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The Crystal Structure of Bistrichloromethylcarbonate, Triphosgene

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The crystal structure of bistrichloromethylcarbonate (triphosgene), $C_3O_3Cl_6$, has been determined from three-dimensional diffractometer-collected single crystal X-ray data. Crystals of triphosgene are monoclinic, space group $P2_1/c$ with unit cell dimensions $a = 9.824 \pm 0.008$ Å, $b = 8.879 \pm 0.004$ Å, $c = 11.245 \pm 0.004$ Å, and $\beta = 91.7 \pm 0.1°$. The compound is unstable, dissociating slowly into phosgene, $COCl_2$. The conformation of the molecule in the crystal is favourable for the cyclic reaction mechanism that has been proposed for this dissociation.[1] Each molecule consists of a planar chain containing the atoms Cl–C–O–CO–O–C–Cl with the remaining four Cl atoms placed approximately symmetrically above and below the plane of the chain. The molecules of the structure are linked together in chains by weak O···Cl charge-transfer bonds.

Bistrichloromethylcarbonate, (triphosgene) $C_3O_3Cl_6$ behaves in most chemical reactions as three molecules of carbonyl chloride. The compound is slightly unstable and is dissociated slowly at room temperature to $COCl_2$. It is prepared by exhaustive chlorination of dimethyl carbonate and forms colourless crystals with m.p. 79°.[2] The formula $(Cl_3CO)_2CO$ has been confirmed spectroscopically by Hales *et al.*[1] The purpose of the structure determination described here was to investigate whether a correlation might be possible between this instability of the molecule and its geometry. Special interest was directed towards the possible presence of charge-transfer bonds in the structure.

EXPERIMENTAL

The space group and cell dimensions were determined from Weissenberg and precession X-ray diffraction photographs. θ values for 45 reflexions were measured and employed in a least squares refinement of the cell dimensions.

Crystallographic data:

Space group: $P\ 2_1/c$, $Z = 4$. $a = 9.824 \pm 0.008$ Å, $b = 8.879 \pm 0.004$ Å, $c = 11.245 \pm 0.004$ Å, $\beta = 91.7 \pm 0.1°$. Calculated density 2.01 g·cm^{-3}. No experimental determination of the density was made owing to the instability of the compound. Linear absorption correction for Mo$K\alpha$ radiation is 17.0 cm^{-1}. No absorption correction was applied.

Intensity data collection: Nonius three-circle automatic diffractometer.
Radiation: Crystal monochromatized Mo$K\alpha$, $\lambda = 0.71069$ Å.
Measuring technique: Moving-crystal-stationary-detector (ω-scan).
Scan speed: 1.2°/min.
θ range: 2.5° – 25°.
Dimensions of the crystal: $0.4 \times 0.4 \times 0.4$ mm³.
Alignment of the crystal: b-axis parallel to ϕ-(goniometer-head) axis; the crystal was mounted in a glass capillary.

Number of independent reflexions: 1729. The number of reflexions with intensities greater than 1.5 times their corresponding *e.s.d.* was 1559. The range of relative F_o^2 values was 0.1 – 550. One reference reflexion was measured after every twenty new intensity measurements to monitor the stability of the instrument. The relative intensities measured for it were used to bring all intensities to the same scale.

Computers: GIER at H.C. Ørsted inst., Copenhagen and IBM 7094 at NEUCC, Lyngby, Denmark.

Computer programs: X-RAY 63.[3] OR TEP.[4] Diffractometer input and output data reduction programs were written by the author.

STRUCTURE DETERMINATION

Approximate positions for the six Cl atoms were postulated from a three-dimensional sharpened Patterson synthesis. After their coordinates had been improved in a series of Fourier refinement calculations an electron density map calculated using the phases of the six Cl atoms was plotted. The positions of all the C and O atoms were postulated from this.

Two cycles of full matrix least squares refinements varying the positional parameters and individual atomic isotropic temperature factors for all atoms were computed. The R value was 0.17. Anisotropic temperature factors were then introduced for all atoms and some cycles of least squares refinements were calculated. The refinement was based on F's, minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weights were calculated as follows: for $0 \leq F_o \leq 6$ then $w = (1 + 0.167F_o)/(100 - 16.4F_o)$; otherwise $w = 1$. This weight function results in a gradually decreasing weight of reflections having relative structure factors less than six. The final R value calculated for 1559 observed reflexions was 0.065. The final atomic parameters are listed in Tables 1 and 2 and bond lengths and angles calculated from these parameters are listed in Tables 3 and 4. Tables of the structure factors are available on request from the laboratory. Please refer to project number C 1076.

