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Short Communications

Conformational Analyses of Some Fused Alicyclics by Means of Gas Phase Electron Diffraction

M. I. DAVIS* and O. HASSEL

Chemistry Department, University of Oslo, Blindern, Oslo 3, Norway

The configurations of the five isomeric perhydroanthracenes have been assigned, by a number of workers, over a period of some 20 years. These assignments were made, largely, from studies of their syntheses by well known chemical mechanisms.[1-4] For three of the isomers (those melting at 30°, 90°, and 120°C, respectively), it was possible to assign conformations, on the basis of the generally accepted greater stability of the chair form for cyclohexane-type rings. The conformations of the remaining two isomers could not be predicted with such a high degree of reliability, because of the sort of steric arguments that were required; although in point of fact both conformations had been correctly predicted.[5,6]

In order that the conformations might be established unequivocally, it was felt necessary to employ the more direct methods of X-ray crystallography and gas-phase electron diffraction. The results of the X-ray investigations, carried out in this department, have been published previously.[7,8]

The electron diffraction investigations were carried out on four of the five perhydroanthracenes and the two decalins. The two latter compounds were included, partly for their own interest but, largely for the useful information that their radial distribution curves were able to offer for the analysis of those of the perhydroanthracenes.

Intensity data, out to $s = 45$ Å^{-1}, were collected by A. Almenningen, with the Oslo sector unit.[9] The handling of the intensity data followed much the same procedure as outlined by Bastiansen and Skancke.[10]

The analyses were made on the radial distribution (r.d.) curves. The major features of the r.d. curves can be ascribed to the contributions of the various C–C atom pairs. These C–C pairs may be split into three general classifications: (a) Where both carbons are in the same ring, giving contributions in the region 1.3–3.2 Å, (b) where the carbons occupy adjacent rings, and (c) where the carbon atoms are found, one in each of the two outer rings. The contributions of the types (b) and (c) occurred generally, but not exclusively in the regions 3.2–5.5 and 5.5–7.5 Å, respectively.

From the inner region of the r.d. curves, it was possible to establish the mean C–C bond lengths and the mean CCC bond angles. The values obtained for these parameters in the various investigations, are set out in Table 1. Despite the comparatively large deviation, from compound to compound, of the mean bond angles, the bond lengths for the six compounds are very consistent. This consistency indicates that in a given molecule there is not any appreciable difference between the lengths of the individual bonds. The mean angles follow a pattern, increasing with increased steric strain. The variations of the mean values from one compound to another would seem to indicate some variation among the individual values in a given molecule. Some idea of the variation among the angles in a given isomer can be obtained from the values given, for the mean vibrational amplitudes for '*meta*' carbon pairs, in Table 1, although these values cannot be claimed to have any high sensitivity.

* Present address: Department of Chemistry, The University of Texas, Austin, Texas.

Table 1.

Compound	C—C(bond)		C—C(*meta*)		CCC°	Conformation
	r_{ij}Å	U_{ij}Å	r_{ij}Å	U_{ij}Å		
Cis Decalin	1.536	0.051	2.549	0.070	112.05°	All-chair
Trans Decalin	1.537	0.048	2.541	0.065	111.50°	»
P.H.A. m.p. 120°	1.538	0.049	2.551	0.071	112.05°	» *cis-anti-cis*
30°	1.538	0.049	2.546	0.070	111.70°	» *cis-trans*
60°	1.537	0.047	2.553	0.074	112.3°	» *cis-syn-cis*
50°	1.537	0.051	2.546	0.074	111.8°	Staggered centre *trans-anti-trans*
Cyclohexane	1.528	0.048	2.527	0.062	111.55°	Chair

Despite the presumed variation of the individual bond angles, it was found to be useful to calculate the dimensions of the various conformational models on the basis of bond lengths and angles with values equal to their respective means.

The r.d. curves for the decalins showed characteristic differences in the region 3.2—5.5 Å, and were fully consistent with the all-chair models.[11] These characteristics were to be found again in the r.d. curves for the perhydroanthracenes.

In the region $r = 5.5-7.5$ Å, the forms of the perhydroanthracene radial distribution curves showed fairly marked differences. In addition to the differences between the various experimental curves, there were also pronounced differences between the theoretical curves for different conformations for a single configuration. Consequently this region provided useful information in the conformational assignment.

