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MOLECULAR AND CRYSTAL STRUCTURE OF THE METHYL ESTER OF 2-CHLOROMERCURI-3-TRIFLUOROACETOXY-2,3-DIPHENYLCYCLOPROPANE-1-CARBOXYLIC ACID

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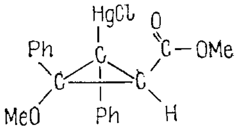
UDC 548.73

The crystal structure was determined for the methyl ester of 2-chloromercuri-3-trifluoroacetozy-2,3-diphenylcyclopropane-1-carbodylic acid using a diffractometer, λMoK_α radiation, and $\theta/2\theta$ scanning with $2\theta_{max} = 60°$ to R = 0.058. The unit cell parameters for the monoclinic crystals are as follows: $a = 17.595(2)$, $b = 11.0454(9)$, $c = 20.933(1)$ Å, $\beta = 97.281(8)°$, $V = 4035.4(7)$ Å³, $Z = 8$, space group $P2_1/c$. The HgCl, CO_2Me, and CO_2CF_3 substituents in both independent molecules (A and B) are located on one side of the plane of the cyclopropane ring, while the phenyl groups are on the other side. All the bond lengths in this molecule are ordinary.

We carried out an x-ray diffraction structural analysis of chloromercuricyclopropane (I) [1]



(I)

in order to determine the arrangement of the substituents relative to the plane of the cyclopropane ring and the possibility of the formation of a secondary Hg...O bond. Indeed, such a secondary bond with the oxygen atom of the carbomethoxy group was found in I.

In the present work, we carried out an x-ray diffraction structural analysis of the methyl ester of 2-chloromercuri-3-fluoroacetoxy-2,3-diphenylcyclopropane-1-carboxylic acid (II), in which the formation of a Hg...O secondary bond is possible with the carbonyl oxygen atom of both the carbomethoxy and trifluoroacetoxy groups.

EXPERIMENTAL

Preparation of II. A sample of 30 ml 0.2 M mercury trifluoroacetate (2.56 g) in acetic acid was added to an equivalent amount of a solution of 1.5 g of the methyl ester of 2,3-diphenylcyclopropenecarboxylic acid of the same concentration. After 72 h, the reaction mixture was poured into a solution of 1.4 g NaCl in 190 ml water. The crystalline precipitate

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TABLE 1. Atomic Coordinates ($\times 10^4$, $\times 10^5$ for Hg) and Isotropic Equivalent Temperature Factors B^{eq}_{iso} (Å^2)

