

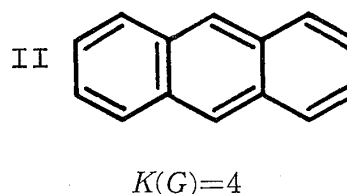
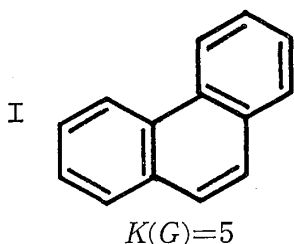
Benzene and Naphthalene Character Diagrams of Polycyclic Aromatic Hydrocarbon Molecules

Maki Shobu and Haruo Hosoya

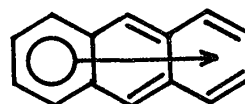
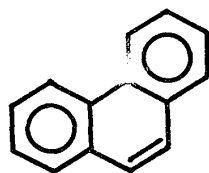
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(Received April 10, 1981)

Introduction

It has long been known that the relative stabilities of polycyclic aromatic hydrocarbons are in parallel with the number of the Kekulé structures, $K(G)$, as exemplified in the case with phenanthrene (I) versus anthracene (II).



According to Clar¹⁾ this ordering can be roughly estimated from the maximum number of the resonant aromatic sextets (a union of six π -electrons as in benzene) of each molecule as



where a circle represents an aromatic sextet and an arrow indicates the movement of the aromatic sextet. Polansky and Derflinger²⁾ gave a molecular orbital (MO) interpretation of the aromatic sextet by defining the benzene character in terms of the π -electronic MO's. A number of independent studies³⁻⁶⁾ have been devoted to get the valence bond (VB) picture of the benzene character in polycyclic aromatic hydrocarbons.

By using both the MO and VB theories the present authors⁷⁾ have extensively analyzed the topological dependencies of the benzene character. Graph-theoretical interpretation of the Clar's aromatic sextet has also been obtained.⁸⁾ In the course of this study it was found that the three highest occupied π -orbitals, if combined together, have a dominant contribution to the benzene character and further the partial electron density distribution made up with

these three highest occupied π -orbitals clearly depicts the local structures of the π -electron distribution and verifies the Clar's idea for representing the ground state of the polycyclic aromatic hydrocarbons. By using the π -MO's the naphthalene character can also be defined, which in turn is shown to have a good correlation with the partial electron density distribution made up with the five highest occupied π -MO's.⁹⁾

In this paper a collection of the contour diagrams showing the partial electron density distributions of three and five highest π -MO's are given for typical polycyclic aromatic hydrocarbons. Benzene and naphthalene characters are also given together with the Clar's aromatic sextet representations. Detailed descriptions will be given elsewhere.⁹⁾

Method of Calculation

Let the total π -electron density $\rho(\mathbf{r})$ at a given point \mathbf{r} be expressed as the sum of the orbital contributions $\rho_n(\mathbf{r})$ with an occupation number g_n for molecular orbital n :

$$\rho(\mathbf{r}) = \sum_n g_n \rho_n(\mathbf{r}),$$

$$\rho_n(\mathbf{r}) = \left\{ \sum_s C_{ns} \chi_s(\mathbf{r}_s) \right\}^2$$

$$\chi_s(\mathbf{r}_s) = (\mu^5/\pi)^{1/2} \mathbf{r}_s \exp(-\mu \mathbf{r}_s) \cos \theta_s$$

where $\chi_s(\mathbf{r}_s)$ is the value of the atomic orbital wavefunction at \mathbf{r} , to which the position vector \mathbf{r}_s is directed from atom s , and μ is the orbital exponent of the carbon $2p\pi$ atomic orbital, 1.5679.¹⁰⁾ The partial electron density is defined as

$$\rho_a^b(\mathbf{r}) = \sum_{n=a}^b g_n \rho_n(\mathbf{r}).$$

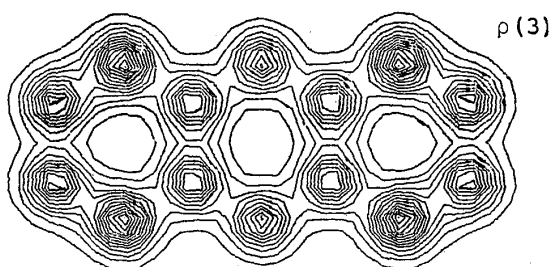
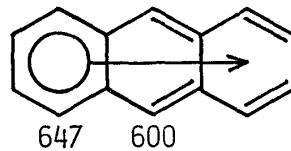
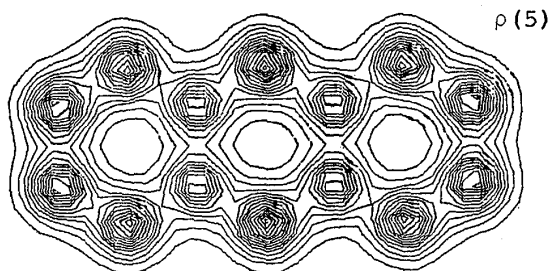
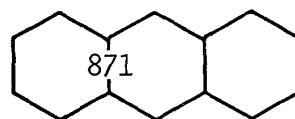
For the section plane parallel to the molecular plane with one atomic unit (Bohr radius) above (or below), two different contour maps of $\rho_a^b(\mathbf{r})$ are given in the following Figures with $b=\text{HOMO}$ and $a=\text{HOMO}-2$ and with $b=\text{HOMO}$ and $a=\text{HOMO}-4$, respectively designated simply as $\rho(3)$ and $\rho(5)$, where the spacings between two contour lines are, respectively, chosen as 0.0002 and 0.0005 e/a_0^3 , where a_0 is the atomic unit and e is the unit charge. The LCAO MO coefficients C_{ns} 's were obtained from the variable- β variant of the PPP method.¹¹⁾

The normalized benzene character is defined⁷⁾ as

$$\bar{r}_L = \frac{1}{3} (2 \sum^L p_{\text{ortho}} - \sum^L p_{\text{para}}) - 2,$$

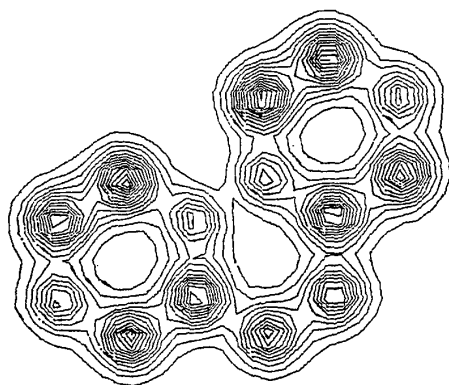
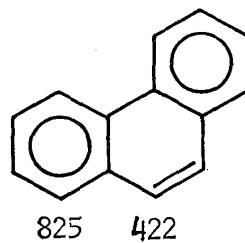
where p_{ortho} and p_{para} indicate the π -electronic bond orders for the pairs of atomic orbitals with ortho and para positions, respectively. The wavefunctions are the same as used in the contour maps. The naphthalene character is defined in terms of the bond orders of the nine different types of atom pairs.⁹⁾ The values given in the Figures are those multiplied by 1000. The Clar's representations are drawn for each compound from the results of the partial electron density distribution and benzene characters.

