Giant benzenoid hydrocarbons. Superphenalene resonance energy†

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We have calculated the molecular resonance energy for "superphenalene," a recently reported giant benzenoid that can be viewed as obtained from three fused "superbenzenes" (hexa-peri-hexabenzocoronenes). Using the method of conjugated circuits we derived quantitative characterization of Clar's qualitative description of the considered benzenoids as composed from disjoint "π-sextets." The calculations show the degree of differentiation between neighboring rings, which decreases as we progressively move towards the center of the molecule.

Recently several very large planar polycyclic aromatic hydrocarbons have been synthesized.[1–3] A subclass of these compounds can be viewed as built by fusion of several hexa-peri-hexabenzocoronene units, just as polycyclic aromatic benzenoids are built by fusion of benzene rings. The smallest members of this series of "superacenes," (starting with hexa-peri-hexabenzocoronene or "superbenzene") are illustrated in Fig. 1. For each molecule we indicate the number of Kekule valence structures it has. Recently, one of us reported on the resonance energy of supernaphthalene.[4] In this report we investigate the next in size giant benzenoid: superphenalene.

To theoreticians these molecules present challenges. Already the simple enumeration of Kekule valence structures (K) for superacenes could be quite tedious. As we see from Fig. 1, supernaphthalene has more Kekule valence structures than buckminsterfullerene, C_{60} (for which $K = 12{,}500$[5]), which undoubtedly owes its stability to the large number of Kekule valence structures. The number of Kekule structures in superphenalene exceeds half a million, and the number of Kekule valence structures of supertriphenylene, the next member of this series, is more than a hundred times larger, giving for K the staggering value of 66,998,000.[6]

Calculation of molecular properties of such large molecules, unless they exhibit high symmetry, is beyond current theoretical means.[7] If, however, one is interested only in getting an insight into the molecular resonance energy (RE), the "method of conjugated circuits"[8–10] allows one to compute RE with a high reliable precision. Therefore, we have undertaken the enumeration of the conjugated circuits in superphenalene in order not only to compute the total molecular RE but also to investigate local variations in the aromaticity. This is done by examining the contributions of individual benzene rings to the molecular RE. Such findings will offer a quantitative numerical characterization of the different rings and will support or point to limitations in the qualitative model of "π-sextets" of benzenoid hydrocarbons elaborated by Clar.[11]

Clar's π-sextet model

Clar's π-sextet model of polycyclic benzenoid hydrocarbons follows from the earlier contemplation of Armit and Robinson.[12] Its basic assumption is that π electrons tend to group, if possible, into disjoint (*i.e.*, isolated) sextets, which coincide with isolated benzene rings of the polycyclic aromatic benzenoid. Apparently, the π-sextet model of Armit, Robinson and Clar has been ignored for the most part by "main stream" theoretical chemists, except for an early attempt to rationalize some of the consequences of this model by MO theory.[13] Nevertheless, the π-sextet model is alive among experimentalists.[14]

With the development of chemical graph theory,[15] interest in Clar's valence structure was revived and many interesting mathematical properties and chemical consequences of such structures have been outlined.[16–39] We should point out that support for the π-sextet Clar model has been based on discussion of experimental data (splitting of NMR signals, shifts of bands in UV spectra among structurally related systems[11]).

The giant hydrocarbons synthesized by Müllen and coworkers[1–3] offer a good opportunity to further explore Clar's qualitative approach of π-sextets in benzenoid hydrocarbons. Clar's model deserves the attention of theoretical chemists, including quantum chemists, despite its lack, or precisely because of its lack, of underlying theoretical justification. Why should *disjoint* π-sextets be the critical structural element for the stability of polycyclic aromatic hydrocarbons? Can this aspect of Clar's model be derived from quantum chemical computations?

In this report Clar's model will be illuminated by using the conjugated circuits method,[8–10,38–46] which is closely connected with Herndon's resonance theory,[47,48] a variant of VB method that has already been considered in a preliminary form by Simpson.[49] The model of Clar has conceptual novelties. First, some benzene rings are viewed as the seat of π-sextets, some are viewed as "empty", that is, empty of resonance contribution to the system. Clar structures received due attention in chemical graph theory. Herndon and Hosoya[50] considered a VB method for the calculation of the molecular resonance energy of benzenoid hydrocarbons using Clar-type valence structures instead of Kekule valence structures. Clar's structures can be obtained by a superposition of several Kekule valence structures; however, recognition of this does not indicate which Kekule structures are preferred. Randić and Pisanski[51,52] examined many Clar's structures for a number of benzenoid hydrocarbons, including several larger benzenoids, and found that using a minimax criterion one can

† This paper is dedicated to Professor W. C. Herndon, one of the pioneers of chemical graph theory.
Non-SI unit employed: 1 eV ≈ 1.6×10^{-19} J.

