A. I. KITAYGORODSKII, Yu. T. STRUCHKOV, G. L. AVOYAN, and M. A. DAVYDOVA

1961

SovietRxiv

Fig. 1. Structure of 1,4,1′,4′-tetrachloronaphthalene. Projection ab

Figure 1: Fig. 1. Structure of 1,4,1′,4′-tetrachloronaphthalene. Projection ab

Abstract

Full Text

CHEMISTRY

A. I. KITAYGORODSKII, Yu. T. STRUCHKOV, G. L. AVOYAN, and M. A. DAVYDOVA

STUDY OF STERIC INTERACTIONS

IN SOME HALOGEN DERIVATIVES OF NAPHTHALENE

(Presented by Academician A. N. Nesmeyanov, 12 X 1960)

The problem of the structure of an organic molecule can be divided, with sufficient clarity, into two parts. The mutual influence of atoms transmitted along a chain of bonds leads to a specific distribution of bond lengths. A number of regularities in bond lengths, concerning aromatic molecules and other cases of bond conjugation, has been established fairly reliably, and a summary of these data may be found in the handbook ([1]).

The second structural problem is connected with the influence of valence-unbonded atoms, which is often called steric interaction. A number of direct and indirect data indicate that these two parts of the structural problem can indeed be clearly separated. The energy of interaction of valence-bonded atoms is greater by 1–2 orders of magnitude than the energy of interaction of valence-unbonded atoms. Therefore, bond lengths depend only to a very slight degree (in any case, by thousandths of an angstrom) on the conformation of the molecule, on strain in rings, and on steric interactions.

Fig. 1. Structure of 1,4,1′,4′-tetrachloronaphthalene. Projection *ab*

The small interference between the interactions of valence-unbonded and valence-bonded atoms makes it possible to formulate the following structural problem: what should the valence angles of a molecule be, and what conformation will it assume, for given bond lengths. An approach to the molecule as a system of electrons and nuclei obeying the laws of quantum mechanics cannot lead to the solution of the indicated problem. A semiempirical approach is expedient ([2]), the essence of which is reduced to finding the minimum of the strain energy of the molecule, understood as the sum of the energies of deviation of the valence angles from their "ideal" values and the energies of

Fig. 2. Structure of 4,4′-dichloroacenaphthene. Projection ab

Figure 2: Fig. 2. Structure of 4,4′-dichloroacenaphthene. Projection ab

interaction of all pairs of valence-unbonded atoms. Obviously, to solve the problem, information is needed on the elasticity of the "ideal" angles and on the interaction potential of valence-unbonded atoms.

A number of more or less successful attempts of this kind are known in the literature. If the problem is formulated quite distinctly for aliphatic compounds, in which it is natural to assume complete isotropy in the deviation $\Delta\alpha$ of an angle from its "ideal" value, then the matter is much more complicated

consists, for aromatics, in the fact that the interaction of π-electrons leads to the advantage of a planar arrangement of atoms. Thus, the energy associated with the angles becomes possible to describe as a sum $k(\Delta\alpha)^2$. Deviations of a bond at different azimuths to the plane of the "ideal" aromatic nucleus undoubtedly have different energetic advantages. Any *a priori* judgments on this matter do not seem possible to us, and certain attempts ([3]) to derive conformations of distorted aromatic systems are, it seems, premature.

Fig. 2. Structure of 4,4′-dichloroacenaphthene. Projection *ab*

In order to make possible the creation of a semiempirical theory, it is necessary first of all to investigate the anisotropy of bond deflection for sterically hindered derivatives of aromatic compounds. Such a systematic investigation has been begun in our laboratory. It is proposed first of all to study the structure of peri-dihalogen derivatives of naphthalene and subsequently the structure of 4,5-dihalogen derivatives of phenanthrene.

In this article we report the first experimental results. By the method of X-ray structural analysis of crystals, the structures of the molecules 1,4,1′,4′-tetrachloronaphthalene and 4,4′-dichloroacenaphthene were determined. Crystals of the first of these belong to the space group $Pccn$ with 4 molecules in the cell, having the parameters $a = 9.45$; $b = 15.20$; $c = 7.05$ Å. In this case the molecules are in special positions on twofold axes (axis 2 perpendicular to the plane of the naphthalene nucleus). The analogous data for the other crystal are as follows: space group $C2/c$, $a = 15.38$; $b = 9.45$; $c = 7.48$ Å; $\beta = 118.5°$; 4 molecules in the cell, occupying special positions on axes 2. The structural investigation was carried out from projections of the electron density on the *ab* faces (Figs. 1 and 2).

The molecules investigated are characterized by substantial steric hindrance: in the "ideal" conformations (i.e., with the direction of the C–Cl bond along the bisector of the valence angle C–C–C of the aromatic ring), the Cl···Cl distance in the tetrachloronaphthalene molecule is 2.49 Å, and in the dichloroacenaphthene molecule 2.56 Å, which is substantially less than the equilibrium van der Waals distance, equal to $\geqslant 3.7$ Å.

The main result of the investigation is that, because of the indicated steric interaction, the atoms of the C—Cl bond in the first compound are deflected by 8°, and in the second by 5°, from the "ideal" directions (the Cl···Cl distances become equal to 2.98 Å and 3.12 Å, respectively). These deflections occur in the plane of the nuclei; the deflections in the perpendicular direction (along the normal to the nuclei) are noticeably smaller and are, respectively, 0.05 and 0.18 Å.

The observed deviations of the bonds depend predominantly on the interaction of neutral chlorine atoms (as is often said, on van der Waals interaction). Indeed, even under the most extreme estimates, the change in electrostatic energy for the indicated change in the Cl···Cl distance is ten times smaller than the change in the energy of van der Waals interaction.

The smaller magnitude of the angle of deviation in the case of dichloroacenaphthene seems to us quite natural. As was shown experimentally [(4)] and explained by calculation [(5)], the valence angle at atom C_5 in the acenaphthene molecule is increased to 128.4° owing to the uniform distribution of strain over the ring. Thus, the bisectors of the valence angles of atoms C_4 and C_4 in the molecule of acenaphthene itself are already deviated from the parallel position by 3.5°. Therefore, the deviations from the positions of the bisectors in dichloroacenaphthene are approximately 3° smaller than in tetrachloronaphthalene. The character of the interaction of the valence-unbonded chlorine atoms in the two compounds studied is undoubtedly the same.

In subsequent communications we hope to give a quantitative estimate of the stiffness of the deviation of the C—Cl bond in different directions, proceeding from the potential of interaction of neutral chlorine atoms.

The authors express their gratitude to V. A. Koptjug for providing the preparations for the investigation.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
4 X 1960

CITED LITERATURE

[1] *Tables of Interatomic Distances and Configuration in Molecules and Ions*, London, 1958. [2] A. I. Kitaigorodskii, *Tetrahedron*, **9**, 183 (1960). [3] *Steric Effects in Organic Chemistry*, N. Y.—London, 1956; M. A. Ali, C. A. Coulson, *J. Chem. Soc.*, 1959, 1558. [4] H. W. W. Ehrlich, *Acta Crystallogr.*, **10**, 699 (1957). [5] A. I. Kitaigorodskii, *DAN*, **124**, No. 6, 1267 (1959).

Note: Figure translations are in progress. See original paper for figures.