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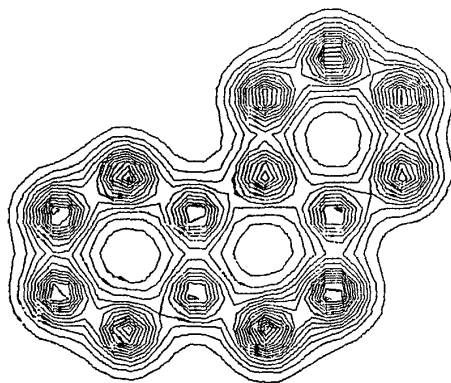
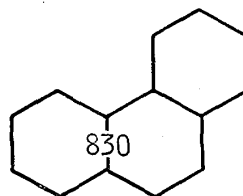
 $\rho(3)$ Benzene Character \bar{r}_L  $\rho(5)$ 

Naphthalene Character

PHENANTHRENE

 $\rho(3)$ 

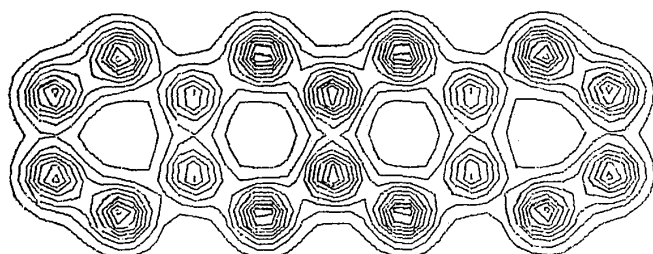
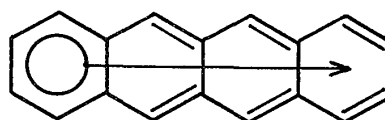
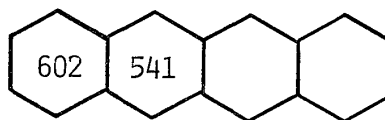
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 $\rho(5)$ 

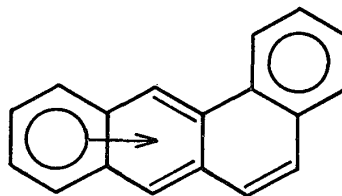
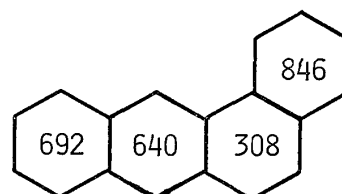
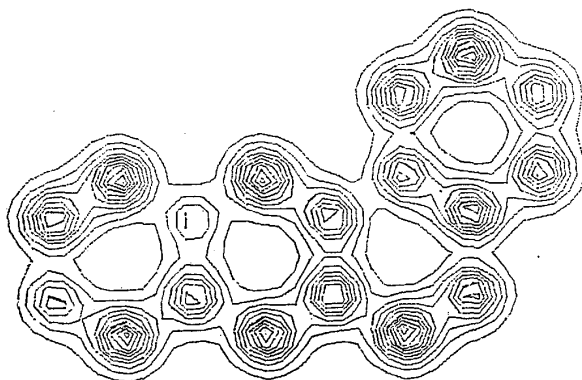
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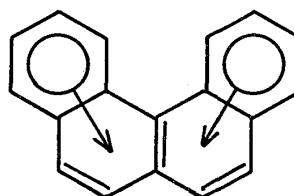
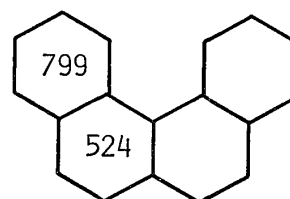
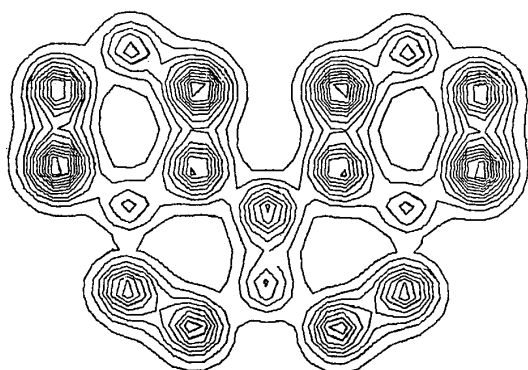
TETRACENE

Benzene Character \bar{r}_L 

BENZANTHRACENE

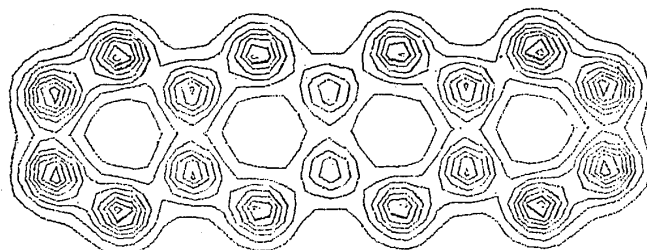


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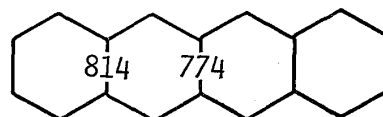


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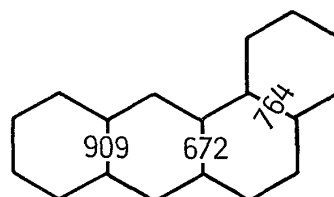
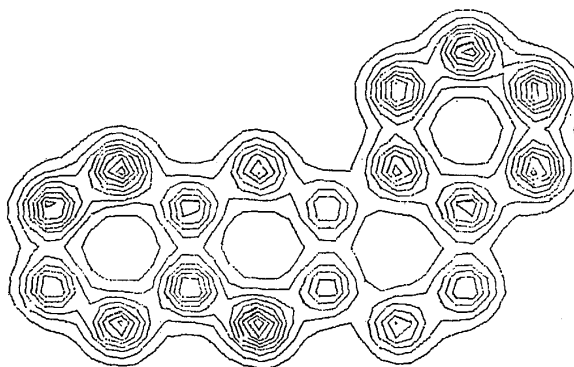
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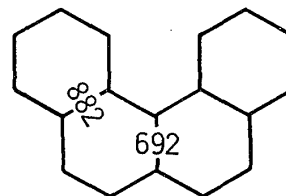
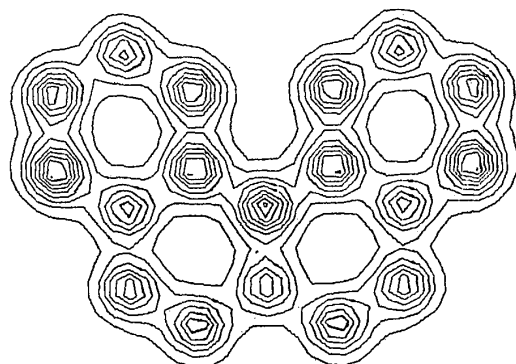
Naphthalene Character



BENZANTHRACENE

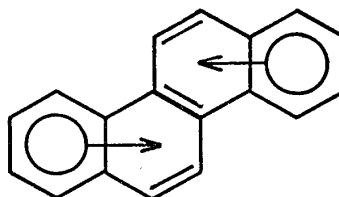
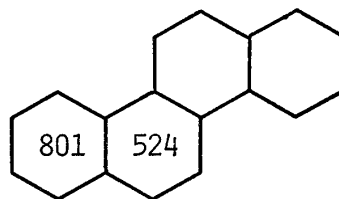
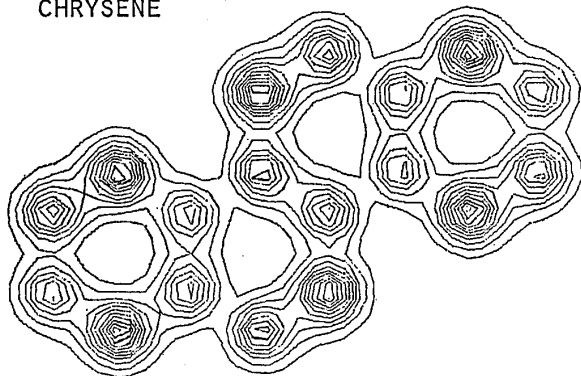


