is, however, very unlikely. Furthermore, additional reflections should appear in the diffraction pattern in this case which would, however, be very weak and might remain unnoticed.

There is reason to assume that this "micro-twinning" phenomenon is rather common in crystalline compounds and is specifically responsible for the disorderliness of crystalline structures which does not occur within individual domains.

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X-RAY DIFFRACTION STRUCTURAL STUDY OF NONBONDING INTERACTIONS AND COORDINATION IN ORGANOMETALLIC COMPOUNDS.

PART XXVIII. CRYSTAL STRUCTURE OF 1-CHLOROMERCURO-1,3-DIPHENYL-2-CARBOMETHOXY-3-METHOXYCYCLOPROPANE

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UDC 548.737

An x-ray diffraction study at –120°C using λMoKα radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max} = 54°$ and correction for the actual crystal shape gave the molecular geometry of 1-chloromercuro-1,3-diphenyl-2-carbomethoxy-3-methoxycyclopropane ($R = 0.0560$, $R_w = 0.0588$). The unit cell parameters of the monoclinic crystals are: $a = 9.501(3)$, $b = 10.591(4)$, $c = 17.716(6)$ Å, $\beta = 98.70(3)°$ $V = 1762(1)$ Å^3, $Z = 4$, space group $P2_1/n$. The ClHg substituent at C(1), the carbomethoxy group at C(2) and the phenyl ring at C(3) are located on one side of the plane of the C(1)C(2)C(3) cyclcopropane ring, while the phenyl ring at C(1) and the methoxy group at C(3) are located on the other side. All the bond lengths in this molecule are ordinary.

An x-ray diffraction structural analysis was carried out for 1-chloromercuro-1,3-diphenyl-2-carbomethoxy-3-methoxycyclopropane $C_{18}H_{17}O_3ClHg$ (I) in order to determine the mutual orientation of the substituents and elucidate the Hg...O nonbonding interaction with the carbonyl oxygen atom of the carbomethoxy group.

EXPERIMENTAL

1. Preparation of I

A solution of 3.41 g mercury trifluoroacetate in 40 ml methanol was poured at room temperature into a solution of 2g of the methyl ester of diphenylcyclopropenecarboxylic acid in 40 ml methanol. The concentration of the reagents in the reaction mixture was 0.1 mole/liter. After 8-12 h, the reaction mixture was poured into a solution of 2 g NaCl in 250 ml water. The crude product was thrice crystallized from 70:30 hexane–chloroform to give the organomercury compound with mp 137.5-138°C.

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0022-4766/86/2701-0107$12.50

TABLE 1. Atomic Coordinates ($\times 10^4$, $\times 10^3$ for H) and Their Isotropic Equivalent Temperature Factors B_{iso}^{eq} (Å^2)*

Atom	x	y	z	B_{iso}^{eq}	Atom	x	y	z	B_{iso}^{eq}
Hg	7665(7)	6795(6)	3887(4)	2,30(2)	C(8)	—1222(18)	3223(17)	2822(10)	3,0(5)
Cl	385(4)	—1369(4)	4333(3)	3,0(1)	C(9)	—2490(18)	3901(17)	2688(10)	3,3(5)
O(1)	2187(11)	4493(10)	4101(6)	2,5(3)	C(10)	—2957(18)	4537(19)	3237(13)	4,1(6)
O(2)	2829(12)	657(10)	3037(6)	3,0(3)	C(11)	—2130(21)	4540(18)	3994(13)	4,2(6)
O(3)	3847(11)	2251(10)	2447(6)	2,5(3)	C(12)	—860(18)	3932(16)	4117(10)	2,8(5)
C(1)	949(15)	2580(15)	3674(8)	2,0(4)	C(13)	3474(16)	2521(14)	4534(9)	2,0(4)
C(2)	2051(15)	2805(15)	3145(8)	1,9(4)	C(14)	4862(17)	2435(15)	4354(9)	2,4(5)
C(3)	2306(17)	3200(16)	3970(9)	2,4(5)	C(15)	5921(17)	1837(18)	4865(11)	3,7(6)
C(4)	3381(18)	5219(16)	3941(10)	3,4(5)	C(16)	5576(20)	1369(17)	5580(11)	3,5(6)
C(5)	2909(16)	1744(18)	2885(8)	2,4(5)	C(17)	4234(19)	1505(15)	5739(9)	2,8(5)
C(6)	4882(19)	1326(18)	2219(11)	4,0(6)	C(18)	3158(17)	2093(15)	5227(9)	2,5(5)
C(7)	—386(16)	3225(15)	3531(9)	2,3(5)					

