Monatshefte für Chemie 113, 1127—1131 (1982)

Monatshefte für Chemie
Chemical Monthly

Kekulé Structures of Polyphenes

Sven J. Cyvin

Division of Physical Chemistry, The University of Trondheim,
N-7034 Trondheim-NTH, Norway

(Received 10 December 1981. Accepted 21 June 1982)

A group-theoretical treatment of the *Kekulé* structures of polyphenes is performed. General expressions in terms of the number of benzene rings are given for the symmetrical structure (Γ_{Kek}) and the characters (χ_{Kek}) of the representation on the basis of the *Kekulé* structures.

(Keywords: Group theory; Kekulé structures; Polyphenes)

Kekulé Strukturen von Polyphenen

Es wurde eine gruppentheoretische Behandlung der *Kekulé*-Strukturen von Polyphenen durchgeführt. Es werden — in Abhängigkeit von der Anzahl der Benzoleinheiten — für die symmetrischen Strukturen (Γ_{Kek}) und die Charaktere (χ_{Kek}) der Darstellung auf Basis der *Kekulé*-Strukturen allgemeine Ausdrücke angegeben.

Introduction

The *Kekulé* structures[1,2] of aromatic molecules are symmetrical; they have either the full symmetry of the molecule in question or lower. On the basis of their symmetry properties a group-theoretical treatment[3] of *Kekulé* structures has been initiated[4]. In this connection the terms χ_{Kek} and Γ_{Kek} have been introduced. With Γ_{Kek} the (reducible) representation and with χ_{Kek} the respective characters of the set of *Kekulé* structures in the point group of the molecule are denoted. They pertain to the representation of the appropriate symmetry group on the basis of the *Kekulé* structures for a given molecule.

The general problem of determining χ_{Kek} or Γ_{Kek} for a given aromatic has not been solved. Special solutions have been reported[4] for

0026-9247/82/0113/1127/$ 01.00

the "straight-chain" aromatics (polyacenes) and "zig-zag chain" aromatics (phenanthrene, chrysene, picene, etc.). In the present work the problem was solved for a class of "bent-chain" aromatics, viz. polyphenes.

As a part of this group-theoretical problem one obtains the number of the *Kekulé* structures as $\chi_{Kek}(E)$, the character of the identity operation.

Results and Discussion

Class of Molecules

The considered class of molecules consists primarily of fused benzene rings in a bent chain, viz. phenanthrene, tetraphene, pentaphene, etc.; see Fig. 1. The number of benzene rings is identified by the symbol Q. The chain should be bent as closely as possible to the centre of the molecule. Consequently the molecules with $Q = 3, 5, 7, \ldots$ possess a vertical plane of symmetry and a two-fold symmetry axis; they belong to the symmetry group C_{2v}. The molecules with $Q = 4, 6, 8, \ldots$ do not possess any symmetry element apart from the molecular plane; they belong to C_s. The molecules naphthalene ($Q = 2$; D_{2h}), benzene ($Q = 1$; D_{6h}) and even ethylene ($Q = 0$; D_{2h}) may also be considered as belonging to this class.

All the molecules considered here have the chemical formula $C_{4Q+2}H_{2Q+4}$.

Number of Kekulé Structures

The number of *Kekulé* structures, K, for a molecule of the class considered here was derived in terms of Q with the result

$$K = \begin{cases} 1 + \frac{1}{4}Q(Q+2); & Q = 0, 2, 4, 6, \ldots \\ 1 + \frac{1}{4}(Q+1)^2; & Q = 1, 3, 5, 7, \ldots \end{cases}$$

The seven *Kekulé* structures of tetraphene ($Q = 4$) are shown in Fig. 2.

Number of Totally Symmetrical Kekulé Structures

For $Q = 4, 6, 8, \ldots$ the symmetry of the considered molecules is C_s. All the K *Kekulé* structures for these molecules are totally symmetrical in the group-theoretical sense.

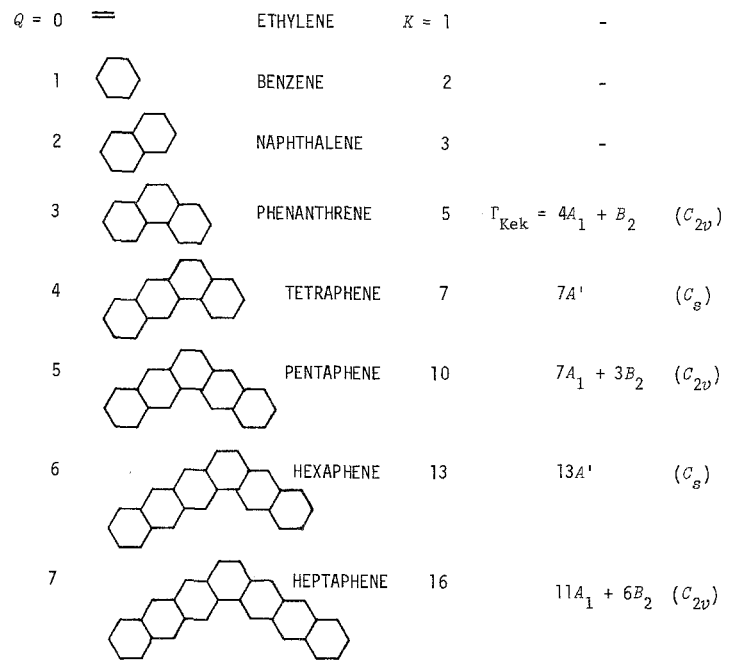

Fig. 1. A class of aromatics including the polyphenes: Number of benzene rings (Q), number of *Kekulé* structures (K), and the symmetrical structure (Γ_{Kek}) for $Q \geq 3$. Symmetry group in parentheses