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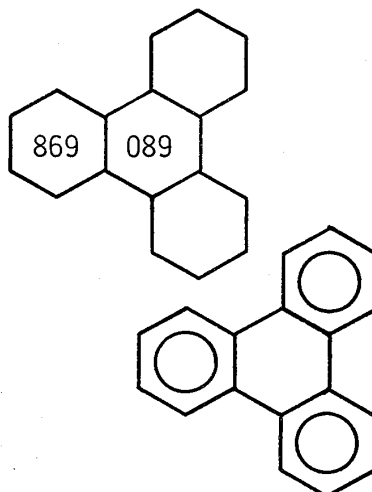
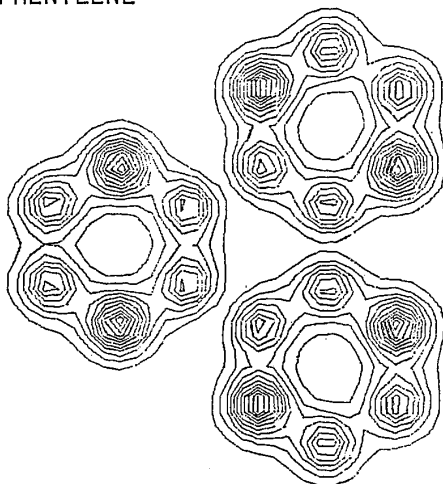


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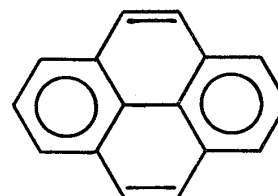
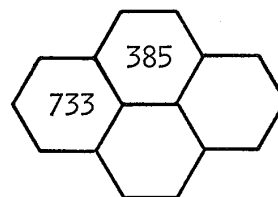
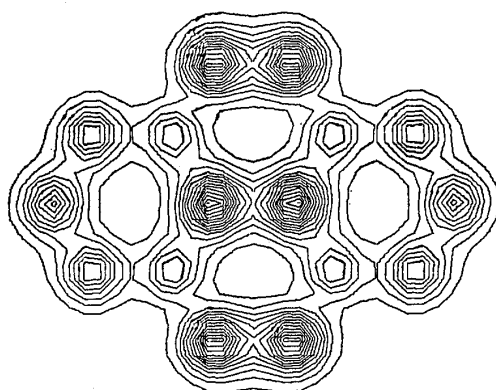
CHRYSENE



TRIPHENYLENE

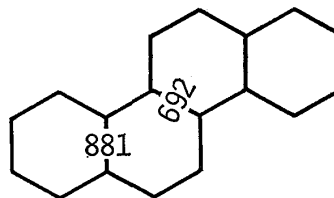
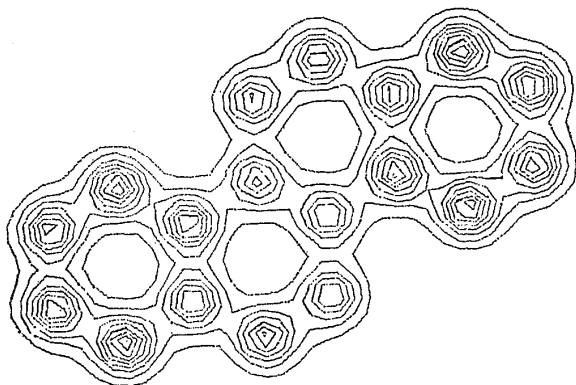


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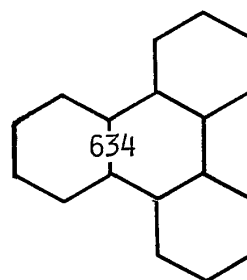
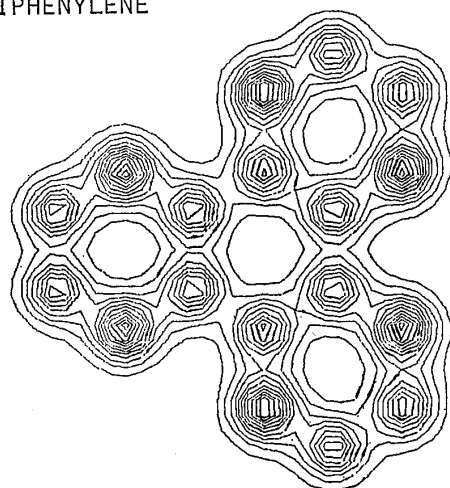


$\rho(5)$

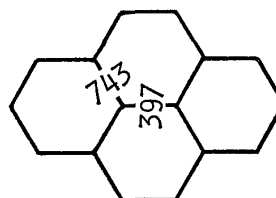
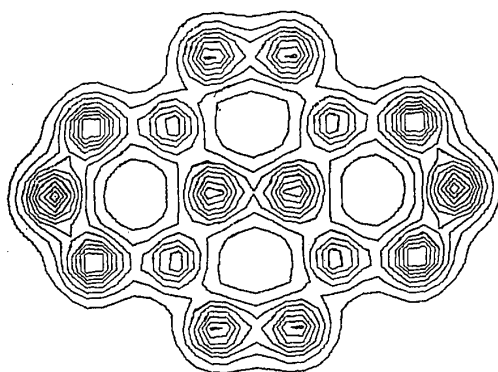
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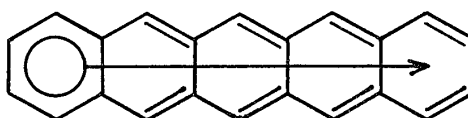
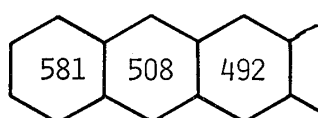
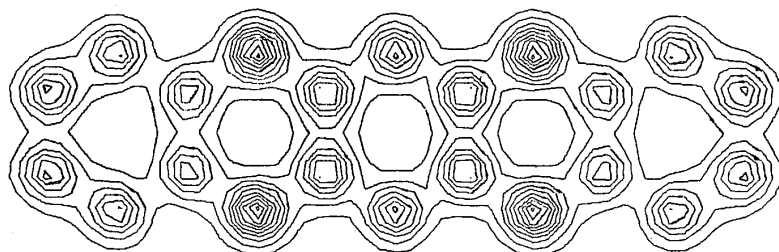
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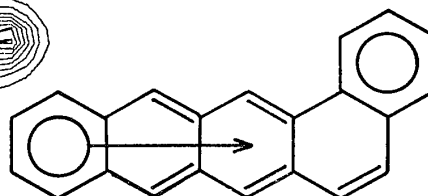
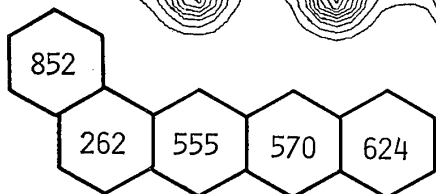
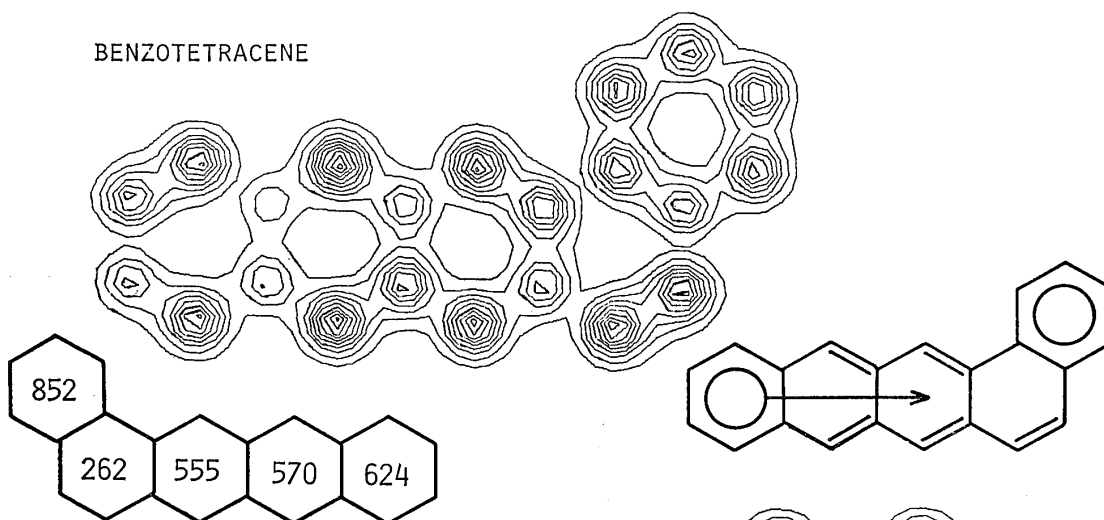
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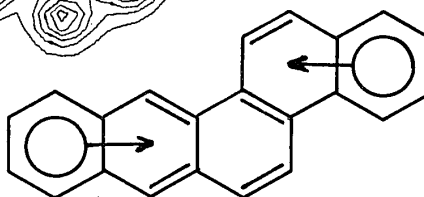
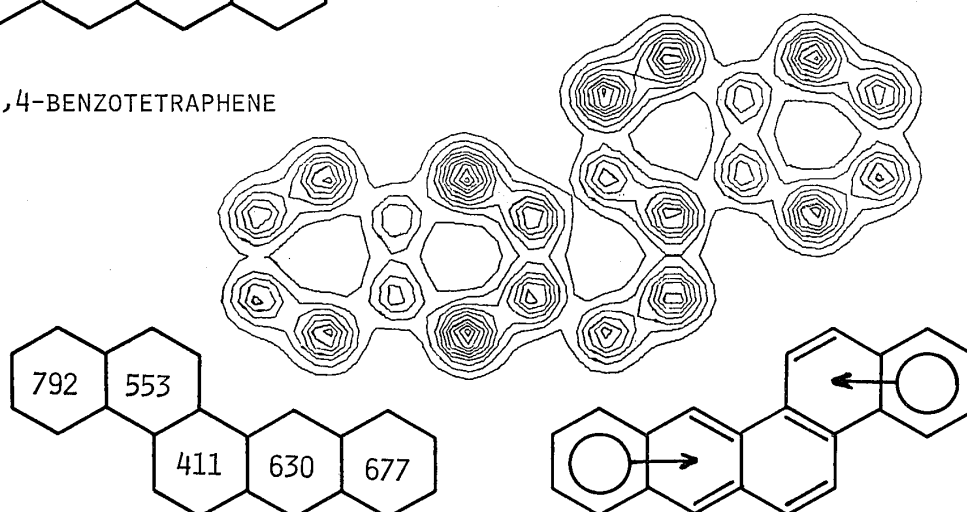
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 $\rho(3)$ 

