81. *The Configuration of Heterocyclic Compounds. Part VIII. The Configuration of Anthracene, 9 : 10-Dihydroanthracene, Phenazine, 9 : 10-Dimethyl-9 : 10-dihydrophenazine, Thianthren, and Selenanthren.*

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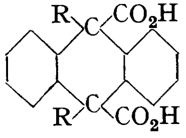
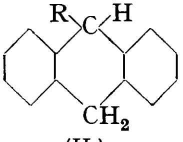
Theoretical considerations show that a molecule of the general formula (VI) will be least strained when it is folded, provided that the atom or group X prefers a valency angle approximating to the tetrahedral angle. For example, 9 : 10-dihydroanthracene (VI; X = CH_2) should be folded, and evidence is given below that the dipole moment of the hydrocarbon is not zero, but is of the same order as that of dibenzyl. The less easily interpreted moment of 9 : 10-dimethyl-9 : 10-dihydrophenazine (VI; X = NMe) could correspond with folding of the molecule about the X—X axis and a certain disposition of the N—Me bonds.

A paper by Schlenk and Bergmann, describing novel stereoisomerism among anthracene derivatives, is discussed.

In 1928, Schlenk and Bergmann (*Annalen*, **463**, 1) stated that in preparing various derivatives of anthracene and dihydroanthracene they had obtained more forms than seemed then to be required by stereochemical theory. They described (*a*) three forms each of 9 : 10-dihydroanthracene-9 : 10-dicarboxylic acid (I; R = H) and of its 9 : 10-diphenyl derivative (I; R = Ph), (*b*) two forms each of 9-phenyl-9 : 10-dihydroanthracene (II;



(I.)



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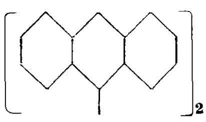

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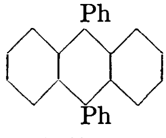
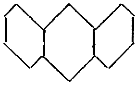
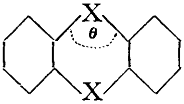


(IV.)

R = Ph) and 9 : 10-dihydroanthracene-9-carboxylic acid (II; R = CO_2H), (*c*) two forms of 9 : 9′-dianthranyl (III) and two forms of 9 : 10-diphenylanthracene (IV). They explained the third form of each of the compounds (I) and the second form of each of the compounds (II), (III), and (IV) as being due to double folding of the molecule *at the two fused bonds*, as indicated in (V).

(V.)





(VI.)

Meerwein and Migge (*Ber.*, 1929, **62**, 1046) showed that Schlenk and Bergmann's second 9 : 10-dihydroanthracene-9-carboxylic acid was probably a mixture and not a second form at all, but did not comment on the general feasibility of the Schlenk–Bergmann space formulæ, although from a footnote in their paper it is clear that they were prepared to *discuss* the possibility that anthracene was not necessarily planar. It may be noted that the Schlenk–Bergmann isomerides were not referred to in Freudenberg's "Stereochemie," 1933.

In 1932, Bergmann and Tschudnowsky (*Ber.*, **65**, 458), finding thianthren (VI; X = S) to possess a considerable dipole moment, suggested, without reference to the disposition of the aromatic nuclei with respect to the centre ring, that the latter was "gewinkelt" about the line joining the sulphur atoms, and this has been interpreted by Bennett and Glasstone (J., 1934, 128) as implying that Bergmann and Tschudnowsky thought, with themselves, that the molecule *as a whole* was folded about the S—S axis. It is at any rate clear that Bergmann and Tschudnowsky did not associate the question of the configuration of thianthren with that of related carbon compounds (VI; X = saturated carbon), and in particular did not associate it with the configuration of their 1928 isomerides (I—IV). Bennett and Glasstone were actually the first to make clear the nature of the folding of thianthren, and their work led Lesslie and Turner (J., 1934, 1170; 1935, 1268; 1936, 730) to attempt, and accomplish, the optical resolution of three different 10-substituted phenoxarsine-2-carboxylic acids, the grounds for this attempt being that the phenoxarsine molecule might be folded with greater rigidity than the thianthren molecule (see below).