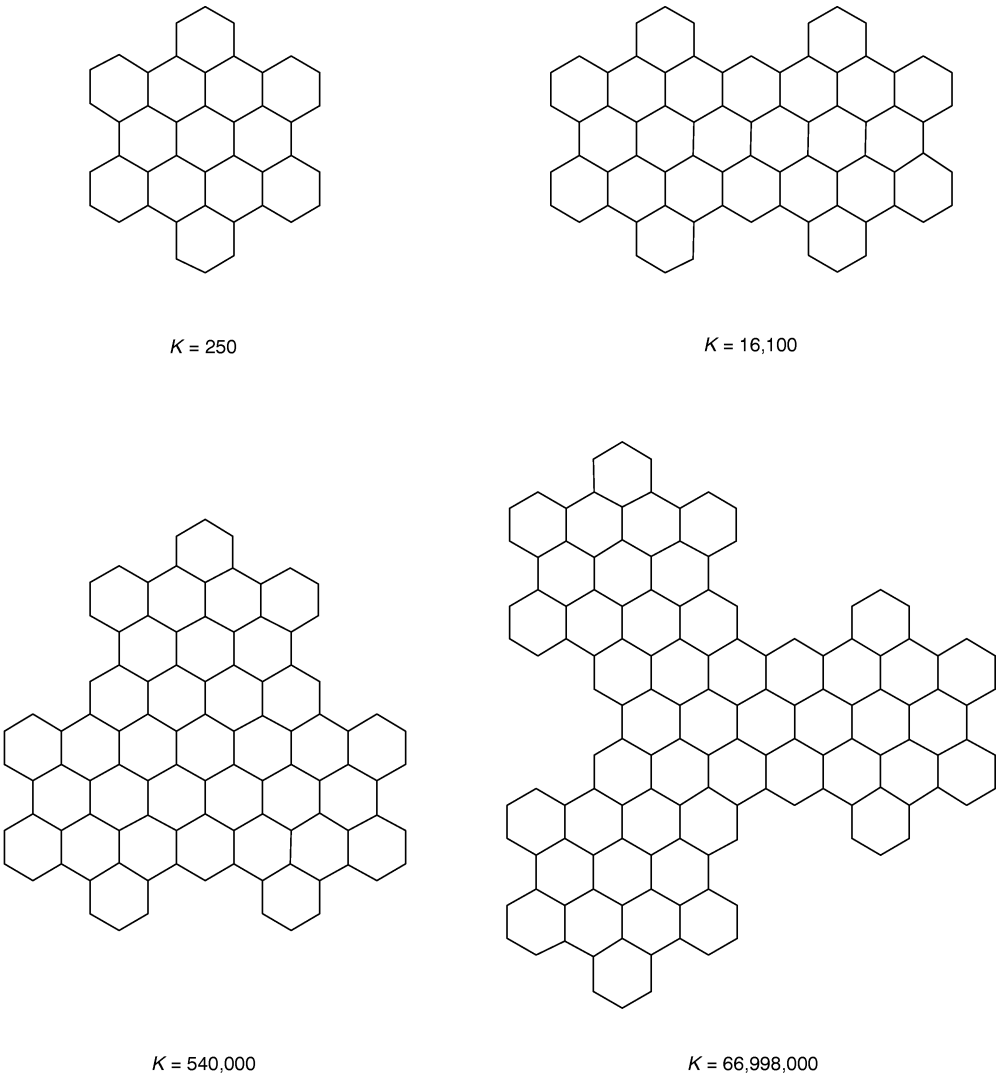

Fig. 1 Smaller superacenes and their number of Kekule valence structures: superbenzene ($K = 250$), supernaphthalene ($K = 16{,}100$), superphenalene ($K = 540{,}000$) and supertriphenylene ($K = 66{,}998{,}000$).

select the Kekule valence structures that contribute to the Clar's structure for many systems. One first assigns to individual Kekule valence structure a weight given by the magnitude of the *smallest* Pauling bond order for the set of CC double bonds defining the valence structure. Then one selects those Kekule valence structures that have the largest weight.

Conjugated circuit model

The expression for the resonance energies of large polycyclic hydrocarbons can be elegantly represented in terms of conjugated circuits.[8–10,38,40–46] Conjugated circuits are those circuits found within individual Kekule valence structures in which there is a regular alternation of C—C single and C=C double bonds. Conjugated circuits in benzenoid hydrocarbons can only be of size $4n + 2$, hence for $n = 1$ we have 6-member conjugated circuits, for $n = 2$ we have 10-member conjugated circuits, for $n = 3$ we have 14-member conjugated circuits, *etc.*

The notion of aromaticity, even if not popular in some circles, is nevertheless still of considerable interest to many organic and theoretical chemists.[53–58] Its quantitative measure has been tied to the molecular resonance energy. Even though *ab initio* computations have been recently reported on some large benzenoids, such computations are usually restricted to molecules of high symmetry.[7] The method of conjugated circuits, however, is not restricted by the presence of a high molecular symmetry, and has been successfully applied to many large benzenoids and fullerenes for which no other calculations were possible. Even though the conjugated circuit method has been outlined between fifteen and twenty years ago, the method is by no means obsolete, as it may appear to some critics. What may be obsolete are the numerical values for the parameters used to calibrate the RE, which are based on Dewar and De Llano's SCF calculations.[59] However, there are no other more recent calculations of the RE for half a dozen smaller benzenoids that could be used to re-calibrate the empirical parameters that the conjugated circuit method requires.

In Fig. 2 we illustrate one of 540,000 Kekule structures of superphenalene and in the molecular diagram at the right we have inscribed in individual benzene rings the number "1" for all rings that have an alternation of CC single and CC double bonds (as in the Kekule formulas of benzene). The benzene rings so identified represent the smallest conjugated circuit, that is they are part of a 6-carbon-atom conjugated circuit. They can be easily enumerated and in this case there are 14 such rings, briefly we write 14 R_1.

As we see from Fig. 2 many benzene rings have not received the label "1", because they do not have three CC double bonds. We continue to examine more closely these "unlabeled" rings. In all benzene rings *adjacent* to "1" rings and which have *two* CC double bonds we now write a label "2", because these rings, when combined together with adjacent "1" rings, give a periphery that has five alternating CC single and CC double bonds. All these rings are shown in the lower part of Fig. 2. Hence, such rings are part of a 10-carbon-

