

# Isomer Enumeration and Topological Characteristics of Benzenoid Quinones

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In addition to a timely review of benzenoid quinones, equations for counting the number of benzenoid quinones are presented. A comparison of the number of benzenoid monoquinone isomers theoretically possible versus the number reported in the chemical literature provides us with a unique perspective of this important group of compounds. If the excised internal structure of a benzenoid hydrocarbon has only one Kekulé structure ( $K = 1$ ) and no more than two methylene groups, then one of the monoquinone isomers of that benzenoid will also have  $K = 1$ . Within the HMO approximation for  $h = k = 1$  for oxygen, if a monoquinone and its benzenoid precursor both have the same number of Kekulé structures, then the quinone has LUMO = 0.

## INTRODUCTION

Benzenoid hydrocarbons are ubiquitous combustion and pyrolytic pollutants. Their quinone derivatives are also pyrolytic coproducts. Benzenoid hydrocarbon pollutants are assimilated in the environment by air and microbial oxidation to quinones and higher oxidized chemical species. Many benzenoid hydrocarbons are synthesized by reduction of their quinone precursors.<sup>1,2</sup> Also, odd-carbon keto benzenoids are condensed into even-carbon benzenoid products.<sup>3</sup> Herein, we study the enumeration of benzenoid quinones (diones) and related molecular species of environmental and synthetic importance.

The atmospheric levels of benzenoid hydrocarbons spewed out as combustion aerosols are determined by the kinetic and thermodynamic conditions under which they are formed and by their inertness toward subsequent ambient reactions.<sup>4</sup> Thus, understanding the relative stabilities and reactivities of benzenoid hydrocarbons and their quinone derivatives is important to environmental issues. Knowing the theoretical number of isomers and their relative stabilities versus those found in the environment will provide us with insight into their mechanism of formation and will allow us to more fully understand consequential cause and effect relationships.

## TERMINOLOGY

Throughout this paper the carbon and hydrogen atoms and the  $\pi$  bonds in all molecular graphs will be omitted and only the C-C  $\sigma$ -bond skeleton will be shown. Methine substructural units will be shown as secondary graph vertices. The molecular graph of benzo[a]pyrene is shown in Figure 1; position 7 is a methine solo position, positions 1, 5, 6, and 12 are duo positions, positions 2, 3, and 4 are trio methine positions, and positions 8-11 are quartet methine positions.

The excised internal structure of a benzenoid hydrocarbon consists of all its connected internal third-degree vertices that remain after all the peripheral carbon vertices have been stripped off.<sup>2</sup> A strictly pericondensed benzenoid hydrocarbon has no catacondensed appendages or disconnected internal vertices.<sup>2</sup> Benzo[a]pyrene and perylene are not strictly pericondensed because the former has a catacondensed appendage (the benzo moiety) and the latter has disconnected internal vertices. Pyrene is a strictly pericondensed benzenoid with an ethene excised internal structure. Since ethene is incapable of having isomers, pyrene has no other benzenoid isomer since it has only one arrangement of its internal third-degree vertices. There are three isomers of the formula  $C_4H_6$ : *s-cis*-1,3-butadiene, *s-trans*-1,3-butadiene, and trimethylenemethane diradical. If an 18-carbon-atom perimeter is circumscribed about each of these  $C_4H_6$  isomers with the resulting species being incremented with 6 hydrogens, one obtains the only three  $C_{22}H_{12}$  benzenoid isomers possible for this formula, i.e., ben-

zo[ghi]perylene, anthanthrene, and triangulene. If these three strictly pericondensed benzenoids are circumscribed by a 30-carbon-atom perimeter followed by incrementation with 6 hydrogens, one obtains the only three benzenoid isomers possible for  $C_{36}H_{18}$ . Because trimethylenemethane is a diradical, triangulene and its  $C_{32}H_{18}$  successor are also diradicals.

## CHEMICAL LITERATURE SEARCHING

Chemistry is the best documented branch of science since most chemical information can be presented by structural formulas that are systematically and uniquely indexed and retrieved. The molecular formula of a chemical compound is a universal invariant that vastly delimits the range of structures to isomers. Molecular formulas can be ordered for indexing purposes according to simple rules. The number and identity of isomers corresponding to a particular formula are the real crux to the documentation/retrieval problem. A similar isomer problem exists in the chemical analysis of natural products and environmental pollutants. The essence of molecular chemistry is the combinatorics of atoms according to definite rules. Thus, the study of isomerism is an important endeavor that impacts not only on the fundamentals of chemistry per se but also on the documentation and retrieval of chemical information.

A formula periodic table for (even carbon) Kekuléan benzenoid hydrocarbons (Table I, PAH6) has been published which contains all the formulas possible for this class of compounds.<sup>2,5</sup> All formulas for benzenoid monoquinones can be obtained from this table by simply substituting two hydrogens by two oxygens. For example, pyrene has the formula  $C_{16}H_{10}$  and all its nine quinone isomers have the formula  $C_{16}H_8O_2$ . Similarly, substitution two hydrogens by two oxygens in the formula of coronene ( $C_{24}H_{12}$ ) gives  $C_{24}H_{10}O_2$ , which corresponds to its five quinone isomers. Also, a table containing all the formulas of odd-carbon radical benzenoid-like reactive intermediates has been published,<sup>5</sup> and substituting one hydrogen by one oxygen gives the formulas for the corresponding ketones. The phenalenyl radical (acena-phenenyl) formula of  $C_{13}H_9$  gives the formula for phenalene ( $C_{13}H_8O$ ) upon replacement of one hydrogen by one oxygen. Thus, using these tables, one can systematically and comprehensively search the literature for all benzenoid quinones and odd-carbon benzenoid ketones. The extension of this approach to diquinones and higher quinones should be obvious.

The number of *Chemical Abstracts* formula listings of benzenoid monoquinones from 1920 to 1986 (Table II) provides us with a unique perspective in regard to their past and current research status. For a benzenoid period (Table I) as molecular size increases, the number of listings decreases. The monoquinones of the catacondensed benzenoids (formulas boldfaced in Table II),  $C_{18}H_{10}O_2$ ,  $C_{22}H_{12}O_2$ ,  $C_{26}H_{14}O_2$ ,  $C_{30}$ -

