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(3-Chloro-2-hydroxy-5-nitrophenyl)(2'-chlorophenyl)iodonium Hydroxide, Inner Salt*

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Abstract. $C_{12}H_6Cl_2INO_3$, $M_r = 410.00$, monoclinic, $P2_1/n$, $a = 15.928$ (9), $b = 4.623$ (2), $c = 18.271$ (6) Å, $\beta = 105.58$ (2)°, $Z = 4$, $D_x = 2.101$, $D_m = 2.11$ Mg m^{-3}; R on $F^2 = 0.055$ (2302 unique reflections). The molecule exists as a zwitterion with an intramolecular $I^+ \cdots O$ distance of 2.755 (4) Å. The I—C bond distances were found to be 2.106 (6) and 2.105 (5) Å, with a C—I—C angle of 98.4 (2)°. Intermolecular ionic attraction between I^+ and O^- causes the formation of infinite chains along the y axis of the cell.

Introduction. The title compound is an intermediate in the preparation of *o*-iododiphenyl ethers. The preparation, NMR data and other chemical information for $C_{12}H_6Cl_2INO_3$ have been reported by Page, Mazzola, Mighell, Himes & Hubbard (1979). Transparent yellow needle-shaped crystals suitable for X-ray analysis were prepared by recrystallization from formic acid. Analysis: calculated for $C_{12}H_6Cl_2INO_3$: C 35.16, H 1.48, N 3.42, Cl 17.30, I 30.95%: composition found: C 35.63, H 1.48, N 3.65, Cl 17.59, I 31.30%. The density was measured by the flotation method using a mixture of halogenated organic liquids. A crystal of dimensions 0.15 × 0.04 × 0.06 mm was

mounted on a four-circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å). Cell dimensions were determined by a least-squares refinement of 15 reflections with 2θ values ranging between 17 and 32°. The monoclinic symmetry was verified by reduction procedures (*International Tables for X-ray Crystallography*, 1969) and the space group $P2_1/n$, which was initially assigned by analysis of precession photographs, was confirmed on the diffractometer by checking 310 systematically absent positions.

Diffraction intensities were measured in the bisecting mode with $4° \leq 2\theta \leq 50°$. The peaks were scanned over a 2θ range of ($K\alpha_1 - 1.0°$) to ($K\alpha_2 + 1.0°$) using variable scan rates of 1.0 to 29.3° min^{-1} depending on the intensity of the preliminary count. Background counts were taken at each end of the scan with a ratio of total background time to scan time of 1.0. Three standard reflections, which were measured periodically, showed a gradual loss of intensity of approximately 9% over the course of data collection. The intensity data were corrected for the drop in the standard reflections. The estimated standard deviation in intensity, $\sigma(I)$, was calculated from $\sigma^2(I) = TC + (0.016TC)^2$, where TC is the total observed counts and the constant was derived from a statistical analysis of the intensity distributions of the three standard reflections. Corrections were applied for Lorentz and polarization factors and for absorption ($\mu = 2.860$ mm^{-1}). Of the 2696 reflections measured, there were 2302 unique reflections with 367 measured more than once. One reflection was either

mismeasured or had its intensity enhanced by simultaneous diffraction: this reflection did not contribute in the refinement. Equivalent observations were then averaged. The internal agreement factors between symmetry-related reflections were: average deviation $= 1/h \sum_h \sum_{i=1}^N ||I(\mathbf{h})_i - \bar{I}(\mathbf{h})_i|/|\sigma(\mathbf{h})_i| = 0.8$ and $wR = (A/B)^{1/2} = 0.032$. where $A = \sum_h \sum_{i=1}^N ||I(\mathbf{h})_i - \bar{I}(\mathbf{h})_i|^2/|\sigma(\mathbf{h})_i|^2$, $B = \sum_h \sum_{i=1}^N ||I(\mathbf{h})_i|^2/|\sigma(\mathbf{h})_i|^2$, and $I(\mathbf{h})_i = i$th intensity of reflection $\mathbf{h}$, $\bar{I}(\mathbf{h})_i =$ mean value of the N equivalent reflections, and $\sigma(\mathbf{h})_i = i$th σ of the reflection $\mathbf{h}$.