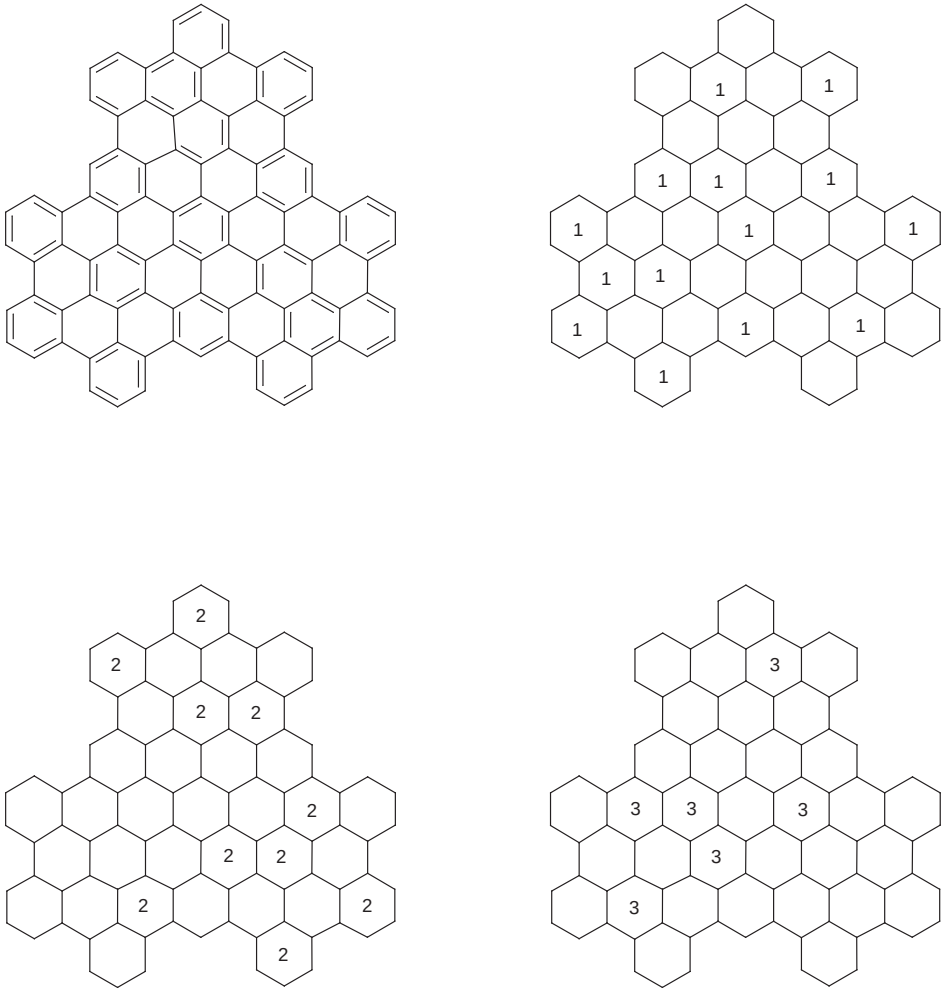

Fig. 2 Location of the smaller conjugated circuits (R_1, R_2 and R_3) for a single Kekule valence structure of superphenalene.

atom conjugated circuit. The count of "2" rings gives the number of 10-conjugated circuits, which for this particular Kekule valence structure gives 10 R_2. We continue to examine rings adjacent to those having labels "1" and/or "2." Such rings may be part of 14-member conjugated circuits if they form the boundary of anthracene or phenanthrene fragments or a pyrene periphery. We have indicated all such rings with the label "3" in the last diagram at the bottom of Fig. 2. Again, once the rings have been identified, their enumeration (for a single Kekule valence structure) is not difficult, and we obtain 6 R_3. The assignment of still larger conjugated circuits to the rings without labels may continue but because as the size of conjugated circuits increases their contribution to the molecular RE diminishes we will stop the enumeration with R_3.

As we have seen, identifying smaller conjugated circuits and their enumeration within a single Kekule valence structure is not a difficult task. The difficulties are due to the large number of Kekule valence structures in large benzenoids. In addition, to the difficult task of enumerating conjugated circuits there are difficulties associated with the presence of linear dependence among conjugated circuits. The smallest conjugated circuits R_1 and R_2 are always linearly independent, which simplifies their enumeration. Since superphenalene has no so-called "fixed" CC double bonds, the number of linearly independent conjugated circuits in a benzenoid hydrocarbon equals the number of fused benzene rings.[60–62] Therefore, we can assign to each ring of a considered Kekule valence structure of a benzenoid hydrocarbon a number (n), which denotes the size of the smallest conjugated circuit of size $4n + 2$ that involves that particular ring. When this is completed for all Kekule valence structures one simply counts separately the rings with different assigned values of n, which immediately leads to the expression for the molecular RE.

The outlined approach is suitable for molecules with a small number of Kekule valence structures. To enumerate conjugated circuits in molecules with a large number of Kekule valence structures it is better to focus attention on the individual benzene rings, rather than on individual Kekule valence structures. To find the contribution of a ring to the molecular RE one erases the selected ring and all rings that constitute the conjugated circuit considered and then one counts the number of Kekule valence structures for the residual structure. No correction of the count thus obtained is required if the conjugated circuits considered are linearly independent (which is, besides the case of R_1 and R_2, also true for R_3 that represent the boundary of anthracene and phenanthrene). However, in the case of conjugated circuits arising from the periphery of pyrene such an efficient counting procedure is marred by the fact that some conjugated circuits (being linearly dependent) may have been counted twice. In order to get the correct count of linearly independent R_3 rings one has to modify the counting so as not to include them,[62] or else one has to subtract conjugated circuits already counted.[63]

To obtain the contribution of the Kekule valence structure of Fig. 2 to the molecular RE we sum the contributions of all the benzene rings in the structure and divide this by the number of Kekule valence structures. Hence we obtain:

$$RE(i) = (14\ R_1 + 10\ R_2 + 6\ R_3)/540{,}000.$$

Here R_1, R_2, and R_3 are the contributions of conjugated circuits of size 6, 10 and 14, respectively, to the molecular RE.

The values $R_1 = 0.869$ eV, $R_2 = 0.247$ eV and $R_3 = 0.100$ eV have been empirically determined[40–42] so that they reproduce satisfactorily the RE in smaller benzenoids as computed by simple SCF MO computations.[59]

The value RE(i) gives the contribution of an ith Kekule valence structure. Different Kekule valence structures generally will make quite different contributions to the molecular RE. In Fig. 3 we depict two Kekule valence structures of superphenalene, one having 25 Kekule benzene rings and the other having only 4. These are the limiting possibilities in this molecule. Clearly the former Kekule valence structure makes a significantly larger contribution to the molecular RE than the latter. If we count (linearly independent) conjugated circuits the first structure gives $25\ R_1 + 9\ R_4$, while the latter gives $4\ R_1 + 9\ R_2 + 6\ R_3 + 6\ R_4 + 3\ R_5 + 6\ R_6$. Comparison between the numerical contributions of these two shows that the first contributes over five times more to the molecular RE than the second structure. This clearly demonstrates the considerable variations of individual Kekule valence structures, which simple models assume to have the same weight.

According to Fries' empirical rule,[64,65] Kekule valence structures with the largest number of formal benzene rings are the most important. The count of the smallest number of choices that one makes in the assignment of CC double bonds to construct a Kekule valence structure, the so called "innate degree of freedom of a structure (f)",[51,66–68] gives another measure of the relative importance of a Kekule valence structure. We obtain for the first Kekule structure of Fig. 3 $f = 16$ (which equals the number of Clar's π-sextets for the molecule) and only $f = 4$ for the second Kekule valence structure. The small value of f suggests a "long-range order" for CC double bonds in that structure. One may view the contributions of individual Kekule valence structures to the molecular RE as the relative weight that the Kekule structure has in the representation of the molecule.

