rows, 3·16, 3·21, 3·30 or 3·51 Å, are not unusually short compared with the normal van der Waals O· · ·Cl distance of 3·20 Å. In the chloro- and bromobenzfuroxans short N· · ·X distances were found. It was our expectation that similar short N· · ·X distances would be found here, but the packing precludes any N· · ·Cl contacts, and replaces them with normal O· · ·Cl contacts. There is one unusually short intermolecular contact, O(1)· · ·C(3)–3·16 Å or O(1)· · ·C(6)–3·33 Å, depending on the disorder. However, these distances are similar to those Donohue (1968) has discussed in detail and rejected as O· · ·H–C hydrogen bonds. In view of the additional uncertainty due to the disorder, there is no reason to regard this as other than an accidentally short distance. It should be mentioned that the refinement in the ordered, acentric arrangement still leaves this distance short, at 3·12 Å. Generally the packing is similar for both the ordered and disordered models; there are no special features in one that are not in the other as well, so that the packing does not appear to favor one arrangement over the other, and we are left accepting the evidence of the r values as the deciding factor in favor of disorder.

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The Crystal Structure of 5-Iodobenzfurazan-1-oxide

By RICHARD C. GEHRZ AND DOYLE BRITTON*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

5-Iodobenzfurazan-1-oxide is monoclinic with $a = 10·413$ (17), $b = 19·787$ (33), $c = 7·596$ (13) Å, and $\beta = 103·4$ (1)°, eight molecules in the unit cell, space group $P2_1/c$ (C_{5h}^2). The structure was solved using film data. Refinement using both film and counter data led to results with large standard deviations in the positional parameters. The final refinement of the diffractometer data, treating the molecules as rigid groups and allowing for anisotropic thermal motion only for the iodine atoms, led to a conventional R value of 0·134. The molecules lie in two independent chains parallel to b. In each chain there is a short O· · ·I intermolecular contact of about 3·1 Å.

Introduction

With the recognition that short intermolecular N· · ·X distances are found in crystalline 5-chloro- and 5-bromobenzfuroxan (see Britton, Hardgrove, Hegstrom & Nelson, 1972) and knowing that the O· · ·I interaction in p-iodonitrosobenzene is strong enough that the molecules occur as loosely polymerized monomers in the crystal rather than as the dimers that are more common with nitroso compounds (Webster, 1956), we have determined the crystal structure of 5-iodobenzfuroxan (= 5-iodobenzfurazan-1-oxide), primarily in order to determine the packing.

Experimental

5-Iodobenzfuroxan was prepared by J. B. Hanson and W. E. Noland by the oxidation of 4-iodo-2-nitroaniline with sodium hypochlorite in basic solution in etha-nol at 0°C. The precipitate was recrystallized from an ethanol/water mixture and then sublimed to give crystals suitable for diffraction studies. The melting point of the sublimed crystals was 72 to 73°C; the infrared spectrum was very similar to that of 5-chlorobenzfuroxan; the analysis was: calculated for $IC_6H_3N_2O_2$; C, 27·50; H, 1·15; N, 10·69; found: C, 27·59; H, 1·23; N, 10·87.

The crystals were examined by Weissenberg and precession photographs and found to be monoclinic, with $a = 10·413$ (17), $b = 19·787$ (33), $c = 7·596$ (13) Å and $\beta = 103·4(1)°$. The errors are those we normally associate with the precession method. Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å) was used for all of the data collection, film or diffractometer. Assuming $Z = 8$, we calculate a molecular volume of 190·3 Å^3, which compares well with the molecular volumes of the chloro and bromo analogs, 176·1 and 185·5 Å^3, respectively (Britton & Noland, 1962). Systematic extinctions ($h0l$, $l = 2n + 1$;