**Table I.** Formula Periodic Table for Benzenoid Polycyclic Aromatic Hydrocarbons (PAH6) ( $N_c = 3N_H - 14 - 2d_s$ )

$N_c = 3N_H + 4$	$N_c = 3N_H + 2$	$N_c = 3N_H$	$N_c = 3N_H - 2$	$N_c = 3N_H - 4$	$N_c = 3N_H - 6$	$N_c = 3N_H - 8$	$N_c = 3N_H - 10$	$N_c = 3N_H - 12$	$N_c = 3N_H - 14$	$N_c = 3N_H - 16$	$N_c = 3N_H - 18$	$N_c = 3N_H - 20$	$(N_c = 2N_H - 6 + N_{1c})$
Forbidden Region			$N_c/N_H < 2$										
$N_c/N_H > 3$			Most Reactive										
Least Reactive			Intermediate Reactive										
$C_{60}H_{20}$	$C_{54}H_{18}$	$C_{48}H_{16}$	$C_{42}H_{14}$	$C_{36}H_{12}$	$C_{30}H_{10}$	$C_{24}H_8$	$C_{18}H_6$	$C_{12}H_4$	$C_6H_2$	$C_4H_2$	$C_2H_2$	$C_0H_0$	$N_c = 2N_H - 6$
$C_{64}H_{22}$	$C_{58}H_{20}$	$C_{52}H_{18}$	$C_{46}H_{16}$	$C_{40}H_{14}$	$C_{34}H_{12}$	$C_{28}H_{10}$	$C_{22}H_8$	$C_{16}H_6$	$C_{10}H_4$	$C_4H_2$	$C_2H_2$	$C_0H_0$	$N_c = 2N_H - 4$
$C_{70}H_{24}$	$C_{64}H_{22}$	$C_{58}H_{20}$	$C_{52}H_{18}$	$C_{46}H_{16}$	$C_{40}H_{14}$	$C_{34}H_{12}$	$C_{28}H_{10}$	$C_{22}H_8$	$C_{16}H_6$	$C_{10}H_4$	$C_4H_2$	$C_2H_2$	$N_c = 2N_H - 2$
$C_{74}H_{26}$	$C_{68}H_{24}$	$C_{62}H_{22}$	$C_{56}H_{20}$	$C_{50}H_{18}$	$C_{44}H_{16}$	$C_{38}H_{14}$	$C_{32}H_{12}$	$C_{26}H_{10}$	$C_{20}H_8$	$C_{14}H_6$	$C_8H_4$	$C_2H_2$	$N_c = 2N_H$
$C_{78}H_{28}$	$C_{72}H_{26}$	$C_{66}H_{24}$	$C_{60}H_{22}$	$C_{54}H_{20}$	$C_{48}H_{18}$	$C_{42}H_{16}$	$C_{36}H_{14}$	$C_{30}H_{12}$	$C_{24}H_{10}$	$C_{18}H_8$	$C_{12}H_6$	$C_6H_4$	$N_c = 2N_H + 2$
$C_{82}H_{30}$	$C_{76}H_{28}$	$C_{70}H_{26}$	$C_{64}H_{24}$	$C_{58}H_{22}$	$C_{52}H_{20}$	$C_{46}H_{18}$	$C_{40}H_{16}$	$C_{34}H_{14}$	$C_{28}H_{12}$	$C_{22}H_{10}$	$C_{16}H_8$	$C_{10}H_6$	$N_c = 2N_H + 4$
$C_{86}H_{32}$	$C_{80}H_{30}$	$C_{74}H_{28}$	$C_{68}H_{26}$	$C_{62}H_{24}$	$C_{56}H_{22}$	$C_{50}H_{20}$	$C_{44}H_{18}$	$C_{38}H_{16}$	$C_{32}H_{14}$	$C_{26}H_{12}$	$C_{20}H_{10}$	$C_{14}H_8$	$N_c = 2N_H + 6$
$C_{90}H_{34}$	$C_{84}H_{32}$	$C_{78}H_{30}$	$C_{72}H_{28}$	$C_{66}H_{26}$	$C_{60}H_{24}$	$C_{54}H_{22}$	$C_{48}H_{20}$	$C_{42}H_{18}$	$C_{36}H_{16}$	$C_{30}H_{14}$	$C_{24}H_{12}$	$C_{18}H_{10}$	$N_c = 2N_H + 8$
$C_{94}H_{36}$	$C_{88}H_{34}$	$C_{82}H_{32}$	$C_{76}H_{30}$	$C_{70}H_{28}$	$C_{64}H_{26}$	$C_{58}H_{24}$	$C_{52}H_{22}$	$C_{46}H_{20}$	$C_{40}H_{18}$	$C_{34}H_{16}$	$C_{28}H_{14}$	$C_{22}H_{12}$	$N_c = 2N_H + 10$
$C_{98}H_{38}$	$C_{92}H_{36}$	$C_{86}H_{34}$	$C_{80}H_{32}$	$C_{74}H_{30}$	$C_{68}H_{28}$	$C_{62}H_{26}$	$C_{56}H_{24}$	$C_{50}H_{22}$	$C_{44}H_{20}$	$C_{38}H_{18}$	$C_{32}H_{16}$	$C_{26}H_{14}$	$N_c = 2N_H + 12$
$C_{102}H_{40}$	$C_{96}H_{38}$	$C_{90}H_{36}$	$C_{84}H_{34}$	$C_{78}H_{32}$	$C_{72}H_{30}$	$C_{66}H_{28}$	$C_{60}H_{26}$	$C_{54}H_{24}$	$C_{48}H_{22}$	$C_{42}H_{20}$	$C_{36}H_{18}$	$C_{30}H_{16}$	$N_c = 2N_H + 14$
$C_{106}H_{42}$	$C_{100}H_{40}$	$C_{94}H_{38}$	$C_{88}H_{36}$	$C_{82}H_{34}$	$C_{76}H_{32}$	$C_{70}H_{30}$	$C_{64}H_{28}$	$C_{58}H_{26}$	$C_{52}H_{24}$	$C_{46}H_{22}$	$C_{40}H_{20}$	$C_{34}H_{18}$	$N_c = 2N_H + 16$
$C_{110}H_{44}$	$C_{104}H_{42}$	$C_{98}H_{40}$	$C_{92}H_{38}$	$C_{86}H_{36}$	$C_{80}H_{34}$	$C_{74}H_{32}$	$C_{68}H_{30}$	$C_{62}H_{28}$	$C_{56}H_{26}$	$C_{50}H_{24}$	$C_{44}H_{22}$	$C_{38}H_{20}$	$N_c = 2N_H + 18$
$C_{114}H_{46}$	$C_{108}H_{44}$	$C_{102}H_{42}$	$C_{96}H_{40}$	$C_{90}H_{38}$	$C_{84}H_{36}$	$C_{78}H_{34}$	$C_{72}H_{32}$	$C_{66}H_{30}$	$C_{60}H_{28}$	$C_{54}H_{26}$	$C_{48}H_{24}$	$C_{42}H_{22}$	$N_c = 2N_H + 20$
$C_{118}H_{48}$	$C_{112}H_{46}$	$C_{106}H_{44}$	$C_{100}H_{42}$	$C_{94}H_{40}$	$C_{88}H_{38}$	$C_{82}H_{36}$	$C_{76}H_{34}$	$C_{70}H_{32}$	$C_{64}H_{30}$	$C_{58}H_{28}$	$C_{52}H_{26}$	$C_{46}H_{24}$	$N_c = 2N_H + 22$
$C_{122}H_{50}$	$C_{116}H_{48}$	$C_{110}H_{46}$	$C_{104}H_{44}$	$C_{98}H_{42}$	$C_{92}H_{40}$	$C_{86}H_{38}$	$C_{80}H_{36}$	$C_{74}H_{34}$	$C_{68}H_{32}$	$C_{62}H_{30}$	$C_{56}H_{28}$	$C_{50}H_{26}$	$N_c = 2N_H + 24$
$C_{126}H_{52}$	$C_{120}H_{50}$	$C_{114}H_{48}$	$C_{108}H_{46}$	$C_{102}H_{44}$	$C_{96}H_{42}$	$C_{90}H_{40}$	$C_{84}H_{38}$	$C_{78}H_{36}$	$C_{72}H_{34}$	$C_{66}H_{32}$	$C_{60}H_{30}$	$C_{54}H_{28}$	$N_c = 2N_H + 26$
$C_{130}H_{54}$	$C_{124}H_{52}$	$C_{118}H_{50}$	$C_{112}H_{48}$	$C_{106}H_{46}$	$C_{100}H_{44}$	$C_{94}H_{42}$	$C_{88}H_{40}$	$C_{82}H_{38}$	$C_{76}H_{36}$	$C_{70}H_{34}$	$C_{64}H_{32}$	$C_{58}H_{30}$	$N_c = 2N_H + 28$
$C_{134}H_{56}$	$C_{128}H_{54}$	$C_{122}H_{52}$	$C_{116}H_{50}$	$C_{110}H_{48}$	$C_{104}H_{46}$	$C_{98}H_{44}$	$C_{92}H_{42}$	$C_{86}H_{40}$	$C_{80}H_{38}$	$C_{74}H_{36}$	$C_{68}H_{34}$	$C_{62}H_{32}$	$N_c = 2N_H + 30$
$C_{138}H_{58}$	$C_{132}H_{56}$	$C_{126}H_{54}$	$C_{120}H_{52}$	$C_{114}H_{50}$	$C_{108}H_{48}$	$C_{102}H_{46}$	$C_{96}H_{44}$	$C_{90}H_{42}$	$C_{84}H_{40}$	$C_{78}H_{38}$	$C_{72}H_{36}$	$C_{66}H_{34}$	$N_c = 2N_H + 32$
$C_{142}H_{60}$	$C_{136}H_{58}$	$C_{130}H_{56}$	$C_{124}H_{54}$	$C_{118}H_{52}$	$C_{112}H_{50}$	$C_{106}H_{48}$	$C_{100}H_{46}$	$C_{94}H_{44}$	$C_{88}H_{42}$	$C_{82}H_{40}$	$C_{76}H_{38}$	$C_{70}H_{36}$	$N_c = 2N_H + 34$
$C_{146}H_{62}$	$C_{140}H_{60}$	$C_{134}H_{58}$	$C_{128}H_{56}$	$C_{122}H_{54}$	$C_{116}H_{52}$	$C_{110}H_{50}$	$C_{104}H_{48}$	$C_{98}H_{46}$	$C_{92}H_{44}$	$C_{86}H_{42}$	$C_{80}H_{40}$	$C_{74}H_{38}$	$N_c = 2N_H + 36$
$C_{150}H_{64}$	$C_{144}H_{62}$	$C_{138}H_{60}$	$C_{132}H_{58}$	$C_{126}H_{56}$	$C_{120}H_{54}$	$C_{114}H_{52}$	$C_{108}H_{50}$	$C_{102}H_{48}$	$C_{96}H_{46}$	$C_{90}H_{44}$	$C_{84}H_{42}$	$C_{78}H_{40}$	$N_c = 2N_H + 38$
$C_{154}H_{66}$	$C_{148}H_{64}$	$C_{142}H_{62}$	$C_{136}H_{60}$	$C_{130}H_{58}$	$C_{124}H_{56}$	$C_{118}H_{54}$	$C_{112}H_{52}$	$C_{106}H_{50}$	$C_{100}H_{48}$	$C_{94}H_{46}$	$C_{88}H_{44}$	$C_{82}H_{42}$	$N_c = 2N_H + 40$
$C_{158}H_{68}$	$C_{152}H_{66}$	$C_{146}H_{64}$	$C_{140}H_{62}$	$C_{134}H_{60}$	$C_{128}H_{58}$	$C_{122}H_{56}$	$C_{116}H_{54}$	$C_{110}H_{52}$	$C_{104}H_{50}$	$C_{98}H_{48}$	$C_{92}H_{46}$	$C_{86}H_{44}$	$N_c = 2N_H + 42$
$C_{162}H_{70}$	$C_{156}H_{68}$	$C_{150}H_{66}$	$C_{144}H_{64}$	$C_{138}H_{62}$	$C_{132}H_{60}$	$C_{126}H_{58}$	$C_{120}H_{56}$	$C_{114}H_{54}$	$C_{108}H_{52}$	$C_{102}H_{50}$	$C_{96}H_{48}$	$C_{90}H_{46}$	$N_c = 2N_H + 44$
$C_{166}H_{72}$	$C_{160}H_{70}$	$C_{154}H_{68}$	$C_{148}H_{66}$	$C_{142}H_{64}$	$C_{136}H_{62}$	$C_{130}H_{60}$	$C_{124}H_{58}$	$C_{118}H_{56}$	$C_{112}H_{54}$	$C_{106}H_{52}$	$C_{100}H_{50}$	$C_{94}H_{48}$	$N_c = 2N_H + 46$
$C_{170}H_{74}$	$C_{164}H_{72}$	$C_{158}H_{70}$	$C_{152}H_{68}$	$C_{146}H_{66}$	$C_{140}H_{64}$	$C_{134}H_{62}$	$C_{128}H_{60}$	$C_{122}H_{58}$	$C_{116}H_{56}$	$C_{110}H_{54}$	$C_{104}H_{52}$	$C_{98}H_{50}$	$N_c = 2N_H + 48$
$C_{174}H_{76}$	$C_{168}H_{74}$	$C_{162}H_{72}$	$C_{156}H_{70}$	$C_{150}H_{68}$	$C_{144}H_{66}$	$C_{138}H_{64}$	$C_{132}H_{62}$	$C_{126}H_{60}$	$C_{120}H_{58}$	$C_{114}H_{56}$	$C_{108}H_{54}$	$C_{102}H_{52}$	$N_c = 2N_H + 50$
$C_{178}H_{78}$	$C_{172}H_{76}$	$C_{166}H_{74}$	$C_{160}H_{72}$	$C_{154}H_{70}$	$C_{148}H_{68}$	$C_{142}H_{66}$	$C_{136}H_{64}$	$C_{130}H_{62}$	$C_{124}H_{60}$	$C_{118}H_{58}$	$C_{112}H_{56}$	$C_{106}H_{54}$	$N_c = 2N_H + 52$
$C_{182}H_{80}$	$C_{176}H_{78}$	$C_{170}H_{76}$	$C_{164}H_{74}$	$C_{158}H_{72}$	$C_{152}H_{70}$	$C_{146}H_{68}$	$C_{140}H_{66}$	$C_{134}H_{64}$	$C_{128}H_{62}$	$C_{122}H_{60}$	$C_{116}H_{58}$	$C_{110}H_{56}$	$N_c = 2N_H + 54$
$C_{186}H_{82}$	$C_{180}H_{80}$	$C_{174}H_{78}$	$C_{168}H_{76}$	$C_{162}H_{74}$	$C_{156}H_{72}$	$C_{150}H_{70}$	$C_{144}H_{68}$	$C_{138}H_{66}$	$C_{132}H_{64}$	$C_{126}H_{62}$	$C_{120}H_{60}$	$C_{114}H_{58}$	$N_c = 2N_H + 56$
$C_{190}H_{84}$	$C_{184}H_{82}$	$C_{178}H_{80}$	$C_{172}H_{78}$	$C_{166}H_{76}$	$C_{160}H_{74}$	$C_{154}H_{72}$	$C_{148}H_{70}$	$C_{142}H_{68}$	$C_{136}H_{66}$	$C_{130}H_{64}$	$C_{124}H_{62}$	$C_{118}H_{60}$	$N_c = 2N_H + 58$
$C_{194}H_{86}$	$C_{188}H_{84}$	$C_{182}H_{82}$	$C_{176}H_{80}$	$C_{170}H_{78}$	$C_{164}H_{76}$	$C_{158}H_{74}$	$C_{152}H_{72}$	$C_{146}H_{70}$	$C_{140}H_{68}$	$C_{134}H_{66}$	$C_{128}H_{64}$	$C_{122}H_{62}$	$N_c = 2N_H + 60$
$C_{198}H_{88}$	$C_{192}H_{86}$	$C_{186}H_{84}$	$C_{180}H_{82}$	$C_{174}H_{80}$	$C_{168}H_{78}$	$C_{162}H_{76}$	$C_{156}H_{74}$	$C_{150}H_{72}$	$C_{144}H_{70}$	$C_{138}H_{68}$	$C_{132}H_{66}$	$C_{126}H_{64}$	$N_c = 2N_H + 62$
$C_{202}H_{90}$	$C_{196}H_{88}$	$C_{190}H_{86}$	$C_{184}H_{84}$	$C_{178}H_{82}$	$C_{172}H_{80}$	$C_{166}H_{78}$	$C_{160}H_{76}$	$C_{154}H_{74}$	$C_{148}H_{72}$	$C_{142}H_{70}$	$C_{136}H_{68}$	$C_{130}H_{66}$	$N_c = 2N_H + 64$
$C_{206}H_{92}$	$C_{200}H_{90}$	$C_{194}H_{88}$	$C_{188}H_{86}$	$C_{182}H_{84}$	$C_{176}H_{82}$	$C_{170}H_{80}$	$C_{164}H_{78}$	$C_{158}H_{76}$	$C_{152}H_{74}$	$C_{146}H_{72}$	$C_{140}H_{70}$	$C_{134}H_{68}$	$N_c = 2N_H + 66$
$C_{210}H_{94}$	$C_{204}H_{92}$	$C_{198}H_{90}$	$C_{192}H_{88}$	$C_{186}H_{86}$	$C_{180}H_{84}$	$C_{174}H_{82}$	$C_{168}H_{80}$	$C_{162}H_{78}$	$C_{156}H_{76}$	$C_{150}H_{74}$	$C_{144}H_{72}$	$C_{138}H_{70}$	$N_c = 2N_H + 68$
$C_{214}H_{96}$	$C_{208}H_{94}$	$C_{202}H_{92}$	$C_{196}H_{90}$	$C_{190}H_{88}$	$C_{184}H_{86}$	$C_{178}H_{84}$	$C_{172}H_{82}$	$C_{166}H_{80}$	$C_{160}H_{78}$	$C_{154}H_{76}$	$C_{148}H_{74}$	$C_{142}H_{72}$	$N_c = 2N_H + 70$
$C_{218}H_{98}$	$C_{212}H_{96}$	$C_{206}H_{94}$	$C_{200}H_{92}$	$C_{194}H_{90}$	$C_{188}H_{88}$	$C_{182}H_{86}$	$C_{176}H_{84}$	$C_{170}H_{82}$	$C_{164}H_{80}$	$C_{158}H_{78}$	$C_{152}H_{76}$	$C_{146}H_{74}$	$N_c = 2N_H + 72$
$C_{222}H_{100}$	$C_{216}H_{98}$	$C_{210}H_{96}$	$C_{204}H_{94}$	$C_{198}H_{92}$	$C_{192}H_{90}$	$C_{186}H_{88}$	$C_{180}H_{86}$	$C_{174}H_{84}$	$C_{168}H_{82}$	$C_{162}H_{80}$	$C_{156}H_{78}$	$C_{150}H_{76}$	$N_c = 2N_H + 74$
$C_{226}H_{102}$	$C_{220}H_{100}$	$C_{214}H_{98}$	$C_{208}H_{96}$	$C_{202}H_{94}$	$C_{196}H_{92}$	$C_{190}H_{90}$	$C_{184}H_{88}$	$C_{178}H_{86}$	$C_{172}H_{84}$	$C_{166}H_{82}$	$C_{160}H_{80}$	$C_{154}H_{78}$	$N_c = 2N_H + 76$
$C_{230}H_{104}$	$C_{224}H_{102}$	$C_{218}H_{100}$	$C_{212}H_{98}$	$C_{206}H_{96}$	$C_{200}H_{94}$	$C_{194}H_{92}$	$C_{188}H_{90}$	$C_{182}H_{88}$	$C_{176}H_{86}$	$C_{170}H_{84}$	$C_{164}H_{82}$	$C_{158}H_{80}$	$N_c = 2N_H + 78$
$C_{234}H_{106}$	$C_{228}H_{104}$	$C_{222}H_{102}$	$C_{216}H_{100}$	$C_{210}H_{98}$	$C_{204}H_{96}$	$C_{198}H_{94}$	$C_{192}H_{92}$	$C_{186}H_{90}$	$C_{180}H_{88}$	$C_{174}H_{86}$	$C_{168}H_{84}$	$C_{162}H_{82}$	$N_c = 2N_H + 80$
$C_{238}H_{108}$	$C_{232}H_{106}$	$C_{226}H_{104}$	$C_{220}H_{102}$	$C_{214}H_{100}$	$C_{208}H_{98}$	$C_{202}H_{96}$	$C_{196}H_{94}$	$C_{190}H_{92}$	$C_{184}H_{90}$	$C_{178}H_{88}$	$C_{172}H_{86}$	$C_{166}H_{84}$	$N_c = 2N_H + 82$
$C_{242}H_{110}$	$C_{236}H_{108}$	$C_{230}H_{106}$	$C_{224}H_{104}$	$C_{218}H_{102}$	$C_{212}H_{10$								

