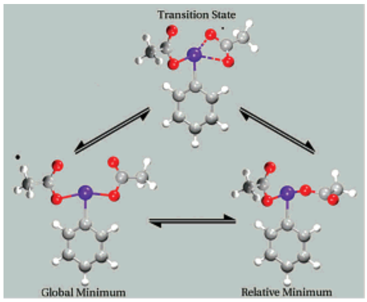

The structure of a series of I−O bonded bis(acyloxy)iodoarenes and benzoiodoxolones in chloroform solution has been investigated by ^{17}O NMR spectroscopy and by density functional theory (DFT) calculations, employing the PBE0 functional together with the LANL2DZ basis set extended with polarization (d) and diffuse (p) functions. This combined approach allowed us to ascertain that, although these classes of λ^3 iodanes maintain in chloroform solution their solid state "T-shaped" structure, a degenerate [1,3] sigmatropic shift of iodine between the two oxygens of the acyloxy groups occurs in solution. The energy barrier involved in this process differs in the two classes, thus causing significant differences in the ^{17}O NMR spectra, at room temperature, of the two classes of compounds.

Introduction

Hypervalent iodine chemistry has experienced in the last few years a fast and important increase of interest, as shown by the accelerated appearance of reviews[1] motivated not only by the pure chemical interest but also by the growing application of many compounds of this class in organic synthesis, especially for their oxidizing properties. Notwithstanding this large body of literature, a full spectroscopic characterization of many I(III) organic derivatives, such as λ^3 iodanes, is lacking in the solution state. The solid-state structure,[2] "T-shaped" and I−O covalently bound, although with a highly ionic character,[1] is usually assumed also in solution. In fact, dipole moment studies[3] by Exner and Plesničar on the conformation of acyloxy groups of some bis(acyloxy)iodoarenes in benzene solution favor this assumption, but definitive evidence is, however, lacking. On the contrary, in recent years, Koser's group[4] has shown that [hydroxy(tosyloxy)iodo]benzene is fully ionized in water solution, originating a monomeric positively charged hydroxy(phenyl)iodonium ion. Ochiai's group[5] has been able to stabilize this cation by interaction with 18-crown-6 ether.

In a recent paper,[6] to justify the observation of only one signal in the ^{17}O NMR for a number of *para*-substituted bis(acetoxy)iodobenzenes in chloroform, we have suggested the possibility that these compounds had an "ion pair" structure, even if other structures (e.g., "chelate") could not be ruled out. Equivalence

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[1] (a) Moriarty, R. M. *J. Org. Chem*. **2005**, *70*, 2893−2903. (b) Zhdankin, V. V. *Curr. Org. Synth*. **2005**, *2*, 121−145. (c) Stang, P. J. *J. Org. Chem*. **2003**, *68*, 2997−3008. (d) Morales-Rojas, H.; Moss, R. A. *Chem. Rev*. **2002**, *102*, 2497−2521. (e) Zhdankin, V. V.; Stang, P. J. *Chem. Rev*. **2002**, *102*, 2523−2584. (f) Zhdankin, V. V. In *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; MYU: Tokyo, 1997; Vol. 17, pp 133−151. (g) Stang, P. J.; Zhdankin, V. V. *Chem. Rev*. **1996**, *96*, 1123−1178. (h) Varvoglis, A. *The Organic Chemistry of Polycoordinate Iodine*; VCH: New York, 1992.

[2] (a) Zanos Gougoutas, J.; Clardy, J. C. *J. Solid State Chem*. **1972**, *4*, 226−229. (b) Etter, M. C. *J. Am. Chem. Soc*. **1976**, *98*, 5326−5331. (c) Alcock, N. W.; Countryman, R. M.; Esperas, S.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans*. **1979**, 854−860.

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10.1021/jo070111h CCC: $37.00