Perhydroanthracene, m.p. 120°C. The form of the experimental curve, in the region 1.5—3.2 Å, was consistent with the existence of 16 C—C bonds, 22 '*meta*' pairs of carbon atoms and 9 chair '*para*' carbon pairs. The region 3.2—5.5 Å showed the general features of the *cis* decalin curve for the same region but lacked the distinctive features of *trans* decalin. This was consistent with the *cis-anti-cis* configurational assignment, with the all-chair conformation. Excellent correlation was observed between the theoretical r.d. curve for this conformational model and the experimental version in the region $r = 5.5-7.5$ Å.

Perhydroanthracene, m.p. 30°C. Again the complete r.d. curve in the region 1.5—3.2 Å, could be accounted for in terms of 16 bonds, 22 '*meta*' and 9 chair '*para*' pairs of carbon atoms. This indicates that there were no boat rings, nor were there any atom pairs, of the adjacent or outer ring type, with contributions in this region. The region 3.2—5.5 Å showed characteristics of both the *cis* and *trans* decalin r.d. curves; in fact the perhydroanthracene curve showed a marked resemblance to the sum of the two decalin curves. These facts were consistent with the all-chair conformation of the *cis-trans* configuration. The theoretical r.d. curve for this model matched well with the experimental version in the region 5.5—7.5 Å, as it did for its entire length.

Perhydroanthracene m.p. 60°C. Unlike the two previous examples, this isomer, with the *cis-syn-cis* configuration, could be ascribed two conformations, for each of which there could be raised fairly strong objections. In one of the possibilities, the central ring is of the boat form, in the other the more stable chair. The objections to the former are on the usual considerations of the greater stability of the chair structure. In the latter, where a purely tetrahedral model is adopted the distance between the hydrogen atoms 4a and 5a is only of the order of 0.7 Å, which is obviously extremely short. The latter model could only be tenable where distortions to the appropriate bond angles lead to a more comfortable separation between the two hydrogen atoms. This sort of distortion can be accomplished, as evidenced by the results of this investigation, but one could not be absolutely sure of this beforehand.

The theoretical r.d. curve corresponding to the boat centre model showed fairly extensive deviations from experimental version, and even appreciable variations to the model failed to produce any really satisfactory improvement.

The appropriate values for those angles, which by their increase, could provide a comfortable H—H separation in the chair centred model, were calculated. The resulting theoretical r.d. curve matched up well with the experimental version in all regions.

Perhydroanthracene, m.p. 50°C. For this, the most recently isolated of the perhydroanthracenes, with the *trans-anti-trans* configuration, there is no possibility of an all chair conformation. The alternatives are between a model in which the centre ring is of the formal boat shape and one in which one has the staggered boat form.

On the basis of the observed mean C—C bond lengths and CCC bond angles two models were calculated and the corresponding theoretical radial distribution curves. It was quite evident that the formal boat structure failed to match up with the experimental r.d. curves, whereas the staggered boat conformation gave good correlation in all regions and represents the correct structure.

The results of the entire series of investigations are presented in Table 1, together with those for cyclohexane.[12] It is interesting to note that the C—C bond distances in the fused ring compounds are consistently longer than that found for cyclohexane.

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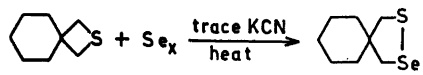
Formation of the 1-Thia-2-selenacyclopentane Ring System from the Thiacyclobutane Ring

AIJA BIEZAIS and GÖRAN BERGSON

Chemical Institute, University of Uppsala, Sweden

Hitherto only two substances have been prepared in which sulphur and selenium are neighbouring atoms in a small saturated ring system,[1,2] namely 1-thia-2-selena-cyclopentane-4-carboxylic acid [1] and 4-(aminomethyl)-1-thia-2-selenacyclopentane.[2] For both the synthesis was rather laborious. A new substance (II) belonging to this class of compounds has now been synthesized in a simple but unusual way. On heating 2-thiaspiro-[3.5]-nonane* (I) with elemental selenium to 180—190° for 16 h in diethylene glycol containing a trace of potassium cyanide, a selenium atom is incorporated in the thiacyclobutane ring and 2-thia-3-selenaspiro-[4.5]-decane (II) is formed in 75 % yield. The product is nicely crystalline and has the characteristic orange-red colour of the thiaselenacyclopentanes.



(I) (II)

The absorption spectrum is given in Fig. 1 along with the spectra of the corresponding disulphide and diselenide. The close similarity between these spectra and those obtained for the carboxylic acids described earlier [1] constitutes a good proof for the structure given to our new compound.

Further, the NMR-spectrum at 60 Mc/s, of (II) shows three peaks with intensity ratio 1:1:5. The stronger peak, originating from the protons in the six-membered ring, appears at 1.28 ppm (δ, relative

* Nomenclature according to The Ring Index, 2nd Ed. Washington 1960.