To obtain the molecular RE one has to add the contributions from all Kekule valence structures. For superphenalene we obtain (*vide infra*):

$$\mathrm{RE} = (7{,}897{,}800\ R_1 + 4{,}772{,}100\ R_2 + 3{,}390{,}000\ R_3)/540{,}000 \quad (1)$$

or

$$\mathrm{RE} = 14.625\,555\ R_1 + 8.837\,222\ R_2 + 6.277\,778\ R_3$$

which, when we substitute the numerical values for R_1, R_2 and R_3 gives RE = 15.5202 eV.

Enumeration of conjugated circuits in superphenalene

Enumeration of conjugated circuits (reported here for superphenalene) is computationally more involved than enumeration of Kekule valence structures. An efficient way to count conjugated circuits in large benzenoids is to consider contributions to the resonance energy from individual benzene rings, rather than individual Kekule valence structures.[60–63] If a molecule has symmetry it suffices only to consider symmetry non-equivalent rings. These have been given the labels A–H for superphenalene (Fig. 4). The molecular resonance energy is then given by:

$$RE = [3(A + E + F) + 6(B + C + D + G) + \mathrm{H}]/\mathrm{K} \quad (2)$$

where A, B, C, ... give the count of conjugated circuits involving the corresponding benzene rings, and K is the total number of Kekule valence structures. We can obtain the con-

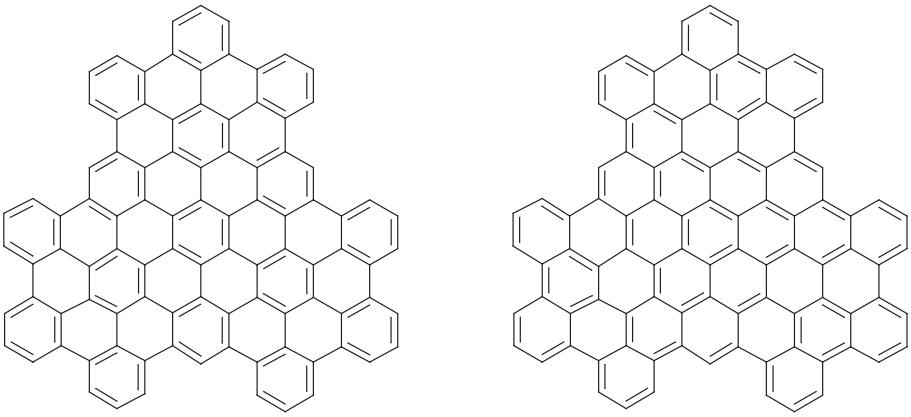

Fig. 3 Two limiting Kekule valence structures of superphenalene. The structure at the left has the largest number of the dominant R_1 conjugated circuits while the structure at right has the smallest number of R_1 conjugated circuits.

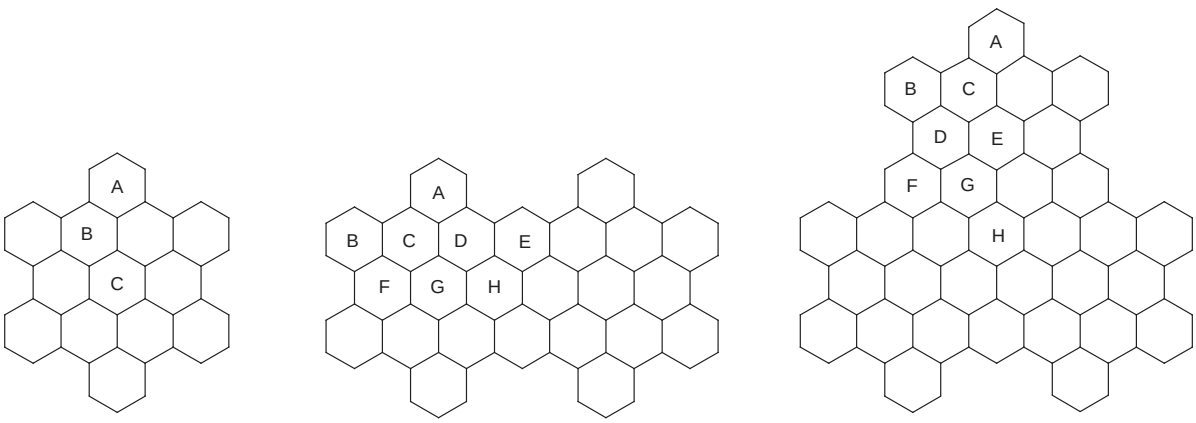

Fig. 4 Labeling of symmetry non-equivalent rings in superbenzene, supernaphthalene and superphenalene.

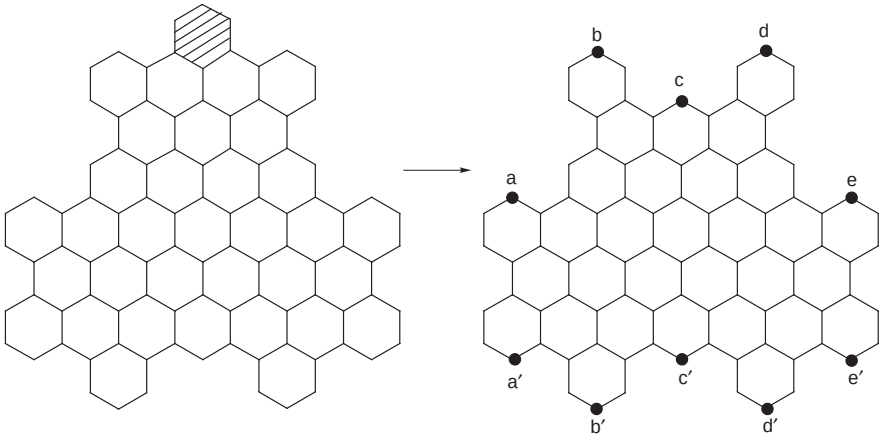

Fig. 5 The residual fragment of superphenalene when ring A and adjacent pendent bonds are erased. Labels a–e indicate the peak carbon atoms and labels a′–e′ indicate the corresponding valley carbon atoms.

tribution to the molecular RE of the benzene ring A by finding separately the contributions of conjugated circuits of size 6 (the coefficient of R_1 in the expression for RE), of size 10 (the coefficient of R_2 in the expression for RE) and of size 14 (the coefficient of R_3 in the expression for RE).