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
H(2)	209	327	258	H(9)	—319	393	215	H(15)	702	169	472
H(1.6)	563	188	188	H(10)	—394	512	327	H(16)	641	90	597
H(2.6)	438	63	188	H(11)	—249	503	454	H(17)	399	103	626
H(3.6)	546	89	272	H(12)	—20	398	472	H(18)	211	226	542
H(8)	—82	276	235	H(14)	514	278	381				

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* $B_{iso}^{eq} = 1/3 \sum_i \sum_j a_i^* a_j^* B_{ij} (a_i a_j)$.

TABLE 2. Bond Angles ω (deg)

Bond angle	ω	Bond angle	ω
ClHgC(1)	176,1(4)	C(1)C(7)C(8)	122(1)
HgC(1)C(2)	114(1)	C(1)C(7)C(12)	120(1)
HgC(1)C(3)	116(1)	C(8)C(7)C(12)	118(2)
HgC(1)C(7)	113(1)	C(7)C(8)C(9)	121(2)
C(2)C(1)C(3)	60(1)	C(8)C(9)C(10)	121(2)
C(2)C(1)C(7)	119(1)	C(9)C(10)C(11)	119(2)
C(3)C(1)C(7)	124(1)	C(10)C(11)C(12)	119(2)
C(5)C(2)C(1)	122(1)	C(11)C(12)C(7)	121(2)
C(5)C(2)C(3)	119(1)	C(3)C(13)C(14)	119(1)
C(1)C(2)C(3)	58(1)	C(3)C(13)C(18)	120(1)
O(1)C(3)C(1)	114(1)	C(14)C(13)C(18)	121(1)
O(1)C(3)C(2)	116(1)	C(13)C(14)C(15)	119(2)
O(1)C(3)C(13)	114(1)	C(14)C(15)C(16)	119(2)
C(1)C(3)C(2)	62(1)	C(15)C(16)C(17)	119(2)
C(1)C(3)C(13)	122(1)	C(16)C(17)C(18)	122(2)
C(2)C(3)C(13)	119(1)	C(17)C(18)C(13)	119(2)
O(2)C(5)O(3)	125(1)	C(4)O(1)C(3)	114(1)
O(2)C(5)C(2)	127(1)	C(6)O(3)C(5)	114(1)
O(3)C(5)C(2)	108(1)		

