



Cyclic Conjugation in Benzo-annelated Ovalenes

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Abstract: The effect of small structural changes on the electronic properties of large benzenoid molecules is studied in the case of ovalene and its benzo-annelated derivatives. Two quantitative indicators of the intensity of cyclic conjugation in individual rings were used: the π -electron content and the energy effect. Most regularities observed can be rationalized by means of the classical Clar aromatic sextet theory, although a few second-order effects point towards the need to go beyond the Clar model.

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INTRODUCTION

Klaus Müllen and his coworkers have recently succeeded to synthesize benzenoid molecules of unprecedentedly large size (Watson et al. 2001). These π -electron systems proved to possess remarkable electronic, optical, and optoelectronic properties, suitable for a variety of technical applications and thus of great commercial value (Berresheim et al., 1999; Li et al., 2010; Figueira-Duarte and Müllen, 2011). The design of large benzenoids with technically desired properties requires the knowledge of the fine details of their electron configuration, in particular of the distribution and energetics of their π -electrons. The present work is the continuation of our earlier efforts to contribute to the better understanding of the electronic properties of large benzenoid molecules, and to help designing such molecules with desired properties (Balaban et al., 2010; Marković et al., 2012; Gutman et al., 2012a, 2012b; Radenković et al., 2012).

It is well known (Gutman and Cyvin, 1989) that the main physical and chemical properties of benzenoid molecules are determined by their π -electrons. These electrons are in a complicated manner cyclically delocalized, and the pattern of their cyclic conjugation can be followed by a variety of theoretical methods. In this work, as well as in our previous studies, we focus our attention to two quantitative indicators of cyclic conjugation, namely the π -electron content (EC) and the π -electron energy effect (ef) of individual rings. Details of the EC -method can be found in the papers (Randić and Balaban, 2004; Balaban and Randić, 2004; Gutman et al., 2004), whereas the details of the ef -method are described in the reviews (Gutman, 2005, 2009).

Ovalene is one of the largest benzenoid hydrocarbons known before Müllen's works. Its structure as well as Clar formula are depicted in the Figure 1. Also shown in Figure 1 are the EC - and ef -values of all rings of ovalene.

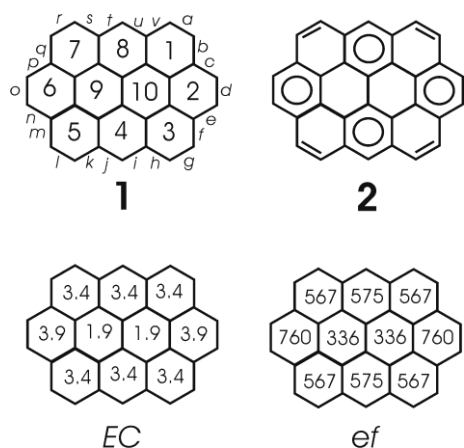


Figure 1: Ovalene (1) and its unique Clar formula (2). According to formula 2 it is expected that there is a strong cyclic conjugation in the rings 2, 4, 6, and 8, and that this conjugation is particularly weak in the rings 9 and 10. This is well reproduced both by the *EC*-values (= the effective number of π -electrons in the underlying ring) and by the *ef*-values (here and later given in β -units, multiplied by 10000; thus the *ef*-value of the ring 1 is 0.0567β , where $\beta \approx 137 \text{ kJ mol}^{-1}$).

NUMERICAL WORK

Ovalene has a total of 23 benzo-annulated derivatives (two mono-, six di-, six tri-, six tetra-, two penta-, and one hexabenzocongener). For all six-membered rings of ovalene and all its derivatives (a total of 312 rings), the *EC*- and *ef*-values were calculated using our in-house software. These numerical results can be obtained from the authors (S.G-S. and M.J.) upon request. In what follows, we discuss in detail only a few selected examples.

In Figure 2 we present the plot of the calculated *EC*-values versus the respective *ef*-values. As expected, there is a reasonably good monotonically increasing correlation between these two measures of cyclic conjugation, reflecting the fact that the (stabilizing) energy-effect of cyclic conjugation is proportional to the π -electron content in the respective ring.