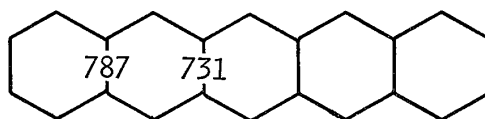
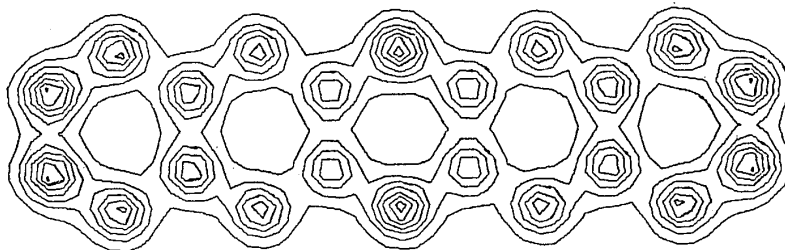
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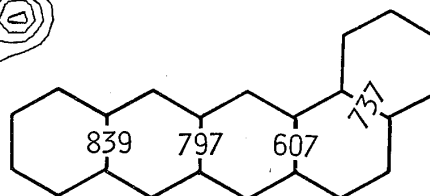
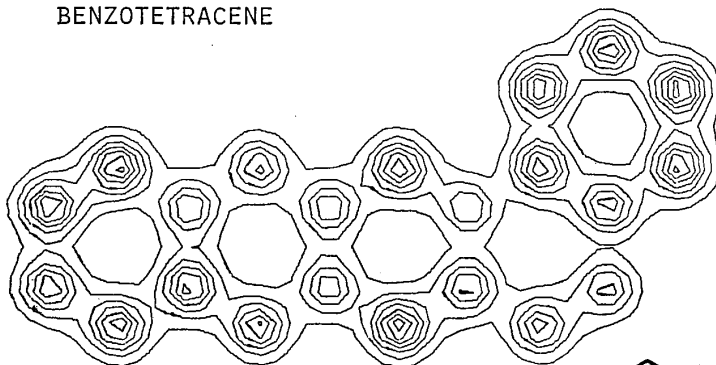
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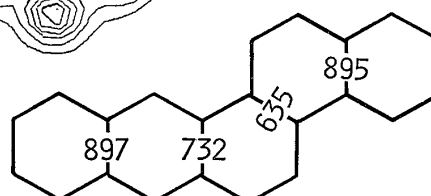
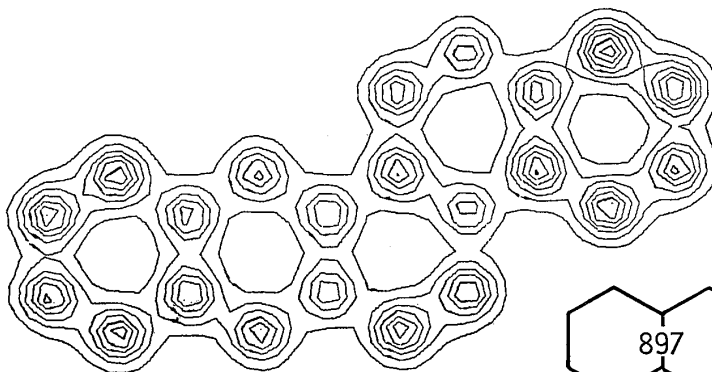
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 $\rho(5)$ 