The contribution of ring A to R_1 is given by twice the number of Kekule valence structures of the molecular fragment of superphenalene in which the ring A, together with the adjacent CC bonds that connect A to other benzene rings, has been deleted. The factor of two comes from two alternative distributions of CC double bonds within a single benzene ring. Other higher conjugated circuits do not involve this factor of two, since the alternative distributions of CC bonds change the size of individual conjugated circuits. In fact, as Gutman and Randić have shown,[69] by changing systematically the alternation of CC single and CC double bonds within individual conjugated circuits (and their linear combinations) one can from a single Kekule valence structure derive all the remaining Kekule valence structures. In Fig. 5 we show the resulting fragment. Now we have to find the number of Kekule valence structures (K') of that fragment.

An elegant way to find K' in larger benzenoids has been outlined by John and Sachs[70,71] and summarized by Cyvin and Gutman.[72] First we identify vertices at the top (a, b, c, d, e in Fig. 5, the so-called "peak" vertices) and at the bottom (a′, b′, c′, d′, e′ in Fig. 5, the so-called "valley" vertices) of the molecular diagram. Next we construct the determinant of a matrix in which the element (x, y') gives the number of monotonous decreasing paths connecting vertex x (at the top) and vertex y' (at the bottom). In Fig. 6 we show several of the corresponding lattices that enumerate paths between pairs of vertices. The number of paths is given by the number of Kekule valence structures of the corresponding lattice.[73] Thus for the fragment of Fig. 5 we have

	a	b	c	d	e
a′	5	11	8	0	0
b′	5	55	21	8	0
c′	0	20	20	20	0
d′	0	8	21	55	5
e′	0	0	8	11	5

which gives $K' = 432{,}000$.

The contributions of ring A to R_2 are given by the count of Kekule valence structures of the molecular fragments of superphenalene in which the ring and the adjacent ring forming conjugated circuits of size 10, together with the CC bonds that connect the two rings to other benzene rings, have been deleted. In this case one can assign CC double bonds to ring B and excise the three rings, which results in the fragment shown in Fig. 7, for which one finds $K' = 54\,000$, but because of the symmetry we obtain 108 000 for the contribution of ring A to R_2.

Finally, the contributions of ring A to R_3 are given by the count of Kekule valence structures of the molecular fragment of superphenalene in which ring A together with neighboring rings forming 14-carbon-atom conjugated circuits and the adjacent CC bonds that connect these rings to the rest of the molecule have been deleted. However, ring A cannot be part of a 14-member conjugated circuit because it is a terminal ring, while rings involved in 14-member conjugated circuits are always in the central part of three-ring fragment. Hence, ring A has contributions only from conjugated circuits R_1 and R_2:

$$\mathrm{RE(A)} = (432{,}000\ R_1 + 108{,}000\ R_2)/540{,}000$$

or

$$\mathrm{RE(A)} = 0.800\,00\ R_1 + 0.200\,00\ R_2\,.$$

Superphenalene resonance energy

In Tables 1 and 2 we give the count of conjugated circuits R_1, R_2 and R_3 for the so-called "full" and "empty" rings, respectively, of superphenalene (at the end of these tables). As we see from Tables 1 and 2, which also include the results for superbenzene and supernaphthalene, there is considerable variation in the contributions of the individual benzene rings of the polycyclic benzenoid hydrocarbons examined, even within the classes of "full" and "empty" rings. Similar variations have been observed in smaller polycyclic benzenoids. A particularly pronounced difference is found in fully benzenoid systems between the rings to which a "π-sextet" is assigned as compared to the "empty" rings, rings devoid of π-sextets.

The molecular resonance energy, given by eqn. (2), equals 15.520 eV. If one wants to compare the resonance stabilization in molecules of different sizes, REPE (the resonance energy *per* π electron, *i.e.*, REPE = RE/n) is more suitable than RE, as suggested by Hess and Schaad.[74] RE is size-dependent and increases with the size of molecules. In contrast, REPE does not depend on the size of the molecule. For superphenalene we obtain REPE = 0.1617 eV. The REPE for benzene is given by 0.869/6 = 0.1448 eV and serves as the standard for comparison of relative stability among benzenoids of different sizes. As we see the REPE for superphenalene is greater than that of benzene, which is typical for fully benzenoid hydrocarbons.