CHART 1. Structures of Compounds 1, 2, and 3

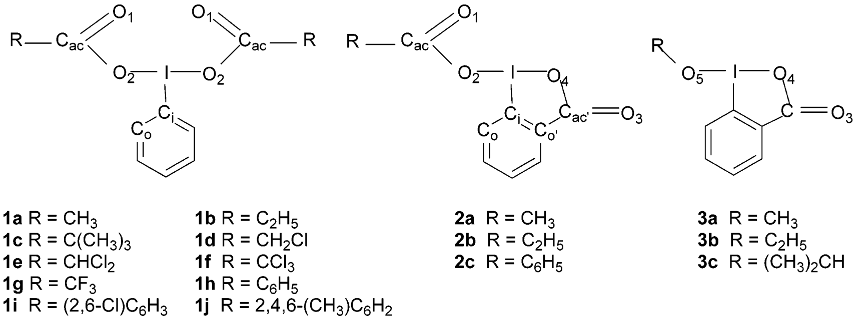

TABLE 1. ^{17}O NMR Data,[a,b] at 25 °C and in $CHCl_3$ Solution, of the Carboxylic Groups of Derivatives 1a−j and of Their Corresponding Free Carboxylic Acids

compound	δ (RCOOI)	$\nu_{1/2}$ (RCOOI)	δ (COOH)	$\nu_{1/2}$ (COOH)	$\Delta\delta$
1a	301	1050	254.2	161	47
1b	298	1350	248.9	218	49
1c	295	1270	242.4	206	43
1d	292	1100	250.2	245	42
1e	281	2150	244.1	226	37
1f	275	∼2200	238.7	240	36
1g	270	1030	246.5	166	24
1h	285	1340	234.1	420	51
1i	307	640	266.3	535	41
1j	303	1365	263.1	465	40

[a] $\delta(^{17}O)$, ppm, from $\delta_{H_2O} = 0$ ppm; $\nu_{1/2}(^{17}O)$ half-height line width, Hz. Because of the lines broadness, δ, for derivatives **1**, and $\Delta\delta$ values are approximated to integer values since the chemical shifts are estimated with a confidence of ±2 ppm. A better estimate (±1 ppm or less) is obtained from the much sharper signal of the free carboxylic acids. [b] ^{17}O NMR spectra had already been reported for **1a**[6,7a] and **1g**;[7a] our measurement is not in complete agreement, in the case of **1g**, with the literature data both for the chemical shift (263 ppm)[7a] and, particularly, with their finding that a "sharp" line is observed when compared to that of **1a**.

in the ^{17}O NMR of the two "estereal" oxygens had already been observed.[7] In the case of compounds **1a** and **1g** (see Chart 1) in CH_2Cl_2 solution, a degenerate [1,3] sigmatropic shift of iodine between the two oxygens was suggested[7a] as not unreasonable, while for some acyloxysilanes[7b] and -germanes[7b] and some Sn(IV) stannane dicarboxylates,[7c] an asymmetric chelate bonding was preferentially suggested. Other possible ways to reach equivalence of the two oxygens are full ionization and intermolecular exchange between the acyloxy groups. Thus it seemed to us of interest to extend our previous observations[6] to seek a better understanding of the I−O bonds and of the structure(s) in solution of acyloxyiodoarenes and related λ^3 iodanes, and, possibly, to ascertain the way leading to the observed[6,7a] equivalence of the oxygens of their acyloxy groups.

Results and Discussion

The structures of studied derivatives are shown in Chart 1. The ^{17}O NMR data of derivatives **1**, collected in Table 1, confirm our previous observation[6] on a series of *p*-substituted bis(acetoxy)iodobenzenes; only one broad signal is observed, in the ^{17}O NMR, for the two oxygens of the carboxylic groups in this class of λ^3 iodanes, not only in the case of the acetoxy derivatives[6,7a] but also for a generality of acyloxy substituents. We note that, although with the possible exception in **1g**, iodine bonding influences ^{17}O chemical shifts of the carboxylic groups roughly to a similar extent ($\Delta\delta = 43 \pm 8$ ppm, excluding **1g**), seemingly irrespective of electronic and/or steric factors. In a qualitative way and for limited and quite homogeneous series, it is, however, possible to distinguish an influence of steric hindrance or of acid strength as it can be deduced from the comparison of the lower $\Delta\delta$ values for **1c** versus **1a**,**b** or **1i**,**j** versus **1h**. The influence of the acid strength is indicated by the lowering of the $\Delta\delta$ values on going from **1d** to **1g**. The quite low $\Delta\delta$ value ($\Delta\delta = 24$ ppm) found for **1g** seems thus due to an unexpected high value of the shift of the trifluoroacetic acid. The relatively high deshielding overall observed ($\Delta\delta > 35$ ppm) on going from the free acids to derivatives **1** indicates the presence of a significant interaction between iodine and the two oxygens of the carboxylic group. This interaction does not seem to be sensitive to changes in the electronic distribution on the phenyl ring since *para*-substitution showed a remarkable constancy of the chemical shifts of the acyloxy group, with a measured $\delta = 299 \pm 3$ ppm.[6]

This constancy and the small changes among the $\Delta\delta$ values, mostly reflecting the influence of the R group in RCOOH, seem to indicate a very small influence of changes in other parts of the molecule on the interactions between iodine and carboxylic groups.