**Table IV.** Cycle Indexes for All the Even-Carbon Benzenoid Symmetry (Sub)Groups ( $n = N_H$ )

symmetry group	cycle index
$C_s$	$Z(C_s) = f_1^n$
$C_{2h}$	$Z(C_{2h}) = \frac{1}{2}(f_1^n + f_2^{n/2})$
$C_{3h}$	$Z(C_{3h}) = \frac{1}{3}(f_1^n + 2f_3^{n/3})$
$C_{2v}$	$Z[C_{2v}(e), C_{2v}(v_3)] = \frac{1}{2}(f_1^n + f_2^{n/2})$ $Z[C_{2v}(v_2)] = \frac{1}{2}(f_1^n + f_1^2 f_2^{(n-2)/2})$
$C_{6h}$	$Z(C_{6h}) = \frac{1}{6}(f_1^n + 2f_6^{n/6} + 2f_3^{n/3} + f_2^{n/2})$
$D_{2h}$	$Z[D_{2h}(e), D_{2h}(v_3)] = \frac{1}{4}(f_1^n + 3f_2^{n/2})$ $Z[D_{2h}(v_2)] = \frac{1}{4}(f_1^n + f_1^2 f_2^{(n-2)/2} + 2f_2^{n/2})$
$D_{3h}$	$Z(D_{3h}) = \frac{1}{6}(f_1^n + 2f_3^{n/3} + 3f_2^{n/2})$
$D_{6h}$	$Z[D_{6h}(v_3), D_{6h}(e)] = \frac{1}{12}(f_1^n + 2f_6^{n/6} + 2f_3^{n/3} + 7f_2^{n/2})$ $Z[D_{6h}(v_2)] = \frac{1}{12}(f_1^n + 2f_6^{n/6} + 2f_3^{n/3} + 3f_1^2 f_2^{(n-2)/2} + 4f_2^{n/2})$

ilarly, one needs to distinguish between the  $D_{2h}(v_2)$ ,  $D_{2h}(v_3)$ ,  $D_{6h}(v_2)$ , and  $D_{6h}(v_3)$  subclasses for a similar reason. Since there are only these symmetry groups for planar benzenoid structures, one can just present their respective isomer-counting equations without having to explicitly work through Polya's theorem for each and every case. Thus, the practitioner can just use these given equations without having to understand the details of Polya's theorem.<sup>7</sup>

Table IV presents the cycle indexes for all the symmetry groups characteristic of benzenoid hydrocarbons. Substitution of the appropriate figure-counting series into these cycle indexes leads to the configuration-counting series. These cycle indexes are applicable to benzenoid skeletons where substitution is only allowed at second-degree vertices. The figure-counting series is  $1 + x$  for one different substituent,  $1 + x + y$  for two different substituents, and so on.

