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Hypervalent Organoiodine. Crystal Structure of Phenylhydroxytosyloxyiodine

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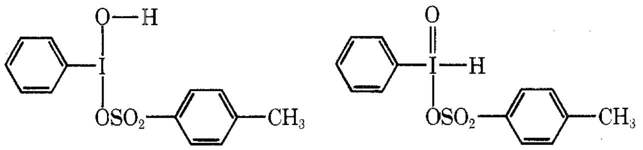
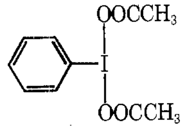
Phenylhydroxytosyloxyiodine was subjected to x-ray analysis and was found to exhibit the three-coordinate iodine(III) structure **1a** in the solid state. The structure of **1a** was refined, and the positions of all hydrogen atoms were determined. H_1 is clearly bonded to O_1 and not to iodine as the four-coordinate iodine(V) structure **1b** would demand.

A number of compounds believed to contain a hydroxy group bound to trivalent iodine are known.[1-8] One such substance, phenylhydroxytosyloxyiodine (**1**), reported in 1970 by Neiland and Karele, is accessible through the action of toluenesulfonic acid on iodosobenzene diacetate (**2**).[9] We wondered about the possibility that **1** may prefer the four-coordinate iodine(V) structure, **1b**, over the three-coordinate iodine(III) structure, **1a**, which had been assigned to it and that such "tautomerism" may be general among compounds thought to contain the >I–OH moiety. We drew analogy from organophosphorus chemistry. For example, dialkylphosphonates may exhibit the four-coordinate phosphorus(V) structure, **3**, as well as the corresponding three-coordinate phosphorus(III) structure, **4**.[10]



a **b**

1



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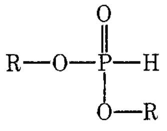

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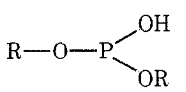

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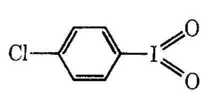


5

A spectroscopic analysis of **1** does not lead to a clear-cut choice between **1a** and **1b**. The infrared spectrum exhibits a strong absorption band which maximizes at 3.25 μ (~3100 cm^{-1}) and extends from 2.9 to 3.9 μ. This may be due to –O–H stretching in **1a**, but, since **1** possesses both aromatic and aliphatic C–H bonds, such an assignment is uncertain. The ^{1}H NMR spectrum of **1** (Me_2SO-d_6) exhibits a singlet at ~δ 9 which belongs to an exchangeable hydrogen atom. There is, however, no reason to presume that hydrogen–deuterium exchange will be possible for **1a** but not for **1b**, especially since **1b** may isomerize to **1a** in solution.

Results and Discussion

Because of this structural dichotomy and because structural studies on hypervalent organoiodine compounds are uncommon, compound **1** was subjected to single-crystal x-ray analysis. The results of our study are summarized in Tables I and II and Figure 1.

It seems clear that, at least in the solid state, phenylhydroxytosyloxyiodine exhibits structure **1a**, a conclusion which rests on the following considerations: (1) The I–O_1 bond distance in **1** was found to be 1.940 Å, consistent with a single bond distance of 1.99 Å computed from covalent radii. *p*-Chloroiodoxybenzene (**5**) has two iodine–oxygen "double bonds", and they exhibit lengths of 1.60 and 1.65 Å.[11] (2) All hydrogen atoms were located in a difference Fourier, and all atoms were included in least-squares refinements. The distance from O_1 to the "tautomeric" hydrogen atom was found to be 0.75 Å while the distance from iodine to the same hydrogen atom was found to be 2.17 Å. This result is consistent with an O–H bond instead of a I–H bond. (3) The geometry about iodine in **1** is T-shaped (refer to the O_1–I–O_2, O_1–I–C, and O_2–I–C bond angles), a configuration which has been observed with other trivalent organoiodine compounds.[12-14] Also, it seems likely that structure **1b** would be tetrahedral about the iodine atom.