Table 1. Fractional atomic coordinates with their estimated standard deviations ($\times 10^4$) in parentheses.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cl(11)	4437(2)	6616(2)	3811(2)	O(1)	3170(4)	4862(5)	2452(4)
Cl(12)	5330(2)	5975(2)	1464(2)	O(2)	2549(5)	4685(5)	0486(4)
Cl(13)	2880(2)	7668(2)	1793(2)	O(3)	1941(4)	3004(5)	1919(4)
Cl(31)	0595(2)	0658(2)	2116(2)	C(1)	3928(6)	6210(7)	2357(6)
Cl(32)	2060(2)	1303(2)	0015(2)	C(2)	2562(6)	4249(7)	1453(6)
Cl(33)	–0287(2)	3066(2)	0582(2)	C(3)	1127(6)	2097(7)	1161(6)

Table 2. Anisotropic thermal parameters β_{ij} with their estimated standard deviations ($\times 10^4$), and the r.m.s. components, R_i, of the thermal displacements of the atoms along the principal axes of the thermal motion (Å). The temperature factor is $\exp[-(h^2\beta_{11}+2hk\beta_{12}+\cdots)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Cl(11)	207(3)	162(3)	85(2)	−77(3)	−20(2)	−16(2)	0.19	0.25	0.35
Cl(12)	100(2)	139(3)	122(2)	−10(2)	−25(2)	−7(2)	0.21	0.24	0.29
Cl(13)	144(3)	89(2)	144(2)	21(2)	−8(2)	−3(2)	0.18	0.27	0,31
Cl(31)	144(3)	87(2)	140(2)	−29(2)	11(2)	26(2)	0.17	0.27	0.30
Cl(32)	142(2)	133(3)	124(2)	2(2)	26(2)	−59(2)	0.18	0.26	0.32
Cl(33)	104(2)	115(2)	125(2)	14(2)	−18(2)	5(2)	0.20	0.23	0.29
O(1)	121(6)	90(6)	68(4)	−38(5)	−8(4)	4(4)	0.17	0.21	0.26
O(2)	138(6)	105(7)	68(4)	−22(5)	−4(4)	9(4)	0.19	0.21	0.27
O(3)	109(6)	75(5)	77(4)	−24(5)	3(4)	5(4)	0.16	0.22	0.24
C(1)	100(8)	86(8)	82(6)	−21(7)	−3(5)	5(6)	0.17	0.22	0.24
C(2)	90(7)	71(8)	72(6)	−4(6)	8(5)	0(6)	0.17	0.20	0.22
C(3)	95(8)	75(8)	77(6)	−9(6)	3(5)	−7(5)	0.17	0.22	0.22

Table 3. Interatomic distances (Å) with their estimated standard deviations ($\times 10^3$) in parentheses. Errors in the unit cell dimensions have been included in the e.s.d.'s. The second columns in the first part of the table give the distances averaged over thermal motion, assuming the second atom to ride on the first.

C(1)−Cl(11)	1.733(7)	1.763	C(1)−O(1)	1.416(8)	
C(1)−Cl(12)	1.742(7)	1.742	C(3)−O(3)	1.405(7)	
C(1)−Cl(13)	1.760(7)	1.783	C(2)−O(1)	1.369(8)	
C(3)−Cl(31)	1.759(7)	1.779	C(2)−O(3)	1.374(7)	
C(3)−Cl(32)	1.752(7)	1.770	C(2)−O(2)	1.154(8)	1.171
C(3)−Cl(33)	1.743(7)	1.762			

Intra- and *inter*molecular distances from C(2) and O(2) to Cl.

C(2)···Cl(12)	3.121(7)	O(2)···C(12)	3.131(6)
C(2)···Cl(13)	3.074(6)	O(2)···Cl(13)	3.041(5)
C(2)···Cl(32)	3.106(6)	O(2)···Cl(32)	3.084(5)
C(2)···Cl(33)	3.120(7)	O(2)···Cl(33)	3.140(5)
O(2)···Cl(12)	3.125(6)	O(2)···Cl(33)	3.195(6)
(x,y,z) $(1-x,1-y,-z)$		(x,y,z) $(x,y-1,z)$	

*Inter*molecular Cl−Cl distances shorter than 3.6 Å.

