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GROUP-THEORETICAL TREATMENT OF KEKULÉ STRUCTURES

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Abstract: A group-theoretical treatment of Kekulé structures for aromatic hydrocarbons is proposed, and exemplified by the case of pyrene. The general problem of deducing the distribution over irreducible representations (Γ_{Kek}) or the characters (χ_{Kek}) of the representation based on the Kekulé structures has not been solved. The solutions are reported for special classes of molecules, viz. (a) "straight chain" aromatics (polyacenes), (b) "bent chain" aromatics (polyphenes) and (c) "zig-zag chain" aromatics (phenanthrene, chrysene, picene, etc.).

INTRODUCTION

Kekulé structures is a well known concept in structural chemistry of aromatic molecules.[1,2] It is a part of the fundamental concept of resonance in the valence bond method. Kekulé structures are symmetrical; they have either the full symmetry of the molecule in question or lower. Their properties are obviously suited for a group-theoretical treatment.[3]

The Kekulé structures of a given aromatic molecule form the basis for a representation of the symmetry group of this molecule. The ultimate goal of the group-theoretical treatment should be to produce a general rule for setting up the characters of this representation, say χ_{Kek}. As one of the applications of this theory one would be able to predict the number of Kekulé structures as $\chi_{Kek}(E)$, the character of the identity operation. Furthermore, the corresponding symmetrical structure, Γ_{Kek}, could be detected by standard methods.[3] The symmetrical structure would prescribe the classification of the Kekulé structures according to their symmetries.

AN EXAMPLE: PYRENE

As an example we have

$$\chi_{Kek}(E) = 6$$

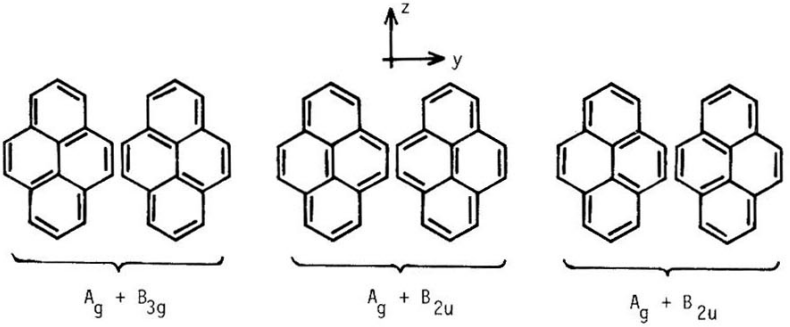

FIG. 1. The six Kekulé structures of pyrene, classified according to symmetry.

and

$$\Gamma_{\text{Kek}} = 3A_g + B_{3g} + 2B_{2u}$$

for pyrene. Fig. 1 shows the six Kekulé structures, classifies according to their symmetries, i.e. the distribution into irreducible representations of the D_{2h} group.

CLASSES OF MOLECULES

The general problem of deducing Γ_{Kek} or χ_{Kek} for a given aromatic molecule has not been solved. Some special solutions are reported in the following for certain classes of aromatics consisting of fused benzene rings in a chain, viz. (a) "straight chain" (polyacenes), (b) "bent chain" (polyphenes) and (c) "zig-zag chain" aromatics; see Fig. 2. Pyrene (Fig. 1) does not belong to these classes.

Number of Kekulé structures

The number of Kekulé structures, $\chi_{\text{Kek}}(E) = K$, was found in terms of the number of benzene rings (Q) in each of the three classes.

Class (a): $$K = Q + 1$$

Class (b): $$K = \frac{1}{8}\left[2Q^2 + 4Q + 9 - (-1)^Q\right]$$

Class (c): $$K = F_{Q+1}$$

Here F_i denotes a member of the Fibonacci series: 1, 1, 2, 3, 5, 8, 13,.... A complete definition of this series reads

$$F_0 = F_1 = 1, \qquad F_n = F_{n-1} + F_{n-2}; \qquad n = 2, 3, 4, \ldots$$

Symmetry of the Kekulé structures

The symmetrical structures, Γ_{Kek}, were also derived for the three classes in question. In the cases of the C_{2v} and D_{2h} symmetries the x axis was chosen as perpendicular to the molecular plane.