It is noteworthy that the I–O_2 bond distance in **1a** (2.473 Å) is significantly longer than the computed covalent single bond distance of 1.99 Å. At the same time, the O_2–S bond distance (1.467 Å) is significantly shorter than the computed distance of 1.70 Å. These facts, coupled with the observation that all three sulfur–oxygen bonds are comparable in length, indicate that the I–O_2 bond in **1a** may possess some ionic character. We know of only one other compound with an >I–OH unit which has been subjected to x-ray analysis, and it is similar

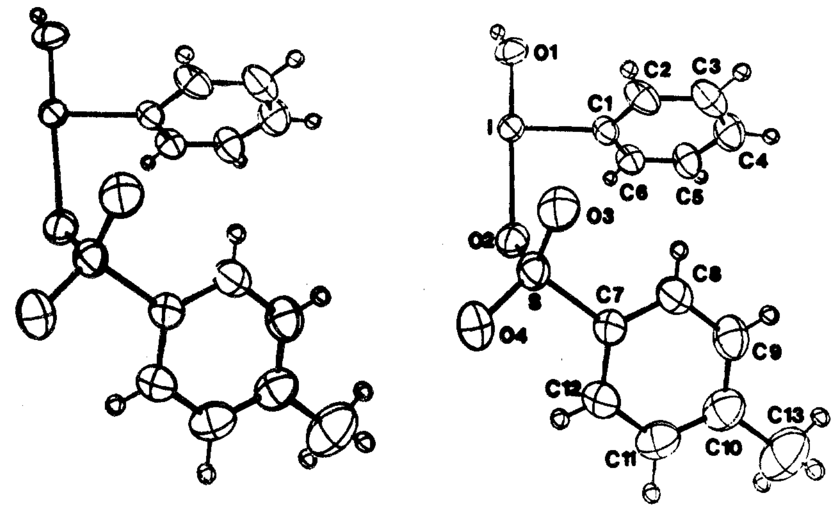


Figure 1. Stereoscopic view of phenylhydroxytosyloxyiodine (**1a**).

Table I.[a] **Bond Distances (Å) in 1a**

Bonding pair	Distance	Bonding pair	Distance
I–O(1)	1.940 (4)	C(6)–H(6)	0.89 (4)
I–O(2)	2.473 (3)	C(7)–C(8)	1.375 (7)
I–C(1)	2.083 (4)	C(7)–C(12)	1.363 (6)
S–O(2)	1.467 (3)	C(8)–C(9)	1.379 (8)
S–O(3)	1.453 (4)	C(8)–H(7)	0.82 (5)
S–O(4)	1.436 (3)	C(9)–C(10)	1.368 (8)
S–C(7)	1.767 (4)	C(9)–H(8)	0.85 (6)
C(1)–C(2)	1.375 (6)	C(10)–C(11)	1.379 (9)
C(1)–C(6)	1.377 (6)	C(10)–C(13)	1.518 (9)
C(2)–C(3)	1.369 (8)	C(11)–C(12)	1.381 (8)
C(2)–H(2)	1.00 (5)	C(11)–H(9)	0.94 (7)
C(3)–C(4)	1.370 (9)	C(12)–H(10)	0.85 (6)
C(3)–H(3)	0.94 (6)	C(13)–H(11)	0.93 (10)
C(4)–C(5)	1.374 (8)	C(13)–H(12)	1.16 (11)
C(4)–H(4)	0.91 (6)	C(13)–H(13)	0.73 (6)
C(5)–C(6)	1.364 (7)	H(1)–O(1)	0.73 (5)
C(5)–H(5)	0.91 (6)	H(1)–O(3)	2.01 (5)

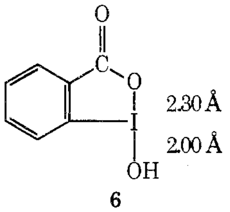
[a] Estimated standard deviations are given in parentheses.