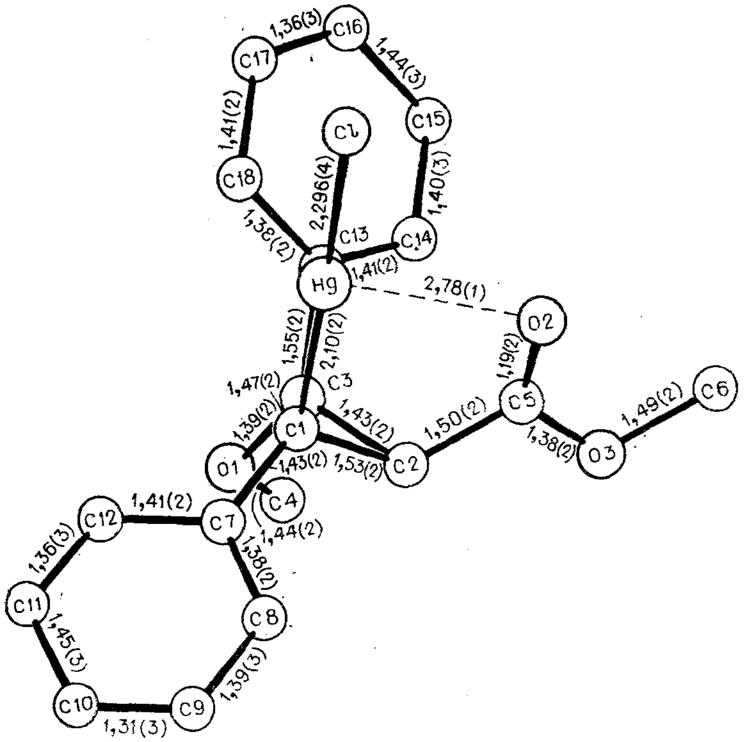


Fig. 1. Molecular structure of I.

2. X-Ray Diffraction Structural Analysis

The unit cell parameters of monoclinic crystals of I are as follows: −120°C a = 9.501(3), b = 10.591(4), c = 17.716(6) Å, β = 98.70(3)°, V = 1762(1) Å^3, Z = 4, d_{calc} = 1.95 g/cm^3, space group P2$_1$/n.

TABLE 3. Plane Equations Ax + By + Cz — D = 0 of Molecular Fragments and Angles between Planes (deg)

Plane	Atoms and their extrusion from the plane	*A*	*B*	*C*	*D*
I	C(1) C(2) C(3)	—0,375	0,892	—0,253	0,841
II	O(2) O(3) C(5) C(6) —0,00(1) 0,00(2) —0,00(2) —0,01(1)	—0,565	—0,122	—0,816	—5,481
III	O(1) C(3) C(4)	—0,308	0,126	—0,943	—6,475
IV	C(7) C(8) C(19) C(10) C(11) —0,01(2) —0,01(2) 0,01(2) 0,00(2) —0,02(2) C(12) 0,02(2)	0,528	0,811	—0,253	0,519
V	C(13) C(14) C(15) C(16) C(17) 0,02(2) —0,02(2) 0,01(2) 0,00(2) —0,00(2) C(18) —0,01(2)	—0,182	—0,886	—0,427	—6,152
VI	Hg C(1) C(2) C(5) O(2) —0,0030(6) 0,00(1) 0,00(1) —0,01(1) 0,01(1)	—0,592	—0,136	—0,794	—5,435

I/II 72,0; I/III 62,2; I/IV 53,9; I/V 127,9; I/VI 72,4

The unit cell parameters and intensities of 2923 reflections with $I > 2\sigma$ were measured on a Syntex $P2_1$ diffractometer at −120°C using λMoK_α radiation, graphite monochromator, $\theta/2\theta$ scanning and $2\theta_{max} = 54°$. The absorption was taken into account using our program [1] for the actual form of the crystal ($\mu(MoK_\alpha) = 90.8\ cm^{-1}$).

The structure was solved by the heavy atom method and refined by the method of least squares initially in the full-matrix isotropic approximation and then in the anisotropic approximation. All the hydrogen atoms of the phenyl rings and the hydrogen atoms of the $C(6)H_3$ group were revealed in the difference map. The hydrogen atoms of the $C(4)H_3$ group could not be localized.

Further refinement of the structure in the anisotropic approximation taking account of the hydrogen atoms of the phenyl rings whose positions were calculated geometrically and the hydrogen atoms of the methyl group localized in the difference map with fixed positional and isotropic temperature parameters ($B_{iso} = 4.5$ Å^2) gave R = 0.0560 and $R_W = 0.0588$ using 2891 reflections with $F^2 > 3\sigma$. The coordinates of the atoms and their isotropic equivalent temperature factors are given in Table 1.