Consider the two  $C_{18}H_{12}$  benzenoid isomers, benz[a]-anthracene ( $C_s$ ) and chrysene ( $C_{2h}$ ), where only the latter has an axis of symmetry. If one desires to know the number of diaza isomers having the benz[a]anthracene or chrysene skeleton, then one simply substitutes the figure-counting series of  $f_1 = x + 1$  and  $f_2 = x^2 + 1$  into the appropriate cycle index found in Table IV which gives the corresponding configuration-counting series. For benz[a]anthracene, one obtains the binomial equation  $Z(C_s; x+1) = (x+1)^{12}$ , and for chrysene one obtains  $Z(C_{2h}; x+1, x^2+1) = \frac{1}{2}[(x+1)^{12} + (x^2+1)^6]$ . The coefficient to the  $x^2$  term for these expanded equations gives the respective number of diaza isomers.<sup>7</sup> For benz[a]-anthracene, there are  $12!/2!10! = 66$  diaza analogue isomers, and for chrysene, there are  $\frac{1}{2}(12!/2!10! + 6!/15!) = 36$  diaza analogue isomers.

In general, the isomer-counting generating function for aza analogues of benzenoid hydrocarbons (azaarenes) without an axis of symmetry is the binomial function and with a single  $C_2$  axis is

$$Z[C_{2h}, C_{2v}(e), C_{2v}(v_3); x+1] = \frac{1}{2}[(x+1)^n + (x^2+1)^{n/2}]$$

For an even number of nitrogens, the above equation is also applicable to aza analogues of  $C_{2v}(v_2)$  benzenoids, but it underestimates the number of isomers of odd-nitrogen azaarenes. Thus, the binomial and the above isomer-counting generating functions take care of over 60% of the possible benzenoid isomer analogues.<sup>7</sup> It is worth noting at this point that these results are also applicable to any per substituted benzenoid isomer set.

Threefold ( $C_{3h}$ ,  $D_{3h}$ ) and sixfold ( $C_{6h}$ ,  $D_{6h}$ ) symmetry among nonradical benzenoid molecular graphs can only be exhibited

**Table V.** Equations for Determining the Number of Benzenoid Monoquinone Isomers ( $n = N_H$ )

symmetry group	no. of benzenoid monoquinone isomers	examples
$C_s$	$Iq(C_s) = n^2/4$	benzo[a]pyrene
$C_{2h}$ and $C_{2v}(e)$	$Iq(C_{2h}) = n(n+2)/8$	chrysene and phenanthrene
$C_{2v}(v_3)$	$Iq(C_{2v}(v_3)) = n^2/8$	benzo[c]phenanthrene
$C_{2v}(v_2)$	$Iq(C_{2v}(v_2)) = (n^2+4)/8$	dibenz[a,j]anthracene
$C_{3h}$	$Iq(C_{3h}) = n^2/12$	tribenzo[a,g,m]-triphenylene
$C_{6h}$	$Iq(C_{6h}) = n(n+2)/24$	hexanaphthocoronene
$D_{2h}(v_3, e)$	$Iq(D_{2h}(v_3)) = n(n+4)/16$	naphthalene
$D_{2h}(v_2, e)$	$Iq(D_{2h}(v_2)) = (n+2)^2/16$	anthracene
$D_{3h}$	$Iq(D_{3h}) = n(n+6)/24$	triphenylene
$D_{6h}(v_3, e)$	$Iq(D_{6h}(v_3)) = \frac{n(n+8)}{48}$	coronene
$D_{6h}(v_2, e)$	$Iq(D_{6h}(v_2)) = \frac{(n+2)(n+6)}{48}$	hexabenzocoronene

when  $N_{1c} \equiv 0 \pmod{6}$  and  $N_c \equiv 0 \pmod{6}$ .<sup>8</sup> This constitutes about one-ninth of all possible benzenoid formulas and considerably less than 10% of all cases. For example, the total resonant sextets of benzene and hexabenzocoronene are the only two benzenoids of 3.5 million with 13 or less rings that belong to the  $D_{6h}(v_2)$  symmetry subgroup.

Inputting the figure-counting series into the appropriate cycle index found in Table IV, one can obtain the configuration-counting series which will give both radical and nonradical quinones of a specified benzenoid skeleton. Since only nonradical benzenoid quinones can stably exist, the enumeration of this subset is of practical importance. For benzenoid skeletons with no element of symmetry (besides its molecular  $\sigma$  plane), the number of possible nonradical quinone isomers ( $Iq$ ) is given by

$$Iq(C_s) = \frac{1}{2} \left[ \frac{n!}{2(n-2)!} + \frac{(n/2)!}{[(n-2)/2]!} \right] = (n/2)^2$$

where  $n = N_H$  is the number of replaceable hydrogens in the corresponding precursor PAH6. For example, benz[a]-anthracene and benzo[a]pyrene in Figure 1 have 66 radical and nonradical quinone isomers (given by the binomial equation) but only 36 nonradical quinone isomers, in agreement with the above equation. In Figure 1 benzo[a]pyrene has a nonstandard numbering to emphasize its parallel relationship to benz[a]anthracene in their one-to-one quinone isomer correspondence. Parenthetically, one should note that the above nonradical quinone isomer counting equation has a form that corresponds to the configuration-counting series for benzenoids of the  $C_{2h}$  symmetry group. Nonradical quinones will have one oxo on a nonstarred carbon and the other on a starred carbon.

Table V presents equations for counting the number of benzenoid monoquinone isomers of various symmetry groups. These equations overestimate the number isomers for benzenoid molecules having essential single and double bonds, as perylene and zethrene derivatives. These equations are exact for all other benzenoids of even carbons. A number of trends are evident in Table V. Because of the bipartite characteristics and the exclusion of diradical quinones, the  $C_s$  benzenoid quinone group has an isomer-counting equation (Table V) with a form corresponding to the  $C_{2h}$  symmetry group (Table IV), and the  $C_{2h}$  quinone group has an isomer-counting equation with a form corresponding to the  $D_{2h}$  symmetry group. In going from  $C_s$  to  $C_{2v}(v_3)$  to  $C_{3h}$ , the isomer-counting equations go from  $n^2/4$  to  $n^2/8$  to  $n^2/12$ , respectively, i.e., the denominator is first doubled and then tripled. In going from  $C_{2h}$  to  $D_{2h}(v_2)$  and  $D_{2h}(v_3)$ , the denominators of the isomer-counting

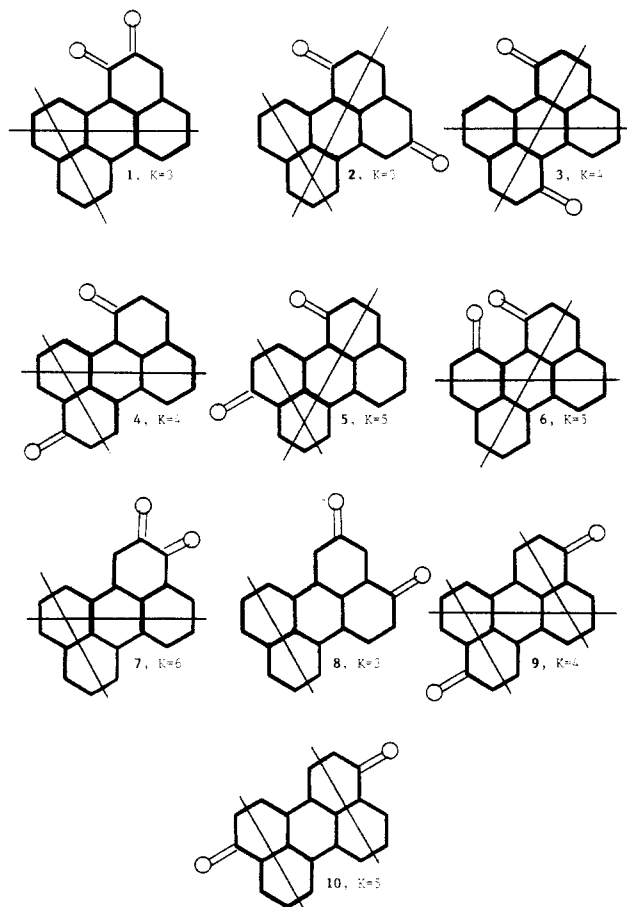
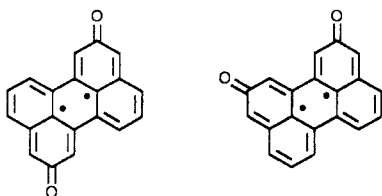


Figure 2. All the monoquinone isomers of perylene.

equations double and the numerators increase by two successively for the first term and then for the second. In going from  $C_{3h}$  to  $C_{6h}$  and  $D_{3h}$ , the denominators double in the isomer-counting equations and a term in the numerator increases by two and six, respectively. Finally, in going from  $C_{6h}$  to  $D_{6h}(v_2)$  and  $D_{6h}(v_3)$ , the denominators double in the isomer-counting equation and the numerators increase by six successively for the first term and then for the second. All these progressive changes agree with our intuition. Table V gives isomer-counting equations for only monoquinones. Similar expressions for diquinones, triquinones, etc. have not been derived.