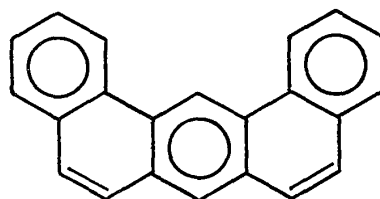
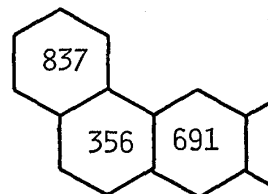
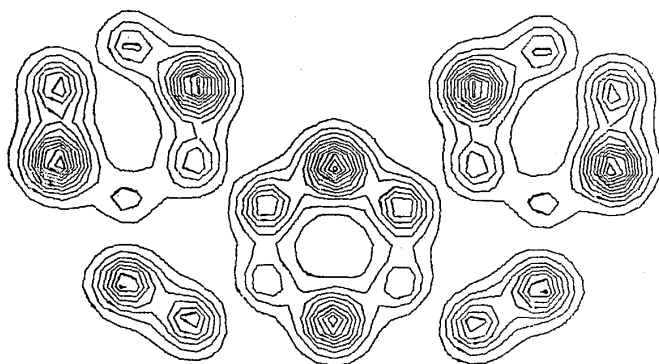
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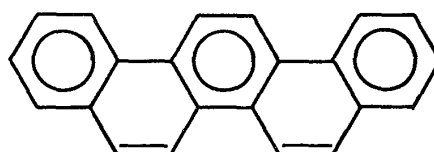
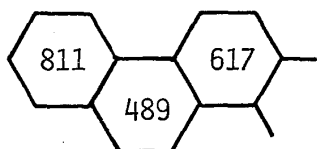
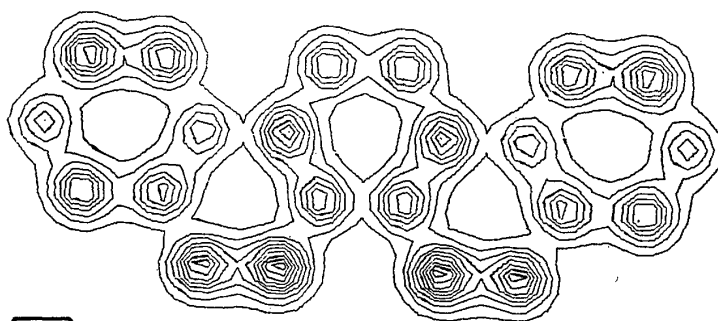
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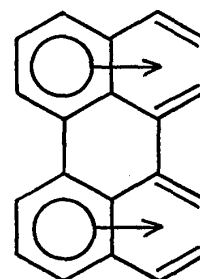
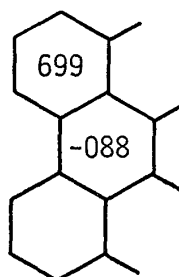
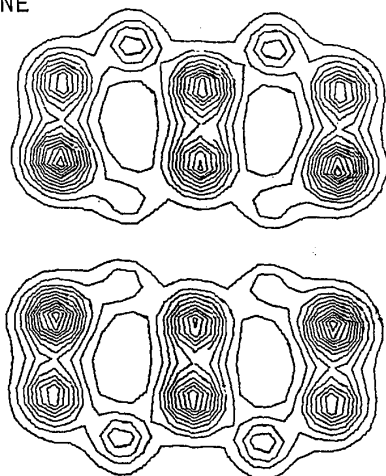
1,2,7,8-DIBENZANTHRACENE

 $\rho(3)$ 

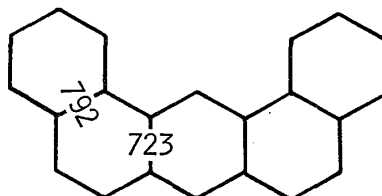
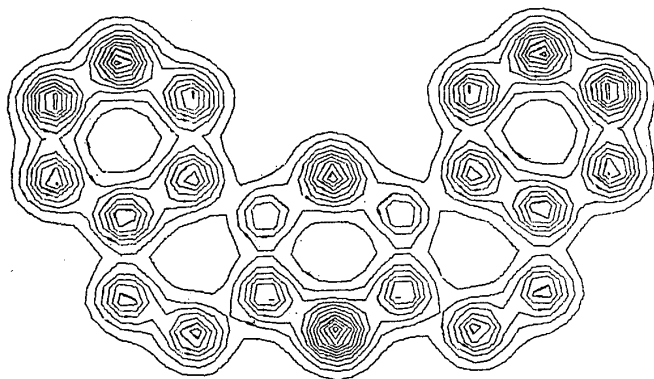
PICENE



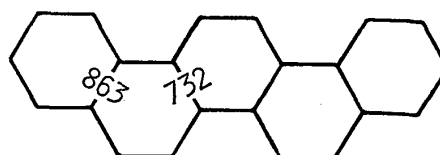
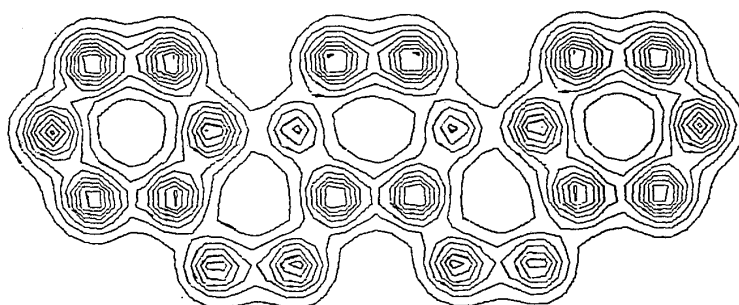
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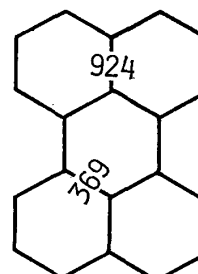
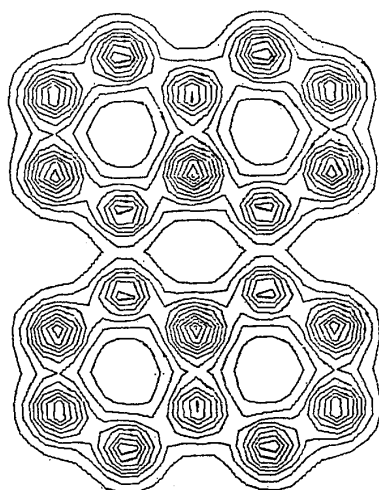
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 $\rho(5)$ 