RESULTS AND DISCUSSION

The structure of I and its bond lengths are shown in Fig. 1. The bond angles are given in Table 2. The ClHg substituent at C(1), the carbomethoxy group at (C2), and the phenyl ring C(13)...C(18) at C(3) are located on one side of the plane of the C(1)C(2)C(3) cyclopropane ring, while the phenyl ring C(7)...C(12) at C(1) and the methoxy group at C(3) are on the other side.

The Hg—C (2.10(2) Å) and Hg—Cl bond lengths (2.296(4) Å) are in accord with the usual values (2.05-2.15 and 2.29-2.33 Å, respectively) in organomercury compounds [2], in mercuric chloride [3] and in organomercury halides [4-8]. The phenyl rings and ester group are planar (Table 3). The bond lengths in the carbomethoxy and methoxy groups and the phenyl rings are in accord with standard values within experimental error [9].

Despite the not very high precision for localization of the light atoms (due to the presence of the heavy mercury atom in the structure of I), we should note the clear difference in the C—C bond lengths in the cyclopropane ring in I (1.43(2), 1.47(2) and 1.53(2) Å). Such asymmetry of substituted cyclopropanes is a general phenomenon due to the electronic interaction of the substituents with the molecular orbitals of cyclopropane.

On the basis of 91 precise structural analyses, Allen [10] carried out a statistical analysis of the bond lengths in substituted cyclopropanes and arrived at results in good accord with qualitative MO concepts. Thus, π-withdrawing substituents cause shortening ($\delta_1 < 0$) of the opposite C_β–C_β' (distal) bond and extension ($\delta_2 \approx \delta_3 \approx -\delta_1/2 > 0$) of both adjacent C_α–C_β and C_α–C_β' (vicinal) bonds in the cyclopropane ring. Data for the effect of electron-donor substituents are sparse but, on the whole, it is oppsite to the effect of electron-withdrawing substituents, i.e., leads to an extension of the distal and shortening of the vicinal bonds. Comparison with the experimental data showed satisfactory addditivity of the substituent effects, although further experimental data are required for electron-donor and the less common π-withdrawing substituents and polysubstituted cyclopropanes, and predominant substituent orientations relative to the cyclopropane ring. Thus, the electron-withdrawing effect of RC(=O) groups is most evident in the case of their bisectorial orientation (see below) although it remains significant upon deviation from this position by ± 30°. Phenyl groups in the bisectorial orientation also withdraw electron density from highest occupied MO of cyclopropane but donate electron density to its lowest vacant MO in the perpendicular orientation. It is significant that in both orientations, the phenyl groups cause physically identical shortening of the distal and extension of the vicinal bonds in the cyclopropane ring.

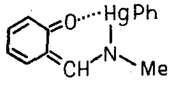
Using Allen's parameters [10] characterizing the effect of the carbonyl group (more precisely, α-carbonyl-containing substituents) $\delta_{C=O} = -0.026(5)$ Å and the phenyl substituent $\delta_{Ph} = -0.018(2)$ Å on cyclopropane geometry, we attempted to evaluate the effect of the OMe and HgCl substituents, whose parameters were not given by Allen [10], and the "theoretical" mean C–C bond length (Δ) in the cyclopropane ring of I assuming additivity of the substituent effects. Using the experimental data for the C–C bond lengths, a system of three equations gave $\delta_{OMe} = 0.032$ Å (which is in accord with the weak electron-donor properties of the MeO group), $\delta_{HgCl} = -0.035$ Å (in accord with the weak electron-donor properties of this substituent) and Δ = 1.477 Å which is identical with the mean value of the experimental bond lengths in I, thereby confirming the applicability of the additivity scheme in our case.

