Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 76 (5) 733–741 (2011)
JSCS–4154
UDC 547.686:54.02+66.095.252.5:547.52
Original scientific paper

Effect of benzocyclobutadieno-annelation on cyclic conjugation in fluoranthene congeners

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(Received 1 December 2010)

Abstract: Earlier studies revealed that benzo-annelation has a peculiar effect on the intensity of cyclic conjugation in the five-membered ring of fluoranthene congeners. Now, the analogous effect of benzocyclobutadieno-annelation was examined and it was found show it is opposite to the effect of benzo-annelation: a benzocyclobutadiene fragment in angular (resp. linear) position with regard to the five-membered ring, decreases (resp. increases) the intensity of cyclic conjugation in the five-membered ring.

Keywords: fluoranthenes; Kekulé structure; polycyclic aromatic hydrocarbon; benzo-annelation; benzocyclobutadieno-annelation.

INTRODUCTION

Attaching a benzene ring to a carbon–carbon bond of a polycyclic conjugated molecule can be performed in two different ways: either as an ordinary benzo-annelation or by connecting the benzene ring *via* two new carbon–carbon bonds, referred to as a benzocyclobutadieno-annelation (or, abbreviated, BCBD-annelation), Fig. 1.

The effect of benzo-annelation on cyclic conjugation in various polycyclic conjugated systems was much studied: in acenaphthylene and fluoranthene congeners,[1–8] in other non-alternant conjugated molecules,[9,10] and in benzenoid hydrocarbons,[11–17] and a general theory thereof was developed.[18] The analogous effect of benzocyclobutadieno-annelation has until now not been examined at all.

In previous works, particular attention was paid to the effect of benzo-annelation on the intensity of cyclic conjugation in the five-membered ring of acenaphthylene and fluoranthene congeners.[1–8] Within these studies, the following five generally valid regularities could be established:

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doi: 10.2298/JSC101201061G

Rule 1. Benzo-annelation in an angular position to the five-membered ring increases the intensity of cyclic conjugation in the five-membered ring.

Rule 2. Benzo-annelation in a linear position to the five-membered ring decreases the intensity of cyclic conjugation in the five-membered ring.

Rule 3. The effects specified in Rules 1 and 2 are proportional to the number of benzo-annelated rings.

Rule 4. The effect of an angular benzo-annelation on the intensity of cyclic conjugation in the five-membered ring is significantly stronger than the analogous effect of linear benzo-annelation.

Rule 5. The effect of annelation at the "male" part of fluoranthene (positions a_3, a_4 and l_3, Fig. 2) is much weaker than the effect of annelation at the "female" part (positions a_1, a_2, l_1, and l_2, see Fig. 2).

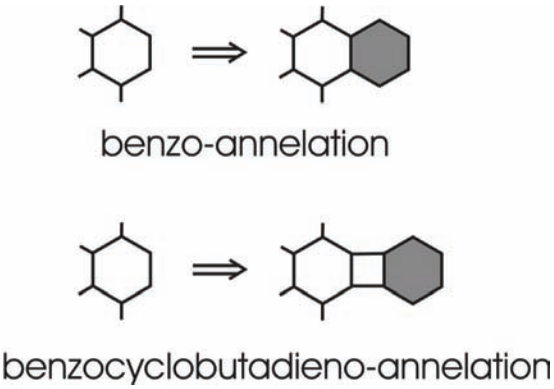


Fig. 1. Two ways in which a benzene ring can be annelated to a polycyclic conjugated system. In this work, the effects of the benzocyclobutadieno (BCBD) annelation on the intensity of cyclic conjugation in a ring of the parent conjugated system were studied for the first time (*cf.* Fig. 2).

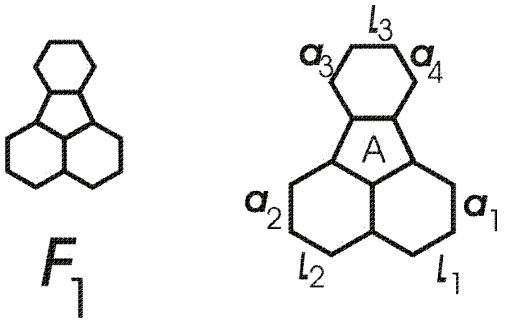


Fig. 2. Fluoranthene $\mathbf{F_1}$ and the sites where a benzo- or BCBD-annelation can occur. Sites marked by *a* and *l* pertain, respectively, to angular and linear annelation relative to the five--membered ring (A).