The general problem concerning the configuration of compounds of type (VI) has, however, never been stated, and it is with this that we are now concerned.

The centres of the carbon atoms in the aromatic nucleus form a regular hexagon. Save for particular reasons in special cases, the extra-annular valency direction of each nuclear carbon atom passes, if produced backwards, through the centre of the hexagon. Formula (V) does not comply with this requirement and is therefore not admissible.

For a compound of the general formula (VI), in which two aromatic nuclei are joined by *single* bonds through two atoms, X, of the same element, whatever the nature of X, two corollaries follow: (1) If the molecule is planar, the angle, θ, at X is 120°. (2) If θ is 109·5°, the tetrahedral angle, the molecule will be folded about the axis X—X, so that the angle of fold (ψ) between the two planes each containing one aromatic nucleus and both atoms X, is approximately 141°. The flexibility of the molecule about the X—X axis will naturally vary from one substance to another.

A compound of type (VI) will therefore be planar when the preferred valency angle of X is equal to or greater than 120°, as has been pointed out by Bennett, Earp, and Glasstone (J., 1934, 1179) for the case of diphenylene dioxide (VI; X = O). More interesting are the numerous examples of compounds of type (VI) in which X is an element which prefers a valency angle less than 120°, *e.g.*, sulphur (as shown by the configuration of thianthren) or *carbon*. It is at once clear that 9 : 10-dihydroanthracene (VI; X = CH_2) will only be strainless when it is folded about the CH_2—CH_2 axis, and this folding should cause the molecule to possess a measurable dipole moment.

We have determined the dipole moment of 9 : 10-dihydroanthracene, and for comparative purposes that of anthracene. We also give details of the experimental work on selenanthren (VI; X = Se) referred to in Part VI (Thompson and Turner, this vol., p. 29). Thianthren has been used as a standard for comparison.

Little information is available as to the preferred nitrogen valency angle, although for ammonia itself values from 94° to 116° have been given (Badger and Mecke, *Z. physikal. Chem.*, 1929, *B*, **5**, 333; Barker, *Physical Rev.*, 1928, **31**, 1131; 1929, **33**, 684; Lueg and Hedfeld, *Z. Physik*, 1932, **75**, 599). It seems probable that 9 : 10-dimethyl-9 : 10-dihydrophenazine (VI; X = NMe) would be folded. The results of examining this phenazine derivative are stated and discussed below.

Dipole-moment Measurements.—The requisite observed data are in Table I under the following headings: w_1, the weight fraction of the solute in the solutions; $\epsilon_{25^\circ}^{1200}$, the dielectric constants of the solutions measured at approximately 1200 kc. and 25°; $d_{4^\circ}^{25^\circ}$; and finally, $r_D^{25^\circ}$. From these are derived $\alpha\epsilon_2$ and βd_2, constants containing the coefficients of change of dielectric constant and density with solute concentration (w_1). Observational irregularities can most easily be discerned in these columns, which also show that the linear relationships relating ϵ_{12} and w_1, and d_{12} and w_1, hold in the present cases. The total polarisations at infinite dilution are calculated (Table II) from the mean values of $\alpha\epsilon_2$ and β, etc., by the formula $(P_1)_\infty = M[p_2(1-\beta) + C\alpha\epsilon_2]$ (compare Le Fèvre and Vine, J., 1937, 1805), in which M is the molecular weight of the solute, and p and C are, for the sample of benzene used in the present work, 0·34086 c.c. and 0·18809, respectively.

The molecular refractions are derived from the appropriate measurements by the mixture rule $[R_L]_D = M_1[r_2 + (r_{12} - r_2)/w_1]$, in which r_2 and r_{12} are the specific refractions of the solvent and solution; $r_2 = 0{\cdot}33503$ for the benzene used.

TABLE I.