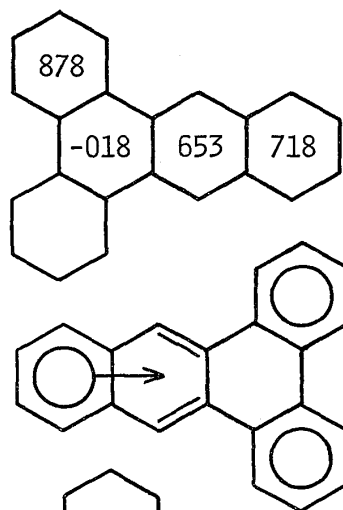
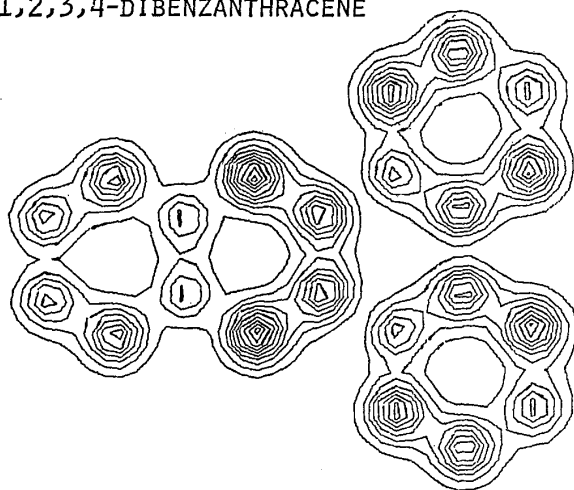
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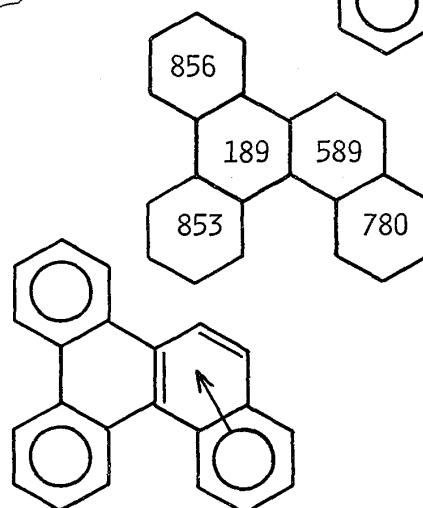
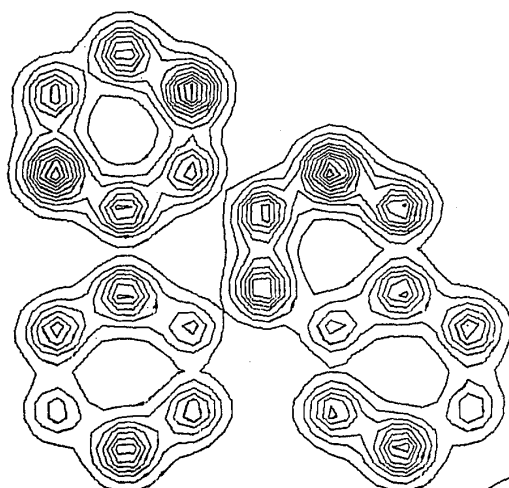
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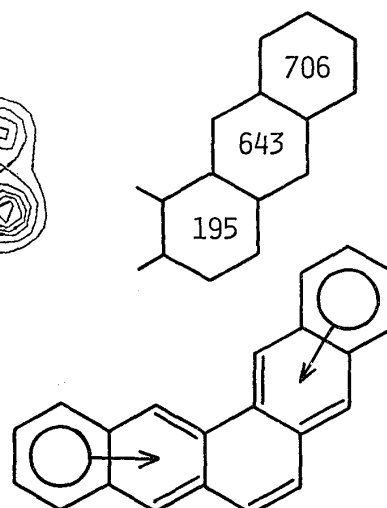
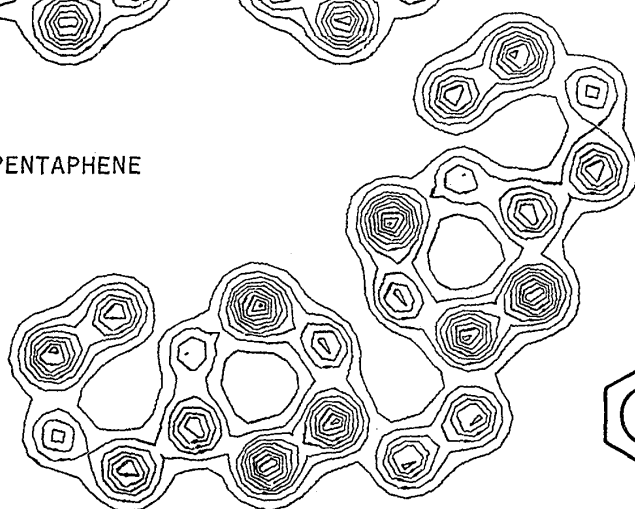
1,2,3,4-DIBENZANTHRACENE

 $\rho(3)$ 

1,2,3,4-DIBENZOPHENANTHRENE

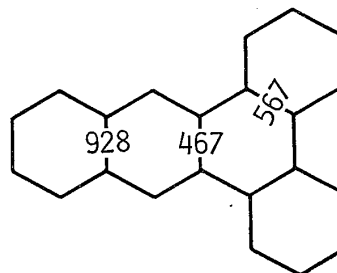
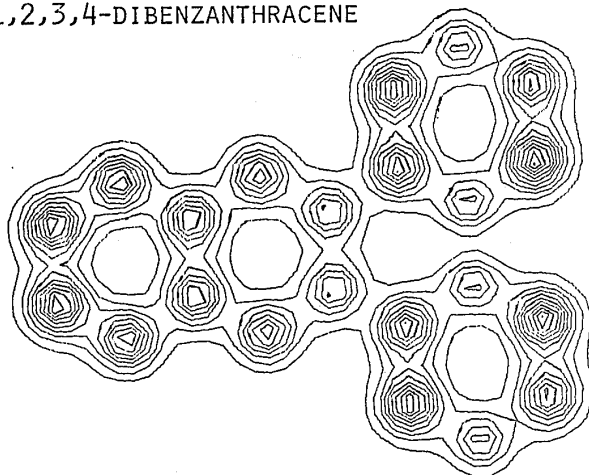


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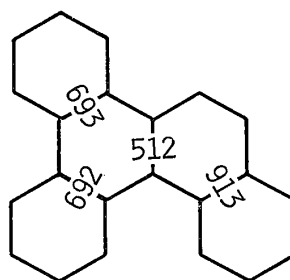
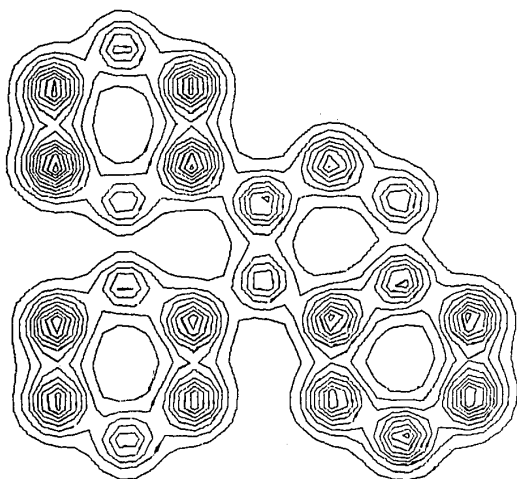


$\rho(5)$

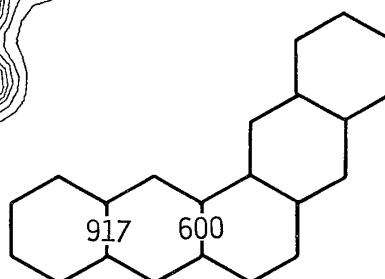
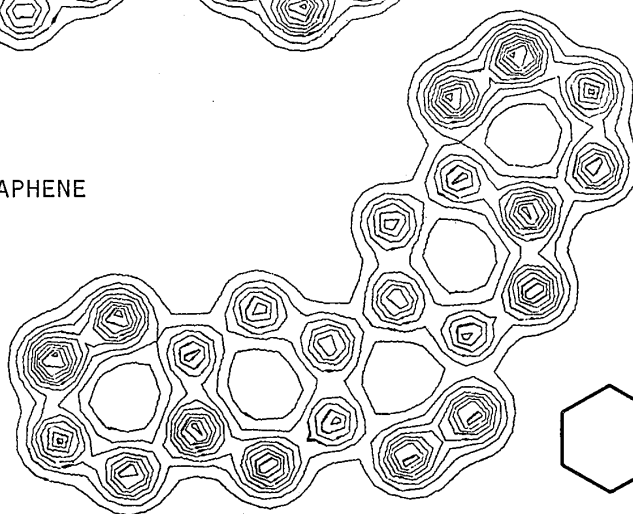
1,2,3,4-DIBENZANTHRACENE



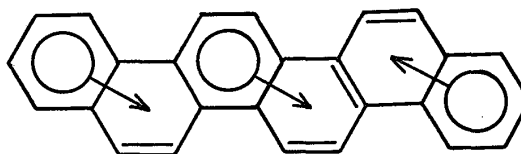
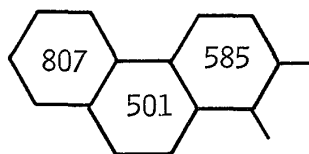
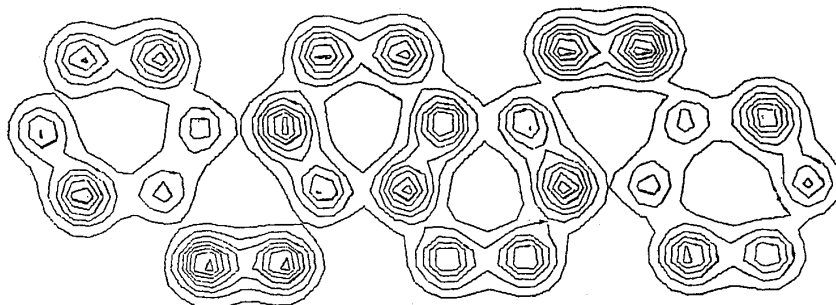
1,2,3,4-DIBENZOPHENANTHRENE



