Monatshefte für Chemie 114, 525—533 (1983)

Monatshefte für Chemie
Chemical Monthly

Number and Symmetry of *Kekulé* Structures for Some Aromatic Chain Molecules

Sven J. Cyvin

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

(Received 14 October 1982. Accepted 3 November 1982)

A class of aromatic molecules with fused benzene rings is considered. It is characterized by one, two or three straight chains of benzene rings meeting at one ring. The group-theoretical problem of symmetry in terms of Γ_{Kek} and χ_{Kek} is solved; explicit formulas are given for the symmetry groups D_{3h} and C_{2v}.

(Keywords: Aromatics; Group theory; Kekulé structures)

Anzahl und Symmetrie von Kekulé-Strukturen für einige aromatische Ketten-Moleküle

Es wird eine Klasse aromatischer Moleküle behandelt, die dadurch charakterisiert ist, daß eine, zwei oder drei gerade Ketten von Benzolringen an einem Ring aufeinandertreffen. Das gruppentheoretische Problem der Symmetrie ist in Form von Γ_{Kek} und χ_{Kek} gelöst; für die Symmetriegruppen D_{3h} und C_{2v} werden explizite Formeln angegeben.

Introduction

The numbers and symmetries of *Kekulé* structures for condensed aromatics have been studied to some extent[1,2]. In a previous work[3] the single-chain aromatics were treated. In those molecules the centers of the fused benzene rings may be connected by a single (unbranched) line. In the present work we consider chain aromatics with one branching point. Only the simplest case is to be treated, assuming that all the subchains are straight.

0026-9247/83/0114/0525/$ 01.80

Results and Discussion

General Theory

Up to three sub-chains may be attached to one benzene ring in chain aromatics; let the number of rings in the sub-chains be designated Q_1, Q_2 and Q_3. We make the convention that

$$Q_1 \geq Q_2 \geq Q_3 \tag{1}$$

Fig. 1 shows examples of chain aromatics of the considered class and with different values of Q_i. Allowance is made for one or more Q_i equal

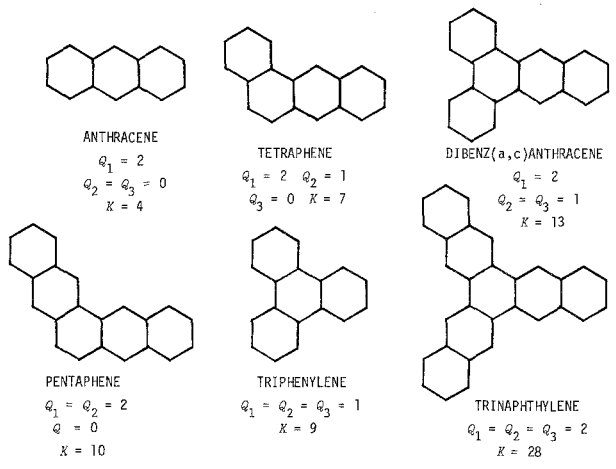

Fig. 1. Some chain aromatics. The number of *Kekulé* structures (K) is given in each case

to zero. Consequently some single-chain aromatics occur among the considered molecules. Some examples are anthracene, tetraphene and pentaphene (see Fig. 1).

The total number of benzene rings in one molecule is obviously

$$Q = 1 + Q_1 + Q_2 + Q_3 \tag{2}$$

The number of *Kekulé* structures is designated by K. It was found

$$K = 1 + (Q_1 + 1)(Q_2 + 1)(Q_3 + 1) \tag{3}$$

Special Cases

Benzene

The benzene molecule ($Q = 1$) is obtained as a trivial special case for

$$Q_1 = Q_2 = Q_3 = 0 \tag{4}$$

The formula (3) gives correctly

$$K = 2 \tag{5}$$

in this case.

Polyacenes

Polyacenes are single-chain aromatics with the fused benzene rings in a straight chain. Anthracene in Fig. 1 is an example. This special case emerges by

$$Q_2 = Q_3 = 0 \tag{6 a}$$

$Q_1 \neq 0$ excludes benzene. The total number of rings is obviously $Q = 1 + Q_1$; cf. eqn. (2). On inserting

$$Q_1 = Q - 1 \tag{6 b}$$

along with (6 a) into eqn. (3) one obtains

$$K = 1 + Q \tag{7}$$

in consistence with previous findings[1].