	Molecule A				Molecule B			
atom	x	y	z	B^{eq}_{iso}	x	y	z	B^{eq}_{iso}
Hg	63669(5)	9081(9)	25454(5)	3,61(2)	86877(5)	15127(9)	24582(5)	3,31(2)
Cl	6866(4)	2024(8)	1769(4)	6,3(3)	8175(3)	241(7)	3172(3)	4,9(2)
F1	6677(9)	—3873(20)	1507(11)	10,9(9)	7449(7)	5351(17)	2895(7)	6,8(6)
F2	7441(9)	—2663(20)	1948(9)	8,2(7)	8206(11)	4624(29)	3609(9)	15(1)
F3	6572(13)	—2068(31)	1342(9)	16(1)	8234(11)	6423(25)	3447(13)	13(1)
O(1)	5268(7)	—470(16)	1843(7)	3,5(5)	9703(7)	2958(17)	3237(7)	4,2(5)
O(2)	4215(7)	—1351(15)	2166(8)	3,8(5)	10779(7)	3870(15)	3014(8)	3,9(5)
O(3)	6457(7)	—1742(13)	2680(7)	3,0(5)	8538(6)	4250(13)	2345(6)	2,7(4)
O(4)	5754(10)	—3347(18)	2340(9)	6,5(7)	9187(11)	5892(19)	2668(9)	7,2(7)
C(1)	5208(10)	—916(21)	2974(10)	2,6(6)	9856(10)	3443(21)	2147(9)	2,4(6)
C(2)	5922(15)	—86(25)	3282(12)	4,8(9)	9136(14)	2637(26)	1796(11)	5,0(8)
C(3)	6016(11)	—1451(23)	3186(12)	3,8(7)	9022(10)	3973(19)	1869(9)	2,2(5)
C(4)	4938(11)	—839(21)	2258(13)	3,5(7)	10049(11)	3365(21)	2855(12)	3,2(7)
C(5)	3821(12)	—1323(23)	1485(11)	3,8(7)	11088(13)	3800(26)	3673(11)	4,7(8)
C(6)	6260(11)	—2665(24)	2329(11)	3,3(7)	8690(11)	5203(26)	2722(11)	4,2(8)
C(7)	6679(12)	—2872(30)	1769(13)	5,7(9)	8139(11)	5329(25)	3170(11)	3,8(7)
C(8)	5942(13)	500(22)	3896(11)	3,9(7)	9192(11)	2131(19)	1148(10)	2,5(6)
C(9)	5201(12)	783(22)	4116(11)	3,6(7)	8571(10)	1936(21)	770(12)	3,3(7)
C(10)	5221(14)	1388(27)	4710(13)	5,3(9)	8574(12)	1539(26)	117(11)	4,4(8)
C(11)	5962(15)	1685(27)	5068(13)	5,6(9)	9238(15)	1343(25)	—99(12)	4,8(8)
C(12)	6596(12)	1385(27)	4807(13)	5,1(8)	9929(12)	1532(25)	305(12)	4,2(7)
C(13)	6583(11)	774(21)	4235(11)	3,4(7)	9944(13)	1929(21)	938(12)	3,8(7)
C(14)	6147(12)	—2267(21)	3758(11)	3,4(7)	8932(11)	4749(21)	1317(10)	2,8(6)
C(15)	5521(13)	—2972(25)	3925(12)	4,3(8)	9581(12)	5209(24)	1025(12)	4,1(8)
C(16)	5647(16)	—3759(26)	4447(15)	6(1)	9456(13)	5922(26)	484(13)	4,8(8)
C(17)	6353(16)	—3882(24)	4775(13)	5,4(9)	8680(14)	6113(23)	166(12)	4,4(8)
C(18)	6966(15)	—3149(24)	4589(14)	5,4(9)	8083(13)	5665(23)	459(14)	4,7(8)
C(19)	6849(13)	—2352(24)	4083(12)	4,4(8)	8201(11)	4994(22)	1005(12)	3,4(7)

of II obtained in 90% yield was recrystallized from 1:3 hexane—chloroform. The first recrystallization gave 1.9 g of the product and subsequent recrystallization gave a sample with mp 153-153.5°C.

X-ray diffraction structural analysis. The unit cell parameters of the monoclinic crystals of II ($C_{19}H_{14}F_3O_4HgCl$) are as follows: a = 17.595(2), b = 11.0454(9), c = 20.933(1) Å, β = 97.281(8)°, V = 4035.4(7) Å^3, Z = 8, d(calc) = 1.97 g/cm^3, space group $P2_1/c$, $\mu(MoK_\alpha)$ = 79.7 cm^{-1}. The unit cell parameters and intensities of 3515 independent reflections with $I > 2\sigma$ were measured on a Hilger—Watts four-circle automatic diffractometer using λMoK_α radiation, graphite monochromator, and $\theta/2\theta$ scanning with $2\theta_{max}$ = 60°.

The structure was solved by the heavy atom method and refined by the method of least squares in the block diagonal isotropic approximation. In this stage, an empirical correction was introduced using the DIFABS technique [2]. Subsequent refinement was carried out in the block diagonal anisotropic approximation to R = 0.058 and R_w = 0.060 using 3440 reflections with $F^2 > 3\sigma$. Attempts to reveal the hydrogen atoms were not undertaken. All the calculations were carried out on an Eclipse S-200 computer using the INXTL programs [3].

Table 1 gives the atomic coordinates of the crystallographically independent molecules A and B and the isotropic equivalent temperature factors. The fluorine atoms of both independent molecules have high temperature factors due either to strong thermal motion or some rotational disorderedness of the CF_3 groups relative to the positions, in which these groups are localized in the F-map.

