[CONTRIBUTION FROM JESUS COLLEGE, OXFORD]

A CALCULATION OF THE NUMBER OF POSITIONAL ISOMERS IN SOME AROMATIC SYSTEMS

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Hill (1, 2, 3) and Polya (4, 5, 6) have given detailed mathematical treatments of position isomerism in simple ring compounds. With the exception of a short table (5), the present authors do not believe that the results for aromatic systems have been published. Part II of this paper is devoted to tables of isomers for all possible modes of substitution in the benzene, naphthalene, anthracene, and phenanthrene systems, together with a table showing only the number of isomers, with all the substituents identical, in a number of more complicated aromatic hydrocarbons. Since the calculations were made before the attention of the authors was drawn to the work of Hill and Polya, a résumé of our treatment of this particular problem is given below.

Method of calculation: The substituents in the aromatic systems to be considered may be either single atoms or univalent groupings, though for ease of explanation, the word "grouping" is used below. Any question, therefore, of isomerism in the side chain is excluded from this discussion. Optical isomers due to restricted rotation are also not counted.

It will be obvious that the number of dimethylnaphthalenes will be the same as that of the hexamethyl compounds: both of these are referred to as the A_6B_2 naphthalenes. The lettering in the final table is arranged so that in the expression $A_aB_bC_c \cdots$, $a \geq b \geq c$, etc. The sum of a, b, c, etc. is equal to n, the number of replaceable hydrogen atoms in the original hydrocarbon.

In every case, the parent hydrocarbon is planar and the symmetry elements within the plane are considered. A symmetry factor S is defined as follows:—

(a) If the hydrocarbon molecule has one or more axes of two-fold symmetry, S is equal to twice the number of such axes.

(b) If the hydrocarbon molecule has a center of two-fold symmetry but no axis, $S = 2$ (for one of three-fold symmetry, $S = 3$).

(c) If the hydrocarbon molecule has neither a center nor an axis of symmetry, $S = 1$.

Thus, for example:—

	TWO-FOLD AXES	TWO-FOLD CENTRE	S
Benzene	6	(1)	12
Coronene	6	(1)	12
Triphenylene	3	—	6
Naphthalene	2	(1)	4
Anthracene	2	(1)	4
Phenanthrene	1	—	2
Chrysene (1:2-Benzphenanthrene)	—	1	2
1:2-Benzanthracene	—	—	1

Now the number of ways in which b groupings of type B can be arranged in n positions, while a groupings of type A fill the remaining $(n - b)$ positions, is

$$C = \frac{n!}{a!\,b!}$$

This would be the number of A_aB_b isomers if the parent hydrocarbon had no elements of symmetry.

For the $A_aB_bC_cD_d \cdots$ isomers, this formula becomes

$$C = \frac{n!}{a!\,b!\,c!\,d! \cdots}$$

If the symmetry factor of the parent hydrocarbon is S, and none of the $A_aB_bC_cD_d \cdots$ isomers derived from it has an element of symmetry, the number of such isomers is given by

$$C = \frac{1}{S} \times \frac{n!}{a!\,b!\,c!\,d! \cdots}$$

In cases where none of the axes of symmetry of the original hydrocarbon passes through a substitutable CH group, the above condition is satisfied if any of the numbers a, b, c, d, etc. is odd. In cases such as benzene or anthracene, where an axis of symmetry can pass through a pair of CH positions, more than two of these numbers must be odd. Another exception must be made in cases such as triphenylene and coronene, where three-fold symmetry is possible if the number of groups of each substituent is a multiple of three.

If all of the $A_aB_bC_cD_d \cdots$ isomers had the same symmetry factor S' (defined in the same way as S for the parent hydrocarbon) then equation [1] would be

$$C = \frac{S'}{S} \times \frac{n!}{a!\,b!\,c!\,d! \cdots}$$

i.e.,

$$\frac{S}{S'}\,C = \frac{n!}{a!\,b!\,c!\,d! \cdots} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [2]$$

Unless $S' = 1$, the isomers will not, in fact, all have the same symmetry factor S'. There will be C_1 isomers of symmetry factor S_1', C_2 isomers of symmetry factor S_2', and so on. Hence the left hand side of equation [2] is actually the sum of terms of the type $\frac{S}{S_1'}\,C_1$. In other words

$$\sum \frac{S_1'}{S}\,C_1 = \frac{n!}{a!\,b!\,c!\,d! \cdots} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [3]$$

The numbers of symmetrical $A_aB_bC_cD_d \cdots$ isomers were found by drawing or inspection, and application of equation [3] gave the number of asymmetrical

compounds. Thus where two of the numbers a, b, $c \cdots$ etc. in the $A_aB_bC_c \cdots$ substituted anthracenes are odd, $S' = 2$ for the symmetrical cases and application of equation [3] shows that the number of $A_aB_bC_c \cdots$ compounds exceeds that given by equation [1] by half the number of symmetrical isomers.

Another equation of some value is the following: if the number of $A_aB_bC_c \cdots$ isomers is N that of $A_{a-1}B_bC_cX \cdots$ is N_1 and that of $A_{a-2}B_bC_cX_2 \cdots$ is N_2

then
$$N_2 = \left(\frac{a}{2} - 1\right) N_1 + \frac{aN}{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots [4]$$

This relation, however, only holds for cases where the quantity N_1 can be obtained from equation [1]. In addition, it is inapplicable to benzene, triphenylene or coronene derivatives, since in these compounds certain arrangements become identical on rotation through 60° or 120° about the centre of symmetry.