Polyphenes with $Q = 1, 3, 5, \ldots$

For polyphenes with an odd number of rings one has

$$Q_1 = Q_2 = \frac{1}{2}(Q - 1), \quad Q_3 = 0 \tag{8}$$

Pentaphene in Fig. 1 is an example. The formula (3) gives in this case

$$K = 1 + \frac{1}{4}(Q + 1)^2 \tag{9}$$

which is identical to a previous result[2].

Polyphenes with $Q = 2, 4, 6, \ldots$

For polyphenes with an even number of rings one has

$$Q_1 = \frac{1}{2}Q, \quad Q_2 = \frac{1}{2}Q - 1, \quad Q_3 = 0 \tag{10}$$

Tetraphene in Fig. 1 is an example. On inserting into eqn. (3) one obtains

$$K = \frac{1}{4} Q (Q + 2) \tag{11}$$

as before[2].

Trigonal Special Cases

For

$$Q_1 = Q_2 = Q_3 = q, \quad K = 1 + (q + 1)^3; \quad q \neq 0 \tag{12a}$$

the considered molecules belong to the symmetry group D_{3h}. In this case

$$Q = 3q + 1 \tag{12b}$$

Fig. 1 shows the examples of $q = 1$ (triphenylene) and $q = 2$ (trinaphthylene).

The group-theoretical problem of symmetries[1,2,4] of the *Kekulé* structures of this class of molecules was solved with the following results.

(i) There are $q + 2$ totally symmetrical *Kekulé* structures. They belong to the irreducible representation A_1'.

(ii) There are $q (q + 1)$ symmetrically equivalent sets with 3 structures in each. Such 3 structures are distributed among the irreducible representations according to $A_1' + E'$.

(iii) There are $\frac{1}{6} q (q + 1) (q - 1)$ symmetrically equivalent sets with 6 *Kekulé* structures in each, having the symmetrical structure $A_1' + A_2' + 2 E'$.

Fig. 2 shows the 9 *Kekulé* structures of triphenylene ($q = 1$). They consist of (i) 3 totally symmetrical ones, (ii) 2 symmetrically equivalent sets with 3 structures in each, and none of the category (iii) above. The 4 totally symmetrically *Kekulé* structures (i) of trinaphthylene ($q = 2$) are shown in Fig. 3. Fig. 4 shows 6 representative structures for the symmetrically equivalent sets belonging to the category (ii). From each of them 3 structures are generated by using the appropriate symmetry operations. Finally the structure in Fig. 5 generates 6 symmetrically equivalent structures belonging to the category (iii). The total number of 28 *Kekulé* structures are hence distributed among the irreducible representations according to $\Gamma_{Kek} = 11 A_1' + A_2' + 8 E'$.

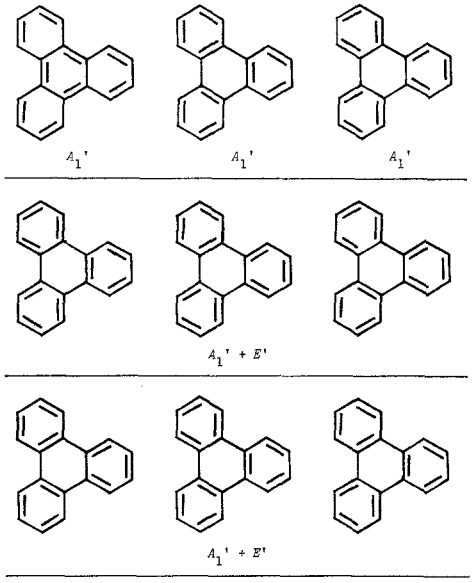

Fig. 2. The nine *Kekulé* structures of triphenylene classified according to symmetry. The total symmetrical structure is $\Gamma_{Kek} = 5\,A_1' + 2\,E'$