$0k0$, $k=2n+1$) indicate the space group to be $P2_1/c$ (C_{5h}^2), so that there must be two independent molecules in the asymmetric unit. In addition to the systematic extinctions hkl reflections with $2h+k+2l=4n$ are stronger than the other reflections, suggesting some relationship between the parameters of the two independent molecules. The crystals grow as needles elongated along c with frequent mirror twinning on the (001) plane. An untwinned crystal $0.01 \times 0.04 \times 0.5$ mm was mounted in a glass capillary tube, which was filled with water and sealed. Weissenberg film data, $hk0-hk7$, were collected and used to solve the structure. When the eventual refinement was unsatisfactory, it was decided to collect diffractometer data. A crystal $0.12 \times 0.14 \times 0.68$ mm, similarly mounted, was used for the diffractometer data. A total of 2114 reflections (1051 independent) was collected over one entire hemisphere for θ between 0 and 18° on a Hilger and Watts 4-circle automated diffractometer. There were virtually no reflections of measurable intensity for $\theta > 18°$. The distance from the source to the crystal was 28 cm, from the crystal to the aperture 20 cm; a 6.0 mm diameter circular aperture was used. The scan was one hundred 0.02° steps in θ and ω, from -1.00 to $+1.00°$ with respect to the calculated setting. The step time was one second; stationary background counts of 50 seconds were taken at each end of the scan. The intensities of two check reflections were measured every 50 reflections; the intensities of these check reflections decreased by about 1% over the entire series of measurements, and the maximum scatter from the mean was about ± 1%. No correction was made for the intensity as a function of time. At the time the data were collected, no absorption correction program was available and it was decided to use the data and return to the absorption correction later if necessary, since the corrections would not be large. As the results below will show, the absorption corrections are not the main source of error, so they were never made. The linear absorption coefficient is 42.1 cm^{-1} for Mo $K\alpha$ radiation.

The data were processed in the manner described by Corfield, Doedens & Ibers (1967); the value of 0.04 was used for p in the $\sigma(I)$ equation.*The average value of $\sigma(F)/F$ was 0.102. Of the 1051 independent reflections, the 483 with $I > 2.4\sigma(I)$ were used in the refinement of the structure.

Solution and refinement

The iodine positions were determined from a three-dimensional Patterson map based on the film data (437 reflections of measurable intensity). As could be expected from the non-space-group condition for the strong reflections, mentioned above, the two independent iodine positions were related by approximately rational fractions of the unit cell; if the first set of iodine coordinates is x,y,z, the second set is approximately $\frac{1}{2}+x,\frac{1}{4}+y,\frac{1}{2}+z$. A Fourier map based on the iodine positions showed generally the positions of the rest of the molecules but with very poor resolution. After several attempts to find a consistent and refinable set of light atom positions the two molecules were put in and refined as rigid groups. The resulting positions showed that the approximate relationship given above between the two sets of iodine positions carried over to the positions of the entire molecules.† Attempts to refine the structure further treating the atoms independently led to convergence with reasonable R values, but the molecules, although recognizable, were very highly distorted. At this stage an automatic diffractometer became available and it was decided to collect a better set of data.

The diffractometer data were collected as described in the experimental section. The relatively small size of the crystal (the largest we were able to grow) and the rapid fall-off in intensity with angle again limited the
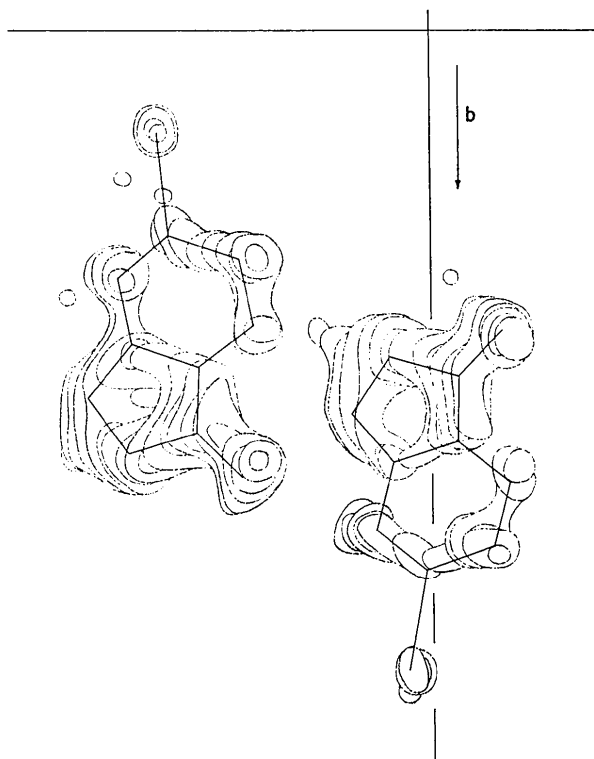
Fig. 1. Composite 3-dimensional difference Fourier map. Contours are shown at 4.0 and 6.0 e.Å^{-3}. The center and right-hand molecules from Fig. 2 are shown in outline. The phases are based on the iodine atoms only.