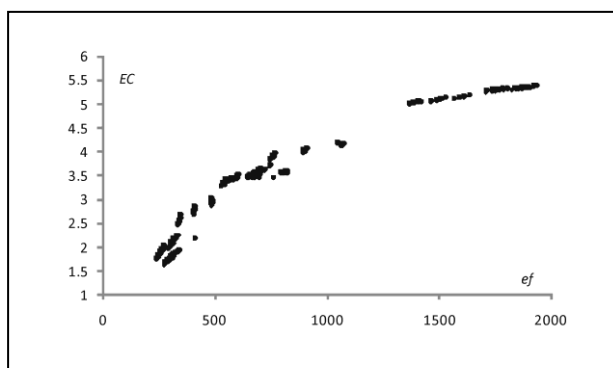


Figure 2: The π -electron contents *EC* of all six-membered rings of ovalene and all its benzo-annulated congeners, plotted versus the respective energy effects *ef*, 312 data points.

DISCUSSION

The simplest and most direct way by which one gets an insight into the modes of cyclic conjugation of a benzenoid molecule is Clar's aromatic sextet theory (Clar, 1972); its details are outlined also in the book (Gutman and Cyvin, 1989). The essence of Clar theory is that so-called "Clar formulas" are constructed by placing "aromatic sextets" into some rings of a benzenoid molecule, obeying certain formal rules (Gutman and Cyvin, 1989; Balaban, 2004). Rings in which "aromatic sextets" are located are predicted to have a high intensity of cyclic conjugation. The original version of Clar's method is qualitative and has no direct foundation in quantum theory. Eventually, much effort has been done to provide a quantitative and theory-based reformulation of Clar theory (Aihara, 2003; Portella *et al.*, 2005; Gutman *et al.*, 2005, 2006; Salem *et al.*, 2009; Randić and Plavšić, 2011). Anyway, recent works (Gutman *et al.*, 2012a, 2012b; Radenković *et al.*, 2012) showed that in some benzenoid systems, Clar theory yields incorrect results. In what follows we will also point at a property of some benzo-annulated ovalenes, violating the predictions of Clar theory.

In Figure 3 are depicted dibenzo[*a,g*]ovalene (3) and its unique Clar formula (4). This is an example of a benzo-annulated ovalene in which the Clar theory is fully applicable.

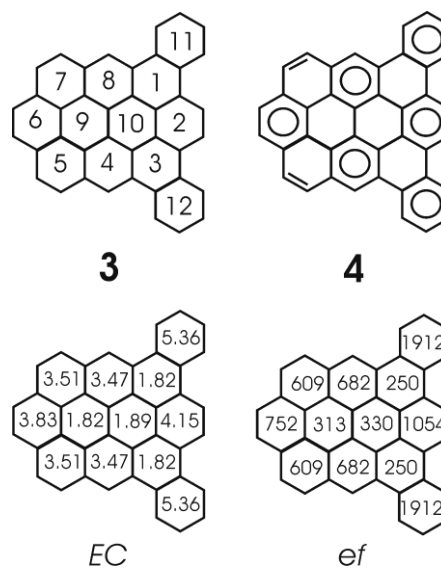


Figure 3: Dibenzo[*a,g*]ovalene (3) and its unique Clar formula (4). The *EC*- and *ef*-values are in good agreement with the predictions of Clar theory: in the rings 2, 4, 6, and 8 cyclic conjugation is strong, and stronger than in ovalene, whereas in the central rings 9 and 10 it is weak and weaker than in ovalene (cf. Figure 1).

From Figure 1 we see that the fixed double bonds in the Clar formula of ovalene are in positions *a*, *g*, *l*, and *r*. Therefore, the benzenoid system obtained by benzo-annulation in any of these positions has a unique Clar formula. Accordingly, cyclic conjugation is increased in the rings 2, 4, 6, and 8, and decreased in the central rings 9 and 10. This regularity in the conjugation pattern of benzo-annulated ovalenes is seen by comparing Figures 1 and 3.

Benzo-annulation in positions *d* and/or *o* causes a significantly different change in the conjugation modes of the ovalene core. As a characteristic example, we consider dibenzo[*d,o*]ovalene. In Figure 4 is depicted its formula (5) and three of its 20 Clar formulas (6,7,8).