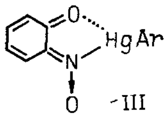
The calculated and experimental values for Δ are significantly less than the mean value for substituted cyclopropanes (1.510(2) Å) [10]. However, Δ values even less than in I are encountered in polysubstituted representatives (down to 1.45 Å [10]). This reduction in Δ indicates a significant (and different) rehybridization of the cyclopropane ring carbon atoms in I. The s character of the shortest C(2)–C(3) bond is significantly enhanced and the correspondingly enhanced p character of the exocyclic C(2)–C(5) bond is likely in accord with its extension to 1.50(2) Å relative to the mean value (1.456(6) Å) in carbonyl-substituted cyclopropanes [10]. Significantly enhanced s character of the C(1)–C(3) bond and, especially, of the C(2)–C(3) bond is in accord with the extension of the C(3)–Ph bond to 1.55(2) Å (which is also facilitated by the inductive effect of the electron-donor MeO group), while the small overall change in the s character of the endocyclic C(1)–C(2) and C(1)–C(3) bonds permits the clear manifestation of the inductive effect of the electron-donor ClHg substituent leading to contraction of the C(1)–Ph bond to 1.43(2) Å. We should note that the mean value of the lengths of both C(cyclopropane)–C(Ph) bond in I (1.49 Å) is close to the mean value in phenyl-substituted cyclopropanes (1.517(3) Å) [10].

The substituent orientation in substituted cyclopropanes is characterized by the torsion angle τ = X(n)–C(n)–Y–Z, where C(n) is a cyclopropane ring atom (n = 1, 2, 3), X(n) is the midpoint of the opposite ring bond, and Y and Z are atoms of the substituent at C(n). The carbomethoxy group in I has vicinal (gauche) orientation i.e., is projected onto the C(1)–C(2) cyclopropane bond (τ = X(2)–C(2)–C(5)–O(2) = 36°, the C(1)–C(2)–C(5)–O(2) torsion angle is 1(2)°, Table 3). Although the cis-bisectorial conformation (τ = 0°) is more often found for cyclopropane carbonyl derivatives, the vicinal conformation (τ = 30°) is also rather common and, in the case of I, it a consequence of an intramolecular secondary bond (see below). The orientation of both phenyl substituents is close to perpendicular (τ = ± 90°): indeed, the X(1)–C(1)–C(7)–C(12) and X(3)–C(3)–C(13)–C(14) torsion angles are 92 and 89°, respectively. Finally, the orientation of the MeO substituent is close to vicinal (the X(3)–C(3)–O(1)–C(4) torsion angle is −110°). In this case, nonoptimal overlap is possible both with the highest occupied and lowest unoccupied MO of the cyclopropane ring. Thus, the orientation of all the substituents in I is in accord with their electronic effects. As noted above, the ClHg and MeO_2C groups are located on the same side of the plane of the three-membered ring. The orientation of the CO_2Me group is such that the carbonyl oxygen atom is most approximated to the mercury atom (the HgC(1)C(2)C(5)O(2) fragment is planar, see Table 3).

The Hg...O distance (2.78(1) Å) is markedly less than the sum of the van der Waals radii (3.0-3.1 Å) of the mercury (1.5-1.6 Å [2]) and oxygen atoms (1.52 Å [11]) and undoubtedly corresponds to a secondary bond giving rise to a five-membered chelate ring. The Hg...O(2) C(5) bond angle is 102(1)°, while the O...HgCl and O...HgCl) angles are 107.8(3) and 75.5 (5)°, which is favorable for the interaction of the sp^2 orbital of the unshared electron pair of the oxygen atom with the vacant 6p orbital of the mercury atom.* As a result of the secondary interaction, there is a slight but completely real rehybridization of the mercury atom bonds: the C(1)HgCl bond angle opposite to O(2) is contracted to 176.3(5)°.

