Technical Papers

Nomenclature and Structure of 1,2,3,4,5,6-Hexachlorocyclohexanes

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A considerable literature has grown up concerning the geometrical structure of the various 1,2,3,4,5,6-hexachlorocyclohexane isomers. The gamma isomer is one of our most potent insecticides. The isomers have been pictured either as planar or nonplanar, and various methods of naming them have been used. It is the purpose of this note to indicate the accepted structures of the isomers using the planar and nonplanar configuration and to suggest that the nomenclature be standardized as shown.

Eight different forms of the 1,2,3,4,5,6-hexachlorocyclohexanes are possible if we assume a planar carbon ring or a nonplanar carbon ring the two configurations of which are interconvertible. One of these forms may exist as an optically active material. Five of the hexachlorocyclohexanes have been isolated from samples of benzene hexachloride obtained by the direct photochlorination of benzene. Recently Kolka *et al.* (*1*) prepared a sixth, designated as the *eta* isomer, by the photochlorination of individual benzene tetrachloride isomers. Evidence has also been offered by these workers that a seventh, designated as the *theta* isomer, can be formed in a similar fashion. The *alpha* isomer is a racemic mixture; the levorotatory form has been isolated by Cristol (*2*).

In Fig. 1 the cyclohexane ring is represented as being planar, with the chlorine substituents perpendicular to and either above or below the plane of the ring. All the possible isomers are indicated, and because it has been postulated at various times that the insecticidal property of the gamma isomer may be due to interference with the normal metabolism of the inositols, the structures of the known inositols are also given.

The nomenclature used is based on a modified Maquenne (*3*) numbering system, as suggested by Fletcher *et al.* (*4*). The configurations are given by a fraction. A particular carbon atom is placed in the numerator or denominator according to whether the substituted group is above or below the plane of the ring. Numbering is clockwise.

The last two configurations in Fig. 1 are optically active modifications of the same form. We have two different numbers for equivalent positions of the optically active compound. However, if we number the structure IX counterclockwise, we can assign the same number to both forms.

Although it is often convenient to use the planar representation, it has been shown by electron-diffraction measurements (*5*) and other physical and chem-

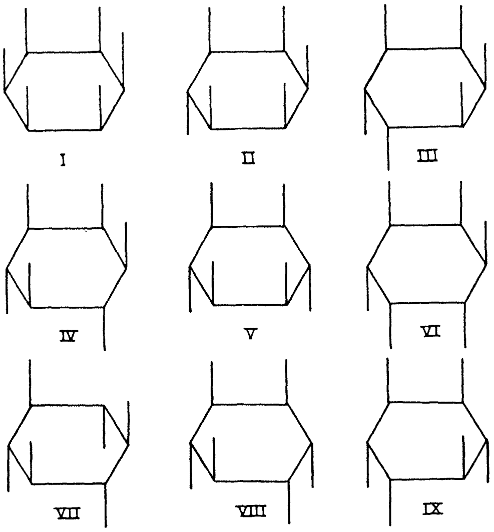

Fig. 1. Hexachlorocyclohexanes (benzene hexachlorides) and hexahydroxycyclohexanes (inositols). For each structure the configuration is given followed by the name of the hexachlorocyclohexane isomer, a dash, and the name of the corresponding inositol. (*I*) 123456/0 unknown–unknown; (*II*) 12345/6 theta–epi; (*III*) 1234/56 eta–allo; (*IV*) 1235/46 delta–myo (meso); (*V*) 1245/36 gamma–muco; (*VI*) 123/456 epsilon–unknown; (*VII*) 135/246 beta–scyllitol; and (*VIII*) 125/346 and (*IX*) 124/356 alpha (a racemic mixture; the levorotatory form has been isolated)–dl inositol.

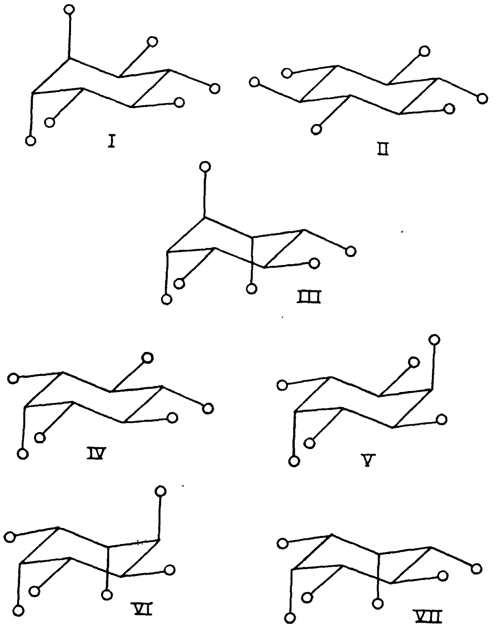

Fig. 2. Isomers of hexachlorocyclohexanes. If the carbons with the substituents parallel to the axis of symmetry are designated *a* and the ones with the equatorial substitution are designated *e*, the configuration can be represented as follows: (*I*) alpha, *aaeeee*; (*II*) beta, *eeeeee*; (*III*) gamma, *aaaeee*; (*IV*) delta, *aeeeee*; (*V*) epsilon, *aeeaee*; (*VI*) eta, *aeaaee*; and (*VII*) theta, *aeaeee*.

ical methods that the cyclohexane ring in the hexachlorocyclohexanes can best be represented as a modified chair form.