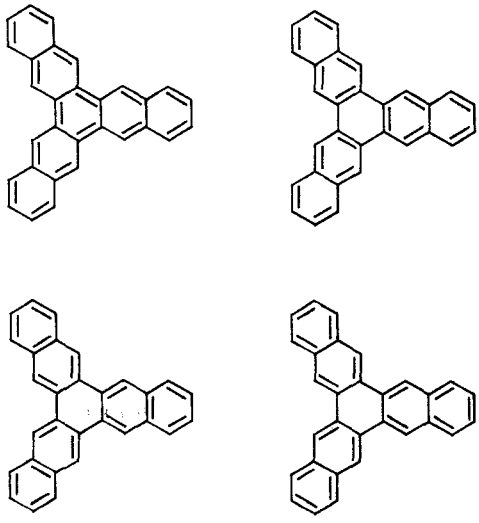

Fig. 3. The four totally symmetrical (A_1') *Kekulé* structures of trinaphthylene

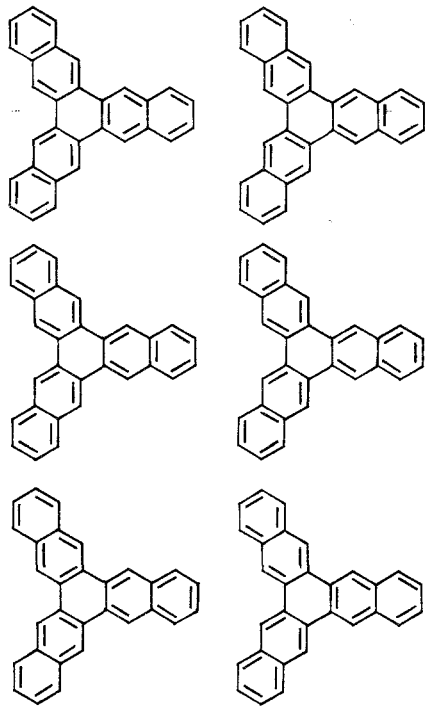

Fig. 4. Six representative *Kekulé* structures of trinaphthylene. Each of them generate three symmetrically equivalent structures belonging to $A_1' + E'$

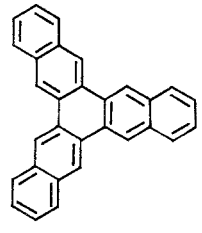

Fig. 5. The only *Kekulé* structure of trinaphthylene which generates six symmetrically equivalent structures ($A_1' + A_2' + 2E'$)

In general the symmetrical structure (Γ_{Kek}) of a trigonal aromatic molecule of the considered type reads

$$\Gamma_{Kek} = \left[1 + \frac{1}{6}(q+1)(q+2)(q+3)\right] A_1' + \frac{1}{6} q(q+1)(q-1) A_2' + \frac{1}{3} q(q+1)(q+2) E' \tag{13}$$

The symmetrical structure may also be given in terms of the characters (χ_{Kek}) of the representation on the basis of the *Kekulé* structures. In this case they are:

$$\begin{gathered} \chi_{Kek}(E) = \chi_{Kek}(\sigma_h) = 1 + (q+1)^3 = K \\ \chi_{Kek}(C_3) = \chi_{Kek}(S_3) = q + 2 \\ \chi_{Kek}(C_2) = \chi_{Kek}(\sigma_v) = 1 + (q+1)^2 \end{gathered} \tag{14}$$

Special Cases of C_{2v} Symmetry

The cases of C_{2v} symmetry among the considered class of molecules are characterized by

$$Q_1 > Q_2 = Q_3 \neq 0 \tag{15 a}$$

or

$$Q_1 = Q_2 > Q_3 \tag{15 b}$$

These types are exemplified by (a) pentaphene and (b) dibenz(a, c) anthracene, respectively; cf. Fig. 1. The z-axis is conventionally taken as the two-fold symmetry axis. Furthermore we adher to the convention of choosing the x-axis perpendicular to the molecular plane. We define q as the number in one of the two symmetrically equivalent sub-chains; cf. Fig. 6. With the aid of eqns. (2) and (3) one obtains

$$Q = 1 + q + 2q', \quad K = 1 + (q+1)(q'+1)^2 \tag{16}$$

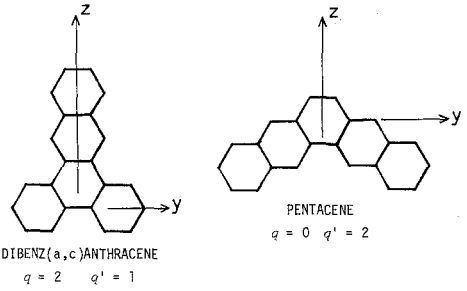

Fig. 6. Two chain aromatics of C_{2v} symmetry, both with $Q = 5$

For this class of molecules it has been found:

(i) There are $1+(q+1)(q'+1)$ totally symmetrical *Kekulé* structures. They belong to A_1.