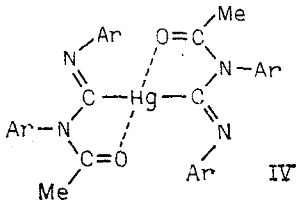
There have not been many reports of as strong an intramolecular Hg...O interaction with a carbonyl group as in the case of I. Thus, for example, six- and five-membered chelate rings are formed in potentially tautomeric phenylmercury salicylalmethyliminate (II) [12] and o-nitrosophenoxyl(o-hydroxy-m-tolyl)mercury (III) [13] due to secondary Hg...O bonds:


II


III

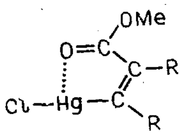
The Hg...O distances in II and III are 2.44 and 2.57 Å while the angle between the covalent bonds of the mercury atom opposite the oxygen atom is contracted to 167 and 174°, respectively.

Two five-membered chelate rings are formed in symmetrical IV with Hg...O distance equal to 2.63 Å [14].


IV

In our previous work [2], we showed that the strength of a secondary bond depends, in particular, on the possibility of the delocalization of electron charge in the chelate ring formed. If such delocalization is possible, the secondary bond is shorter. There are apparently no examples in the literature of organomercury compounds, in which chelate rings containing a secondary Hg...O bond contain groups not transmitting conjugation such as the $-CH_2-$ group. The inclusion of such a group in a chelate ring formed due to the usually stronger Hg...N secondary bond leads to a significant weakening of this bond.

Since cyclopropane in its chemical and physical behavior is not an analog of cycloalkanes but rather of ethylene [15], this fragment of I containing a five-membered chelate ring is an analog of a system, in which electron density delocalizaion in its chelate ring is possible:



Thus, we may now understand the formation of the rather strong Hg...O secondary bond in I.

The structure of I is molecular with ordinary van der Waals distances between the molecules.

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*Attainment of the Hg...O–C (120°) and O...Hg–C (and O...Hg–C) bond angles (90°) optimal for the secondary interaction in the five-membered chelate ring is impossible but the observed angles are rather close to these ideal values.

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STRUCTURE OF ORGANOPHOSPHOROUS COMPOUNDS. PART XXXIII.* MOLECULAR STRUCTURE OF N-[P'-1-ADAMANTYL-P'-BIS(TRIMETHYLSILYL)AMINO]PHOSPHINO-P-IODO-P,P-DI(TERT-BUTYL)IMIDOPHOSPHINATE

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UDC 548.737

An x-ray diffraction structural analysis was carried out for N-[P'-1-adamantyl-P'-bis(trimethylsilyl)amino]phosphino-P-iodo-P,P-di(tert-butyl)imidophosphinate using λMo radiation and 4069 reflections (R = 0.037). The unit cell parameters for these triclinic crystals at -120°C are: $a = 8.958$, $b = 12.493$, $c = 13.883$ Å, $\alpha = 102.04$, $\beta = 93.41$, $\gamma = 96.68°$, space group $P\bar{1}$, Z = 2. The central part of the molecule is nonplanar. The P(1)N(1)P(2)N(2) and IP(1)N(1)P(2) torsion angles are 117.7 and 47.2°, respectively. The mjaor geometrical parameters are: P(1)=N(1), 1.539; amide P(2)—N(2), 1.742; imide P(2)—N(1), 1.691 Å; P(1)N(1)P(2) 131.1°; N(1)P(2)N(2), 105.9°. The bond length distribution in the $\rightarrow P(1){=}N(1){-}P(2){<}$ system indicates the lack of conjugation between the unshared electron pair of tricoordinated P(2) and the π-system of the P(1)-N(1) double bond. Steric overloading of the molecule leads to extension of the P(1)—C(Bu^t) bond to 1.872, of the P(2)—C(Ad) bond to 1.879, and of the P(1)—I bond to 2.511 Å, a slight distortion of the tetrahedral coordination of P(1) and significant nonequivalence of the P(2)N(2)Si bond angles (112.1 and 129.0°).

Significant interest in organophosphorus chemistry has recently focused on the structure and properties of compounds of dicoordinated phosphorus, especially, of λ^3-iminophosphines.

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*For part XXXII, see [1].

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