There is an alternating axis of symmetry in the structure, and the bond between any carbon atom and its constituent may be parallel to this axis or in an equatorial position somewhat above or below the perpendicular to the axis. The configurations assigned to the different isomers on this basis are shown in Fig. 2. Various designations, such as polar, equatorial, epsilon, and gamma, have been given to these bonds. It is suggested that the positions be named according to a recent proposal by Barton *et al.* (*6*). The term *axial* is used for substituents parallel to the axis of symmetry and is symbolized *a*; equatorial substituents are symbolized *e*.

References

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Partial Charges on Atoms in Organic Compounds

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The recent development of a simplified theory and method of estimating quantitatively the contribution to charge distribution made by atomic electronegativities (*1–3*) should be of especial interest in organic chemistry. This paper outlines the fundamental ideas and methods of calculation, presents numerical data for facilitating application, and discusses the interpretation of chemical phenomena.

The chief quantitative indication of molecular charge distribution hitherto available has been the experimentally determinable electric dipole moment. This value indicates only the over-all charge distribution, with no evidence of the relative importance, or even of the existence, of the several factors involved (*4*). In addition to the atomic charges and bond polarity introduced by the initial differences in atomic electronegativity, there are also possible effects arising from differences in atomic radius, from hybridization unsymmetric with respect to the nucleus, from polarization of nonbonding electron pairs, from the interaction of separate bonds to the same atoms, from electrostatic interaction between atoms not directly joined, and from the mobility of electrons of multiple bonds.

The reason for listing these factors now is to emphasize at once the complexity of charge distribution and the folly of expecting too much from the evaluation of the dipole moment or of any of its contributing factors, such as bond polarities and atomic charges. Nevertheless, such data are useful where they are helpful in interpreting chemical phenomena.

The method of estimating the charge distribution that would result from the effect of initial electronegativity differences on bond polarity is speculative. However, it introduces some ideas whose demonstrated utility in inorganic applications (*3*) justifies careful consideration in organic chemistry.

One of the most important of these ideas is the principle of electronegativity equalization: *When two or more atoms initially different in electronegativity combine chemically, their electronegativities become equalized in the molecule.* The intermediate electronegativity of the molecule is taken as the geometric mean of the electronegativities of all the atoms before combination. The equalization of electronegativities occurs through the adjustment of the polarity of the bonds, which is pictured as resulting in a partial charge on each atom. That is, electron loss causes increase and electron gain causes decrease in electronegativity. If it is assumed (*2*) that the electronegativity of an atom changes linearly with charge, and that, as an arbitrary standard, the bond in an isolated molecule of NaF is 75-percent ionic, it is possible to determine that change in the electronegativity of an atom that would correspond to the complete gain or loss of one electron. The partial charge on an atom in a molecule is then estimated as the ratio of the change in electronegativity that is undergone when the free atom joined the molecule to the change that the atom would have undergone in acquiring unit electronic charge.

Data for calculating approximate partial charges on atoms in organic molecules are given in Tables 1 and 2. Table 1 lists the electronegativities [expressed as stability ratio (SR) values (*1*)] of some elements commonly occurring in organic compounds, together with logarithms of the electronegativities (for use in calculating geometric mean values for molecules), and the changes in electronegativity corresponding to the acquisition of unit charge. Table 2 simplifies the calculation of molecular values by listing the log SR sums for a number of common organic radicals and functional groups.

Table 1. Electronegativities of some elements and data for estimating the charge on combined atoms; $\delta_E = (SR_{compound} - SR_E)/\Delta SR_{E \to E^+}$.

Element (E)	SR_E	Log SR_E	ΔSR $E \to E^+$
C	3.790	0.5786	4.050
H	3.550	.5502	3.919
O	5.210	.7168	4.749
N	4.490	.6522	4.408
F	5.750	.7597	4.988
Cl	4.930	.6928	4.618
Br	4.530	.6561	4.426
I	3.840	.5843	4.077
P	3.340	.5237	3.802
S	4.110	.6138	4.216
Si	2.620	.4183	3.418