Local aromaticity

Our results (Tables 1 and 2) are not surprising to those fam-

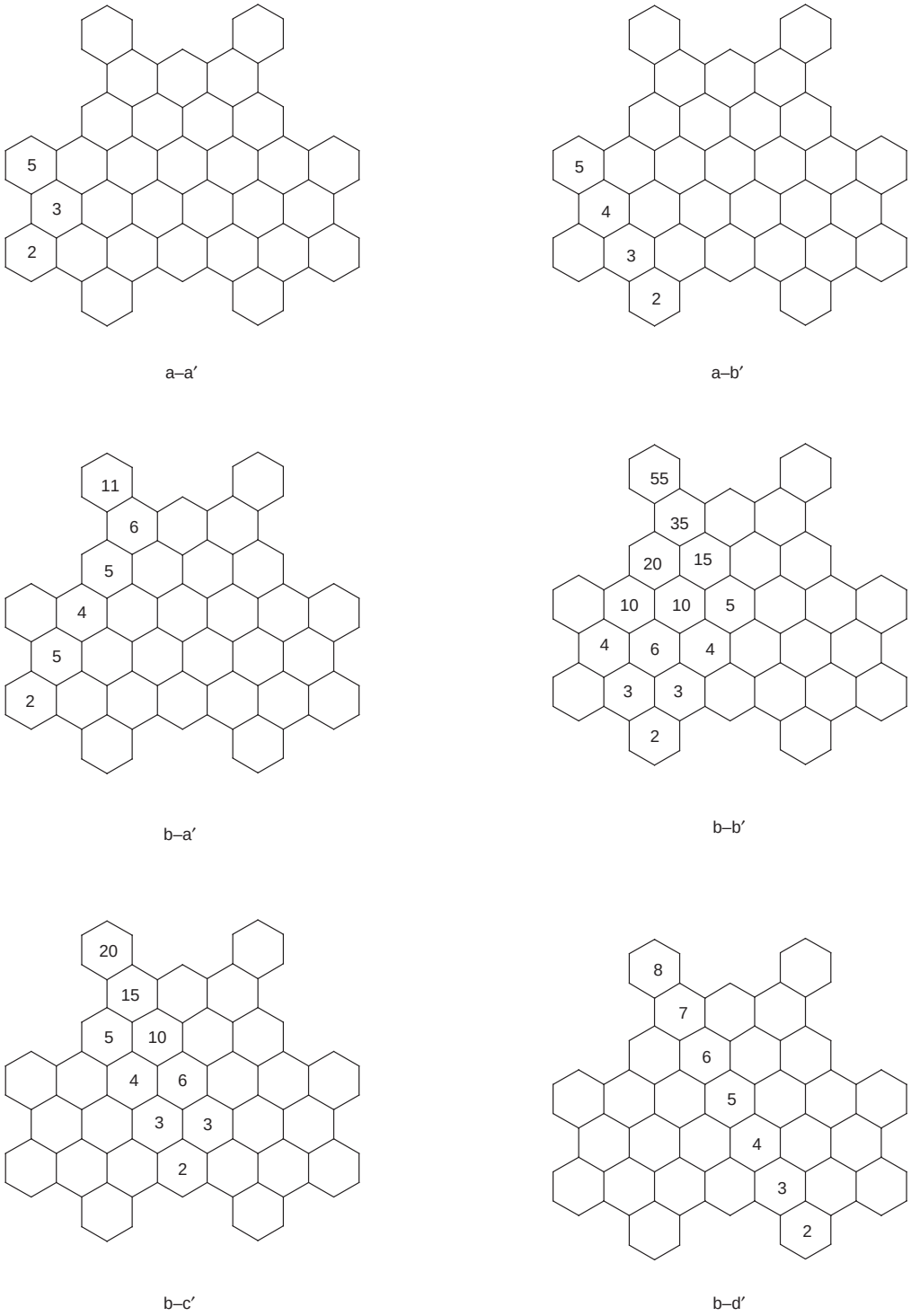

Fig. 6 The count of paths for selected "peak" and "valley" carbon atoms in superphenalene.

iliar with Clar's model of benzenoids. The benzene rings that have been assigned π-sextets in Clar's formalism have been found, by the totally independent approach that the conjugated circuits model is, to have a considerably larger role in contributing to the molecular stability than have other rings devoid of π-sextet content. We thus fully confirm the expectations that Clar would have foreseen for superphenalene when he adopted the notion of the π-sextets. Our approach, however, raises this model to a quantitative level. We see that "full" rings of a Clar's structure of superphenalene are not all equivalent. The largest contribution to RE comes from the A rings, which are slightly more "aromatic" than the B rings, both however being more "aromatic" than the remaining peripheral ring F, and considerably more "aromatic" than the inner π-sextet rings E and H. A similar discrimination can be made between non-equivalent "empty" rings. According to the conjugated circuit model the "empty" rings are not totally devoid of π-sextet character. They also make a contribution to the molecular RE. In comparison to the π-sextet rings, the so called "empty" rings make a considerably smaller contribution to the molecular RE, about 1/3 of the contribution of the π-sextet rings.

It is interesting to observe that the "empty" rings at the molecular periphery are "more empty" than the "empty" rings closer to the molecular center. It thus appears that the difference in resonance contribution between the π-sextet rings and the "empty" rings is attenuated as we move from the molecular periphery towards the molecular center. We can

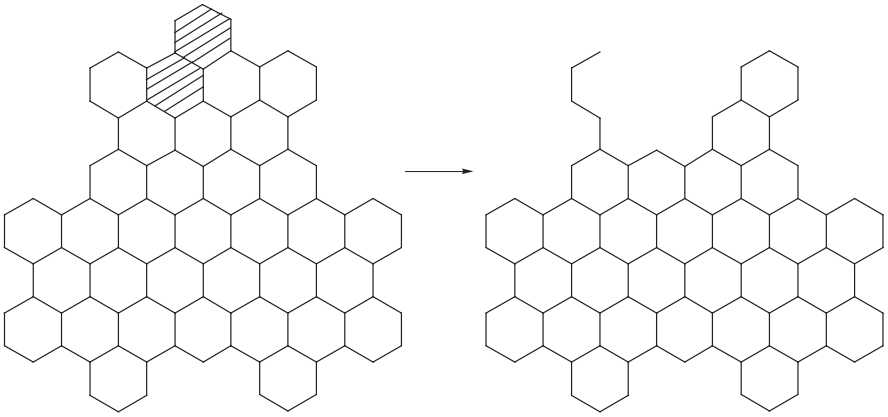

Fig. 7 The residual fragment of superphenalene when the rings A and C (representing a 10-member conjugated circuit) and adjacent pendent bonds are erased.

express the degree of "fullness" and the "emptiness" of individual rings (terms that correspond to Clar's molecular model of benzenoids) by a local aromaticity measure defined as the quotient[62,75–77]: $\{RE(R_1) - [RE(R_2) + RE(R_3)]\}/RE$. The index is a measure of the departure of each ring from the ring of benzene, for which Clar's index equals 1 (or 100%).

Discussion

A comparison of ring resonance energies of superbenzene, supernaphthalene and superphenalene is of some interest. We observe that the ring RE for ring A in superbenzene and superphenalene are precisely the same as is the ring RE of ring B in supernaphthalene (see Fig. 4 for the labeling of rings). These rings make the largest ring contribution to RE and are the rings in which only R_1 and R_2 conjugated circuits arise. If we compare between different superacenes the ring resonance energies of the "π-sextet" rings in the molecular interior we see that the ring RE in larger superacenes decreases as the size of the molecule increases. Thus, we find the smallest ring RE for supernaphthalene to be 0.5367 eV and for superphenalene to be 0.4983 eV, as compared with the smallest value for a superbenzene ring of 0.5494 eV. The decrease is particularly apparent if the results are compared with smaller fully benzenoid systems, shown in Fig. 8 for which the corresponding ring RE are listed in Table 3.

