also the fragment C(6)C(1)N(1)O(1)N(2), but to a lesser extent.

The contacts shorter than the sum of the van der Waals radii are: O(3)···D(42) 2·44 (8), N(3) ($\bar{x}, 1-y, 1-z$)···H(3) 2·24 (8), N(3) ($\bar{x}, 1-y, 1-z$)···O(3) 2·864 (9) Å, N(3) ($\bar{x}, 1-y, 1-z$,)···H(3)···O(3) 140 (4)°.

We intend to proceed with the analysis of the other isomer in order to compare the effect of the relative position of the *N*-oxide and the oxime groups on the geometry of the furoxan moiety.

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Phenylmercury(II) Cyanide

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Abstract. Tetragonal, $P4_2/n$ (No. 86), $a=15{\cdot}161$ (3), $c=6{\cdot}146$ (1) Å, formula C_7H_5NHg, $Z=8$, $D_c=2{\cdot}87$ g cm^{-3}, μ(Mo $K\bar{\alpha}$)$=222{\cdot}4$ cm^{-1}. The structure consists of discrete molecular units. The C–Hg–C–N group is approximately linear, with Hg–C(phenyl) and Hg–C(cyanide) bond distances of 2·05 and 2·09 Å respectively. An upper limit of 1·50 Å is suggested for the van der Waals radius of the Hg atom.

Introduction. $Hg(CN)_2$, Ph–Hg–CN and Ph_2Hg (Ph= C_6H_5) are known to form 1:1 adducts with neutral bidentate ligands whose stability decreases with the decreasing electronegativity of the R groups in the R_2Hg molecule. The adducts of $Hg(CN)_2$ with phen (1,10-phenanthroline) and DMP (2,9-dimethyl-1,10-phenanthroline) have been recently studied by Cano & Santos (1976). The crystal structures of two crystalline adducts of $HgPh_2$ with phen and TMP (2,4,7,9-tetramethyl-1,10-phenanthroline) have been previously reported (Canty & Gatehouse, 1972) and more recently the formation of the adducts of Ph–Hg–CN with phen and DMP has been proved (Santos & Cano, 1975).

A first stage in the elucidation of the stereochemistry of these adducts is the determination of the molecular structure of the acceptors. The molecular structure of $Hg(CN)_2$ has been determined three times both by X-ray and neutron diffraction, the most accurate structure having been reported by Seccombe & Kennard (1969) (by neutron diffraction). Also the geometry of the Ph_2Hg group is known as several structures containing this group have been determined. To date the best data of its geometry are possibly those obtained by Mathew & Kunchur (1969) for di-*p*-tolylmercury. The structure of Ph–Hg–CN is not known and the present paper deals with its determination.

Crystals of Ph–Hg–CN were prepared by reaction of $Hg(CN)_2$ and Ph_2Hg in ethanol in a sealed tube and recrystallization from ethanol.

A crystal of dimension 0·09 × 0·10 × 0·40 mm, sharply delimited by the faces {110} and {001}, was mounted along the *c* axis. Intensity data were collected on an automatic Philips PW 1100 four-circle diffractometer using monochromated Mo $K\bar{\alpha}$ radiation and the $\omega/2\theta$ scan technique. Out of the 2056 reflexions measured ($\theta \le 30°$), 996 were unobserved, a reflexion being considered unobserved when $I_o \le 2\sigma(I_o)$. Irradiated crystals were rather unstable and an appreciable intensity shift of the two standard reflexions was observed during the data collection, while the crystal was turning from colourless to dark gray.

An absorption correction was applied with the program *ORABS* and minimum and maximum transmission factors were 0·112 and 0·188. Polarization and Lorentz corrections were applied as usual. Scattering factors were taken from Cromer & Waber (1965). Allowance was made for the f' and f'' terms of the Hg atom (Cromer, 1965). Computations were carried out mainly with the X-RAY 71 system of crystallographic programs.

The structure was solved by Patterson methods and refined by full-matrix least squares minimizing $\sum[|F_o|-(1/k)|F_c|]^2$ and refining Hg, C and N atoms anisotropically. Unobserved reflexions were used only if $|F_c|>|kF_o|$. Positions of the H atoms were calculated assuming a C–H bond length of 1·08 Å. Weights for the last cycle were calculated as $w=1/(31{\cdot}0-0{\cdot}44|F_o|+0{\cdot}0023|F_o|^2)$. In this cycle the largest shift/error, R (= $\sum|\Delta|/\sum|F_o|$) and $R_w[=(\sum w|\Delta|^2/\sum w|F_o|^2)^{1/2}]$ were respectively 0·02, 0·045 and 0·049.