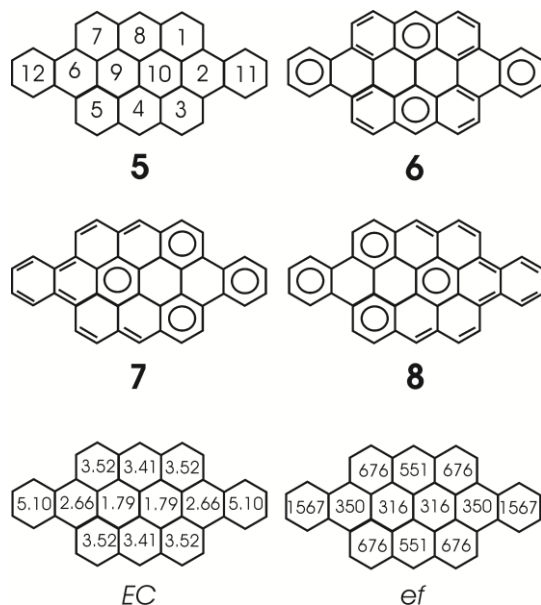


Figure 4: Dibenzo[*d,o*]ovalene (5) and three of its 20 Clar formulas (6,7,8). Formula 6 seems to be in the best agreement with the calculated *EC*- and *ef*-values. Therefore, our guess is that this is the dominant Clar representation. According to the formulas 7 and 8, some cyclic conjugation should exist also in the rings 9 and 10, which would require that the *EC*- and *ef*-values of these rings be greater than in unsubstituted ovalene (cf. Figure 1). The fact that this is not the case, points towards a limitation of the Clar model.

Already the fact that dibenzo[*d,o*]ovalene has 20 different Clar formulas, implies that the application of the Clar model to this benzenoid hydrocarbon is neither simple nor unambiguous. The assumption that the all Clar formulas are equally important (Randić and Balaban, 2006, 2008; Randić and Plavšić, 2011) is evidently an oversimplification. From the *EC*- and *ef*-data shown in Figure 4, we conclude that the Clar formula 6 provides the best representation of the true π -electron configuration. In other words, 6 would be the dominant Clar formula of dibenzo[*d,o*]ovalene. Within the Clar model, the remaining 19 aromatic sextet formulas would cause only small perturbations of the initial pattern of cyclic conjugation. If so, then based on formulas 7 and 8, we would expect that cyclic conjugation in the rings 9 and 10 is stronger than in the unsubstituted ovalene (cf. Figure 1). This, however, is not the case: *d,o*-annulation decreases the intensity of cyclic conjugation in the central rings, a phenomenon violating Clar theory. This second-order effect in the pattern of cyclic conjugation of benzo-annulated ovalenes is one more example for the recently discovered limitations of the Clar model (Gutman et al., 2012a, 2012b). A theoretical explanation of these violations has not yet been achieved.

CONCLUSIONS

Our analysis of cyclic conjugation in benzo-annulated ovalenes can be summarized by the following general regularities. If annulation is done in positions *a*, *g*, *l*, and/or *r* (cf. Figure 1), then the respective benzo-derivative has a unique Clar formula which well reproduces the dominant modes of cyclic conjugation, and to some extent also their intensity. For these benzenoid systems, Clar theory is fully applicable. If annulation is done in positions *d* and/or *o*, then there exist several (sometimes quite numerous) Clar formulas, whose interpretation is difficult and ambiguous. The *EC*- and *ef*-values, calculated in this work, make it possible to single out the Clar formula that provides the best representation of the distribution and energetics of π -electrons. However, some of the fine details of the pattern of cyclic conjugation of such ovalene congeners cannot be correctly predicted by applying the Clar model.

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Summary/Sažetak

Istraživani su uticaji malih strukturnih promjena na elektronske osobine velikih benzenoidnih molekula, i to na primjeru ovalena i njegovih benzo-aneliranih derivata. Ispitivanja su vršena pomoću dva kvantitativna indikatora intenziteta ciklične konjugacije u pojedinačnim prstenovima, i to: π -elektronski sadržaj i energetski efekat. Većina uočenih pravilnosti može se objasniti pomoću klasične Clarove teorije aromatičnog sekteta, iako neki manje izraženi efekti ukazuju na potrebu da se proširi originalni Clarov model.