* The programs used for the calculations were the same as in the three preceding papers (Britton & Noland, 1972; Britton, Hardgrove, Hegstrom & Nelson, 1972; Britton, Konnert, Hammer & Trefonas, 1972). R and r also have the same definitions.

† If the relationship that for each atom at x, y, z there were one at $\frac{1}{2}+x$, $\frac{1}{4}+y$, $\frac{1}{2}+z$ were exact, all reflections with $2h+k+2l=4n+2$ would be extinct. This is not inconsistent with the observed pseudo condition.

amount of data. The total number of independent re-
flections with $I > 2\cdot4\sigma(I)$ was 483, which is rather less
than we would have liked for a structure with 22 inde-
pendent atoms, and it was decided to again start with
group refinement. The two independent molecules were
put in as rigid groups with parameters based on those
of 5-methylbenzfuroxan (before libration corrections;
see the preceding papers) with the methyl group re-
placed by an iodine atom at a distance of 2·070 Å from
the ring. Group refinement with all atoms isotropic led
to $R = 0\cdot213$ and $r = 0\cdot445$.* A difference Fourier map
at this point showed a number of peaks approximately
one-third the height of a carbon atom peak on the cor-
responding Fourier map. Several of these peaks were
near the iodine atom positions and were strongly in-
dicative of anisotropic thermal motion for these atoms;
others were near the heterocyclic ring positions but we
could see no obvious interpretation for these. The next
series of refinements was with the same rigid groups as
before but with anisotropic thermal parameters for the
iodine atoms. This converged with $R = 0\cdot134$ and $r =$
$0\cdot051$; we estimate that about two-thirds of the im-
provement was due to the deletion of the faint reflec-
tions. Further refinement with all atoms independent
with isotropic thermal parameters for the light atoms
and anisotropic for the iodine atoms converged with
$R = 0\cdot120$ and $r = 0\cdot034$. Again the distortions in the
molecule were large; the average e.s.d. for the bond
lengths was 0·13 Å, the average discrepancy between
the calculated bond lengths and those used in the rigid
body model was 0·15 Å. From this we conclude that
the group refinement gives better atomic parameters
than the individual atom refinement and accordingly
we report the group refinement results. The group par-
ameters are given in Table 1, the atomic parameters
from the group refinement in Table 2, and the observed
structure factors in Table 3. Since some of the isotropic
temperature factors are rather high, we have calculated
a three-dimensional difference Fourier synthesis based
only on the iodine atoms with anisotropic thermal par-

* Up to this point we were using the 569 independent
reflections with $I > 2\cdot0\sigma(I)$. After this point in the refinement
the number of reflections was reduced by the more severe
restriction that only reflections with $I > 2\cdot4\sigma(I)$ would be accep-
ted. This change was based on a comparison of the observed and
calculated structure factors for the faint reflections.

Table 1. Group parameters

The origin of the group is on the iodine atom in each case.
The angles are in radians. δ, ε and η are angles that bring
about alignment (except for translation) of an internal co-
ordinate system within the group with a fixed external system.

Molecule	x	y	z
1	$-0\cdot0459$ (15)	$0\cdot6542$ (9)	$0\cdot2472$ (25)
2	$0\cdot4730$ (15)	$0\cdot1053$ (9)	$0\cdot2223$ (25)

	δ	ε	η
1	$-1\cdot392$ (7)	$-2\cdot801$ (22)	$-0\cdot037$ (6)
2	$-1\cdot725$ (5)	$-2\cdot933$ (21)	$3\cdot106$ (5)

ameters. A composite view of the Fourier map is shown
in Fig. 1 and verifies the overall correctness of the struc-
ture in spite of the unsatisfactory R values at the end
of the refinement.

(a)

