# Hexachloro-Cyclohexane, M. P. 145° C

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Hexachloro-cyclohexane of m. p. 145° C obtained by chlorination of cyclohexane in artificial light has been found to have zero dipole moment [1]. At the time when this result was obtained nothing was known about the dipole moment of ε benzene hexachloride, and the molecular structure of this compound had not yet been determined. Bastiansen and Hassel [1] therefore suggested that the 145° substance might be the second benzene hexachloride (besides the β isomer) possessing a centro-symmetric structure.

Later on electron diffraction [2,3] and X-ray crystallographic work [4] have conclusively proved that ε benzene hexachloride has the configuration $\varepsilon\varkappa\varkappa\varepsilon\varkappa\varkappa$ and therefore it became necessary to reject the possibility that the 145° substance is a member of the series of benzene hexachlorides [2]. The 145° substance must therefore contain at least *one* carbon atom attached to *two* chlorine atoms. If the lack of a dipole moment means that the molecule is rigorously centro-symmetric only *one* structural alternative is possible, corresponding to the two interconvertible configurations (1) and (2):

(1) $1(\varkappa,\varepsilon),2\varkappa,4(\varkappa,\varepsilon),5\varkappa$ (2) $1(\varkappa,\varepsilon),2\varepsilon,4(\varkappa,\varepsilon),5\varepsilon$
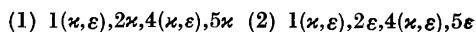
The vanishing of the dipole moment might, however, also be due to a chance compensation of partial moments. Although the electron diffraction results (see below) are strongly in favour of the first alternative, with the configuration (1), the result was not decisive. Additional X-ray crystallographic measurements revealed however, that the monoclinic unit cell reported earlier [1] and containing four molecules, is B-centered. The smallest possible cell thus contains *two* molecules, its lattice constants being $a = 8.25$ Å, $b = 6.72$ Å, $c = 9,41$ Å with $\beta = 103.7°$. The space group is $C_{2h}{}^5\text{-}P2_1/n$ and the molecules are therefore strictly centrosymmetric. The substance is consequently the 1,1', 2, 4, 4',5-hexachloro-cyclohexane capable of existing in the two steric configurations (1) and (2) given above. Our present knowledge about the relative stability of interconvertible forms of cyclohexane derivatives would suffice, we think, to predict the configuration (1) in the crystal-

cause an increase of the periodate consumption at the non-reducing terminal residue only.

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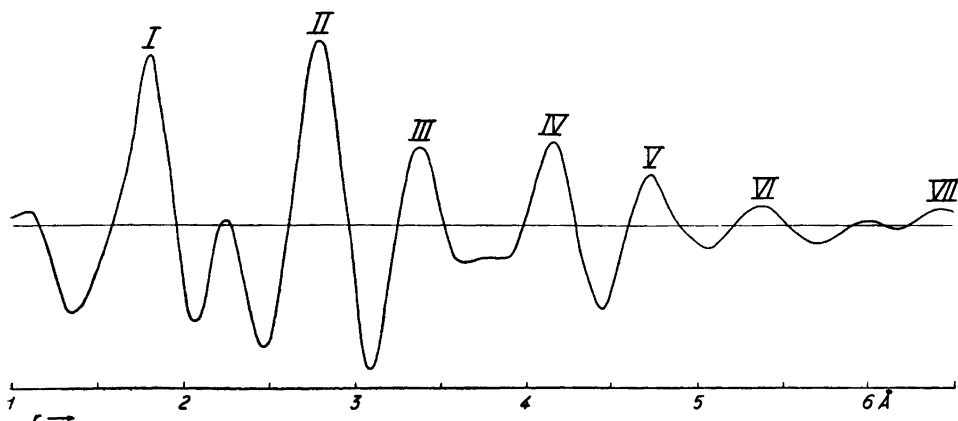
line state, and even in the vapour state quite negligible amounts of the configuration (2) would be expected.

As mentioned above this expectation has been confirmed by an electron diffraction analysis. The $\dfrac{\sigma(r)}{r}$-curve given in Fig. 1 corresponds to the curves reproduced in an earlier communication dealing with the benzene hexachlorides[3]. The scales have been so adjusted that both position and height of the peaks I to VII may easily be compared with those of the corresponding peaks of the benzene hexachloride curves. The pronounced peak numbered II (at about 2.8 Å) besides being considerably higher than the corresponding peaks of the hexachlorides is also somewhat displaced towards greater r-values. This observation is in excellent agreement with the formula of 1,1′,2,4,4′,5-hexachlorocyclohexane which contains *two* CCl_2-groups. An in-spection of the peaks VI and VII now enables us to make a decision between the two possible configurations (1) and (2) mentioned above. The first peak (at about 5.4 Å) corresponds in height to peak VI of a and ε benzene hexachloride, thus indicating the presence of *two* $Cl_{1\varkappa}-Cl_{3\varkappa}$ distances. Moreover, the height of peak VII (6.4 Å) corresponds to that observed for δ and ε benzene hexachloride which indicates *two* $Cl_{1\varkappa}-Cl_{4\varkappa}$ distances. This observation proves, we think, that at least the greater part of the molecules have the configuration (1) in the vapour phase.

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