In the case of the "empty" rings (in Clar's model), we see that the contributions, at least of some of the "empty" rings, increase with the increasing size of the molecule. The increase is particularly apparent if the results are compared with

Table 1 The count of conjugated circuits R_1, R_2 and R_3 for symmetry non-equivalent "full" benzene rings of superacenes and the corresponding ring resonance energies

Ring			Ring RE/eV	Clar index
Superbenzene				
A	1	$(200\ R_1 + 50\ R_2)/250$	0.7446	86.73
C	2	$(128\ R_1 + 96\ R_2 + 24\ R_3)/250$	0.5494	61.98
Supernaphthalene				
A	1	$(12{,}750\ R_1 + 3225\ R_2 + 125\ R_3)/16{,}100$	0.7384	86.39
B	2	$(12{,}880\ R_1 + 3220\ R_2)/16{,}100$	0.7446	86.73
E	3	$(9900\ R_1 + 5200\ R_2 + 1000\ R_3)/16{,}100$	0.6203	72.28
G	4	$(8000\ R_1 + 6120\ R_2 + 1770\ R_3)/16{,}100$	0.5367	60.91
Superphenalene				
A	1	$(432{,}000\ R_1 + 108{,}000\ R_2)/540{,}000$	0.7446	86.73
B	2	$(426{,}000\ R_1 + 108{,}500\ R_2 + 5375\ R_3)/540{,}000$	0.7362	86.25
E	3	$(257{,}600\ R_1 + 201{,}600\ R_2 + 68{,}700\ R_3)/540{,}000$	0.5195	59.60
F	4	$(322{,}000\ R_1 + 171{,}500\ R_2 + 43{,}000\ R_3)/540{,}000$	0.6046	71.42
H	5	$(243{,}000\ R_1 + 201{,}000\ R_2 + 517{,}750\ R_3)/540{,}000$	0.4983	56.96

Table 2 The count of conjugated circuits R_1, R_2 and R_3 for symmetry non-equivalent "empty" benzene rings of superacenes and the corresponding ring resonance energies

Ring			Ring RE/eV	Clar index
Superbenzene				
B	1	$(50\ R_1 + 66\ R_2 + 61\ R_3)/250$	0.2644	31.96
Supernaphthalene				
C	1	$(3250\ R_1 + 4250\ R_2 + 4875\ R_3)/16{,}100$	0.2709	29.51
D	2	$(3200\ R_1 + 3950\ R_2 + 4515\ R_3)/16{,}100$	0.2614	32.17
F	3	$(3190\ R_1 + 3440\ R_2 + 4875\ R_3)/16{,}100$	0.2552	34.92
H	4	$(3750\ R_1 + 4370\ R_2 + 5040\ R_3)/16{,}100$	0.3008	34.60
Superphenalene				
C	1	$(108{,}000\ R_1 + 140{,}200\ R_2 + 159{,}750\ R_3)/540{,}000$	0.2675	29.94
D	2	$(109{,}000\ R_1 + 132{,}775\ R_2 + 146{,}825\ R_3)/540{,}000$	0.2633	33.22
G	3	$(127{,}000\ R_1 + 139{,}825\ R_2 + 183{,}450\ R_3)/540{,}000$	0.3023	35.21

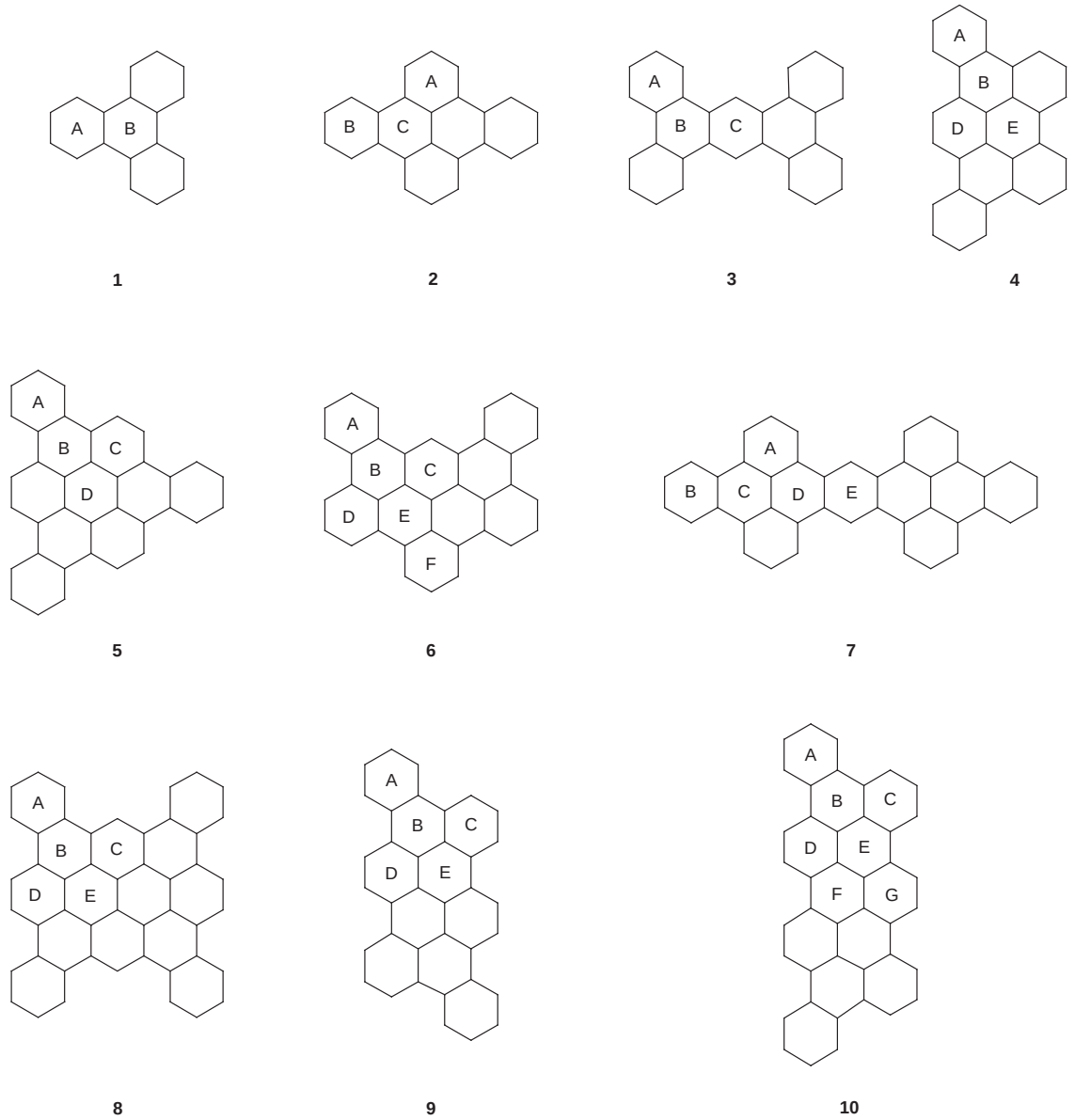

Fig. 8 Smaller fully benzenoid hydrocarbons whose ring resonance energies are listed in Tables 3 and 4.

smaller fully benzenoid systems for which corresponding ring RE are listed in Table 4.