The measured chemical shifts and the signals' half-height line widths of derivatives **1** are clearly different from those of the free acids, thus ruling out both a full ionization or an "accidental" hydrolysis, as a possible cause of observing only a single signal, in the ^{17}O NMR, for the two oxygens of the estereal group. The lack of ionization is also in agreement with results based on conductivity and freezing point measurements.[8]

A systematic study of carboxylic acids by ^{17}O NMR seems not to be present in the literature. A contribution to the observed deshielding ($\Delta\delta > 35$ ppm) of derivatives **1** compared to that of the free acids could be partly given by the rupture of the intermolecular hydrogen bonds present in the free acids.

Intermolecular exchange between acyloxy groups can also be discharged; in fact, when studying, in $CDCl_3$ solution, a degenerate isomerization of acetoxy ligands about iodine in some chiral acetoxyiodo(III)binaphthyls,[9] Ochiai and co-workers clearly demonstrated the absence of bimolecular ligand exchange. We further checked this point on our derivatives, measuring a ^{13}C NMR spectrum of an equimolar mixture of **1a** and **1g**, and not observing any changes from the spectra of these derivatives measured as pure compounds.

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TABLE 2. **^{17}O NMR Data,[a] at 25 °C, of Derivatives 1a, 2, and 3**

compound	$\delta(O_1)$	$\nu_{1/2}(O_1)$	$\delta(O_2)$	$\nu_{1/2}(O_2)$	$\delta(O_3)$	$\nu_{1/2}(O_3)$	$\delta(O_4)$	$\nu_{1/2}(O_4)$	$\delta(O_5)$	$\nu_{1/2}(O_5)$
1a	301	1050	301	1050						
2a	360	800	219	520	323	425	203	440		
2b	370	1500	190	1700	324	630	203	700		
2c[b]	340		198		325		198			
3a					308	470	213	280	22	600
3b					310	440	216	285	53	650
3c					309	580	219	325	80	585

[a] $\delta(^{17}O)$, ppm, from $\delta_{H_2O} = 0$ ppm; $\nu_{1/2}(^{17}O)$ half-height line width, Hz. Because of the lines broadness observed in most cases, all δ values are approximated to integer values with a confidence of ±2 ppm. [b] The value of $\nu_{1/2}$ could not be estimated due to partial signals overlapping.