100 w_1.	$\epsilon_{25^\circ}^{1200}$.	$d_{4^\circ}^{25^\circ}$.	$\alpha\epsilon_2$.	βd_2.	$n_D^{25^\circ}$.	$[R_L]_D$.
0	2·2725	0·87378	—	—	1·49724	—
Anthracene.						
0·1623	2·2735	0·87410	0·616	0·197	—	—
0·4821	2·2756	0·87471	0·643	0·194	1·49820	66·7
0·6003	2·2762	0·87494	0·616	0·193	—	—
0·6015	2·2762	0·87495	0·615	0·195	1·49966	67·4
9 : 10-Dihydroanthracene.						
0·89325	2·2765	0·87532	0·445	0·173	—	—
0·8942	2·2765	0·87533	0·447	0·174	1·49813	58·5
0·8981	2·2765	0·87535	0·445	0·173	1·49820	59·5
0·9493	2·2767	0·87541	0·442	0·172	1·49828	59·7
Phenazine.						
0·5503	2·2757	0·87517	0·581	0·253	1·49828	62·3
0·66045	2·2762	0·87544	0·560	0·251	1·49850	62·5
0·6715	2·2763	0·87546	0·571	0·251	—	—
0·6856	2·2764	0·87551	0·569	0·253	—	—
9 : 10-Dimethyl-9 : 10-dihydrophenazine.						
0·1475	2·2734	0·87412	0·610	0·230	—	—
0·1924	2·2736	0·87422	0·590	0·228	—	—
0·4649	2·2752	0·87485	0·580	0·230	—	—
0·8928	2·2778	0·87585	0·594	0·232	1·49873	71·5
1·0673	2·2788	0·87623	0·590	0·230	1·49894	70·9
Thianthren.						
0·2474	2·2766	0·87450	1·657	0·291	1·49761	66·3
0·3279	2·2780	0·87476	1·677	0·299	1·49773	65·8
0·4385	2·2800	0·87507	1·710	0·294	1·49788	66·0
0·4801	2·2806	0·87524	1·687	0·304	1·49795	65·2
Selenanthren.						
0·2906	2·2756	0·87509	1·067	0·451	1·49761	(73·0)
0·4821	2·2776	0·87596	1·058	0·452	1·49781	71·2
0·5211	2·2780	0·87616	1·055	0·457	1·49790	71·8
0·5613	2·2784	0·87632	1·051	0·453	1·49793	71·9

TABLE II.

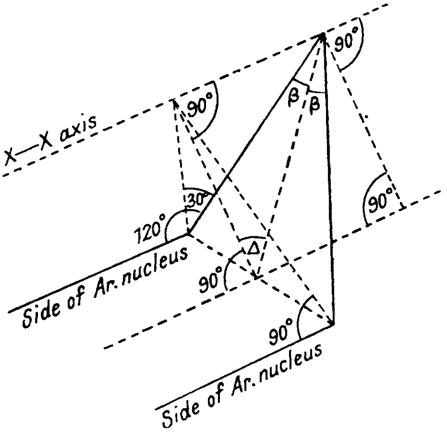
Substance.	M.	Mean values of $\alpha\epsilon_2$.	β.	$(P)_\infty$.	$[R_L]_D$.	μ.
Anthracene	178	0·622	0·223	67·9	67	*ca.* 0
Dihydroanthracene	180	0·445	0·198	64·3	60	*ca.* 0·4
Phenazine	180	0·570	0·288	63·0	63	*ca.* 0
Dimethyldihydrophenazine	210	0·593	0·263	76·2	72	*ca.* 0·4
Thianthren	216	1·683	0·340	117·0	66	1·57
Selenanthren	310·5	1·058	0·518	112·8	72	1·41

Remarks.—Measurements previously recorded for phenazine and thianthren are:

	Thianthren.					Phenazine.
Temp.	21·8°.	25°.	50°.	24·92°.	24°.	14·9°.
Solvent	C_6H_6	C_6H_6	C_6H_6	CCl_4	CS_2	C_6H_6
Moment	1·7 [1]	1·41 [2]	1·41 [2]	1·54 [3]	1·47 [3]	0 [4]

[1] Bergmann and Tschudnowsky, *loc. cit.* [2] Smyth and Walls, *J. Chem. Physics*, 1933, **1**, 337.
[3] Bennett and Glasstone, *loc. cit.* [4] Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446.