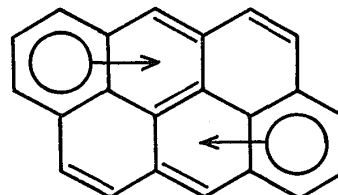
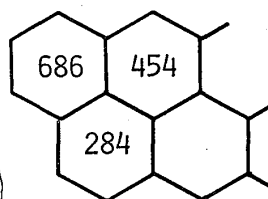
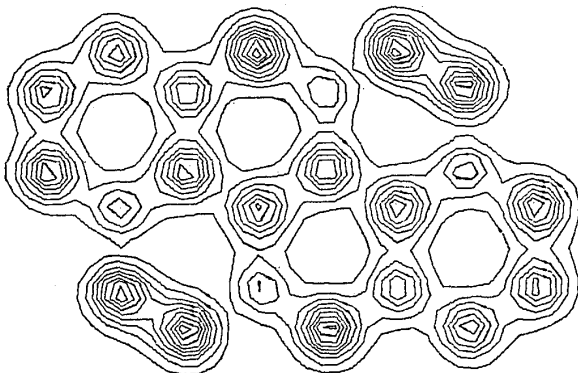
PENTAPHENE



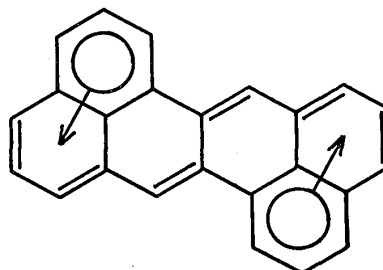
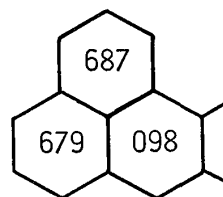
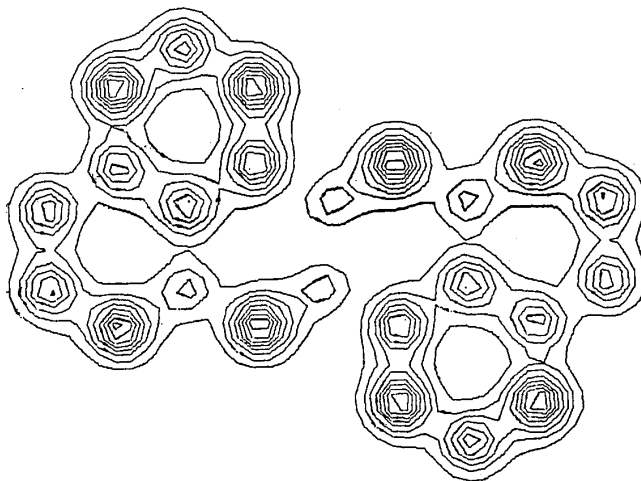
FULMINENE

 $\rho(3)$ 

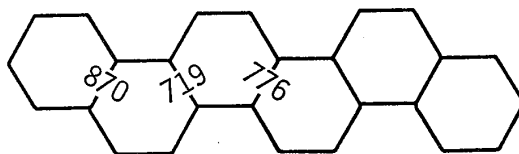
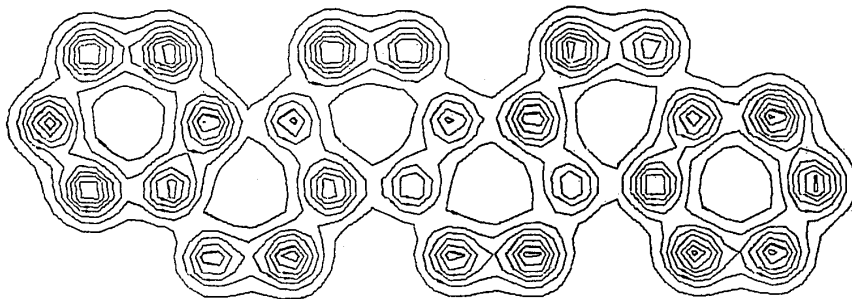
ANTHANTHRENE



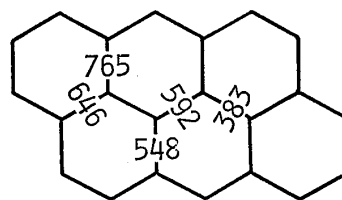
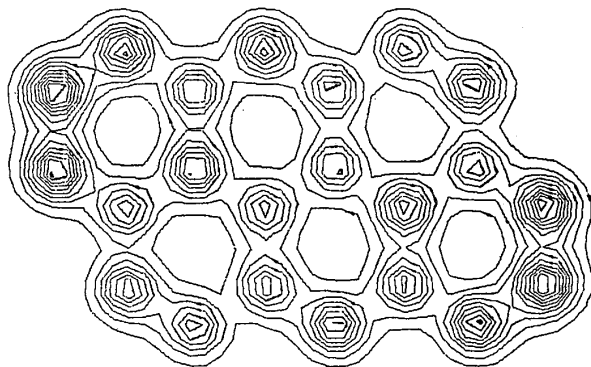
ZETHRENE



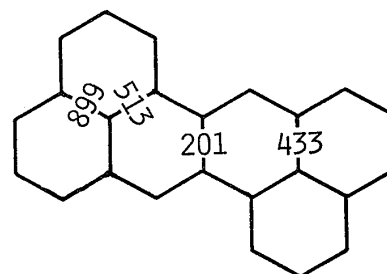
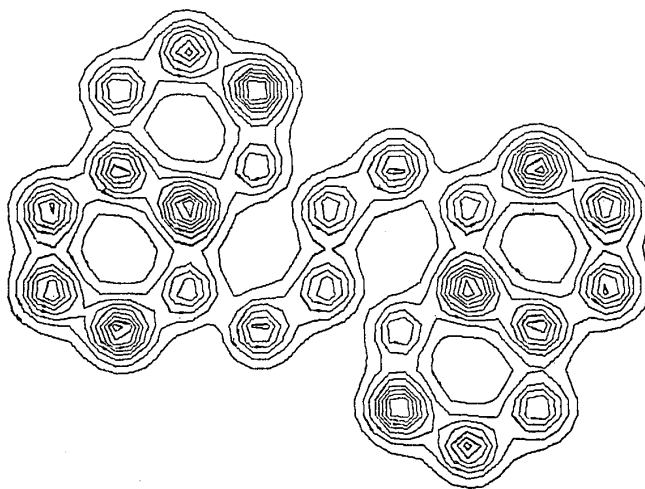
FULMINENE

 $\rho(5)$ 

ANTHANTHRENE

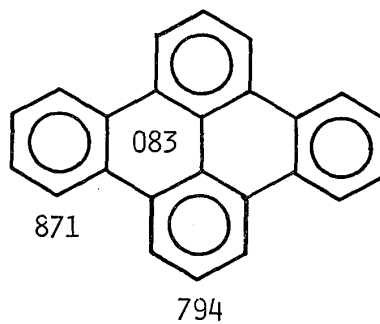
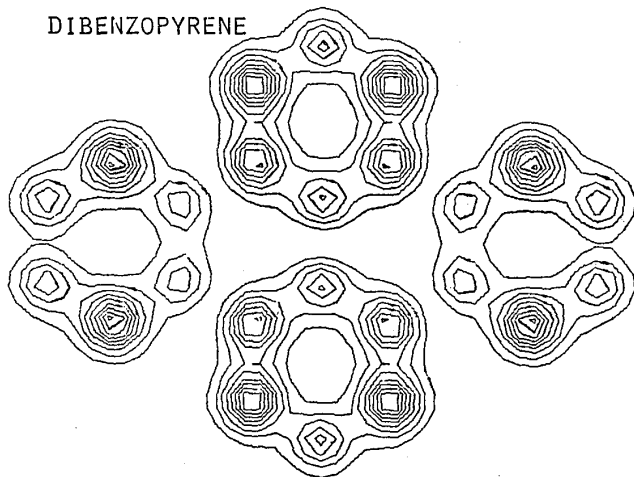