(ii) All the other *Kekulé* structures occur in $\frac{1}{2}(q+1)q'(q'+1)$ pairs, each pair being a symmetrically equivalent set with the symmetrical structure A_1+B_2.

Fig. 7 shows the 7 totally symmetrical *Kekulé* structures of dibenz(a,c)anthracene. The remaining 6 *Kekulé* structures of this molecule occur in pairs; one member of each is shown in Fig. 8. The total number of 13 *Kekulé* structures follow $\Gamma_{Kek}=10\,A_1+3\,B_2$.

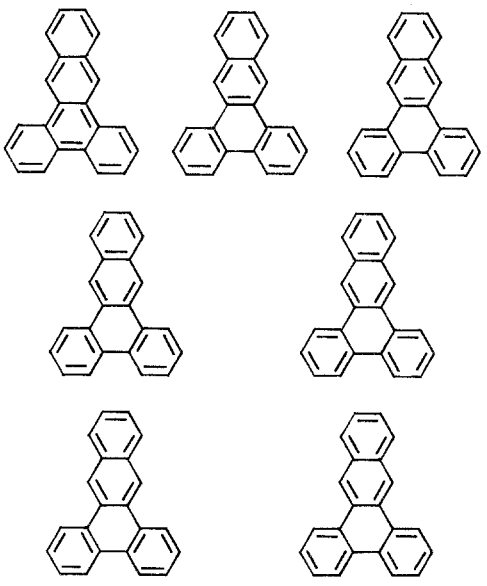

Fig. 7. The seven totally symmetrical (A_1) *Kekulé* structures of dibenz(a,c)-anthracene

In general the symmetrical structure of a molecule of the considered type reads

$$\Gamma_{Kek}=\left[1+\frac{1}{2}\left(q+1\right)\left(q'+1\right)\left(q'+2\right)\right]A_1 + \frac{1}{2}\left(q+1\right)q'\left(q'+1\right)B_2 \qquad (17)$$

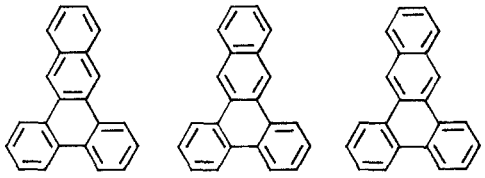

Fig. 8. Three representative non-totally symmetrical *Kekulé* structures of dibenz(a,c)anthracene. The mirror image of each is the other member of a symmetrically equivalent set belonging to $A_1 + B_2$

In terms of the characters:

$$\chi_{Kek}(E) = \chi_{Kek}(\sigma_{yz}) = 1 + (q+1)(q'+1)^2 = K$$
$$\chi_{Kek}(C_2) = \chi_{Kek}(\sigma_{zx}) = 1 + (q+1)(q'+1) \qquad (18)$$

The symmetrical polyphenes (e.g. pentaphene) are special cases of the molecules considered here when

$$q = 0; \quad Q = 1 + 2q', \quad K = 1 + (q'+1)^2 \qquad (19)$$

These relations are consistent with eqns. (8) and (9); one has namely $q = Q_3$, $q' = Q_1 = Q_2$. When the number of totally symmetrical *Kekulé* structures is denoted S one obtains

$$S = 1 + (q+1)(q'+1) = \frac{1}{2}(Q+3) \qquad (20)$$

in consistence with a previously reported formula[2].

Note added in proof: After this paper was in press a very interesting theorem concerning *Kekulé* structures was published by *I. Gutman*, Communications in mathematical Chemistry (match) **13**, 173 (1982). The paper contains also a useful bibliography to previous developments.

References

[1] *Cyvin S. J.*, Acta Chim. Hung., in press.
[2] *Cyvin S. J.*, Monatsh. Chem. **113**, 1127 (1982).
[3] *Cyvin S. J.*, Monatsh. Chem. **114**, 13 (1983).
[4] *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.