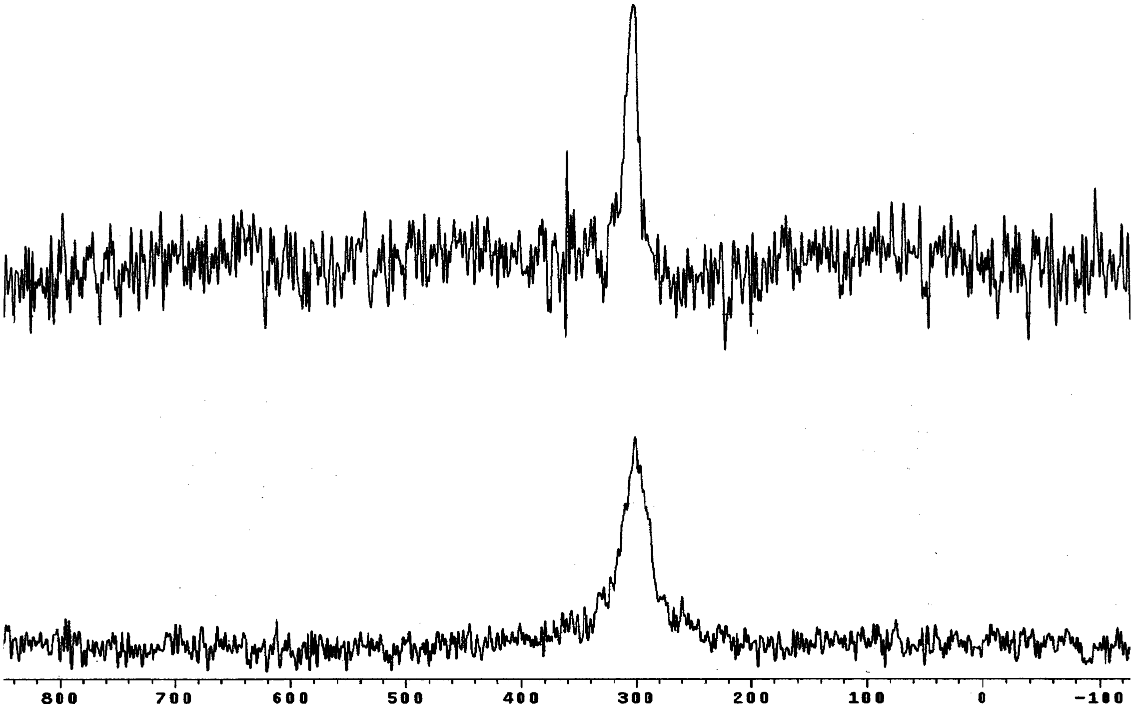

FIGURE 1. ^{17}O NMR spectra of **1a** at 25 °C (bottom) and 45 °C (top).

To discriminate among the remaining hypotheses, that is, chelate or ion pair structures, or a degenerate [1,3] sigmatropic shift, and to gain a better comprehension of the phenomenon, at least in the case of these classes of λ^3 iodanes, we extended our ^{17}O NMR investigation of bis(acyloxy)iodobenzenes **1** to the related benzoiodoxolones **2** and **3** (Table 2) and modeled compounds **1a**, **2a**, and **3a** using DFT calculations.

An important difference is found in the ^{17}O NMR spectra of derivatives **2** and **3** versus that of **1**. The carboxylic group now part of the iodoxolone ring of derivatives **2** and **3** originates two different signals. This feature is not completely surprising since stabilization of the I−O bond by ring closure could be expected. Much more unexpectedly, also the other carboxylic group in derivatives **2** showed two different signals. A comparison of the ^{17}O signals in compounds **2** and **3** with the only signal of derivatives **1** allows a safe attribution of the resonances. The average values of the chemical shifts assigned to O_1 and O_2 of each of derivatives **2** are similar to the corresponding values measured for compounds **1**, while those assigned to O_3 and O_4 better match the corresponding unequivocal signals of compounds **3**. We also note that the signals of **2** and **3** are, in most cases, sharper than those of **1** and that in derivatives **2** the pair of signals assigned to O_3 and O_4 is sharper than that assigned to O_1 and O_2. Moreover, in the ^{17}O NMR spectra obtained at 45 °C, O_1 and O_2 signals of derivatives **2** broadened beyond detection, while those of O_3 and O_4 and that of derivatives **1** sharpened, as shown for **1a** in Figure 1 and for **2a** in Figure 2.

The behavior (and the uniqueness) of oxygens O_1 and O_2 of derivatives **1** is typical of a dynamical phenomenon *after* coalescence, while that of oxygens O_1 and O_2 of derivatives **2** indicates a situation *before* coalescence. The fact that these signals become undetectable at 45 °C seems to indicate that they reach coalescence around this temperature. The sharpening of the signals of O_3 and O_4 is simply what is expected by increasing the temperature in the case of quadrupolar nuclei as ^{17}O.[10] A proper dynamic NMR analysis is prevented by the severe broadening (quantitatively not predictable) of the oxygen signals with temperature lowering; in fact, obtaining decoalescence of the signal of derivatives **1** would be, for these reasons, useless or even impossible. However, a rough estimate of the energy barriers for the oxygens exchange in compounds **1a** and **2a** has been obtained assuming, for both compounds, as chemical shift difference between O_1 and O_2 in the absence of exchange, the chemical shift difference between O_3 and O_4 of **2a**, and a $\nu_{1/2}$ value of 500 Hz; under these assumptions, the exchange rate constant was varied until the best fitting of

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(10) Butler, L. G. In *^{17}O NMR Spectroscopy in Organic Chemistry*; Boykin, D. W., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 1, p 2.