The equations in Table V give only upper bounds for the number of monoquinone isomers for perylene and zethrene derivatives. Perylene has  $D_{2h}(v_3)$  symmetry with  $n = N_H = 12$ , and using the equation given in Table V, one should expect that it would have 12 quinone isomers. However, perylene only has 10 quinone isomers (Figure 2) because its essential single bonds bridging two naphthalene units leads to additional diradicals such as



which were counted by this equation. Similarly, benzo[*a*]perylene of  $C_s$  symmetry and  $n = N_H = 14$  is predicted to have 49 quinone isomers by the relevant equations in Table but has only 43 isomers, and naphtho[2,3-*a*]perylene, naphtho[1,2-*a*]perylene, and naphtho[2,1-*a*]perylene all have 56 quinone isomers rather than 64. Zethrene ( $C_{2h}$ ,  $n = N_H = 14$ ) has 23

quinone isomers rather than 28, and phenanthro[1,10,9,8-*opqra*]perylene ( $D_{2h}$ ,  $n = N_H = 14$ ) has 14 quinone isomers instead of 16.

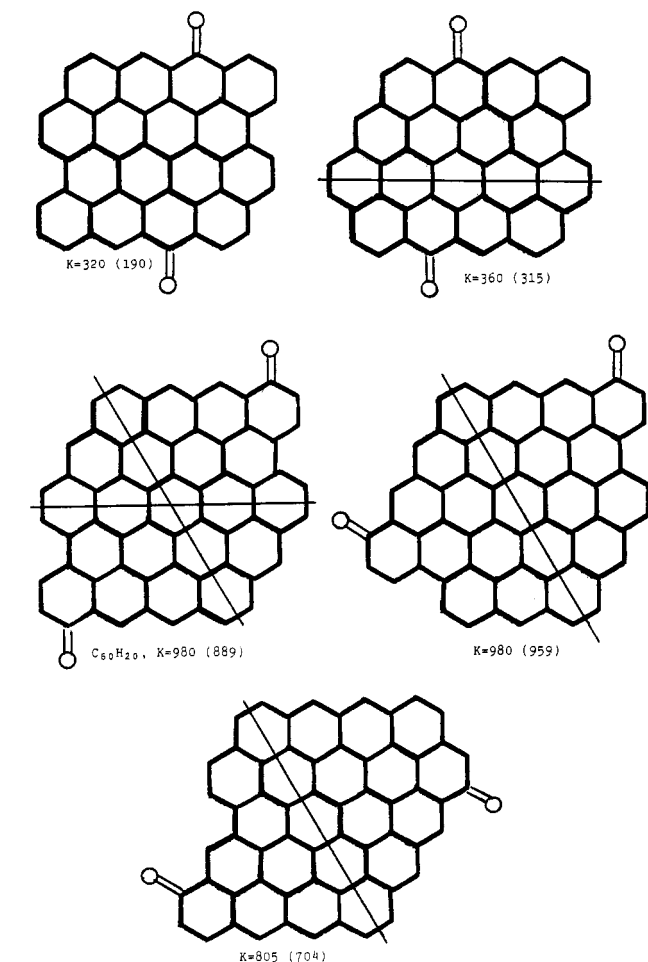
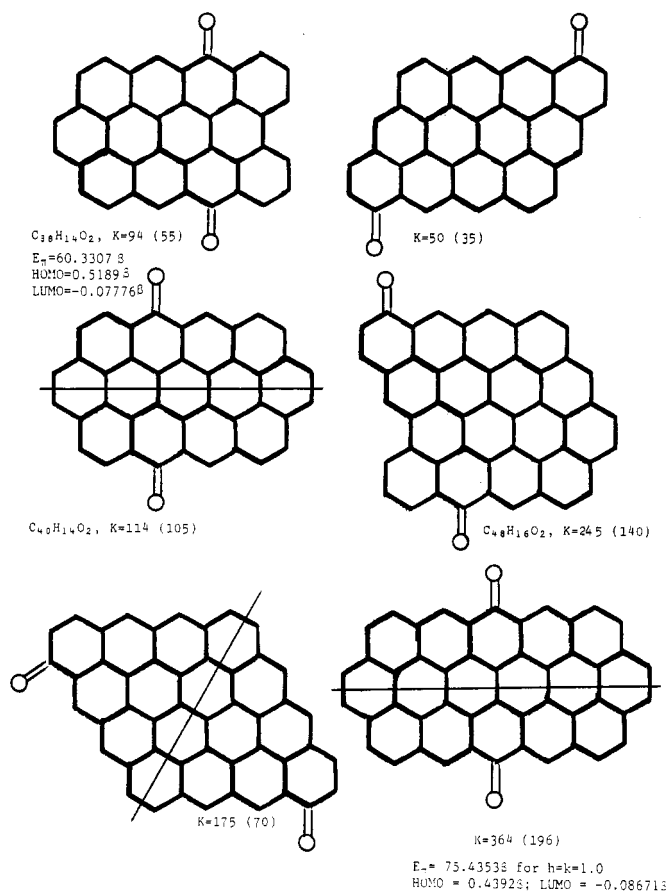
While the equations in Table V give the number of non-radical benzenoid monoquinones possible, one should expect the synthesis and isolation of less stable ones to be unlikely. Of the 36 possible monoquinones of benzo[*a*]anthracene, 2 have  $K = 6$ , 3 have  $K = 5$ , 4 have  $K = 4$ , 7 have  $K = 3$ , 7 have  $K = 2$ , and 13 have  $K = 1$ . Similarly, of the 36 benzo[*a*]pyrene monoquinones, 1 has a  $K = 8$ , 1 has  $K = 7$ , 7 have  $K = 6$ , 3 have  $K = 5$ , 3 have  $K = 4$ , 11 have  $K = 3$ , 3 have  $K = 2$ , and 7 have  $K = 1$ . Of the five benzo[*a*]anthracene monoquinone isomers found in the literature,<sup>9</sup> none have  $K < 4$ , and of the nine benzo[*a*]pyrene monoquinone isomers found in the literature,<sup>10</sup> none have  $K < 5$ . The very few monoquinones found in the literature with  $K = 1$ , as 1,5- and 2,6-naphthoquinones, are reported to be unstable.<sup>11</sup> SCF molecular orbital calculations suggest that all quinodimethanes which can exist only as a single classical structure are antiaromatic.<sup>12</sup>

#### RELATIVE STABILITY AND ELECTRONIC PROPERTIES OF BENZENOID MONOQUINONES

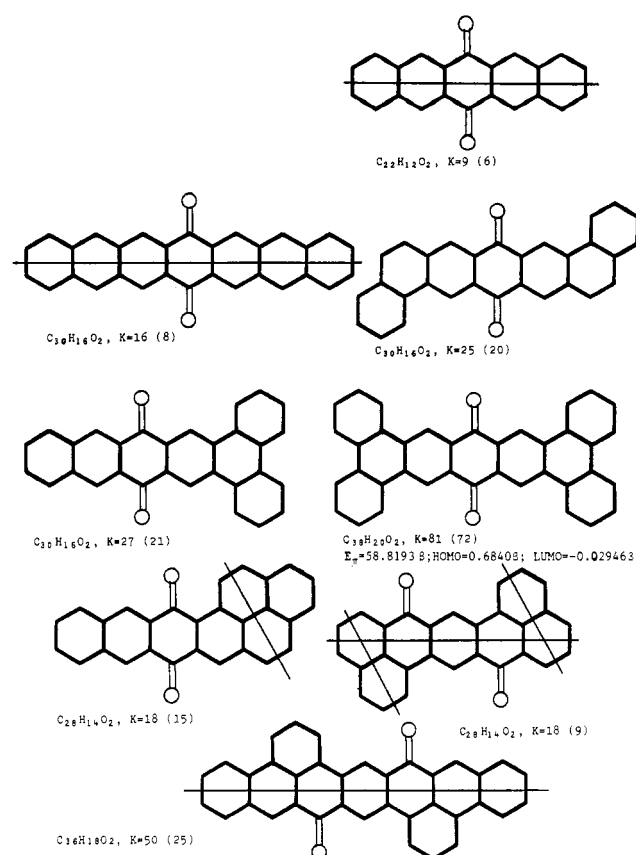
Frequently, there is an increase in the number of Kekulé structures ( $K$ ) in going from a benzenoid hydrocarbon to its corresponding quinone derivative. The number of Kekulé structures ( $K$ ) for acenes increases in going to its most symmetrical *p*-quinone derivative. For example, naphthacene (tetracene) has  $K = 5$  and its 5,12-quinone has  $K = 6$ . Other examples of the increase in  $K$  values in going from a precursor benzenoid hydrocarbon to its quinone derivative are given in Figures 3 and 4. From the Randić/Wheland equation<sup>13</sup> of  $K(G) = K(G - e) + K(G - (e))$ , one must conclude that no *o*-quinone (equivalent to  $G - (e)$ ) will ever have a larger  $K$  value than its precursor benzenoid hydrocarbon since  $K(G - (e)) < K(G)$ . If a benzenoid hydrocarbon has a quinone derivative of a larger  $K$  value, then it is likely that it will have a tendency toward air oxidation to it, and this process is probably operating in the environmental assimilation of benzenoid-laden aerosols. Triangulene diradical ( $C_{22}H_{12}$ ,  $K = 0$ ) is unknown, whereas its 4,12-quinone ( $K = 8$ ) has been synthesized.<sup>14</sup> Pyrolytic processes may well generate quinone derivatives of diradical benzenoid hydrocarbons since they may occur as reactive intermediates in the overall mechanism of carbonization.<sup>15</sup>