Table II.[a] **Bond Angles (deg) in 1a**

Triad	Angle	Triad	Angle
O(1)–I–O(2)	178.8 (1)	C(1)–C(6)–H(6)	123.1 (26)
O(1)–I–C(1)	92.8 (2)	C(5)–C(6)–H(6)	117.0 (26)
O(1)–I–H(1)	19.4 (14)	C(8)–C(7)–C(12)	120.5 (5)
O(2)–I–C(1)	86.0 (1)	C(7)–C(8)–C(9)	119.1 (5)
O(2)–I–H(1)	161.0 (14)	C(7)–C(8)–H(7)	120.5 (33)
C(1)–I–H(1)	100.0 (15)	C(9)–C(8)–H(7)	120.2 (33)
O(2)–S–O(3)	110.8 (2)	C(8)–C(9)–C(10)	121.8 (5)
O(2)–S–O(4)	111.0 (2)	C(8)–C(9)–H(8)	115.2 (40)
O(2)–S–C(7)	105.5 (2)	C(10)–C(9)–H(8)	123.0 (39)
O(3)–S–O(4)	115.1 (2)	C(9)–C(10)–C(11)	117.8 (5)
O(3)–S–C(7)	107.0 (2)	C(9)–C(10)–C(13)	121.5 (7)
O(4)–S–C(7)	106.8 (2)	C(11)–C(10)–C(13)	120.7 (8)
C(2)–C(1)–C(6)	121.4 (4)	C(10)–C(11)–C(12)	121.4 (6)
C(1)–C(2)–(3)	118.3 (5)	C(10)–C(11)–H(9)	121.6 (44)
C(1)–C(2)–H(2)	128.0 (27)	C(12)–C(11)–H(9)	116.1 (44)
C(3)–C(2)–H(2)	113.7 (27)	C(7)–C(12)–C(11)	119.4 (6)
C(2)–C(3)–C(4)	120.7 (5)	C(7)–C(12)–H(10)	118.9 (38)
C(2)–C(3)–H(3)	117.1 (35)	C(11)–C(12)–H(10)	121.5 (39)
C(4)–C(3)–H(3)	122.2 (35)	C(10)–C(13)–H(11)	108.2 (100)
C(3)–C(4)–C(5)	120.6 (5)	C(10)–C(13)–H(12)	115.4 (44)
C(3)–C(4)–H(4)	126.7 (41)	C(10)–C(13)–H(13)	99.4 (53)
C(5)–C(4)–H(4)	112.6 (41)	H(11)–C(13)–H(12)	113.8 (113)
C(4)–C(5)–C(6)	119.3 (5)	H(11)–C(13)–H(13)	128.0 (112)
C(4)–C(5)–H(5)	118.4 (37)	H(12)–C(13)–H(13)	91.2 (72)
C(6)–C(5)–H(5)	122.2 (37)	I–O(1)–H(1)	98.1 (46)
C(1)–C(6)–C(5)	119.7 (5)	O(1)–H(1)–O(3)	166.7 (63)

[a] Estimated standard deviations are given in parentheses.

in this regard.[15] Thus, 1,3-dihydro-1-hydroxy-3-oxo-1,2-benziodoxole (**6**) exhibits an external I–O bond length of 2.00 Å and an internal I–O bond length of 2.30 Å.[15,16] The hydrogen atoms in **6** were not located, but the molecule is T-shaped about iodine and appears to exhibit a three-coordinate iodine(III) structure.[15,16]



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Experimental Section

General. ^1H NMR spectra were recorded on a Varian Model A-60 NMR spectrometer with Me_4Si as an internal reference. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer and were calibrated with polystyrene. Melting points are uncorrected.

Phenylhydroxytosyloxyiodine (1a). This material was synthesized by a procedure similar to that described by Neiland and Karele, who subjected iodosobenzene diacetate (**2**) to the action of $TsOH-H_2O$ in hot dichloroethane.[9] We employed acetonitrile as the reaction solvent instead of dichloroethane, and we allowed the reaction to proceed at room temperature.

Compound **1a** was purified by its initial dissolution in a minimum quantity of methanol. To that solution was added diethyl ether until a cloud point was reached. Upon standing at room temperature, the Et_2O-CH_3OH solution yielded **1a** as colorless prisms, mp 136–138.5 °C (lit.[9] mp 140–142 °C).

Spectral Data for 1a. ^1H NMR (Me_2SO-d_6) δ 2.38 (s, $-CH_3$), 6.9–8.3 (complex multiplet, aromatic hydrogens), this multiplet exhibits *apparent* singlets at δ 7.08, 7.22, and 7.53, an *apparent* triplet with lines at δ 7.59, 7.62, and 7.65, and distorted *apparent* doublets centered at δ 8.13 and 8.25; ~δ 9.1 (s, –OH), this singlet disappeared when D_2O was added to the sample with the concomitant appearance of a "new" singlet at δ 4.64. Also, the chemical shift of the –OH singlet fluctuates from sample to sample. Finally, machine integration yielded an area ratio of 40 mm:131 mm:14 mm for the three types of resonances described above.

Crystal Data. $C_{13}H_{13}O_4SI$, mol wt 392.21. A colorless prism, 0.20 × 0.22 × 0.25 mm, was mounted in a glass capillary such that the crystal orientation was random. The width at half height from ω scans was 0.15°.