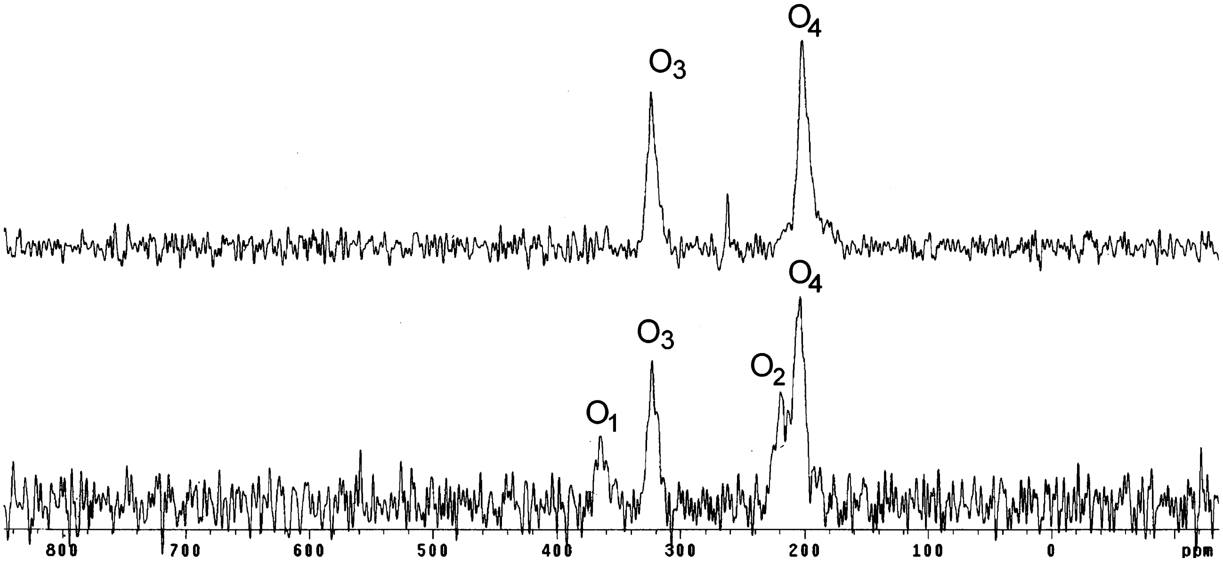


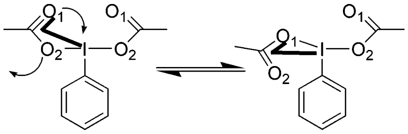
FIGURE 2. ^{17}O NMR spectra of **2a** at 25 °C (bottom) and 45 °C (top), showing the vanishing of the O_1 and O_2 signals at 45 °C.

computed and experimental spectra was obtained. The $\Delta G^{\ddagger}$ values estimated by this crude approximation are **1a** $\cong$ 44 kJ/mol and **2a** $\cong$ 54 kJ/mol.

To obtain further evidence that the equivalence of the ^{17}O NMR observed signals is due to a dynamic phenomenon and to explain the difference between the classes of compounds **1** and **2**, DFT calculations were performed on derivatives **1a**–**3a**, studying both the equilibrium structures and the preferential path to mutual exchange of the estereal oxygens in **1a** and **2a**. DFT calculations were performed at the hybrid PBE0 level[11] using the LANL2DZ[12] basis set extended with polarization (d) and diffuse (p) functions.[12c,d] Because of the low dielectric constant of $CHCl_3$ (4.8 at 293 K), it seemed reasonable to carry on the calculations in vacuo; however, possible solvent effects were checked by employing the polarizable continuum model (PCM)[13] in single-point energy calculations on the in vacuo optimized geometries.

Geometry optimization of compounds **1a**–**3a** reveals that, as in the solid state,[2] also in vacuo the stable conformers of the modeled derivatives have a T-shaped structure. We found four stable conformers for **1a**, two for **2a**, and only one for **3a**; the conformations differ in the orientation of the acetoxy groups plane, which can be either coplanar or perpendicular to the I–C bond. In all cases, the most stable conformer is analogous to that found in the solid state:[2] in **1a** and **2a**, the acetoxy group plane is coplanar with the I–C bond, while in **3a**, the plane containing the methoxy group carbon and oxygen and the iodine is perpendicular to the I–C bond. Molecular models of all the optimized structures are shown in Figure 1S of the Supporting Information; total energies and optimized coordinates are also provided as Supporting Information.

CHART 2. Schematic Representation of the [1,3] Sigmatropic Shift of Iodine between the Two Oxygens of an Acyloxy Group in 1a (I–C_{ac}–O_1 Angle Bolded)



Considering that the [1,3] sigmatropic shift of iodine between the acetoxy oxygens necessarily involves the variation of the I–C_{ac}–O_1 angle (see Chart 2), we calculated the potential energy profile for this process by varying this angle in step of 5°, from the computed equilibrium value of ca. 77°, found in the most stable conformers of **1a** and **2a**, up to 45°. For each constrained value of the I–C_{ac}–O_1 angle, the structures were optimized leaving all of the other geometrical parameters free to vary. To better estimate the energy barriers, further calculations were performed to locate the transition states (TS) close to the maximum energy point.