The I and Cl atoms were located by using a three-dimensional Patterson map. The structure was then solved by conventional heavy-atom techniques. The model was refined by full-matrix anisotropic least-squares analysis. In the final cycles of refinement, the H atoms on the benzene rings were held fixed at their ideal calculated positions assuming trigonal geometry and a C—H bond length of 1.0 Å. The function minimized was $\sum w(F_{obs}^2 - F_{calc}^2)^2$, where $w = |Lp/\sigma(I)|^2$. The final R factors based on F^2 are $R = \sum |F_{obs}^2 - F_{calc}^2|/\sum |F_{obs}^2| = 0.055$ and $wR = [\sum w(F_{obs}^2 - F_{calc}^2)^2/\sum wF_{obs}^4]^{1/2} = 0.068$. The average and maximum shift divided by error were 0.002 and 0.01, respectively. The scattering factors used were those of Cromer & Mann (1968) for the heavy atoms and those of Stewart, Davidson & Simpson (1965) for H. Corrections for anomalous dispersion were applied for Cl and I (*International Tables for X-ray Crystallography*, 1974). A difference Fourier map was calculated and no peak in the vicinity of O(1) was detected (see Fig. 1 for atom numbering). An analysis of the difference map showed ripples less than 1 Å from both I

and Cl(2) and one peak ($\simeq 1$ e Å^{-3}) 1 Å from R1C(4) and 1.5 Å from R1C(5). The presence of the peak and ripples in the difference map suggests that small errors exist in scattering factors and absorption corrections. No other map feature exceeded 0.4 e Å^{-3}. Table 1 lists the final atomic parameters.* Calculations were performed with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. The bond distances and angles for the title compound are illustrated in Fig. 1. The two I—C distances of 2.106 (6) and 2.105 (5) Å are comparable with those found in diphenyliodonium nitrate $|2.114$ (9) Å| (Wright & Meyers, 1972) and diphenyliodonium chloride $(2.08$ Å) (Khotsianova & Struchkov, 1957). The C—I—C angle $[98.4\ (2)°]$ is appreciably greater than the theoretical value of $90°$, primarily due to the effects of steric hindrance. Similar deviations from $90°$ have also been observed in diphenyliodonium fluoroborate $(94°)$ (Struchkov & Khotsianova, 1960), diphenyliodonium chloride and

Table 1. *Positional parameters and isotropic thermal parameters* (Å^2) *with estimated standard deviations in parentheses*

Equivalent isotropic temperature factors for the non-hydrogen atoms were calculated from $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U
I	-0.14202 (2)	0.20796 (8)	0.70536 (2)	0.0470 (2)
Ring 1 (R1)				
C(1)	0.0235 (3)	0.0122 (12)	0.7027 (3)	0.044 (3)
C(2)	0.0194 (4)	0.0746 (13)	0.6472 (3)	0.051 (3)
C(3)	0.0998 (4)	-0.0496 (15)	0.6526 (4)	0.065 (4)
C(4)	0.1370 (4)	0.2341 (15)	0.7135 (4)	0.077 (5)
C(5)	0.0951 (4)	-0.2937 (15)	0.7685 (3)	0.065 (4)
C(6)	0.0129 (4)	-0.1680 (13)	0.7629 (3)	0.051 (3)
Cl(1)	0.02699 (10)	0.2939 (4)	0.57171 (8)	0.0666 (10)
H(3)*	0.131	-0.008	0.613	0.080
H(4)	0.195	-0.324	0.717	0.080
H(5)	0.123	-0.424	0.812	0.080
H(6)	-0.019	-0.210	0.802	0.080
Ring 2 (R2)				
C(1)	-0.2261 (3)	-0.0350 (12)	0.6185 (3)	0.039 (3)
C(2)	-0.3085 (3)	0.0008 (12)	0.6323 (3)	0.043 (3)
C(3)	-0.3744 (3)	-0.1671 (13)	0.5808 (3)	0.044 (3)
C(4)	-0.3587 (3)	-0.3357 (12)	0.5241 (3)	0.044 (3)
C(5)	-0.2751 (3)	-0.3417 (12)	0.5144 (3)	0.043 (3)
C(6)	-0.2065 (3)	-0.1892 (13)	0.5621 (3)	0.045 (3)
O(1)	0.3195 (2)	0.1634 (8)	0.6842 (2)	0.052 (2)
Cl(2)	-0.47843 (9)	-0.1563 (4)	0.59386 (8)	0.0621 (9)
N	-0.2600 (3)	0.5106 (12)	0.4527 (3)	0.056 (3)
O(2)	0.1892 (3)	-0.4901 (12)	0.4399 (2)	0.090 (4)
O(3)	-0.3174 (3)	-0.6680 (11)	0.4170 (2)	0.078 (3)
H(4)	-0.407	-0.452	0.490	0.080
H(6)	0.146	-0.193	0.555	0.080

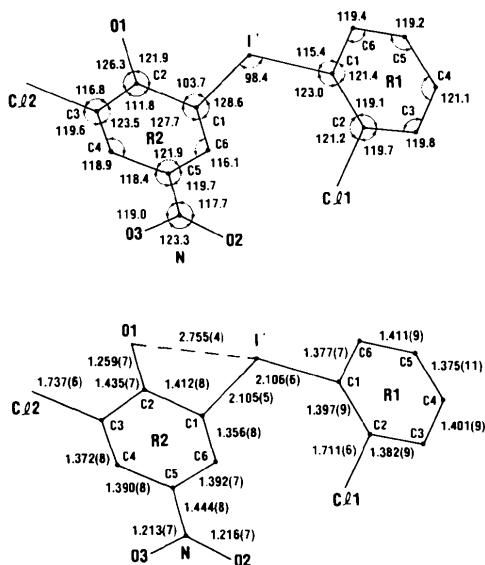* The C atom and the bonded H atom are assigned the same number.