ZETHRENE

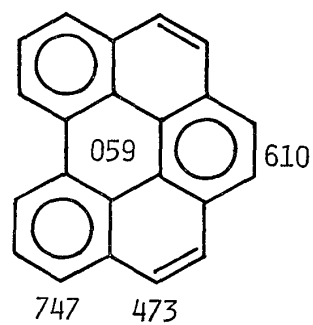
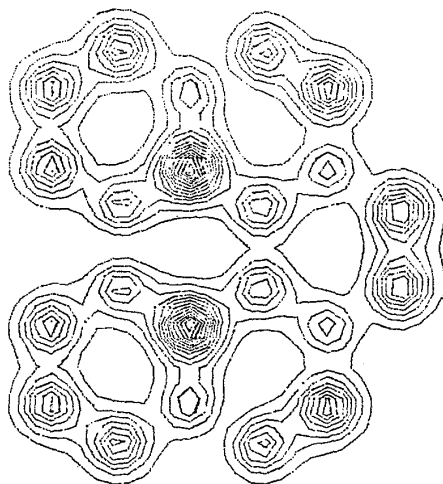


$\rho(3)$

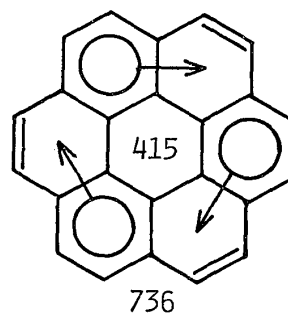
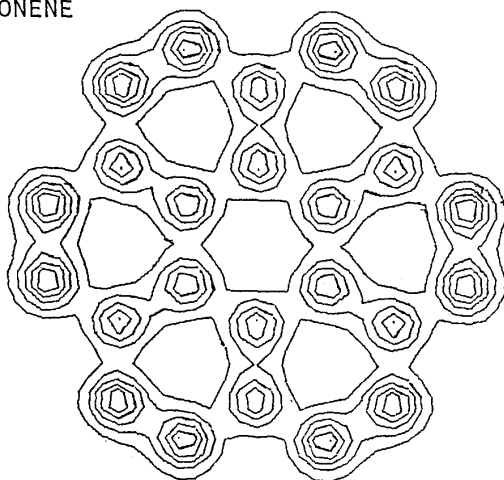
DIBENZOPYRENE



1,2-BENZOPERYLENE

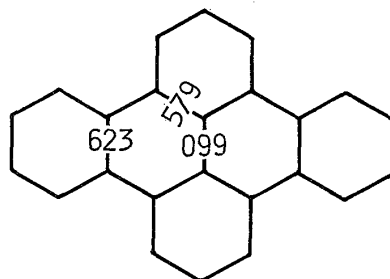
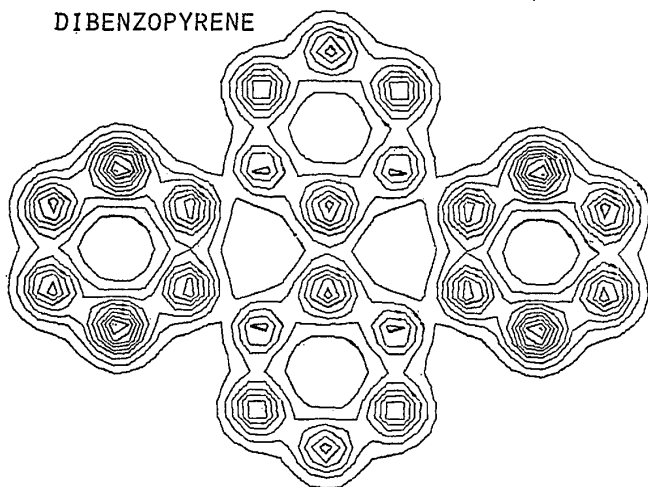


CORONENE

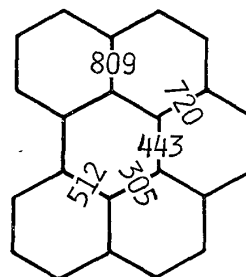
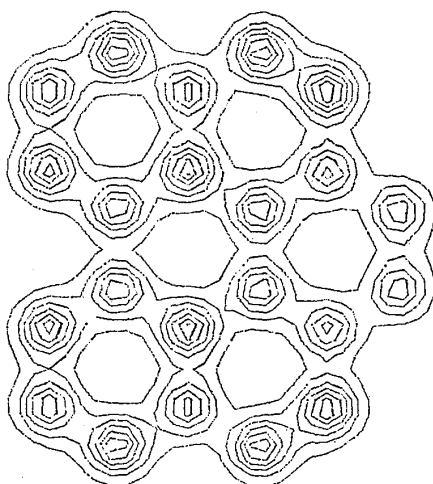


$\rho(5)$

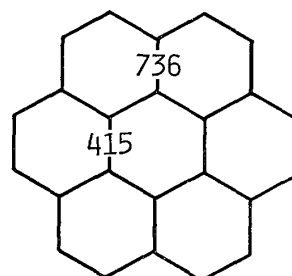
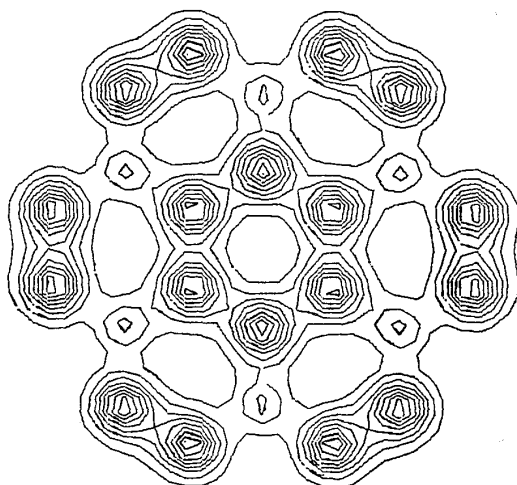
DIBENZOPYRENE



1,2-BENZOPERYLENE



CORONENE



References

- [1] E. Clar: "The Aromatic Sextet", John Wiley & Sons, London (1972).
- [2] O.E. Polansky and G. Derflinger, *Int. J. Quantum Chem.*, **1**, 379 (1967).
- [3] W.C. Herndon and M.L. Ellzey, Jr., *J. Am. Chem. Soc.*, **96**, 6631 (1974).
- [4] M. Randić, *Tetrahedron*, **31**, 1477 (1975).
- [5] J. Aihara, *Bull. Chem. Soc. Jpn.*, **49**, 1429 (1976).
- [6] H. Hosoya and T. Yamaguchi, *Tetrahedron Lett.*, **1975**, 4659.
- [7] M. Aida and H. Hosoya, *Tetrahedron*, **36**, 1317 (1975).
- [8] N. Ohkami and H. Hosoya, *Tetrahedron*, **37**, 1113 (1981).
- [9] M. Shobu, M. Aida, and H. Hosoya, to be published.
- [10] E. Clementi and D.L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
- [11] K. Nishimoto and L.S. Forster, *Theor. Chim. Acta (Berl.)*, **3**, 407₂ (1965).