In general, among the set of benzenoid nonradical monoquinone isomers of a specific nonbranched or minimally branched catacondensed skeleton, there will be at least one monoquinone structure that has  $K = 1$  such as triphenylene-1,6-dione and dibenzo[*g,p*]chrysene-2,12-dione. Strictly pericondensed benzenoids having an excised internal structure with  $K = 1$  and no more than two methylene groups will have a monoquinone isomer with  $K = 1$ . This is a necessary and sufficient condition. Pyrene has the excised internal structure of ethene ( $K = 1$ ), and pyrene-2,7-dione has  $K = 1$ . Similarly, benzo[*ghi*]perylene has the excised internal structure of *s-cis*-1,3-butadiene ( $K = 1$ ), and benzo[*ghi*]perylene-6,9-dione has  $K = 1$ . Figure 5 gives further examples of this generalization. For quinodimethane-like excised internal structures having  $K = 1$ , the dimethane groups point at the peripheral positions which when functionalized with oxo groups generate the benzenoid monoquinone isomer with the  $K = 1$ . Needless to say, the monoquinones with  $K = 1$  are expected to be unstable, and their rapid recognition is only useful for eliminating them from further consideration. If the excised internal structure has  $K > 1$ , then the corresponding benzenoid has only monoquinone isomers with  $K > 1$ .

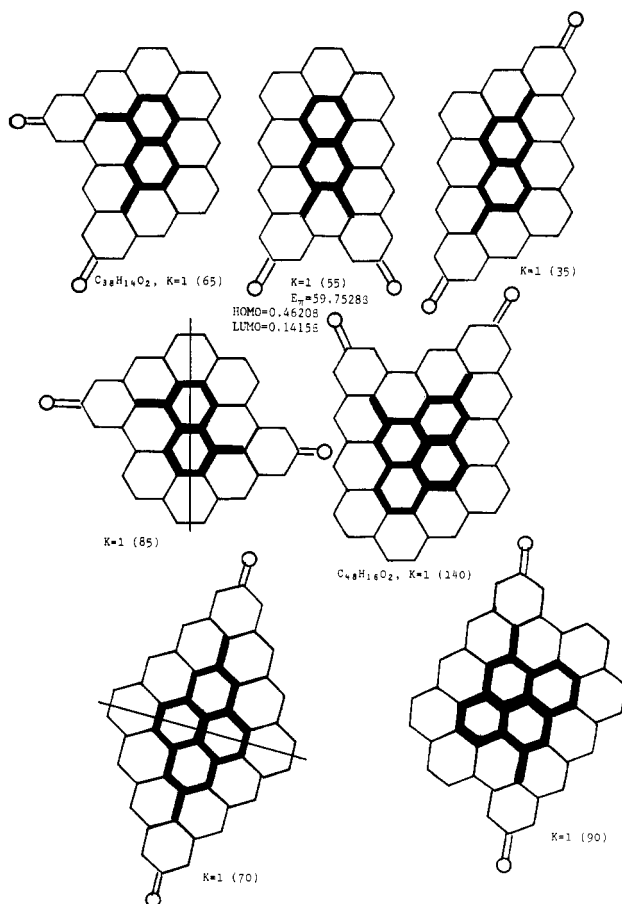
For benzenoid hydrocarbons having quinodimethane-like excised internal structures, the monoquinones of lowest possible



**Figure 3.** Monoquinones whose  $K$  values increase compared to their benzenoid precursors.



**Figure 4.** Benzenoid monoquinones known not to form vat dyes.



**Figure 5.** Monoquinones that have only one Kekulé structure ( $K = 1$ ).

Kekulé structure counts is usually formed by placing the oxo groups on the peripheral benzenoid positions that are pointed

at by (or coaxial with) the dimethane groups of the excised internal structure. Consider the  $C_{60}H_{20}$  benzenoids ( $K = 1001$  and 889) in Figure 6. Both form monoquinones, as prescribed above, with  $K = 6$ . Alternatively, replacing the noncentral hydrogens of two trio groups by oxo groups in both these  $C_{60}H_{20}$  benzenoids gives monoquinones with  $K = 980$  (Figure 3); note that only one isomer of the three possible monoquinones with  $K = 980$  is shown. Needless to say, there should be a strong preference for formation of the latter monoquinones.

An algorithm for finding the benzenoid monoquinone of smallest  $K$  value involves the following strategy. Place the oxo groups on the benzenoid hydrocarbon perimeter in such a way as to generate as many essential double bonds as possible. If possible, perform this operation while preserving the essential double bonds present in the associated excised internal structure. One oxo group must be placed on a starred position, while the other is placed on a nonstarred position, and substitutions on solo position are to be avoided, if possible. Typical examples would involve placing an oxo group on a leading duo or central trio ring perimeter position that is followed by a succession of solo positions. Figure 7 gives a number of examples that were obtained by this algorithm.

To obtain the benzenoid monoquinone of largest  $K$  value, place the oxo groups on positions that produced as few essential double bonds as possible. One oxo group must be placed on a starred position and the other on a nonstarred position. Solo positions and noncentral trio positions should be investigated first. Figure 8 presents a number of examples that were derived via this method. On this basis, of the 73 strictly pericondensed benzenoids previously enumerated,<sup>2,8</sup> it is suggested that compounds 1, 2, 7, 10, 12, 14, 17, 21, 25, 27, 28, 33, 35, 38, 42, 43, 45, 46, 59, 65, 67, 68–70, and 73 will resist quinone formation and will likely be enduring pyrolytic products. Analogously, of these 73 strictly pericondensed benzenoid hydrocarbons, it is predicted that compounds 5, 6, 13, 20, 32, 36, 41, 49, 50, and 64 will rapidly form the monoquinones shown in Figure 3 during or shortly after combustion/pyrolytic formation. It is speculated that the monoquinones in Figure 8 will likely form vat dyes.

Many benzenoid quinones are vat dyes. Insoluble benzenoid quinones are converted into soluble form by reduction (vatting) into their base reactive hydroxy analogues. Cotton fibers absorb this soluble reduced dye. Air or sodium perborate oxidation of the fiber-absorbed dye converts it back into insoluble form which acquires maximum fastness after treatment in a hot detergent bath. Figure 9 presents the structures for well-known vat dyes, and Figure 4 presents the structures of monoquinones that do not form vats.<sup>1,9</sup> The number of Kekulé structures ( $K$ ) for the monoquinones in Figure 9 and 4 are given (the number in parentheses gives the  $K$  values of the corresponding benzenoid hydrocarbon). Of 58 monoquinones reviewed, it appears that if the  $K$  value of the quinone was lower than the  $K$  value of its corresponding hydrocarbon, then it formed a vat; if the  $K$  values for the quinone was larger than for its corresponding hydrocarbon, then it may or may not form a vat.

One criterion for aromatic character is the enhanced magnetic susceptibility ( $\chi_m$ ) shown by benzenoid compounds.<sup>16</sup> Most benzenoid quinones that form vats have lower magnetic susceptibilities than their corresponding hydrocarbons. Dibenz[fg,op]anthanthrene-7,1-dione forms a vat only with difficulty by the addition of sodium dithionite reinforced by Zn dust. Dibenz[fg,op]anthanthrene-7,14-dione shows a greater magnetic susceptibility than its corresponding arene and is the parent quinone system of hypericin, which is a promising HIV AIDS inhibitor.<sup>17</sup>