(b)
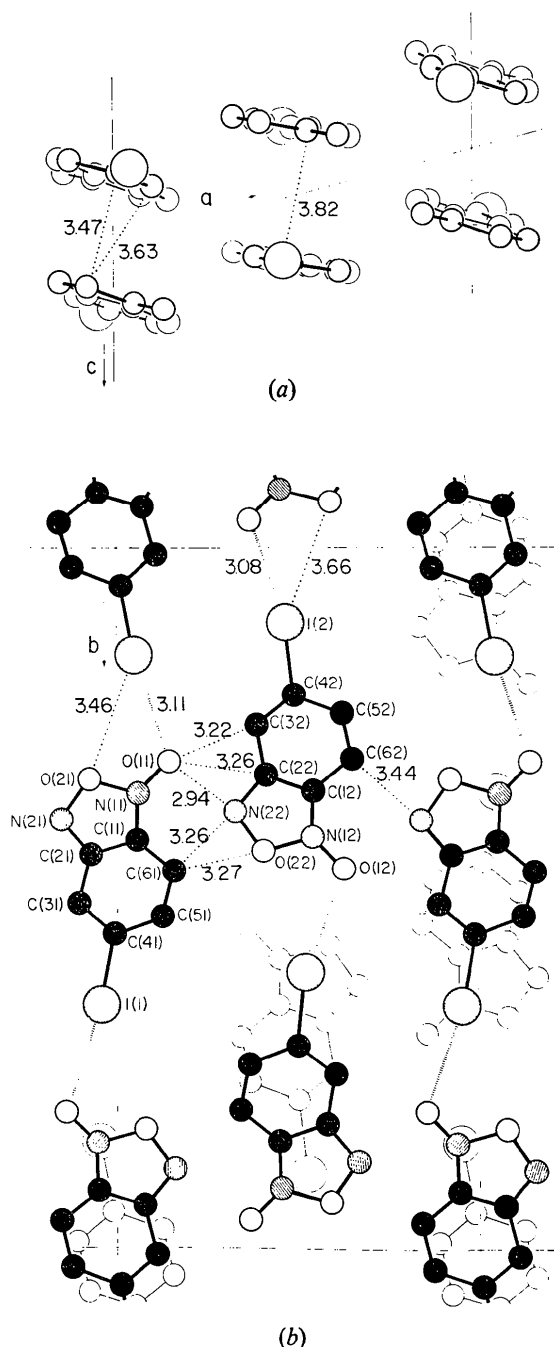
Fig. 2. (a) Projection along **b**. Only half the molecules are
shown in this projection since they overlap badly. At the
left are those centered near $y = \frac{1}{2}$, in the center those near
$y = \frac{1}{4}$, and at the right those near $y = 0$. (b) Projection along **c**.
The molecules centered near $z = \frac{1}{4}$ are emphasized. Some of
the molecules centered near $z = -\frac{1}{4}$ are shown lightly. Inter-
atomic distances are given in Å.

Table 2. *Positional parameters* ($\times 10^3$) *and temperature factors for the atoms*

	x	y	z	B
I(1)	−46	654	247	*
O(11)	136	304	295	21·6
O(21)	−75	330	138	10·3
N(11)	53	349	243	8·0
N(21)	−152	387	94	4·0
C(11)	51	416	259	−0·7
C(21)	−75	438	167	2·9
C(31)	−106	508	161	11·4
C(41)	−12	551	246	9·7
C(51)	117	527	340	−0·4
C(61)	150	461	347	0·0
I(2)	473	105	222	*
O(12)	626	458	318	6·3
O(22)	410	431	187	−0·8
N(12)	545	412	269	3·3
N(22)	336	373	142	5·5
C(12)	549	345	270	4·0
C(22)	421	322	193	2·0
C(32)	396	252	177	1·1
C(42)	498	209	238	0·4
C(52)	629	234	317	1·5
C(62)	656	302	335	7·8

* The anisotropic thermal parameters of the form

$$\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+\ldots+2B_{12}hka^*b^*+\ldots)\right] \text{ are:}$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I(1)	6·1	2·9	4·6	1·4	1·7	0·3
I(2)	8·5	2·9	4·6	−0·4	3·6	−0·3

Results and discussion

The crystal structure is shown in Fig. 2. The molecules occur in two independent chains parallel to **b**. All of the intermolecular distances near the expected van der Waals contact distances are shown. Only two of these are noteworthy: O(11)···I(1) is 3·11 Å and O(12)···I(2) is 3·08 Å, both of which are significantly shorter than the expected O···I van der Waals distance of 3·65 Å. We interpret these as Lewis acid–base interactions between the atoms. A similar O···I intermolecular interaction has been reported by Webster

(1956) in the structure of *p*-iodonitrosobenzene, where the usual dimerization through the nitroso groups is absent, but where weak infinite polymers, built from monomeric molecules and bound through O···I contacts 3·2 Å in length, are present.

The most unexpected feature of our structure is that the interaction is through O···I rather than N···I since the inspiration for this work came from the structures of 5-chloro- and 5-bromobenzfuroxan, where short N···X distances were found. This difference is most likely a secondary effect arising from the difference in size of the halogen atoms, which generally leads to differences in packing between iodides, on one hand, and the corresponding bromides and chlorides, on the other. In this case the difference in packing happens to coincide with allowing oxygen to function as a base with the iodide, and nitrogen to function as a base with the others. Presumably, if other halobenzfuroxans were looked at, for example, the 4-halobenzfuroxans, nitrogen or oxygen might serve as the base in this sort of interaction in an unpredictable way.