Cl(13)···Cl(31)	3.503(3)	Cl(33)···Cl(31)	3.483(3)
(x,y,z) $(x,y+1,z)$		(x,y,z) $(-x,\frac{1}{2}+y,\frac{1}{2}-z)$	

DESCRIPTION OF THE STRUCTURE

The bond lengths are very close to normally accepted values. The geometries of the two chemically similar halves of the molecule, although not constrained by symmetry to be so, are identical within experimental errors. The C−Cl distances have been corrected for riding motion effects assuming that the Cl atoms ride on C(1) and C(3). The distance O(2)−C(2) was similarly corrected

Table 4. Valency angles and some *inter*molecular angles (°), with their estimated standard deviations (× 10) in parentheses.

*Intra*molecular angles.

C(1) – O(1) – C(2)	119.5(5)	O(3) – C(3) – Cl(31)	102.7(4)
C(3) – O(3) – C(2)	118.7(5)	O(3) – C(3) – Cl(32)	112.1(4)
O(1) – C(2) – O(2)	129.2(6)	O(3) – C(3) – Cl(33)	112.1(4)
O(2) – C(2) – O(3)	129.6(6)	Cl(11) – C(1) – Cl(12)	111.0(4)
O(1) – C(2) – O(3)	101.2(5)	Cl(11) – C(1) – Cl(13)	109.6(4)
O(1) – C(1) – Cl(11)	104.0(4)	Cl(12) – C(1) – Cl(13)	110.1(4)
O(1) – C(1) – Cl(12)	111.7(4)	Cl(31) – C(3) – Cl(32)	109.2(4)
O(1) – C(1) – Cl(13)	110.2(4)	Cl(31) – C(3) – Cl(33)	109.8(4)
		Cl(32) – C(3) – Cl(33)	110.7(4)

*Inter*molecular angles.

C(2) – O(2) ··· Cl(12)	127.5(4)	O(2) ··· Cl(12) – C(1)	169.3(2)
(x,y,z) (1−x,1−y,−z)		(x,y,z) (1−x,1−y,−z)	
C(2) – O(2) ··· Cl(33)	123.5(4)	O(2) ··· Cl(33) – C(3)	170.5(2)
(x,y,z) (x,y−1,z)		(x,y,z) (x,y−1,z)	
Cl(12) ··· O(2) ··· Cl(33)	108.9(2)		
(1−x,1−y,−z) (x,y,z) (x,1−y,z)			

with O(2) assumed to ride on C(2). The valency angles deviate appreciably from the ideal values, forming molecules with somewhat curved backbones, to make room for O(2), Cl(12), Cl(13), Cl(32), and Cl(33). Each molecule contains a planar chain from Cl(11) to Cl(31) and Cl(12), Cl(13), Cl(32), and Cl(33) are placed approximately symmetrically around this plane; Figs. 1 and 2. A least squares plane through O(1), O(2), O(3) and C(2) was calculated according to Schomaker *et al.*[5] The equation of this plane with respect to the *a*, *b* and *c* axes is:

$$8.129x - 4.767y - 2.133z = -0.261 \text{ Å}$$

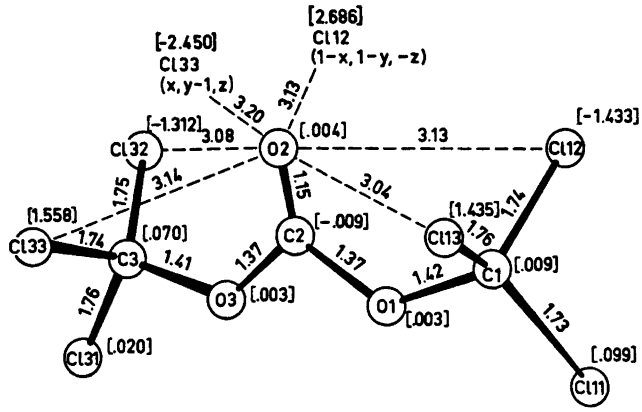

Fig. 1. Triphosgene, *intra-* and some *inter*molecular distances, and distances of the atoms from the least squares plane computed through O(1), O(2), O(3) and C(2).