Our result for thianthren is in good agreement with that of Bennett and Glasstone. In both cases the orientation polarisation is the same, *viz.*, 51 c.c., from which, without further correction, the moment is calculable as 1·57 D. For phenazine, Bergmann, Engel, and Meyer reported a molecular refractivity in excess over the total polarisation by more than 10 c.c. Our figures have a greater *prima facie* probability and indicate a zero moment for the substance.

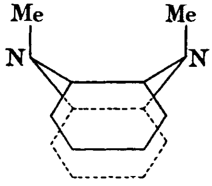


The moments of dihydroanthracene and dimethyldihydrophenazine are too small to evaluate accurately. This arises because their calculation involves square roots, which, being small differences between two relatively large numbers, are liable to contain the accumulated errors of both. These uncertainties are not only experimental in origin, but are inherent in the method, which accepts the molecular refraction as the sum of the electronic and the atomic polarisation.

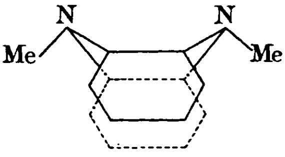
On the other hand, the fact that anthracene and phenazine, with flat molecules, show total polarisations which are practically equal to the corresponding refractions (so that $\mu = 0$) strengthens the likelihood that the two dihydro-derivatives have finite moments greater than zero.

The present results therefore support the conclusion that certain molecules of type (VI) exist largely in non-planar configurations, stabilised by the adoption by the atom or group X of preferred valency angles ($\theta = 2\beta$) of about 110°. The simple construction given in the figure shows that if $\theta = 2\beta = 110°$ and the extra-nuclear valency angles are 120°, $\sin \Delta = 1/(2 \cos \beta)$, whence $\Delta = 61°$, *i.e.*, the resultant moments of these compounds should arise from two vectors compounded at 122°. Approximate values for each of the latter would be the moment of the corresponding substance: Ph_2S, Ph_2Se, Ph_2CH_2 and Ph_2NMe. The last is not yet available, but for the first three, $\mu \doteqdot 1{\cdot}5$, 1·4, and 0·4 D., respectively. The moments of thianthren, selenanthren, and dihydroanthracene calculated from these figures are 1·45, 1·36, and 0·39, respectively, in close agreement with the present experimental results.

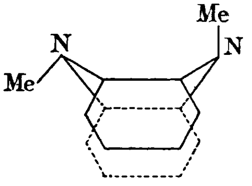
The Small Moment of Dimethyldihydrophenazine.—Three probable configurations for this substance, involving three different dispositions of the N—Me bonds, are shown in exaggerated perspective. In type *A* the Me→N links would subtend an angle of about 120° with the planes containing the two associated pairs of Ar→N links. This is a highly probable arrangement and would give a molecular model in which the Me→N link moments together would oppose in *nearly antiparallel alinement* the resultant moment



(*A*.)



(*B*.)



(*C*.)

arising from the four Ar→N vectors. Such a structure might well have only a small molecular resultant moment, so that the value now found for dimethyldihydrophenazine does not necessarily disprove occurrence of folding in the molecule. Moreover, it seems unlikely that the dipole moment observed owes its origin merely to a *cis*-disposition of N—Me valencies in a non-folded structure : the only examples of *cis-trans*-isomerism among such derivatives of tervalent nitrogen are the "quinoline dicyanides" of Mumm and Ludwig (*Annalen*, 1934, **514**, 34).

In view of the failure of attempts (Bennett, Lesslie, and Turner, J., 1937, 444; Keats, *ibid.*, p. 1592) to resolve substituted thianthrens, it seems unlikely that nuclear substituted dihydroanthracenes would (usually) be configurationally stable enough to be resolvable. At the same time, although a configuration such as (V) for anthracene is inadmissible, for reasons stated above, yet a molecule of type (I), if *stably* folded about the 9 : 10-axis, should exist in three forms, and one of type (II) in two forms, corresponding with the experimental evidence of Schlenk and Bergmann. On the other hand, anthracene, a compound not belonging to type (VI), is beyond doubt planar (Robertson, *Proc. Roy. Soc.*, 1933, **140**, 79), and for (III) and (IV) only one form in each case is conceivable, contrary to the experimental evidence of Schlenk and Bergmann.