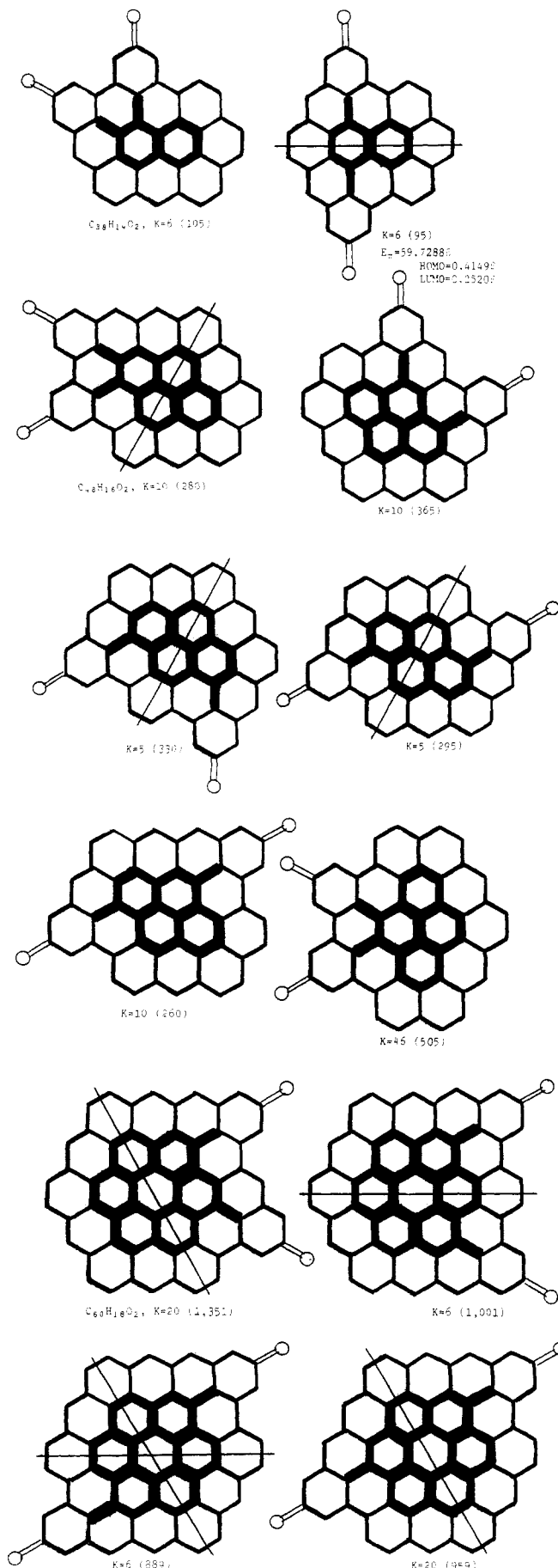
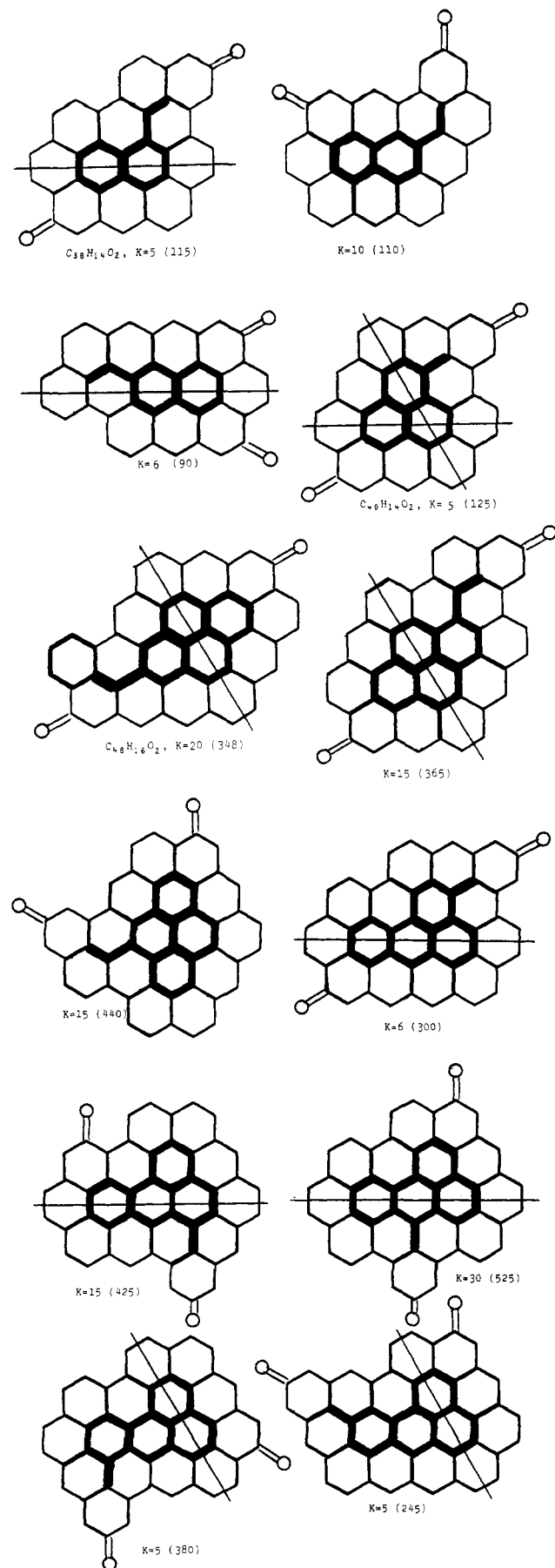
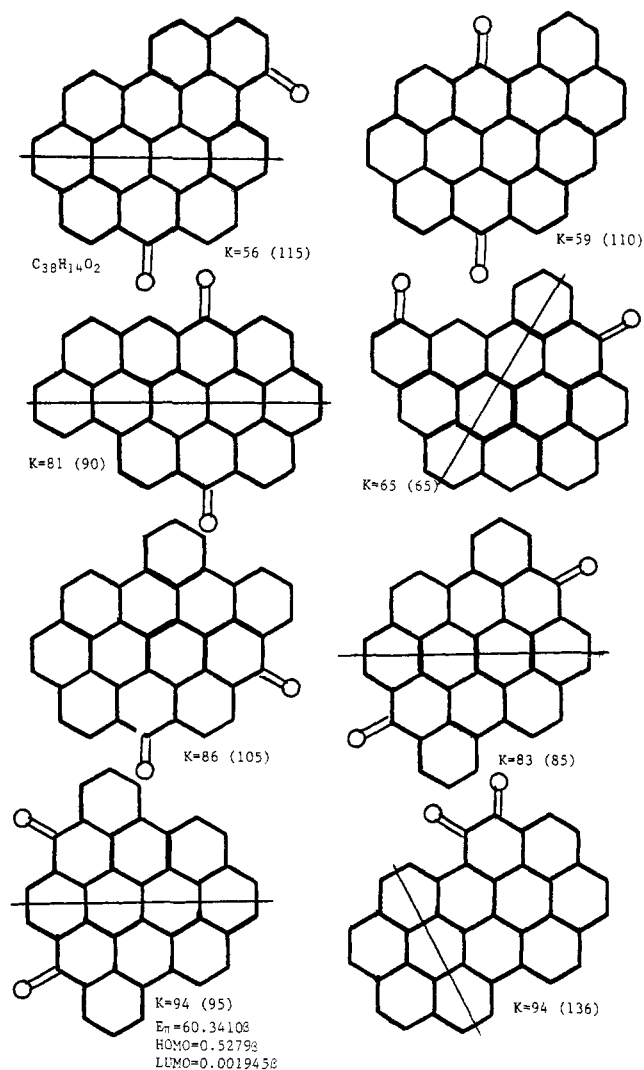


Figure 6. Monoquinones having minimum  $K$  values and quinodimethane-like excised internal structures.

Figure 7. Benzenoid monoquinones with minimum  $K$  values.

Whenever a benzenoid structure can have a succession of edges (bonds) bisected with a straight line drawn from one side of the molecule to the other with the terminal rings being

Figure 8. Benzenoid monoquinones with maximum  $K$  values.

symmetrically convex relative to the line, then those rings intersected by the line can be embedded by a perpendicular succession of ethene substructures, and the benzenoid structure as a whole will have at least one eigenvalue pair of  $\pm 1$ .<sup>2,18</sup> This straight line is called a selective lineation. All monoquinones in this paper scored with straight lines have no eigenvalue pair of  $\pm 1$  for each line. In the absence of overlapping bands, the photoelectron (PE) spectra of these monoquinones are expected to have relatively sharp ionization peaks at approximately 8.8 eV.<sup>19</sup> Several selective lineations or degeneracy should lead to relatively more intense sharp ionization peaks at about 8.8 eV.<sup>20</sup>

A few representative HMO results are presented below the corresponding monoquinone structures given in Figures 3–6, 8, and 9. The tail coefficient ( $a_N$ ) in the characteristic polynomials of monoquinones is given by  $|a_N(G_{xx})| = K^2(G) - hK^2(B)$ , where  $G_{xx}$  is the monoquinone group,  $G$  is its isoconjugate,  $B$  is the corresponding precursor benzenoid, and  $h$  is the weight of vertex  $x$ . For the results given  $h = k = 1$ . Thus, for  $K(G) > K(B)$  LUMO has a negative value, for  $K(G) < K(B)$  LUMO has a positive value, and for  $K(G) = K(B)$  LUMO is 0. For  $K(G) < K(B)$ , one should expect that  $n \rightarrow \pi^*$  electronic transitions to be more favorable, leading to greater color intensity, another attribute of known vat dyes (Figure 9).

#### MONOQUINONE SYNTHESSES

The major syntheses of quinones include controlled oxidation or Friedel–Crafts condensation with maleic, phthalic, or

