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Bonds Connecting Group VI Donor Atoms and Halogen Atoms in Ethylene Derivatives

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Several crystal structures of addition compounds exhibiting bonds between group VI donor atoms and halogen atoms of organic molecules are known, but in-

formations are lacking for halogen derivatives of ethylene. One addition compound of this kind has been described, however; the 1:1 compound containing 1,4-dioxan and tetraiodoethylene.¹

We have prepared this compound and also some new compounds in which oxygen is replaced by other group VI atoms. For X-ray investigation we first chose the 1,4-diselenane-tetraiodoethylene compound. In crystals of this kind we expected the presence of endless chains of alternating acceptor and donor molecules, with a nearly linear arrangement donor atom, halogen, carbon. Further that the chain halogen atoms of the acceptor molecule might be *trans* situated. In this case both donor and acceptor molecule would be expected to occupy centrosymmetrical sites in the crystal. These expectations were actually confirmed for the compound investigated. The other moiety of iodine atoms are also linked to selenium atoms, however, but these iodine atoms belong to neighbour chains. The I...Se distances are equal (3.43 resp. 3.40 Å) and the C-I...Se arrangements both nearly linear. In the (1:1) diiodoacetylene compound where each selenium atom is linked to *one* iodine atom only, the distance is a little shorter (2.35 Å).² In this compound no indication of a

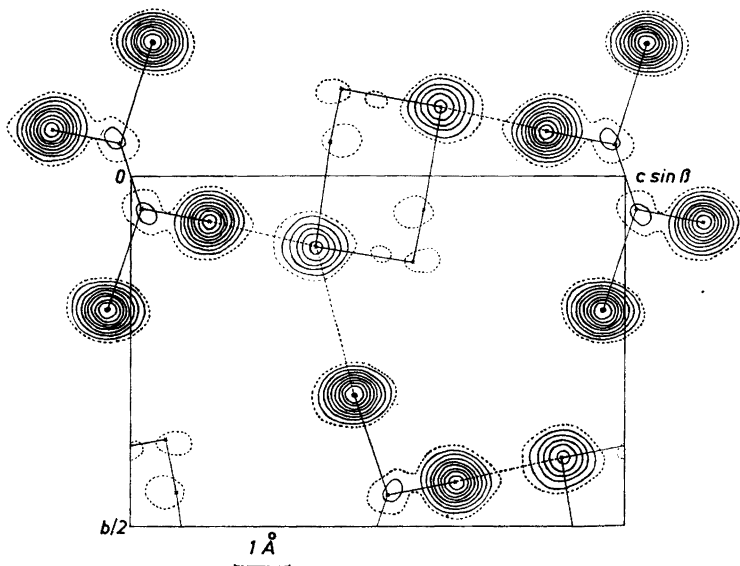


Fig. 1. Fourier projection along the *a* axis. Contour intervals of $10 \text{ e}/\text{Å}^2$; the dotted contour corresponds to $5 \text{ e}/\text{Å}^2$.

distortion of the diselenane molecule is observed, but a minor deformation is indicated in the case of particularly strong Se...I bonds (in the iodine compound) and when each sulphur atom forms two bonds to iodine, from a lengthening of the intramolecular Se...Se distance by a few hundredths of an Å U.³⁻⁵ The four iodine atoms form a planar rectangle with sides 3.53 and 3.68 Å long. The carbon coordinates are of course not so accurately determined, but it appears that the C-C bond direction runs approximately parallel to the longer side of the iodine rectangle and the C-I distance and the angle ICI are not sensitive to a deviation from strict parallelity. Assuming the C-C distance to be 1.34 Å the figures obtained are C-I = 2.12 Å, the angle ICI = 113°.

The crystals belong to the space group $P2_1/c$ and the lattice parameters are: $a = 6.50$, $b = 12.80$, $c = 9.21$, $\beta = 99.6^\circ$. The number of formula units in the unit cell is 2. The intensity data for the $0kl$ -zone were collected from integrated Weissenberg diagrams and measured photo-metrically. For the $h0l$ -zone a diffractometer with counter was employed. Absorption corrections were applied in both cases, although MoK-radiation was used. The final R factors were 5.5 % ($0kl$) and 7.7 % ($h0l$).

In Fig. 1 the Fourier map for the a -axis projection is reproduced and visualizes the chains of alternating donor and acceptor molecules running along the $[10\bar{1}]$ direction.

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Preparation of [¹⁵N]- and [4-¹³C]-Pyridine

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As a pre-requisite for the determination of the r_s -structure of pyridine by microwave technique, milligram quantities of [¹⁵N]- and [4-¹³C]-pyridine were prepared.

[¹⁵N]-Pyridine. Anhydrous sodium glutacondialdehyde (I) was prepared.^{1,2} A 32 % yield has been claimed. The yields obtained by us varied between 10 and 25 %. 640 mg 33 % enriched ¹⁵NH₄NO₃ (8 mmole) was dissolved in 240 ml dry methanol to which 8 g anhydrous MgSO₄ was added for immediate removal of water under the subsequent reaction. After 15 min of stirring, 9.5 g (80 mmole) (I) was added. The flask was closed and left to itself at room temperature for 2 weeks under continued stirring. MgSO₄ was separated by filtering and washed by methanol. 10 ml 12 N aqueous HCl was added to the combined methanolic solutions, from which methanol was removed *in vacuo*. The almost dry residue was again dissolved in 14 ml 4 N HCl and the water and the remaining methanol removed *in vacuo*. For separation from polymerized glutacondialdehyde the residue was dissolved in 7 ml 4 N HCl and transferred to a Claysen flask together with 2 g NaOH. At 1 atm, 50 ml water-pyridine-ammonia mixture was distilled off into 14 ml 4 N HCl. The water was removed *in vacuo* at a final temperature of 40°C and the residue transferred with 250 ml water to an Erlenmeyer flask. 1 g KBr and 0.5 g NaHCO₃ was added and dissolved. A small quantity of ammonia was oxidized to nitrogen by addition of 2 ml of a solution containing 0.4 mmole OCl⁻ per ml. Hereafter, water and bromine was removed *in vacuo*. A solution of 3 g NaOH in 70 ml water was added, and 50 ml water-pyridine mixture was distilled off at 1 atm into 14 ml 4 N HCl. After renewed evaporation to dryness, the residue was dissolved in 0.7 ml water. A warm solution of 1.1 g HgCl₂ in 7 ml water was added. The crystalline precipitate, C₅H₅N, HCl,