A possibility which has always received our consideration becomes a probability as a result of the present study of dimethyldihydrophenazine, and this is that in a phenoxarsine the folding of the molecule and the natural disposition of the valencies of the arsenic atom tend to a mutual stabilisation of configuration.

EXPERIMENTAL.

Preparation of Phenazine.—This was found to be less readily effected than would be gathered from the literature. Ris's method (*Ber.*, 1886, **19**, 2206) of heating catechol with *o*-phenylenediamine under pressure was extremely unsatisfactory. The condensation of *o*-nitrodiphenylamine with *o*-aminodiphenylamine in presence of sodium acetate (Kehrmann and Havas, *Ber.*, 1913, **46**, 341) gave a very poor yield. The method of Wohl and Aue (*Ber.*, 1901, **34**, 2246), in which aniline is heated with nitrobenzene in presence of alkali, was tedious and gave poor yields of phenazine. We found, however, that distillation of *o*-aminodiphenylamine with litharge (Fischer and Heiler, *Ber.*, 1893, **26**, 383) provided a convenient method (contrast McCombie, J., 1928, 353). The details of our synthesis are as follows :

o-Nitrodiphenylamine was prepared by a modification of the method of Kehrmann and Havas (*loc. cit.*) : we noted that when a mixture of 100 g. of *o*-chloronitrobenzene, 140 g. of aniline, and 52 g. of fused sodium acetate was heated under reflux in a bath kept at 225—230°, the reaction mixture remained at a temperature of about 183° for the first 6 hours and finally rose to about 200° during the next 9 hours. Following the instructions of Kehrmann and Havas, we obtained poor yields, but operating as described above our yield of pure *o*-nitrodiphenylamine was 88 g.

The nitro-compound (150 g.) was reduced at boiling water-bath temperature with one part of iron filings in presence of water and a little acetic acid. Extraction of the reaction mixture with alcohol, followed by filtration and addition of water, gave the base, which, after being crystallised from alcohol, was pure (110 g.).

The conversion of aminodiphenylamine into phenazine was effected by heating an intimate mixture of 20 g. of the base with 200 g. of litharge in a wide combustion tube until no more material distilled. The crude distillate was crushed, mixed with 2 parts of litharge, and slowly sublimed through a layer of litharge in an evaporating basin covered with a clock-glass. After being crystallised from alcohol, the phenazine was pure (8 g.).

Phenazine methosulphate. The procedure of Kehrmann and Havas (*loc. cit.*) was modified : 10 g. of pure methyl sulphate were added to a solution of 10 g. of phenazine in 50 c.c. of dried nitrobenzene at 120°. The mixture was kept at 100—110° for 10 minutes, by which time the methosulphate began to crystallise. Pure ether was added to the cooled mixture. The solid was collected, washed with ether, and crystallised from the least absolute alcohol (yield, 10—11 g.).

9 : 10-Dimethyl-9 : 10-dihydrophenazine was obtained by the method outlined by McIlwain (J., 1937, 1711), but since we had considerable difficulty with the preparation we give the actual conditions used. A Grignard reagent, prepared from 1·2 g. of magnesium and 3·2 c.c. of methyl iodide in 80 c.c. of ether, was slowly added to a suspension of 8 g. of finely ground phenazine methosulphate in 400 c.c. of ether. A vigorous current of dry nitrogen was passed through the mixture, which was well cooled. After addition of the reagent, the whole was boiled under reflux for 2 hours and then allowed to cool in a slow current of nitrogen. Ice and water were added. The ethereal layer was separated, and washed with water and dilute sodium bisulphite solution [washing with 5% sulphuric acid (McIlwain) diminished the yield]. The ether was removed, and the residue crystallised 3 times from absolute alcohol. The dimethyl base (1 g.) formed prisms, m. p. 152—153°. McIlwain's yields were never attained, in spite of the fact that we found that the dimethyl base was extracted to some extent from an ethereal solution by 5% sulphuric acid.

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