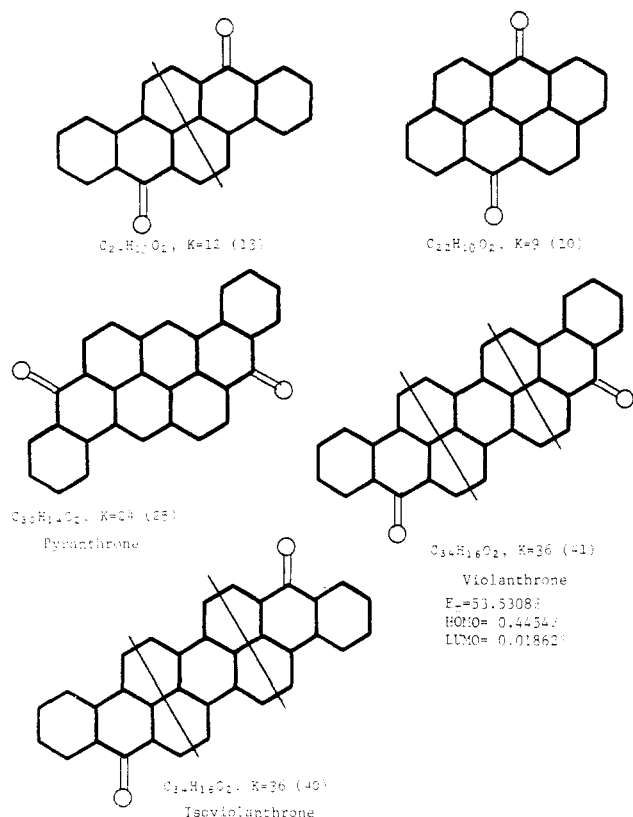


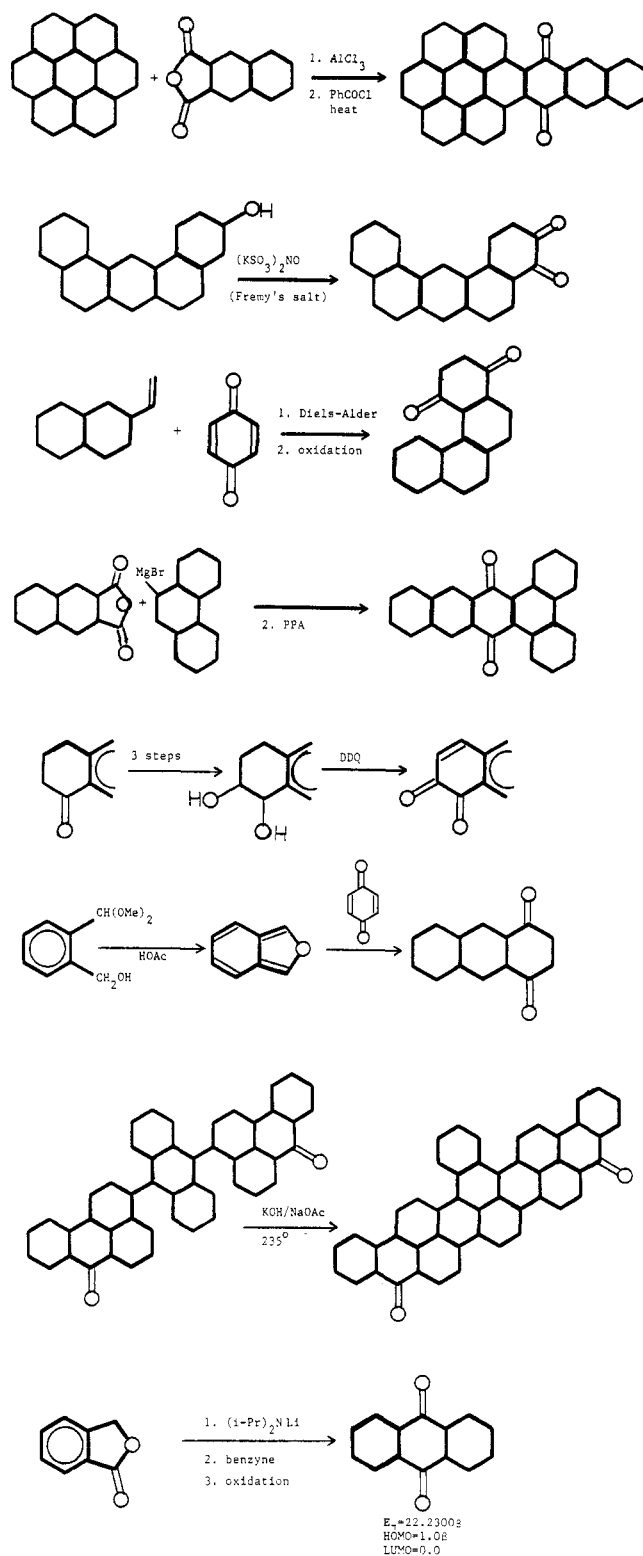
Figure 9. Benzenoid monoquinones known to form vat dyes.

naphthalene-2,3-dicarboxylic anhydride of an appropriate benzenoid hydrocarbons.<sup>21</sup> Oxidation of appropriate hydroxy-substituted benzenoids results in the production of quinone isomers whose oxo group positions are determined by the location of the initial hydroxy substituent that becomes oxidized to one of the oxo groups.<sup>22</sup> Vinyl benzenoids undergo Diels-Alder reaction with naphthoquinone followed by dehydrogenation with quinone (benzoquinone) to give select benzenoid quinones.<sup>23</sup> Reaction of aryl bromide Grignards with phthalic or naphthalene-2,3-dicarboxylic anhydrides followed by polyphosphoric acid catalyzed condensation leads to control of the substitution positions by virtue of the initial location of the bromo group.<sup>24</sup> Direct oxidation of benzenoids leads to monoquinones that should be common to samples of environmental/pyrolytic origin. In general, this latter synthesis will lead to the more stable monoquinone isomers which will usually have their nonadjacent oxo groups located on solo ( $n_1$ ) or noncentral trio ( $n_3$ ) peripheral benzenoid positions.<sup>25</sup> Non  $K$  region  $o$ -quinones of benzenoid hydrocarbons are prepared in four steps from cyclic ketones via dehydrogenation of tetrahydriols with 2,3-dichloro-5,6-dicyano-1,4-benzoquinones.<sup>10</sup> Diels-Alder condensation/oxidation reaction of in situ generated isobenzofuran with 1,4-monoquinones leads to two-ring augmented successor quinone products.<sup>26</sup> Condensation of bis(arylphenone) derivatives in either molten KOH or  $\text{AlCl}_3$  or photolysis leads to quinone products.<sup>27</sup> Addition of lithium phthalide to the benzyne generated in situ by reaction of the appropriate bromaryl with lithium diisopropylamide has been used to produce quinones.<sup>28</sup> Scheme I gives specific examples of these quinone syntheses.

#### SUMMARY

In addition to a timely review of benzenoid quinones, their topological properties have been deciphered. This class of compounds is of considerable importance to environmental and industrial economies. Herein, while presenting a novel perspective of quinones, we emphasize aspects not covered by Patai and Rappoport.<sup>29</sup> In general, the number of possible

#### Scheme I. Representative Monoquinone Syntheses



monoquinone isomers ( $I_q$ ) of benzenoids with no axis of symmetry is estimated by  $n^2/4$  and with a twofold axis of symmetry by  $\geq n^2/8$ . These two equations cover about two-thirds of all possible cases.

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## Benzenoid Series Having a Constant Number of Isomers

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By use of the formula periodic table for benzenoids and the excised internal structure concept several new strictly pericondensed benzenoid series possessing an identical number of isomers have been identified. These constant-isomer series are conjectured to be probable carbonization/pyrolytic benzenoid species.

### INTRODUCTION

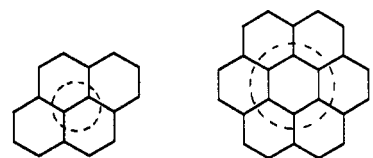
The number and identity of benzenoid (PAH6) isomers are important problems in both environmental analysis and documentation/retrieval of chemical literature of this class of compounds.<sup>1</sup> The knowledge of the absence and presence of benzenoid isomers in the environment should present novel insights and will allow one to speculate why. The recent availability of extended tables<sup>2,3</sup> on the number of benzenoid isomers makes it now possible for us to clarify and extend our previous work on enumeration of select benzenoid families of potential importance to pyrolytic processes.<sup>4,5</sup>

### RESULTS AND DISCUSSION

**Terminology.** The formula periodic table for even-carbon benzenoids is given in Table PAH6 and for odd-carbon benzenoids in Table PAH6(odd). Throughout this paper the carbon and hydrogen atoms and the  $p\pi$  and C-H bonds will be omitted, leaving only the C-C  $\sigma$ -bond skeleton to represent the benzenoid structure. Methine substructural units will be shown as secondary graph vertices. All the remarks and generalizations presented herein are restricted to systems that are exclusively polyhexagonal and essentially planar.

The number of carbon atom vertices will be denoted  $N_c$ , the number of internal carbon vertices bounded by three hexagonal rings  $N_{ic}$ , and the net number of disconnections (positive values) and/or rings (negative values) among the internal edges (edges bounded by two rings)  $d_s$ . For example anthracene/phenanthrene has  $d_s = 1$  and  $N_{ic} = 0$  and pyrene has  $d_s = 0$  and  $N_{ic} = 2$ . A strictly pericondensed benzenoid hydrocarbon has all its internal third-degree vertices mutually connected ( $d_s = 0, -1, -2, \dots$ ) and has no catacondensed appendages. An excised internal structure is the set of connected internal vertices usually associated with a strictly pericondensed ben-

zenoid which has a formula found at the extreme left-hand boundary of the formula periodic table for benzenoid polycyclic aromatic hydrocarbons (PAH6s).<sup>4</sup> For example, the excised internal structure of pyrene is ethene and of coronene is benzene, as shown in the structures by the dotted line. Constant-isomer benzenoids have no proximate bay regions and on a per carbon basis have the fewest number of bay regions and among the highest  $p\pi$  electronic energy.<sup>6</sup>



pyrene (ethene)

coronene (benzene)

There are only three conjugated polyene isomers of the formula  $C_4H_6$ : rotamers *s-cis*-1,3-butadiene and *s-trans*-1,3-butadiene and trimethylenemethane diradical (Figure 1). If an 18-carbon-atom perimeter is circumscribed about each of these  $C_4H_6$  isomers with the resulting species being incremented with 6 hydrogens, one obtains the only three  $C_{22}H_{12}$  benzenoid isomers possible for this formula, i.e., benzo[ghi]perylene, anthanthrene, and triangulene.<sup>4</sup> If these three latter strictly pericondensed benzenoids are circumscribed by a 30-carbon-atom perimeter followed by incrementation with 6 hydrogens, one obtains the only three benzenoid isomers possible for  $C_{52}H_{18}$ . Because trimethylenemethane is a diradical, triangulene and its  $C_{52}H_{18}$  successor are also diradicals.<sup>4</sup>

In using excised internal structures for benzenoid enumeration, one must make sure that the perimeter of the excised internal structures has no less than two-carbon gaps.<sup>4</sup> For example, *s-cis*-1,3-butadiene in Figure 1 has a two-carbon-gap