Fig. 1. Bond distances (Å) and angles (°). E.s.d.'s in bond distances are given in parentheses. E.s.d.'s in bond angles range from 0.2 to $0.6°$.

Table 2. Summary of the results of the least-squares-planes analyses

Atoms used to define the planes are marked with asterisks. The estimated standard deviations for the distances to the planes are in the range 0·003–0·005 Å.

	Ring 1 (R1)				Ring 2 (R2)		
*C(1)	0·003 Å	I	0·131 Å	*C(1)	0·022 Å	I	0·126 Å
*C(2)	0·003	Cl(1)	0·029	*C(2)	0·016	Cl(2)	0·028
*C(3)	0·000			*C(3)	0·002	O(1)	0·058
*C(4)	0·002			*C(4)	0·014	N	0·047
*C(5)	0·002			*C(5)	0·011	O(2)	0·211
*C(6)	0·000			*C(6)	-0·008	O(3)	0·104

Table 3. Angles between the normals to the least-squares planes of the two benzene rings, the nitro group and the iodine plane

Plane	R2	Nitro group†	Iodine plane‡
R1*	74·3°	79·7°	74·8°
R2	–	8·48	21·2
Nitro group	–	–	28·4

* R1: ring defined by C(1)···C(6); R2: ring defined by C(1)···C(6).

† Nitro group: N(1), O(2), O(3).

‡ Iodine plane: I, R1C(1), R2C(1).

iodide (both 98°) (Khotsianova & Struchkov, 1957), and in 4,5-dicyano-2-imidazolyl(phenyl)bromonium yl-ide |99·3 (3)°| (Atwood & Sheppard, 1975). The least-squares-planes results (Table 2) show that the two benzene rings are planar. The distances of the I atom from the planes of the benzene rings [0·131 (3) and 0·126 (3) Å] are similar to the out-of-plane distances |0·13 (2) and −0·09 (2) Å| found for diphenyliodonium fluoroborate (Struchkov & Khotsianova, 1960). Table 3 provides a summary of the angles formed between the normals to the various planes.

X-ray analysis has shown that the molecule exists as a zwitterion. The presence of a negative charge on the O atom was deduced from the fact that a hydroxy H atom was not found, from the length of the C—O bond, and from changes in the geometry of the benzene ring (R2). The C(2)—O(1) bond distance [1·259 (7) Å] is consistent with data on bond distances in nitrophenols and nitrophenolates in which the 0·1 Å difference observed between the average C—O bond lengths (1·355 and 1·248 Å, respectively) was attributed to the loss of a phenolic proton (Hough, 1976). In the nitrophenolate compounds, Hough observed that delocalization of the negative charge produced geo-metrical changes in the benzene ring. Similar geometri-cal changes are evident in ring 2 of the title compound |C(1)—C(2)—C(3) = 111·8 (5)°; and C(1)—C(2) = 1·412 (8), C(2)—C(3) = 1·435 (7) Å|.

The zwitterion configuration permits both intra- and intermolecular ionic attraction between I⁺ and O⁻. The
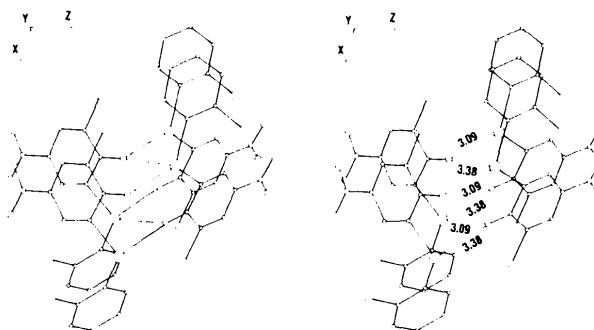

Fig. 2. Stereoscopic view illustrating the intermolecular ionic attraction between iodine and oxygen (ORTEP: Johnson, 1965).

intramolecular ionic attraction causes a relatively large difference in the exocyclic angles associated with C(1) in ring 2, with I—C(1)—C(2) = 103·7 (3) and I—C(1)—C(6) = 128·6 (4)°. The intermolecular ionic attraction creates infinite chains along the y axis (Fig. 2). Each O atom is associated with two I atoms of different molecules; similarly, each I atom is associated with two O atoms. The short–long ionic attraction between I and an external anion (in this case, an O atom) has also been observed in diphenyliodonium chloride and nitrate (Wright & Meyers, 1972).

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