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THE STRUCTURE OF THE PRODUCTS OF THE IODINATION OF ACENAPHTHENE WITH IODINE MONOCHLORIDE

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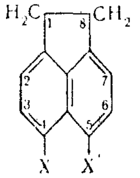
The molecules of 4,5-dihaloacenaphthenes are of interest for the development of the theoretical aspects of conformational analysis [1] since they are hindered systems. In fact, with the ideal valence angles the X...X' distance would be ~2.5A, which is considerably less than the normal van der Waals distance:



The structure of 4,5-diiodoacenaphthene would be especially interesting because the intermolecular radius of iodine (2.1 A) is larger than that of any other monatomic substituent.

We have attempted to obtain this compound by iodination of acenaphthene with iodine monochloride. This method of iodination [2] has not previously been applied to acenaphthene, the 2-iodoacenaphthene [3] and 4-iodoacenaphthene [4] described in the literature having been obtained by the action of elemental iodine in the presence of mercuric oxide.

Iodine monochloride was prepared by a known method [5]. Acenaphthene was dissolved in glacial acetic acid at 60-70° and a solution of the calculated quantity of iodine chloride in glacial acetic acid was added dropwise to the constantly stirred solution at this temperature over 2-3 h. In the first experiment 2 moles of ICl were used per mole of acenphthene. The solution was steam distilled to remove the acetic acid and elemental iodine which usually separated in large quantities. The residual oil was extracted with benzene, the solution dried over calcium chloride, and the benzene evaporated off. The residue was distilled in vacuum. The main solid yellow fraction (b.p. 170-178°/2 mm) was crystallized from glacial acetic acid. The almost colorless substance obtained had m.p. 61.8-62° and an analysis corresponding to a monoiodoacenaphthene (Found: C 51.25, H 3.25, I 45.62; calculated for $C_{16}H_9I$: C 51.45; H 3.24, I 45.34%). The literature data for 4-iodoacenaphthene are m.p. 63-63.5° and 65° [4].

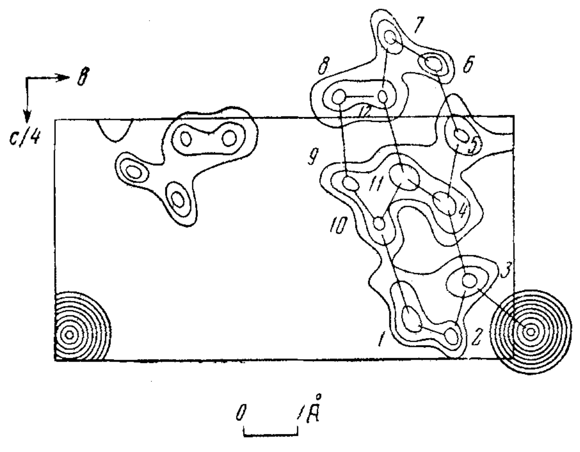


Fig. 1.

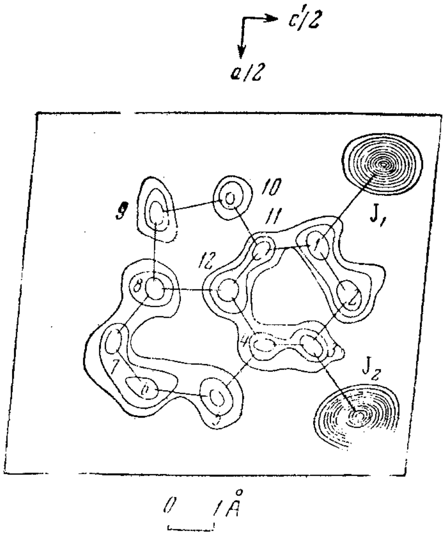


Fig. 2.

A second experiment was carried out in the same way as the first but with 4 moles of ICl per mole of acenaphthene. The extract after evaporation of the benzene was subjected to molecular distillation. Eight fractions were collected: fractions I-IV were liquids ($5 \cdot 10^{-2}$ mm) with $n_D^{20} \approx 1.68$ and an iodine analysis corresponding to about 1.5 I atoms per molecule; fractions V, VI ($4 \cdot 10^{-3}$) and VII, VIII ($2 \cdot 10^{-4}$) were very viscous; the color of these fractions varied from light yellow to brownish. A second distillation of VIII gave a solid yellowish substance with the analysis of a diiodoacenaphthene (Found: C 36.03, H 1.93, I 62.29%; calculated for $C_{12}H_8I_2$: C 35.49, H 1.98, I 62.52%). After many attempts this oily product crystallized, but we had no success in determining the m.p. The x-ray study was carried out on several transparent yellowish crystals. However, it is very possible (and even probable) that the oily product obtained was not a single substance, but rather a complex mixture of isomeric products with different degrees of iodination with an average iodine content corresponding to a diiodoacenaphthene. No diiodoacenaphthene has been described in the literature.