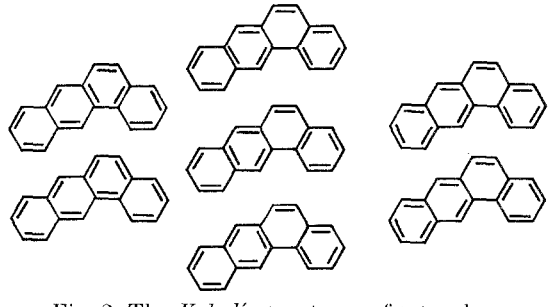

Fig. 2. The *Kekulé* structures of tetraphene

For $Q = 3, 5, 7, \ldots$ the appropriate symmetry is C_{2v}. For the number of totally symmetrical *Kekulé* structures (S) it has been found

$$S = \frac{1}{2}(Q+3); \qquad Q = 3, 5, 7, \ldots$$

The four totally symmetrical structures of pentaphene ($Q = 5$) are shown in Fig. 3.

The symmetry properties of the cases for $Q = 0, 1, 2$ are not treated here since the corresponding molecules do not follow the general scheme as far as their symmetries are concerned.

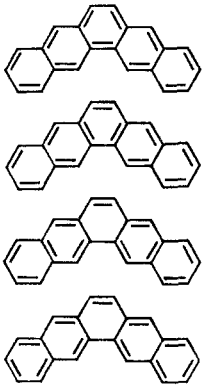

Fig. 3. The totally symmetrical *Kekulé* structures of pentaphene

Group-Theoretical Treatment of the Kekulé Structures

The symmetrical structure, Γ_{Kek}, or the characters, χ_{Kek}, are easily found when the *Kekulé* structures first are derived for a given molecule.

For $Q = 4, 6, 8, \ldots$ (symmetry C_s) one has simply

$$\Gamma_{Kek} = K\,A'$$

and

$$\chi_{Kek}(E) = \chi_{Kek}(\sigma) = K$$

For $Q = 3, 5, 7, \ldots$ (symmetry C_{2v}) it has been found

$$\Gamma_{Kek} = \frac{1}{2}(K + S)\,A_1 + \frac{1}{2}(K - S)\,B_2$$

The numbers K and S are given above in terms of Q. Here the x-axis was chosen as perpendicular to the molecular plane, while the z-axis as usual is the two-fold symmetry axis. The characters of the corresponding representation of the C_{2v} group are:

$$\chi_{Kek}(E) = \chi_{Kek}(\sigma_{yz}) = K, \qquad \chi_{Kek}(C_2) = \chi_{Kek}(\sigma_{zx}) = S$$

Fig. 4 shows the non-totally symmetrical *Kekulé* structures of pentaphene ($Q = 5$). They may be grouped into pairs, K_i and K'_i, where each member is the mirror image of the other; the linear combinations

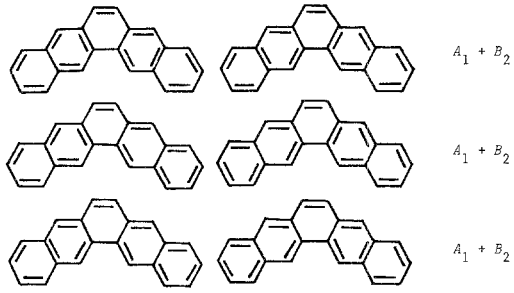

Fig. 4. The non-totally symmetrical *Kekulé* structures of pentaphene

$(K_i + K'_i)$ belongs to A_1 while $(K_i - K'_i)$ belongs to B_2. Figs. 3 and 4 together show all the ten *Kekulé* structures of pentaphene. Their symmetries are consistent with the symmetrical structure $\Gamma_{Kek} = 7\,A_1 + 3\,B_2$.

References

[1] Standard text-books in organic chemistry, e.g.: *Smith L. O., Jr., Christol S. J.*, Organic Chemistry. New York: Reinhold/London: Chapman & Hall. 1966. *Hendrickson, J. B., Cram D. J., Hammond G. S.*, Organic Chemistry, 3rd ed. Tokyo: McGraw-Hill Kogakusha. 1970.

[2] Text-books in structural and quantum chemistry, e.g.: *Pauling L.*, The Nature of the Chemical Bond, 3rd ed. Ithaca: Cornell University Press. 1960. *Coulson C. A.*, Valence, 2nd ed. London: Oxford University Press. 1961. *Murrell J. N., Kettle S. F. A., Tedder J. M.*, Valence Theory, 2nd ed. London: Wiley. 1970.

[3] *Cotton F. A.*, Chemical Applications of Group Theory, 2nd ed. New York: Wiley-Interscience. 1971. *Vincent A.*, Molecular Symmetry and Group Theory. London: Wiley. 1977.

[4] *Cyvin S. J.*, to be published.