The total energy (electronic + nuclear repulsion energy) differences of the in vacuo or solvated structures from that of the corresponding most stable rotamer obtained with unconstrained minimization are reported in Table 3, together with the values of the dihedral angles that are affected by the I–C_{ac}–O_1 angle variation.

The energy profiles do not vary substantially including the solvent in the energy calculation, making us confident that the equilibrium geometry and the exchange path should be similar in vacuo and in chloroform; the estimated energy barriers, including the solvent contribution, are 48 and 59 kJ/mol for **1a** and **2a**, respectively. Should the entropic contribution to the free energy barriers be negligible in comparison to the total energy term, then the calculated barriers must be quite close to the free energy barriers. In fact, the ΔE values found for the transition structures are close to the $\Delta G^{\ddagger}$ values roughly estimated from the ^{17}O NMR spectra (**1a** $\cong$ 44 kJ/mol, **2a** $\cong$ 54 kJ/mol). The difference of the energy barriers for the

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TABLE 3. Selected Dihedrals and PBE0/LANL2DZDP Total Energy Differences, from That of the Most Stable Rotamer, at Variable $I-C_{ac}-O_1$ Angle. Energies were Calculated Either in vacuo or Using the PCM Model for $CHCl_3$

	1a				2a			
$I-C_{ac}-O_1$ (deg)	ΔE (kJ/mol)		Dihedral angles (deg)		ΔE (kJ/mol)		Dihedral angles (deg)	
	in vacuo	solvated	$C_i-I-O_1-C_{ac}$[a]	$C_o-C_i-I-O_2$[a,b]	in vacuo	solvated	$C_i-I-O_1-C_{ac}$	$C_o-C_i-I-O_2$[a]
76.2	0	0[c]	−1.0	53.5				
77.0					0	0	0.0	0.0
70	3.3	5.7	−1.3	56.4	4.4	5.0	0.0	0.0
65	11.8	12.2	0	89.8	14.0	14.9	0.0	0.0
60	25.7	26.6	0.1	89.4	29.6	31.3	−0.1	0.0
55	34.7	35.1	−79.2	84.9	48.2	50.8	−0.2	0.0
50	17.5	19.7	−80.5	85.6	30.0	27.7	−87.2	−0.5
45	5.8	8.2	−80.4	83.3	16.5	14.9	−87.3	−0.5
55.8, TS	45.2	48.3	−42.7	74.1				
53.6, TS					57.0	59.0	−42.4	2.7

[a] For a direct comparison among the dihedrals of the considered atomic configurations of **1a**, the conformational enantiomers with the smallest $C_o-C_i-I-O_2$ angle between the unconstrained acetoxy unit and the clockwise C_o were considered. [b] O_2 belongs to the unconstrained moiety, while C_o is the closest one in the clockwise direction. [c] As discussed in the Supporting Information when taking into account the solvent effect on the energy, the conformer with $C_o-C_i-I-O = 90°$ is predicted to be the more stable; accordingly, the values reported in this column are relative to that structure.

exchange of the oxygens in the acetoxy groups of the two compounds is thus estimated to be ca. 10 kJ/mol experimentally and 11 kJ/mol theoretically and explains the different number of oxygen signals observed experimentally. It is worth noting that, while in the unconstrained global minimum energy structure of both **1a** and **2a** the two carboxylic groups (i.e., the two acetoxy moieties in **1a**, and the acetoxy moiety and the iodoxolone in **2a**) lay in the same plane, in the transition state of both compounds the acetoxy group involved in the exchange moves out from the plane, as can be seen in Table 3 considering the variation of the $C_i-I-O_1-C_{ac}$ dihedrals. For values of $I-C_{ac}-O_1$ larger than that of the TS, the considered dihedral is nearly 0° in both compounds, while for smaller values, it is ca. 80° in **1a** and 87° in **2a**. We also point out that for $I-C_{ac}-O_1 \cong 40°$ the conformation is stable and the rotation around the I−O bond from this value to that of the most stable conformer has a very low barrier (see Supporting Information). It is thus apparent that a degenerate [1,3] sigmatropic shift of iodine between O_1 and O_2 is the actual pathway leading to the equivalence observed by the ^{17}O NMR for compounds **1**, and this observation rules out chelate or ion pair structures.