The mono- and diiodoacenaphthenes prepared were subjected to x-ray investigation to establish their structures.

Monoiodoacenaphthene. The needle-like yellowish crystals were elongated along the b axis. The lattice parameters were: a=7.27 ± 0.04, b = 8.54 ± 0.04, c = 17.38 ± 0.07 A; β = 110° ± 0.5°; d_{meas} = 1.83, d_{calc} = 1.87 g/cm^3, N = 4, space group $P2_1/c$. The structural formula was determined on the basis of a yz projection (Fig. 1); the method of photographing the reciprocal lattice, λM-oK, 112 reflections; a series of interatomic vectors and two cycles of refinement of the electron density; B = 3.9 A^2, R_{okl} = 17.8% (including zero reflections). The relative coordinates of the atoms of one molecule (using the numeration of Fig. 1) were:

Atom	y	z	Atom	y	z
I	1,0290	0,2231	C_7	0,732	—0,082
C_1	0,772	0,212	C_8	0,618	—0,020
C_2	0,862	0,227	C_9	0,642	0,067
C_3	0,895	0,170	C_{10}	0,705	0,111
C_4	0,852	0,091	C_{11}	0,760	0,061
C_5	0,880	0,020	C_{12}	0,715	—0,022
C_6	0,828	—0,053			

It is clear that our monoiodoacenaphthene is the previously described 4-derivative (Fig. 1).

Diiodoacenaphthene. Thin needles along the b axis. Lattice parameters: a = 15.39 ±0.11, b = 4.32 ± 0.02, c = 17.73 ± 0.12 A, β = 95.5° ± 1.0°, d_{meas} = 2.25 d_{calc} = 2.31 g/cm^3, N = 4, space group $P2_1/c$. The structural formula (Fig. 2; c' = c/2) was established on the yz projection; by the method of photographing the reciprocal lattice, λMoK, 202 reflections; a series of interatomic vectors and two cycles of refinement of the electron density; B=3.8 A^2, R_{hol} = 19.3% (including zero reflections). The relative coordinates of the atoms of a single molecule (numeration as in Fig. 2) were:

Atom	x	z	Atom	x	z
I_1	0,0722	0,1847	C_6	0,378	0,498
I_2	0,4181	0,1846	C_7	0,315	0,370
C_1	0,180	0,114	C_8	0,243	0,417
C_2	0,253	0,160	C_9	0,138	0,411
C_3	0,320	0,114	C_{10}	0,120	0,001
C_4	0,322	0,059	C_{11}	0,190	0,045
C_5	0,388	0,006	C_{12}	0,243	0,009

It is clear that our diiodoacenaphthene is the 2,4-derivative (Fig. 2).

Thus the attempt to prepare the interesting 4,5-diiodoacenaphthene has been unsuccessful; instead, just as with bromination of acenaphthene [6], the 2,4-isomer was obtained. It is pertinent to note the great crystal chemical similarity of 2,4-dibromo- and 2,4-diiodo-acenaphthene which appears not only in the similarity of the lattice parameters but also in the atomic coordinates:

Bromoderivative	Iododerivative
$a = 15{,}21$ Å	$a = 15{,}39$ Å
$b = 4{,}14$	$b = 4{,}32$
$c = 16{,}48$	$c = 17{,}73$
$\beta = 90°$	$\beta = 95{,}5°$

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A THEORETICAL DISCUSSION OF THE STEREOCHEMISTRY OF COMPLEX COMPOUNDS OF ELEMENTS WITH f-ELECTRONS

1. TRANSFORMATIONS OF f-ORBITALS OF THE CENTRAL ATOM

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The calculation of the molecular integrals for the quantum mechanical description of the configuration of complexes of elements with f-electrons requires a knowledge of the transformations of the hydrogen-like functions. The transformations of p- and d-orbitals during arbitrary rotation of the system of coordinates have been reported [1]. In the present work the transformation formulas for f-orbitals are given, the orbitals being taken in the cubic harmonic form of Eisenstein [2], which is convenient for subsequent development:

$$\begin{aligned} f_{\beta} &= -i\sqrt{2\pi}\,\{Y_3^2 - Y_3^{-2}\} \\ f_{\delta_1} &= 2\sqrt{\pi}\,Y_3^0 \\ f_{\delta_2} &= \sqrt{\frac{5\pi}{4}}\{Y_3^3 + Y_3^{-3}\} - \sqrt{\frac{3\pi}{4}}\{Y_3^1 + Y_3^{-1}\} \end{aligned} \tag{1}$$