RESULTS AND DISCUSSION

The structure of one (A) of the two independent molecules is shown in Fig. 1. The bond lengths are given in Table 2, while the bond angles are given in Table 3.

The structures of both independent molecules coincide within the experimental precision with the exception of some torsion angles. The arrangement of the substituents at C(1) and C(2) of the cyclopropane ring coincides with that found in I. On the other hand, the

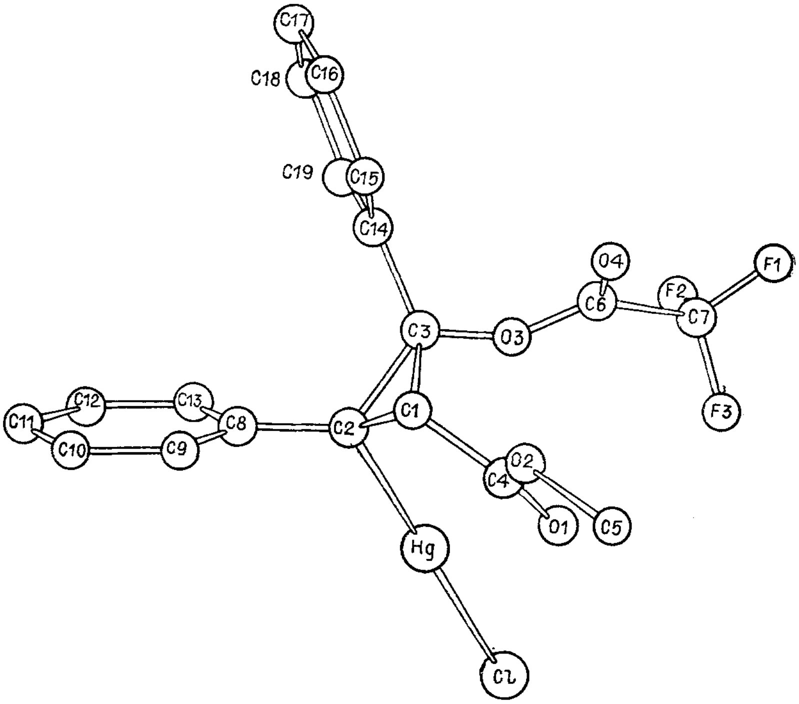

Fig. 1. Structure of molecule A.

TABLE 2. Bond Lengths d (Å)

Bond	d		Bond	d	
	A	B		A	B
Hg—Cl	2,30(1)	2,32(1)	C(7)—F(1)	1,19(6)	1,28(4)
Hg—C(2)	2,12(4)	2,12(3)	C(7)—F(2)	1,38(4)	1,19(5)
O(1)—C(4)	1,19(4)	1,15(4)	C(7)—F(3)	1,22(6)	1,36(5)
O(2)—C(4)	1,39(4)	1,39(3)	C(8)—C(9)	1,44(4)	1,32(4)
O(2)—C(5)	1,49(4)	1,42(4)	C(9)—C(10)	1,45(5)	1,43(5)
O(3)—C(3)	1,41(4)	1,40(3)	C(10)—C(11)	1,45(5)	1,33(5)
O(3)—C(6)	1,23(4)	1,30(4)	C(11)—C(12)	1,32(5)	1,37(5)
O(4)—C(6)	1,19(4)	1,21(4)	C(12)—C(13)	1,42(5)	1,38(5)
C(1)—C(2)	1,71(5)	1,62(4)	C(13)—C(8)	1,26(5)	1,46(4)
C(1)—C(3)	1,59(4)	1,67(4)	C(14)—C(15)	1,36(4)	1,44(4)
C(1)—C(4)	1,47(4)	1,50(4)	C(15)—C(16)	1,40(6)	1,34(5)
C(2)—C(3)	1,56(6)	1,49(5)	C(16)—C(17)	1,37(6)	1,45(5)
C(2)—C(8)	1,39(5)	1,47(4)	C(17)—C(18)	1,43(6)	1,33(5)
C(3)—C(14)	1,52(5)	1,44(4)	C(18)—C(19)	1,40(6)	1,36(5)
C(6)—C(7)	1,51(5)	1,38(4)	C(19)—C(14)	1,29(4)	1,39(4)