We can speculate that in large superacenes the trend of equalization of the interior rings will continue and that eventually, as we approach the model of graphite, the difference between the "empty" and the π-sextet rings will gradually disappear. Hence, because of the observed trend in equalization of their contribution to the molecular RE, except for the rings at the molecular periphery, which reflect the asymmetrical immediate environment (the edge effect), the resonance energy of a large graphite-like single layer of fused benzenoids will be ring-additive. However, the average ring contribution, or more correctly the REPE, apparently increases with the size of the system. The same has already been observed in the case of families of infinite polymers that correspond to fully benzenoid systems.[78–81] It remains to be seen if the model of conjugated circuits would lead to a limiting value for the REPE of graphite and what that limit will be when graphite is viewed as a giant Clar's system. Hence the variations in ring RE can be viewed as the "edge" or border effect on rings in large systems. We will approach the limit of graphite when the difference between the "full" and the "empty" rings in the molecular interior vanishes or becomes insignificant. Hence, calculation of the ring RE may offer a novel route to the characterization of graphite.

In summary, though the molecules studied appear to exhibit usual chemical behavior, except that indeed they are very large, and the theoretical results reported may equally appear usual, our computation offers a *quantitative* measure for the predicted variations in local properties of individual rings, particularly as rings are more and more removed from the molecular periphery. No such information was available prior to this work. Similar results on smaller benzenoid hydrocarbons cannot offer the information on the change of local ring RE as rings are located "deeper" towards the molecular center, because all rings in smaller benzenoid hydrocarbons are on the molecular periphery or are too close to the molecular periphery.

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Table 3 The count of conjugated circuits R_1, R_2 and R_3 for symmetry non-equivalent "full" benzene rings and the corresponding ring resonance energies of the fully benzenoid hydrocarbons shown in Fig. 8

Molecule	Ring		Ring RE/eV
1	A	$(8\ R_1 + R_{12})/9$	0.7999
2	A	$(18\ R_1 + 2\ R_2)/20$	0.8068
	B	$(16\ R_1 + 4\ R_2)/20$	0.7446
3	A	$(36\ R_1 + 4\ R_2)/40$	0.8068
	C	$(32\ R_1 + 8\ R_2)/40$	0.7446
4	A	$(40\ R_1 + 5\ R_2)/45$	0.7999
	C	$(36\ R_1 + 9\ R_2)/45$	0.7446
	D	$(32\ R_1 + 12\ R_2 + R_3)/45$	0.6860
5	A	$(90\ R_1 + 13\ R_2 + R_3)/104$	0.7839
	C	$(72\ R_1 + 28\ R_2 + 4\ R_3)/104$	0.6720
6	A	$(90\ R_1 + 10\ R_2)/100$	0.8068
	C	$(80\ R_1 + 20\ R_2)/100$	0.7446
	D	$(64\ R_1 + 32\ R_2 + 4\ R_3)/100$	0.6392
	F	$(80\ R_1 + 20\ R_2)/100$	0.7446
7	A	$(178\ R_1 + 20\ R_2)/198$	0.8062
	B	$(160\ R_1 + 38\ R_2)/198$	0.7496
	E	$(126\ R_1 + 36\ R_2)/198$	0.5971
8	A	$(460\ R_1 + 56\ R_2 + 4\ R_3)/520$	0.7961
	C	$(320\ R_1 + 128\ R_2 + 32\ R_3)/520$	0.6017
	D	$(360\ R_1 + 146\ R_2 + 148\ R_3)/520$	0.6685
9	A	$(90\ R_1 + 11\ R_2)/101$	0.8013
	C	$(80\ R_1 + 21\ R_2)/101$	0.7397
	D	$(72\ R_1 + 27\ R_2 + 2\ R_3)/101$	0.6875
10	A	$(202\ R_1 + 25\ R_2)/227$	0.8005
	C	$(180\ R_1 + 47\ R_2)/227$	0.7402
	D	$(160\ R_1 + 62\ R_2 + 5\ R_3)/227$	0.6822
	G	$(162\ R_1 + 61\ R_2 + 4\ R_3)/227$	0.6883

Table 4 The count of conjugated circuits R_1, R_2, and R_3 for symmetry non-equivalent "empty" benzene rings and the corresponding ring resonance energies of the fully benzenoid hydrocarbons shown in Fig. 8

Molecule	Ring		Ring RE/eV
1	B	$(2\ R_1 + 3\ R_2 + 3\ R_3)/9$	0.2754
2	C	$(4\ R_1 + 6\ R_2 + 7\ R_3)/20$	0.2829
3	B	$(8\ R_1 + 12\ R_2 + 13\ R_3)/40$	0.2804
4	B	$(10\ R_1 + 15\ R_2 + 15\ R_3)/45$	0.3088
	E	$(8\ R_1 + 12\ R_2 + R_3)/45$	0.2226
5	B	$(26\ R_1 + 34\ R_2 + 32\ R_3)/104$	0.3288
	D	$(18\ R_1 + 27\ R_2 + 15\ R_3)/104$	0.2290
6	B	$(20\ R_1 + 28\ R_2 + 32\ R_3)/100$	0.2750
	E	$(20\ R_1 + 28\ R_2 + 26\ R_3)/100$	0.2690
7	C	$(40\ R_1 + 60\ R_2 + 69\ R_3)/198$	0.2853
	D	$(36\ R_1 + 54\ R_2 + 67\ R_3)/198$	0.2592
8	B	$(112\ R_1 + 160\ R_2 + 164\ R_3)/520$	0.2947
	E	$(112\ R_1 + 146\ R_2 + 148\ R_3)/520$	0.2850
9	B	$(22\ R_1 + 31\ R_2 + 35\ R_3)/101$	0.2998
	E	$(20\ R_1 + 28\ R_2 + 30\ R_3)/101$	0.2703
10	B	$(50\ R_1 + 70\ R_2 + 76\ R_3)/227$	0.3011
	E	$(44\ R_1 + 62\ R_2 + 79\ R_3)/227$	0.2707
	F	$(50\ R_1 + 65\ R_2 + 76\ R_3)/227$	0.2956

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