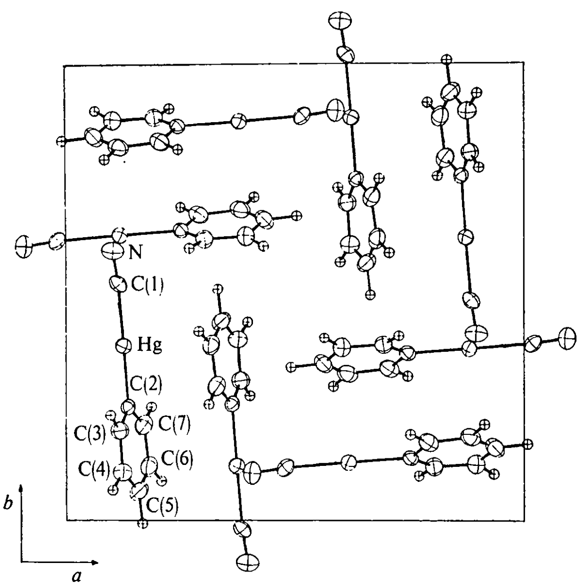

Fig. 1. Projection of the structure along **c**, showing the thermal ellipsoids at 40% probability (Johnson, 1965).

The final values of the positional and vibrational parameters are listed in Table 1.*

A parallel refinement was carried out using the intensities not corrected for absorption. The two refinements are compared in the Appendix.

Discussion. A projection of the structure along the c axis is shown in Fig. 1. The structure consists of discrete molecular units without significant intermolecular contacts. Each Hg atom is surrounded by two N atoms displaced up and down along the c axis, with intermolecular distances of 3·14 (2) and 3·10 (2) Å and angles C(1′)–N′···Hg of 97·7 and 99·3° respectively. This allows an estimation of the van der Waals radius of mercury, r_w(Hg), for which values in the range 1·5–1·73 Å have been proposed (Mak & Trotter, 1962; Grdenič, 1965). The $r_w(N)$ in the cyano group is known to be anisotropic, ranging from 1·40 Å in the direction of the bond to 1·70 Å normal to the bond (Bondi, 1964). Assuming $r_w(N) \ge 1{\cdot}60$ Å for an angle C–N···Hg of about 100°, a value of $r_w(\mathrm{Hg}) \le 1{\cdot}50$ Å is obtained, which is in agreement with the value of 1·50 Å determined by Mak & Trotter (1962) for methoxycarbonylmercury(II) chloride.

The group C(2)–Hg–C(1)–N is approximately linear (Table 2). The deviation of the angle C(2)–Hg–C(1)

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31776 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond distances* (Å) *and angles* (°)

E.s.d.'s in parentheses.

Hg—C(1)	2·094 (16)	C(4)–C(5)	1·38 (4)
Hg—C(2)	2·051 (15)	C(5)–C(6)	1·39 (3)
C(1)–N	1·13 (2)	C(6)–C(7)	1·39 (3)
C(2)–C(3)	1·35 (3)	C(7)–C(2)	1·40 (3)
C(3)–C(4)	1·39 (3)		
Hg—C(1)–N	176 (1)	C(2)–C(3)–C(4)	121 (2)
C(1)–Hg—C(2)	177·5 (7)	C(3)–C(4)–C(5)	121 (2)
Hg—C(2)–C(3)	121 (1)	C(4)–C(5)–C(6)	118 (2)
Hg—C(2)–C(7)	119 (1)	C(5)–C(6)–C(7)	121 (2)
C(7)–C(2)–C(3)	119 (2)	C(6)–C(7)–C(2)	119 (2)

Table 1. *Positional* (×10[4]) *and thermal* (×10[2]) *parameters of the non-hydrogen atoms*