However, the phenanthrene system may be quoted as one where equation [4] has been useful. Thus, for example,

Number of A_8B_2 = 4 × (Number of A_9B) + 5 × (Number of A_{10})

Number of $A_6B_2C_2$ = 3 × (Number of A_7B_2C) + 4 × (Number of A_8B_2) and Number of $A_6B_2C_2$ = (Number of A_6B_3C) + 2 × (Number of A_6B_4) the third equation being used to obtain the value for A_6B_4.

PART II. RESULTS

TABLE I

NUMBERS OF ISOMERS IN THE BENZENE SERIES

A_6	1						
A_5B	1						
A_4BC	3	A_4B_2	3				
A_3BCD	10	A_3B_2C	6	A_3B_3	3		
A_2BCDE	30	A_2B_2CD	16	$A_2B_2C_2$	11		
$ABCDEF$	60						

TABLE II

NUMBERS OF ISOMERS IN THE NAPHTHALENE SERIES

A_8	1						
A_7B	2						
A_6BC	14	A_6B_2	10				
A_5BCD	84	A_5B_2C	42	A_5B_3	14		
A_4BCDE	420	A_4B_2CD	210	A_4B_3C	70	A_4B_4	22
A_3BCDEF	1,680	A_3B_2CDE	840	A_3B_3CD	280		
$A_2BCDEFG$	5,040	A_2B_2CDEF	2,520				
$ABCDEFGH$	10,080						
		$A_4B_2C_2$	114				
		$A_3B_2C_2D$	420	$A_3B_3C_2$	140		
		$A_2B_2C_2DE$	1,260				
		$A_2B_2C_2D_2$	648				

TABLE III

NUMBERS OF ISOMERS IN THE ANTHRACENE[a] SERIES

A_{10}	1						
A_9B	3						
A_8BC	23	A_8B_2	15				
A_7BCD	180	A_7B_2C	92	A_7B_3	32		
A_6BCDE	1,260	A_6B_2CD	632	A_6B_3C	212	A_6B_4	60
A_5BCDEF	7,560	A_5B_2CDE	3,780	A_5B_3CD	1,260	A_5B_4C	318
$A_4BCDEFG$	37,800	A_4B_2CDEF	18,900	A_4B_3CDE	6,300	A_4B_4CD	1,578
$A_3BCDEFGH$	151,200	A_3B_2CDEFG	75,600	A_3B_3CDEF	25,200		
$A_2BCDEFGHI$	453,600	$A_2B_2CDEFGH$	226,800				
ABCDEFGHIJ	907,200					A_5B_5	66
		$A_6B_2C_2$	330				
		$A_5B_2C_2D$	1,896	$A_5B_3C_2$	636		
$A_4B_2C_2D_2$	4,770	$A_4B_2C_2DE$	9,456	$A_4B_3C_2D$	3,156	$A_4B_4C_2$	810
$A_3B_2C_2D_2E$	18,912	$A_3B_2C_2DEF$	37,800	$A_3B_3C_2DE$	12,600		
$A_2B_2C_2D_2EF$	56,712	$A_2B_2C_2DEFG$	113,400				
		$A_4B_3C_3$	1,056				
$A_3B_3C_2D_2$	6,312	$A_3B_3C_3D$	4,200	$A_2B_2C_2D_2E_2$	28,440		

[a] Since the symmetry properties of pyrene and diphenyl are identical with those of anthracene, this table also applies to them.

TABLE IV

NUMBERS OF ISOMERS IN THE PHENANTHRENE SERIES

A_{10}	1						
A_9B	5						
A_8BC	45	A_8B_2	25				
A_7BCD	360	A_7B_2C	180	A_7B_3	60		
A_6BCDE	2,520	A_6B_2CD	1,260	A_6B_3C	420	A_6B_4	110
A_5BCDEF	15,120	A_5B_2CDE	7,560	A_5B_3CD	2,520	A_5B_4C	630
$A_4BCDEFG$	75,600	A_4B_2CDEF	37,800	A_4B_3CDE	12,600	A_4B_4CD	3,150
$A_3BCDEFGH$	302,400	A_3B_2CDEFG	151,200	A_3B_3CDEF	50,400		
$A_2BCDEFGHI$	907,200	$A_2B_2CDEFGH$	453,600				
ABCDEFGHIJ	1,814,400					A_5B_5	126
$A_6B_2C_2$	640						
$A_5B_2C_2D$	3,780	$A_5B_3C_2$	1,260			$A_4B_2C_2D_2$	9,480
$A_4B_2C_2DE$	18,900	$A_4B_3C_2D$	6,300	$A_4B_4C_2$	1,590	$A_3B_2C_2D_2E$	37,800
$A_3B_2C_2DEF$	75,600	$A_3B_3C_2DE$	25,200			$A_2B_2C_2D_2EF$	113,400
$A_2B_2C_2DEFG$	226,800						
		$A_4B_3C_3$	2,100				
$A_3B_3C_2D_2$	12,600	$A_3B_3C_3D$	8,400			$A_2B_2C_2D_2E_2$	56,760

TABLE V

OTHER AROMATIC SYSTEMS

	A_{12}	$A_{11}B$	$A_{10}B_2$	A_9B_3	A_8B_4	A_7B_5	A_6B_6
Naphthacene and perylene	1	3	21	55	135	198	246
Triphenylene	1	2	14	38	90	132	166
3:4-Benzphenanthrene, 3:4-benzpyrene, and chrysene	1	6	36	110	255	396	472
1:2-Benzanthracene and 1:2-benzpyrene	1	12	66	220	495	792	924
Coronene	1	1	9	19	50	66	90
	A_{14}	$A_{13}B$	$A_{12}B_2$	$A_{11}B_3$	$A_{10}B_4$	A_9B_5	A_8B_6	A_7B_7
2:3-Benznaphthacene and *p*-Diphenylbenzene (Terphenyl)	1	4	28	94	266	508	777	868

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