substituents at C(3), namely, Ph and OR (R = Me in I and $COCF_3$ in II) in I and II have opposite orientation: the phenyl group in I is found on the same side of three-membered ring plane as the ClHg and CO_2Me groups, while the MeO substituent is on the opposite side. On the other hand, the $OCOF_3$ group in II is located on the same side as the ClHg and CO_2Me substituents and the phenyl group is located on the opposite side.

Of the two substituents (CO_2Me and $OCOCF_3$) which are potentially capable of forming a secondary Hg...O secondary bond, only one, specifically, the CO_2Me group has a suitable orientation. The $OCOCF_3$ substituent is rotated about the O(3)—C(6) bond such that the carbonyl oxygen atom O(4) is oriented away from the mercury atom.

The distances of the mercury atom to O(1) of the carbomethoxy group are 2.74(2) Å in A and 2.77(2) Å in B and are less than the sum of the van der Waals radii of the mercury atoms (1.5-1.6 Å [4]) and oxygen atoms (1.52 Å [5]) (the sum is 3.0-3.1 Å) and virtually coincide with the corresponding distance (2.78 Å) in I. However, in contrast to I, the HgC(2)C(1) C(4)O(1) "chelate" ring is nonplanar in both independent molecules in II. The C(2)C(1)C(4) O(1) torsion angle (τ) is 19(2) and −13(2)° in molecules A and B, respectively. This

TABLE 3. Bond Angles ω (deg)

Angle	ω		Angle	ω	
	A	B		A	B
ClHgC(2)	178,4(7)	178,7(7)	O(4)C(6)C(7)	112(2)	125(2)
C(2)C(1)C(3)	58(1)	55(1)	C(6)C(7)F(1)	121(2)	113(2)
C(2)C(1)C(4)	119(2)	119(2)	C(6)C(7)F(2)	109(2)	115(2)
C(3)C(1)C(4)	118(2)	118(2)	C(6)C(7)F(3)	114(2)	108(2)
HgC(2)C(1)	110(2)	111(1)	F(1)C(7)F(2)	103(2)	111(2)
HgC(2)C(3)	111(2)	117(1)	F(1)C(7)F(3)	109(3)	104(2)
HgC(2)C(8)	117(2)	117(2)	F(2)C(7)F(3)	97(2)	105(2)
C(1)C(2)C(3)	59(2)	62(1)	C(2)C(8)C(9)	117(2)	118(2)
C(1)C(2)C(8)	123(2)	118(2)	C(2)C(8)C(13)	121(2)	120(2)
C(3)C(2)C(8)	125(2)	119(2)	C(13)C(8)C(9)	122(2)	121(2)
C(1)C(3)C(2)	63(2)	64(1)	C(8)C(9)C(10)	117(2)	122(2)
C(1)C(3)O(3)	111(2)	115(2)	C(9)C(10)C(11)	119(2)	119(2)
C(1)C(3)C(4)	120(1)	121(2)	C(10)C(11)C(12)	118(3)	120(2)
C(2)C(3)O(3)	113(2)	112(2)	C(11)C(12)C(13)	124(2)	122(2)
C(2)C(3)C(14)	120(2)	121(2)	C(12)C(13)C(8)	121(2)	115(2)
O(3)C(3)C(14)	115(2)	115(2)	C(3)C(14)C(15)	119(2)	122(2)
C(1)C(4)O(1)	128(2)	130(2)	C(3)C(14)C(19)	119(2)	120(2)
C(1)C(4)O(2)	106(2)	108(2)	C(19)C(14)C(15)	122(2)	118(2)
O(1)C(4)O(2)	125(2)	123(2)	C(14)C(15)C(16)	119(2)	120(2)
C(4)O(2)C(5)	115(2)	116(2)	C(15)C(16)C(17)	120(3)	120(2)
C(3)O(3)C(6)	118(2)	120(2)	C(16)C(17)C(18)	119(3)	118(2)
O(3)C(6)O(4)	131(2)	124(2)	C(17)C(18)C(19)	122(2)	122(2)
O(3)C(6)C(7)	117(2)	111(2)	C(18)C(19)C(14)	118(2)	122(2)