E.s.d.'s in parentheses. The anisotropic temperature factor has the form
$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	1258·0 (4)	3814·4 (4)	1964·7 (10)	4·85 (4)	4·53 (3)	4·73 (3)	−0·14 (3)	−0·12 (3)	−0·01 (3)
C(1)	1144 (10)	5191 (10)	1978 (28)	5·8 (9)	5·4 (9)	4·5 (9)	−1·5 (7)	0·7 (8)	1·3 (8)
C(2)	1358 (9)	2467 (10)	1811 (27)	4·2 (7)	4·8 (7)	4·9 (9)	0·3 (6)	−0·6 (7)	−0·8 (8)
C(3)	1168 (12)	1953 (12)	3550 (32)	6·0 (10)	5·6 (9)	6·3 (12)	0·0 (7)	1·4 (8)	0·2 (8)
C(4)	1228 (13)	1042 (14)	3436 (52)	6·8 (12)	5·7 (10)	14·3 (25)	0·1 (9)	0·7 (14)	1·5 (14)
C(5)	1588 (14)	638 (13)	1637 (43)	6·7 (11)	6·4 (11)	9·8 (19)	2·0 (9)	−1·1 (12)	−1·1 (12)
C(6)	1816 (12)	1164 (14)	−122 (40)	5·2 (10)	7·8 (13)	8·6 (16)	0·9 (9)	−1·1 (10)	−2·8 (12)
C(7)	1701 (12)	2076 (13)	−64 (34)	5·8 (10)	7·0 (11)	6·8 (12)	1·1 (9)	−0·2 (9)	−0·8 (10)
N	1030 (11)	5926 (10)	2001 (26)	9·4 (11)	5·6 (8)	4·4 (8)	−0·3 (7)	−0·1 (9)	0·5 (7)

from 180° does not seem to be significant and the angle, 177·5 (7)°, can be compared with the 180 and 180 (2)° observed in di-*p*-tolylmercury(II) (Mathew & Kunchur, 1969) and methylmercury(II) cyanide (Mills, Preston & Kennard, 1968; by neutron diffraction). A similar value, 175·0 (2)°, has been found for $Hg(CN)_2$ (Seccombe & Kennard, 1969; by neutron diffraction) in spite of the interactions between Hg and the neighbouring cyanide groups observed in this compound.

The bond distance C(1)–N (1·13 Å) is strictly comparable with the same distance (1·137 Å) in $Hg(CN)_2$ while the Hg–C(1) bond distance is considerably longer, being 2·015 in $Hg(CN)_2$ and 2·09 Å in the present structure. This lengthening is in agreement with the difference in IR stretching frequencies of the Hg–C(cyanide) bond observed for $Hg(CN)_2$ ($\nu_s=412$, $\nu_a=436$ cm^{-1}; Llevellyn, 1971) and for Ph–Hg–CN ($\nu=385$ cm^{-1}; Santos & Cano, 1975).

On the other hand the Hg–C(2) bond distance of 2·05 Å is possibly shorter than the Hg–C(methyl) distance in methylmercury(II) cyanide (2·08 Å; Mills, Preston & Kennard, 1968) and than the average Hg–C(phenyl) distance of 2·09 (2) Å determined from four structures containing the diphenyl group (Mathew & Kunchur, 1969; Canty & Gatehouse, 1972; Küpper & Lindner, 1968).

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APPENDIX

A parallel refinement has been carried out using intensities not corrected for absorption (final values $R=0·055$, $R_w=0·077$, e.s.d.'s on average 15% greater than in the previous refinement) and the results of the two refinements have been compared by means of half-normal probability (HNP) plots (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972).

The use of HNP plots can be questioned as the two parameter sets are not really independent, being derived from the same set of observed intensities. However, it has been assumed that only the meaning of the slope (*i.e.* the correct assignment of e.s.d.'s) can be lost in consequence of this fact and that the possibility of detecting systematic errors from a non-zero intercept and/or deviations from linearity remains unchanged.

The parameters of the regression line through the points of the HNP plots for positional and vibrational parameters are listed in Table 3. The plots for all the positional parameters and intramolecular distances (lines 1 and 2 of Table 3) are essentially linear with zero intercept, suggesting that no systematic difference between the two sets is present. The HNP plot for the U_{ij} of all the atoms (line 3) seems to show a systematic difference in the vibrational parameters of all the atoms. However, a separate treatment of the U_{ij} of heavy and light atoms (lines 4 and 5) shows that strong systematic differences are limited to the U_{ij} of the Hg atom.

Table 3. *Parameters of the regression line through the points of the HNP plots, with e.s.d.'s in parentheses*

Parameters tested	Atoms included	Number of points	Intercept	Slope
x,y,z	all	27	−0·03 (2)	0·52 (2)
$d<4·65$ Å	all	28	0·00 (2)	0·53 (2)
U_{ij}	all	54	−0·29 (6)	0·99 (6)
U_{ij}	Hg	6	−0·63 (43)	2·36 (45)
U_{ij}	C/N	48	−0·12 (3)	0·67 (3)

In conclusion, positional and thermal parameters derived from data corrected or not corrected for absorption are statistically indistinguishable, with the exception of the U_{ij}'s of the Hg atom.

At present it seems impossible to say if this result can be extended to other structures containing heavy atoms with comparable transmission factors or if it has to be related to the poor quality of the crystals, which were slowly decomposing during the data-collection.

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