The origin of the difference in the energy barrier between compounds **1a** and **2a** seems to be related to the structural constraint imposed by the iodoxolone ring, which in compounds **2** forces the $I-O_4$ bond and, consequently, the $I-O_3$ bond to lay in the plane of benzene. To verify this point, we calculated the energy barrier for the exchange in **1a** constraining one of the two $I-O_2$ bonds to be coplanar with benzene ($C_o-C_i-I-O = 0°$) and studying the acetoxy oxygens exchange in the same way as discussed above. The total energy difference between the transition state and the minimum energy constrained structure is (in vacuo) 57.7 kJ/mol, a value much higher than that of 46.0 kJ/mol observed in the unconstrained geometry and very close to that of 57.0 kJ/mol found for **2a** at the same theory level; this result confirms the structural constraint as the reason for the difference in the exchange energy barrier.

To further investigate the dependence of the barrier on the $C_o-C_i-I-O_2$ angle, calculations were performed on **1a** studying the exchange imposing a constraint of 45°, a value intermediate between that of 0 and ca. 90° (a value found in most of the configurations involved in the unconstrained exchange; see Table 3). As it could be expected, constraining this dihedral to 45° leads, in vacuo, to an exchange barrier of 50.7 kJ/mol, intermediate between the situations described above.

The sigmatropic shift is impossible for the exchange between O_3 and O_4 for evident geometrical reasons; thus the breaking of the $I-O_3$ bond could not be compensated by the simultaneous formation of the $I-O_4$ bond, and in fact, the barrier for the exchange is calculated to be ca. 173 kJ/mol.[14] The height of this barrier is consistent with the observation of two ^{17}O NMR signals for the oxygens of the iodoxolone ring in either compounds **2** and **3**.

A dynamic phenomenon with an energy barrier similar to those of the sigmatropic shift had been observed by Ochiai, who gave evidence[9] of the stereochemical nonrigidity in λ^3 iodanes through pseudorotation on iodine. However, while pseudorotation leads to equivalence of a pair of ligands in a chiral situation, the [1,3] sigmatropic shift leads to equivalence of the two oxygens in the same ligand, and the two phenomena are independent each other.

As far as the ^{13}C NMR spectra of these derivatives are concerned, it has already been observed and discussed[15] in a systematic way that, in λ^3 and λ^5 iodanes, the usual "heavy atom effect" of iodine on the ^{13}C chemical shift of the *ipso* carbon C_i is compensated or overwhelmed. This point has been empirically related to the oxidation state of iodine. We can add that the range of ^{13}C chemical shift of the *ipso* carbon is very narrow, with the δ values being equal to 122.6 ± 1.1 ppm for derivatives **1** and 118.6 ± 0.4 ppm in the case of **2** and **3**.

Conclusions

Coupling the ^{17}O NMR spectroscopy to quantum mechanics calculations allowed us to gain a deeper understanding about the structural and dynamical aspects of bis(acyloxy)iodoarenes and benzoiodoxolones in chloroform, giving substantial evidence that the T structure observed in the solid state is also adopted

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(14) The barrier was estimated as the total energy difference between the structure of **2a** with the carboxylate plane parallel and perpendicular to that of benzene; the latter has been obtained constraining the $C_i-C_o-C_{ac}-O_3$ dihedral angle to 90° while the first is the global minimum energy structure.

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in solution; further, the "free" carboxylic groups of derivatives **1** and **2** show a dynamic behavior, observable only in the ^{17}O NMR. This behavior is ascribed to a [1,3] sigmatropic shift of the iodine atom between the two oxygen atoms of the carboxylic groups, and the energy involved in this process varies significantly between bis(acyloxy)iodoarenes and benzoiodoxolones.

Experimental Section

The new compounds **2b** and **3c** were prepared by the following procedures.

1-Propionoxy-1*H*-1λ^3-benzo[*d*][1,2]iodoxol-3-one (2b) was obtained by modification of Merkushev's method[16] used to obtain derivatives **1**. To **2a** (1.0 g, 3.2 mmol), obtained by Baker's method,[17] were added a stoichiometric amount of dry propionic acid (0.237 g, 3.2 mmol) and then 3 mL of dry chloroform, obtaining a clear solution. This solution was then heated to 45 °C under a residual pressure of 35 mmHg, until dryness. The white solid obtained in this way was washed with cold, dry acetonitrile and filtered under vacuum, to leave, in quantitative yield, pure **2b** as a white powder. As far as the melting point is concerned, we observed a first transition point at 120−122 °C, characterized by a sensible volume increase with partial melting, and a second transition point at 220−223 °C, when melting is complete. This last melting point coincides with that of 2-iodosobenzoic acid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (dd, $J = 7.6$, 1.3 Hz, 1H), 8.00 (d, $J = 8.4$ Hz, 1H), 7.95 (td, $J = 8.4$, 1.5 Hz, 1H), 7.72 (td, $J = 7.6$, 1.3 Hz, 1H), 2.56 (q, $J = 7.6$ Hz, 2H), 1.25 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 179.2, 168.0, 135.9, 132.8, 131.0, 129.1, 128.8, 118.3, 27.0, 9.5. Anal. Calcd for $C_{10}H_9IO_4$: C, 37.50; H, 2.83. Found: C, 37.25; H, 2.91.