orientation of the CO_2Me orientation is intermediate between the two optimal orientations for the conjugation of the carbonyl group with the system of cyclopropane banana bonds: one of these optimal orientations is vicinal ($\tau = 0°$) and the other is cis-bisectorial ($\tau = 30°$) [6].

The orientation of the two phenyl substituents is also intermediate between the two limiting cases (bisectorial and perpendicular). The X(2)C(2)C(8)C(9) torsion angle (X(2) is the midpoint of the C(1)–C(3) bond) in molecules A and B is equal to −60(2) and −119(3)°, respectively (in the case of bisectorial) orientation, this angle should be 0 or 180°, while it should be 90° in the case of perpendicular orientation [6]). The X(3)C(3)C(14)C(15) torsion angle (X(3) is the midpoint of the C(1)–C(2) bond) in molecules A and B is 65 and −43°, respectively. Thus, the orientation of the substituents in II is apparently mainly a factor of the packing conditions for these molecules in the crystal and, possibly, of the steric and electrostatic interactions between the substituents and not fine electronic effects involving conjugation with the cyclopropane system.

The length of the Hg–Cl bonds (2.30(1) Å in A and 2.32(1) Å in B and of the Hg–C(2) bonds (2.12(4) Å in A and 2.12(3) Å in B) coincide with those found in I and with the normal values for these bonds [4, 7-12]. The ClHgC bond angle is 178.4(7) and 178.7(7)° in molecules A and B, respectively. The lengths of the bonds between the light atoms were obtained with large errors due mainly to the disorderedness of the CF_3 groups and the poor quality of the crystal and their detailed discussion is not justified.

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CRYSTAL STRUCTURE OF ORGANOSILICON COMPOUNDS.

XLVII.*

1-(CHLORODIMETHYLSILYLMETHYL)-2-PIPERIDONE

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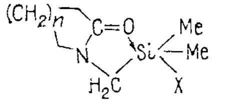
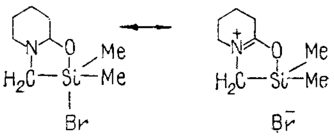
UDC 548.737

An x-ray diffraction structural analysis was carried out for 1-(chlorodimethylsilylmethyl)-2-piperidone using 1608 reflections to R = 0.0274. The silicon atom has trigonal bipyramidal [3 + 2] coordination with the oxygen and chlorine atoms in the axial positions. The Si–O bond length is 1.954(2) Å and the Si–Cl bond length is 2.307(2) Å.

INTRODUCTION

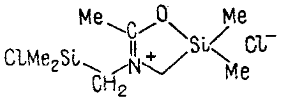
In a study of a new type of pentacoordinated silicon compounds, namely, N-(halodimethylsilyl)methyl lactams (I) which were recently discovered in our laboratory [2, 3], we found that the coordination of the silicon atom in bromo derivative (Ia) in the crystal is satisfactorily described as [4 + 1] with an additional Si ← Br interaction [3].

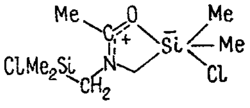

I (n=1-3, X=Cl (b), Br (a))


Ia Ia'

This indicates a significant contribution of "ionic" resonance from (Ia') to the actual structure of this compound and explains the rather high electrical conductivity of its solution in methylene chloride.

We should note that an analogous "ionic" structure II' is possible for N,N-bis(chlorodimethylsilylmethyl)acetamide (II) [4] but an x-ray diffraction structural analysis [5] and an NMR and IR spectral study [6] showed the predominant contribution of structure II".


II'


II''

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*For Part XLVI, see [1].

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