The other feature of the determination that requires further discussion is the poor value of *R* at the final refinement. We would generally find a lower value of *R* and smaller errrors in the parameters from diffractometer data, although we recognize that with the limited number of data collected here, good accuracy in the bond lengths is not to be expected. Making absorption corrections should improve the situation slightly, but our experience with crystals of this size has been that absorption corrections lead to significant changes in the thermal parameters, but not in general in the positional parameters, and not in the *R* factors. An alternative explanation, which seems to us to deserve more consideration, is that this is an example of an order–disorder structure similar to those types discussed by Dornberger-Schiff (1956) and Dornberger-Schiff & Grell-Niemann (1961). The translational relationship between the two independent molecules is only approximate, see for example the top view in Fig. 2, but it is the type of relationship that, according to

Table 3. *Observed structure factors for* 5-iodobenzfurazan-1-oxide

Dornberger–Schiff, can lead to stacking faults. These stacking faults would have to be very occasional in this case since there is no evidence for them in the Fourier maps. However, we do not intend to carry out further work on this compound, and a more complete set of data would be needed to pursue this point.

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The Molecular Structure of Nitrosyltris(trifluorophosphine)rhodium in the Gas Phase, Determined by Electron Diffraction

BY D. M. BRIDGES AND D. W. H. RANKIN

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

AND D. A. CLEMENT AND J. F. NIXON

The Chemical Laboratory, University of Sussex, Falmer, Brighton BN1 9QJ, England

The structure of nitrosyltris(trifluorophosphine)rhodium, $Rh(NO)(PF_3)_3$, has been determined by gas phase electron diffraction. The molecular intensity functions derived from photographically recorded sectored diffraction patterns were fitted by full-matrix least-squares refinements of a molecular model. Assuming that the molecule has a threefold axis of symmetry, the principal parameters have been found to be: N–O $1\cdot149\pm0\cdot019$, P–F $1\cdot558\pm0\cdot003$, Rh–P $2\cdot245\pm0\cdot005$, Rh–N $1\cdot858\pm0\cdot018$ Å, $\angle$ PRhP $110\cdot4\pm0\cdot5$, $\angle$ FPF $100\cdot1\pm0\cdot7°$. The trifluorophosphine groups are twisted by about $10°$ from the configuration in which each PF_3 group is eclipsed with respect to the RhP_2N group.

Introduction

Although well over a hundred transition metal complexes of trifluorophosphine have been characterized (Nixon, 1970), very little structural work on them has been reported. The complexes generally are low melting, and are therefore unsuitable for crystallographic study except at low temperatures. However, fairly high volatilities make many of the compounds, particularly those possessing some symmetry, suitable for structure determination by electron diffraction. Results have been published for tetrakis(trifluorophosphine)nickel (Marriott, Salthouse & Ware, 1970; Almenningen, Andersen & Astrup, 1970) and for tetrakis(trifluorophosphine)platinum (Marriott *et al.*, 1970), tetrahedrally coordinated derivatives of first and third series transition metals, and for hydridotetrakis(trifluorophosphine)cobalt (Frenz & Ibers, 1970). The only structure of a trifluorophosphine complex of a second transition series metal reported to date is that of the octahedral complex pentacarbonyl(trifluorophosphine)mo-

lybdenum (Bridges, Holywell, Rankin & Freeman, 1971).

The most striking feature of these results concerns the metal—phosphorus bond lengths. In the nickel and cobalt complexes, these bonds are about 0·12 Å shorter than in most phosphine complexes of these metals. The molybdenum complex shows a similar shortening of about 0·10 Å, but the platinum compound has metal—phosphorus bonds which are very little, if at all, shorter than usual.

In this present investigation of a tetrahedrally coordinated derivative of a second transition series metal, nitrosyltris(trifluorophosphine)rhodium, $Rh(NO)(PF_3)_3$, the rhodium–phosphorus bond lengths have been found to be about 0·10 Å shorter than the average reported length, but they are not the shortest of all.

Experimental

Nitrosyltris(trifluorophosphine)rhodium is an orange volatile liquid, first obtained in 50–60% yield (Kruck & Lang, 1967) by passing carbon dioxide into an