1-*iso*-Propoxy-1*H*-1λ^3-benzo[*d*][1,2]iodoxol-3-one (3c) was prepared according to the method described[17] for obtaining **3a**,**b**. To compound **2a** (1.0 g. 3.2 mmol), obtained by Baker's[17] method, was added 5 mL of isopropyl alcohol; the obtained dispersion was boiled until complete solubilization and was then left for 12 h in the refrigerator. Colorless needles of **3c** separated and were filtered and washed with cold, dry MeCN to obtain 0.97 g (quantitative yield) of **3c** as a white solid, mp 192−195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (dd, $J = 7.7$, 1.1 Hz, 1H), 7.88 (m, 2H), 7.69 (td, $J = 7.3$, 1.1 Hz, 1H), 4.33 (h, $J = 6.2$ Hz, 1H), 1.35 (d, $J = 6.2$ Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 167.9, 134.8, 132.7, 130.8, 130.7, 126.0, 119.1, 75.5, 25.2. Anal. Calcd for $C_{10}H_{11}IO_3$: C, 39.22; H, 3.62. Found: C, 39.05; H, 3.70.

Computational Methods. Structure optimizations of compounds **1a**, **2a**, and **3a** were performed at the DFT level employing the recently developed parameter free PBE0 functional,[11] as implemented in the commercially available Gaussian 03 suite of programs.[18] As discussed in the Supporting Information, the PBE0 functional was chosen over the popular B3LYP[19] functional after comparing its capability of reproducing the relevant experimental structural parameters of the studied compounds. The effective core potential valence basis set LANL2DZ[12] (i.e., D95V[12a] basis set for the first row elements and the Los Alamos ECP plus DZ on iodine[12b]) extended with polarization (d) and diffuse (p) functions[12c,d] was employed for all atoms. The LANL2DZ basis set was chosen in view of the previous literature on I(III) hypervalent compounds,[20] and the addition of polarized and diffuse functions improves the results, obtaining geometrical parameters closer to those found experimentally (see Table S4 in Supporting Information). Numerical integration was performed using a pruned grid having 99 radial shells and 509 angular points per shell. For unconstrained geometry (both minimum energy and transition structures), vibrational analysis was carried out at the same level of theory to check the character of the stationary point; the normal mode corresponding to the imaginary frequency in the transition structure is similar in compounds **1a** and **2a** and clearly involves the oxygens exchange.

In order to find the global minima, we optimized the geometry of the studied compounds starting from several conformations, constructed with the freely available program Molden,[21] differing each by 90° in the value of the dihedral angle around the I−O bonds.

The three TSs (two for **1a**, unconstrained or with the plane of one of the acetoxy groups constrained to be coplanar with the $I-C_i$ bond, and one for **2a**) were obtained starting from the atomic configuration where the $I-C_{ac}-O_1$ angle is 55° and the plane of the acetoxy group involved in the iodine shift is parallel to the $I-C_i$ bond.

The solvent effect has been studied by employing the polarizable continuum model (PCM)[13] in single-point energy calculations on the in vacuo optimized geometries, using the current implementation[13a] in Gaussian 03 of PCM, performing a reaction field calculation using the IEF-PCM model.[13b−d] All PCM calculations were carried out at 298.15 K using an average tesserae area of 0.2 Å^2.

Graphics of molecular models were generated using the freely available VMD[22] software.

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Supporting Information Available: Extended and detailed computational results (comparison of the B3LYP and PBE0 functionals performance, rotational barriers, Cartesian coordinates, and energies of constrained and unconstrained optimized geometry). General synthetic procedures for the known compounds, their ^{1}H and ^{13}C NMR data, copies of the ^{1}H and ^{13}C NMR spectra of the new compounds **2b** and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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