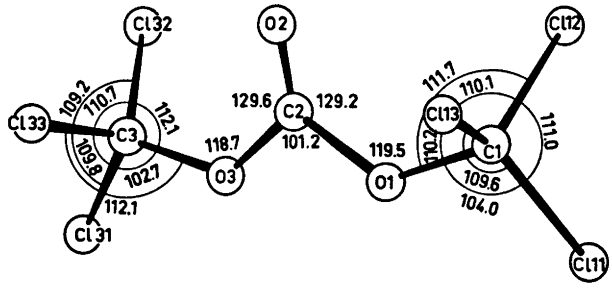

Fig. 2. Triphosgene, *inter*atomic angles.

and the distances of the atoms from it are given in Fig. 1. The symmetrical conformation produces a very compact molecular structure with short distances from O(2) and C(2) to Cl(12), Cl(13), Cl(32), and Cl(33) which are all 0.1 – 0.16 Å shorter than the sum of the corresponding van der Waals radii. The conformation can be described as an equilibrium state: on the one hand there is a repulsion between O(2) and the surrounding Cl atoms whilst on the other there is a tension in the molecular backbone tending to normalize the bond angles.

Four of the Cl atoms are placed so that a reaction between the electrophilic C(2) and one of the Cl atoms is possible. This reaction has been suggested [1] as the initial step in a cyclic mechanism by which the molecule is dissociated into $COCl_2$ and $Cl-CO-OCCl_3$. Cl(13) forms the longest C – Cl bond and also, independently, the shortest contact Cl···C(2), so this could be the reactive centre, however, the experimental data are not sufficient to prove this hypothesis.

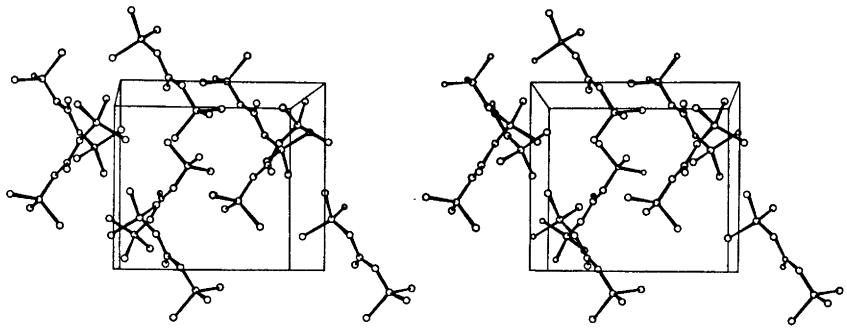

Fig. 3. Stereoscopic pair of figures showing the structure as seen along the *c*-axis.

O(2) forms close contacts to Cl(12) and Cl(33) in neighbouring molecules, thereby linking the molecules together in chains. The O(2)···Cl(12) distance of 3.125 Å is significantly shorter than the van der Waals distance (3.20 Å), probably indicating a weak charge-transfer bond. The angles in this possible charge-transfer system are given in Table 4. The C – Cl···O angles are about

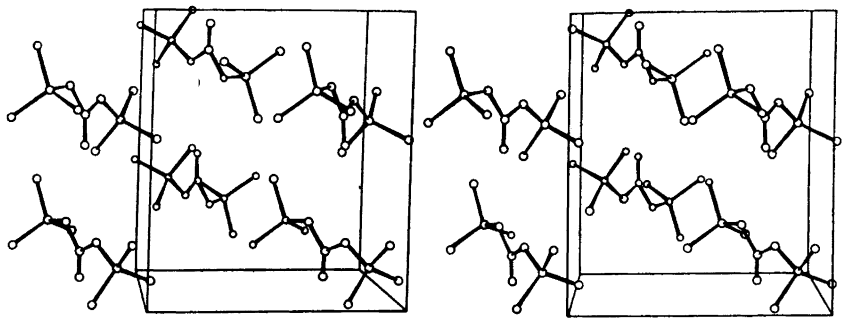

Fig. 4. Stereoscopic pair of figures showing the structure as seen along the *b*-axis.

170° and agree rather well with the linear arrangement found in many charge-transfer complexes.[6]

Two intermolecular Cl···Cl distances are about 0.1 Å shorter than twice the van der Waals radius, all other intermolecular distances are equal to or greater than the corresponding van der Waals distances.

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