Space Group and Cell Data. System, monoclinic; centering, primitive; space group, $P2_1/n$; extinctions, $h0l$, $h + l \neq 2n$, $0k0$, $k \neq 2n$; cell constants, $a = 15.165$ (8) Å, $b = 6.055$ (3) Å, $c = 16.488$ (4) Å, $v = 1451.6$ (2) Å^3, $\lambda = 0.71073$, $\alpha = 90.°$, $\beta = 106.50$ (2)°, $\gamma = 90.°$, $\rho = 1.795$ g/cm^3, $Z = 4$, μ 23.78 cm^{-1}, $F(000) = 768$.

Data Collection. Syntex $P\bar{1}$ diffractometer, Mo Kα radiation filtered by a graphite-crystal incident-beam monochromator; temperature 23 ± 1 °C; crystal to detector distance 19 cm; counter aperature width 2.0 mm; incident beam collimator diameter 1.5 mm; take-off angle 3°; technique, θ–2θ scan; scan rate, 4–24°/min; the variable scan rate permits rapid data collection for intense reflections where a fast scan rate is employed and assures good counting statistics for weak reflections when a slow scan rate is employed. For intense reflections when the counting rate floods the scintillation detector, a coincidence correction is automatically applied to the data. Stationary-crystal stationary-counter background counts were taken at each end of the scan range. The ratio R of scan time to background counting time was 2.0; range of data, $0 <$ (Mo Kα) ≤ 45; scan range 2θ (Mo Kα1) $- 0.8°$ to 2θ (Mo Kα2) $+ 0.8°$; total number of reflections collected, 2309; number of independent reflections collected, 2219; as a check on crystal and electronic stability, three representative reflections were measured periodically. A linear decrease in all three standard reflections to ca. 60% of their original intensity was observed.

Data Reduction. Intensities and standard deviations on intensities were calculated with the formulas

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, and the parameter p is a factor introduced to downweight intense reflections. In our case, p was set to 0.07. Lorentz and polarization corrections were applied to the data. A correction for changes in intensity of the standard reflections was applied and was based on the linear decrease in intensity of these reflections. Each standard reflection exhibited the same percent decrease in intensity during data collection. An extinction correction was found not to be necessary. Also, an absorption correction was not necessary because of the nearly spherical geometry of the crystal.

Structure Solution. The structure was solved by the Patterson method. The Patterson map showed the position of the iodine atom. Least-squares refinement of the atoms resulted in agreement factors (defined below) of $R_1 = 0.35$ and $R_2 = 0.43$. The remaining nonhydrogen atoms were located in succeeding difference Fourier synthesis.

Least-Squares Refinement. In full-matrix least-squares refinement, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized where the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2B. Anomalous dispersion effects were included in F_c, the values of $\Delta f'$ and $\Delta f''$ being those of D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970). Only the 1566 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The following values pertain to the final cycle of least-squares refinement.

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.032$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.042$$

Number of observations, 1566; number of atoms, 32; number of variable parameters, 224; esd of an observation of unit weight, 1.089; maximum parameter shift, 1.0 times its esd in H11, H12, and H13, all other shifts were less than 0.2 times their esd's.

Other Criteria. The final difference Fourier map showed no residual electron density as high as hydrogen atoms on a previous difference Fourier map. Plots of $\Sigma w(|F_o| - |F_c|)^2$ vs. $|F_o|$, $\lambda^{-1} \sin \theta$, reflection order in data collection, and various classes of indices showed no unusual trends.

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Registry No.—**12**, 27126-76-7.

Supplementary Material Available. Tables of temperature factors, thermal vibration amplitudes, weighted least-squares planes, and listings of h, k, l, F_o, and F_c (5 pages). Ordering information is given on any current masthead page.

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Molybdenum Hexacarbonyl Catalyzed Rearrangement of Epoxides

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Epoxides rearrange to aldehydes in the presence of a catalytic amount of molybdenum hexacarbonyl. Vinyl epoxides afford α,β-unsaturated aldehydes via the anticipated β,γ-unsaturated aldehyde. The isomerization of the latter is postulated to occur via a hydrido π-allylmolybdenum carbonyl intermediate. A by-product of all reactions is a deoxygenated olefin of retained stereochemistry with respect to the epoxide.

The acid- or base-catalyzed rearrangement of epoxides (oxiranes) is a subject of considerable interest.[1] Several reports have appeared in the literature concerning the use of metal carbonyls as rearrangement catalysts. Under drastic conditions (210 °C, sealed tube), chlorocarbonylbis(triphenylphosphine)rhodium and Wilkinson's catalyst convert stilbene