Benzene (Q = 1): This molecule falls outside the present systematization inasmuch as it is the only one of them with D_{6h} symmetry. For the two Kekulé structures it was obtained

$$\Gamma_{\text{Kek}} = A_{1g} + B_{2u}$$

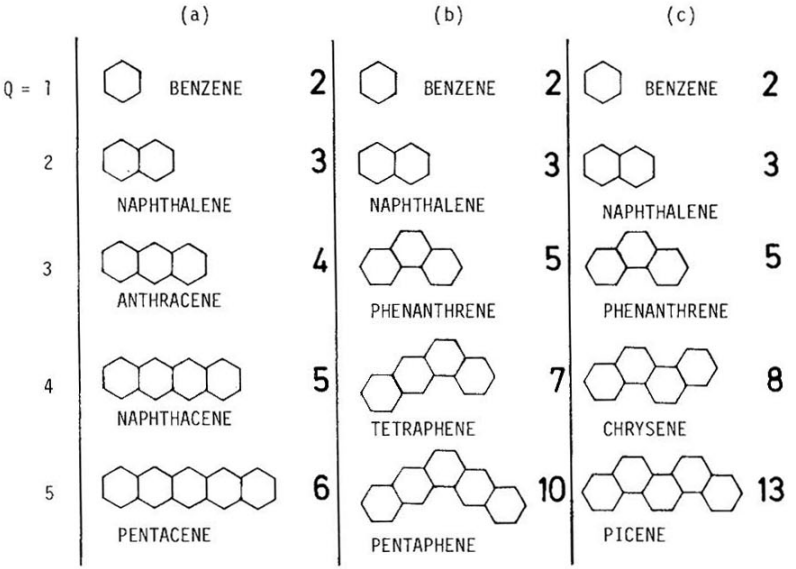

FIG. 2. Number of Kekulé structures for three classes of aromatics with (a) "straight chain", (b) "bent chain" and (c) "zig-zag chain". The cases up to Q (number of benzene rings) = 5 are listed. Notice that benzene and naphthalene may be considered as belonging to all the three classes, while phenanthrene belongs to both (b) and (c).

TABLE 1

Γ_{Kek} for the molecules with $Q = 2,\ldots 7$ belonging to the classes of Fig. 2.

	(a)	(b)	(c)
$Q = 2$	$2A_g + B_{2u}$	$2A_g + B_{2u}$	$2A_g + B_{2u}$
3	$2A_g + 2B_{2u}$	$4A_1 + B_2$	$4A_1 + B_2$
4	$3A_g + 2B_{2u}$	$7A'$	$5A_g + 3B_u$
5	$3A_g + 3B_{2u}$	$7A_1 + 3B_2$	$9A_1 + 4B_2$
6	$4A_g + 3B_{2u}$	$13A'$	$12A_g + 9B_u$
7	$4A_g + 4B_{2u}$	$11A_1 + 6B_2$	$21A_1 + 13B_2$

Class (a), $Q = 2, 3, 4, 5, \ldots$; *symmetry* D_{2h}:

$$\Gamma_{Kek} = \frac{1}{4}[2Q + 3 + (-1)^Q]A_g + \frac{1}{4}[2Q + 1 - (-1)^Q]B_{2u}$$

Class (b), $Q = 3, 5, 7, \ldots$; *symmetry* C_{2v}:

$$\Gamma_{Kek} = \frac{1}{8}(Q^2 + 4Q + 11)A_1 + \frac{1}{8}(Q^2 - 1)B_2$$

Class (b), $Q = 4, 6, 8, \ldots$; *symmetry* C_s:

$$\Gamma_{Kek} = \frac{1}{4}(Q^2 + 2Q + 4)A'$$

Class (c), $Q = 3, 5, 7, \ldots$; *symmetry* C_{2v}:

$$\Gamma_{Kek} = \frac{1}{2}[F_{Q+1} + F_{(Q+3)/2}]A_1 + \frac{1}{2}[F_{Q+1} - F_{(Q+3)/2}]B_2$$

Class (d), $Q = 4, 6, 8, \ldots$; *symmetry* C_{2h}:

$$\Gamma_{Kek} = \frac{1}{2}(F_{Q+1} + F_{Q/2})A_g + \frac{1}{2}(F_{Q+1} - F_{Q/2})B_u$$

Table 1 shows some applications of the above formulas of Γ_{Kek}.

REFERENCES

1. Standard text-books in organic chemistry, e.g.: L. O. Smith, Jr. and S. J. Christol, *Organic Chemistry*, Reinhold, New York, and Chapman &

Hall, London 1966; J. B. Hendrickson, D. J. Cram and G. S. Hammond, *Organic Chemistry*, Third Edition, McGraw-Hill Kogakusha, Tokyo 1970.

2. Text-books in structural and quantum chemistry, e.g.: L. Pauling, *The Nature of the Chemical Bond*, Third Edition, Cornell University Press, Ithaca 1960; C. A. Coulson, *Valence*, Second Edition, Oxford University Press, London 1961; C. W. N. Cumper, *Wave Mechanics for Chemists*, Heinemann, London 1966; J. N. Murrell, S. F. A. Kettle and J. M. Tedder, *Valence Theory*, Second Edition, Wiley, London 1970.
3. R. McWeeny, *Symmetry*, Pergamon Press, Oxford 1963; F. A. Cotton, *Chemical Applications of Group Theory*, Second Edition, Wiley-Interscience, New York 1971; A. Vincent, *Molecular Symmetry and Group Theory*, Wiley, London 1977.