# Molecular Structure of Monochloromethyl Chloroformate

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The molecular structure of monochloromethyl chloroformate molecule in the gas phase was determined by electron diffraction studies. The sample was prepared by passing a mixture of methylformate vapour and chlorine through a silica tube exposed to the light from a mercury lamp, and redistilled at 52.5—53° under 100 mm.Hg. The photographs were taken in the usual way with an electron wave lengh of about 0.06 Å. and a camera distance of 8.5 cm.

The interatomic distances and valence angles determined are as follows:

$ClCOOCH_2Cl$.

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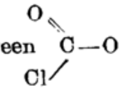
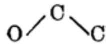
|---|---|
| Cl-C | 1.74 ± 0.02 Å. |
| Cl—C (chloromethyl) | 1.74 ± 0.02 Å. |
| C=O | 1.20 ± 0.03 Å. |
| C—O (carboxyl) | 1.40 ± 0.04 Å. |
| C—O (methoxyl) | 1.40 ± 0.04 Å. |
| ∠Cl—C—O | 112 ± 4° |
| ∠O=C—O | 126 ± 4° |
| ∠C—O—C | 110 ± 4° |
| ∠O—C—Cl (chloromethyl) | 109.5 ± 3° |

An angle between  and  plane is 0°∼90°, and the chlorine atom in the-$CH_2Cl$ group is *trans* to the carboxyl carbon atom.

The carboxyl C—O bond in this molecule is about 0.03 Å. shorter than the normal bond, corresponding about 5% of Pauling double bond character and thus in fair agreement with its non-planar constellation. J. M. O. Gorman *et al.* reported the structures of the methyl formate, methyl acetate and methyl chloroformate molecules by means of electron diffraction.(1) According to their investigation, all these molecules have approximately planar configurations with the ester methyl group *cis* to the carbonyl oxygen atom, and they have shorter carboxyl C—O distance (1.35-1.37 Å.), and longer methoxyl C—O distance (1.46-1.47 Å.), than the normal bond. The contrasting results for these esters are in agreement with the conclusions from dipole-moment studies for aliphatic carboxylic esters(2), (3), (4) but not for methyl carbonate and methyl and ethyl chloroformates, these molecules according to the dipole studies(5), (6) having rather large amplitudes of libration. However, the dipole moment data are not incompatible with a mainly planar structure, either *cis* or *trans*, with considerable libration and considerable resonance, the various, possibly large, resonance moment contributions having been neglected.(5), (6) Accordingly, the carboxylic C—O bond seems to have less double bond character and hindrance to

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(1) J. M. O. Gorman, W. Shand, Jr. and V. Schomaker, *J. Am. Chem. Soc.*, **72**, 4222 (1950).

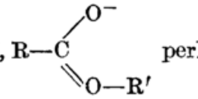
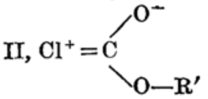
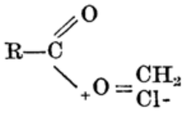
(2) A. Eucken and L. Meyer, *Physik. Z.*, **30**, 397 (1927).

(3) C. T. Zahn. *ibid.*, **33**, 730 (1933).

(4) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.* **1936**, 1383.

(5) M. Kubo, Y. Morino and S. Mizushima, *Sci. Papers. Inst. Phys. Chem. Research (Tokyo)*, **32**, 129 (1937).

(6) S. Mizushima and M. Kubo, This Bulletin, **13**, 174 (1938).

libration in methyl chloroformate than in the simple esters, but more than in chloromethyl chloroformate; correspondingly, chlorine in either position probably diminishes the net contribution of the $\mathrm{C}\dot{-}\mathrm{O}$ (carboxyl) structures such as I,  $\mathrm{R{-}}\overset{\diagup \mathrm{O}^{-}}{\underset{\diagdown\!\!\diagdown \mathrm{O{-}R'}}{\mathrm{C}}}$ perhaps by giving rise predominantly to competing structures such as II,  $\mathrm{Cl}^{+}{=}\overset{\diagup \mathrm{O}^{-}}{\underset{\diagdown \mathrm{O{-}R'}}{\mathrm{C}}}$ and III,  $\mathrm{R{-}}\overset{\diagup\!\!\diagup \mathrm{O}}{\underset{\diagdown {}_{+}\mathrm{O}{=}\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{\mathrm{Cl^-}}}{\mathrm{C}}}$ as well as by the destabilizing (inductive) effect of the chloromethyl dipole on structure I. Structure III would also account for the shortening of methoxyl C—O in monochloromethyl chloroformate.

The details of this research will be published elsewhere.

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