The intensity of cyclic conjugation can be assessed by means of the energy--effect (*ef*) of the respective ring. The theory of the *ef*-method has been outlined in two reviews.[19,20] For additional details see an older paper,[21] more recent articles,[16,17,22,23] and elsewhere.[4,11] For the present considerations it is sufficient to recall that the *ef*-values are expressed in units of the HMO carbon–carbon resonance integral β. Therefore, positive *ef*-values indicate thermodynamic sta-

bilization caused by cyclic conjugation, and the greater is *ef*, the stronger is the cyclic conjugation in the considered ring.

It should be noted that in previous works,[1–8] instead of "angular" constellation of a five- and a six-membered ring, their "PCP" constellation (where PCP is the abbreviation of "phenyl-cyclopentadienyl") was used. In these works,[1–8] RuAle 1 was referred to as the "PCP rule" or the "PCP effect". Since in the present work, we are going to consider benzocyclobutadieno-annelation will be considered, the term "PCP" would be misleading, and, therefore, the more plausible term "angular" is used (*cf*. Fig. 1).

The regularities stated here as Rules 1–4 were first discovered by calculating the *ef*-values of the five-membered ring. Eventually, these regularities were confirmed by a number of other, independent, theoretical approaches.[3,6,8,13]

In this paper, the regularities analogous to Rules 1–4 in BCBD-derivatives of fluoranthene (**F_1**) are studied. BCBD-annelation in fluoranthene may occur in the angular or in the linear mode, relative to the five-membered ring, as shown in Fig. 2.

NUMERICAL WORK

There exist four monobenzocyclobutadieno- (**F_2**–**F_5**), ten dibenzocyclobutadieno- (**F_6**––**F_{15}**), nine tribenzocyclobutadieno- (**F_{16}**–**F_{24}**), and three tetrabenzocyclobutadieno-fluoranthenes (**F_{25}**–**F_{27}**), *i.e.*, a total of 26 BCBD-annelated species. These, together with the labeling of their rings, are depicted in Figs. 3a and 3b.

The calculated energy effects of the five-membered ring (A) and of the attached benzene rings (R, S, T, U) of fluoranthene and its 26 BCBD-annelated derivatives are given in Table I. The analogous data for benzo-annelated fluoranthenes can be found in the literature.[2]

SOME REGULARITIES OBSERVED

By examining the data given in Table I, a number of regularities for the cyclic conjugation in BCBD-annelated fluoranthene-derivatives can be recognized.

The main observed regularities are the following.

Rule 1*. BCBD-annelation in an angular position to the five-membered ring decreases the intensity of cyclic conjugation in the five-membered ring.

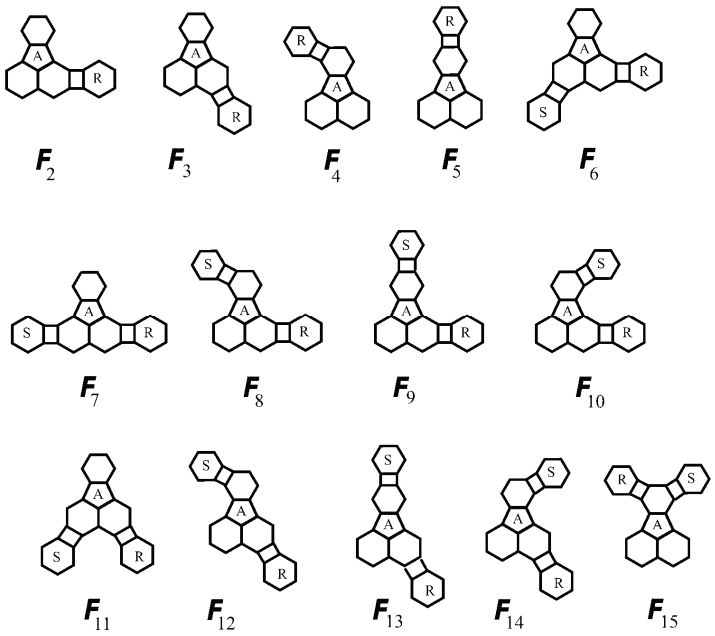
Rule 2*. BCBD-annelation in a linear position to the five-membered ring increases the intensity of cyclic conjugation in the five-membered ring.

Rule 3*. The effects specified in Rules 1* and 2* are proportional to the number of benzo-annelated rings.

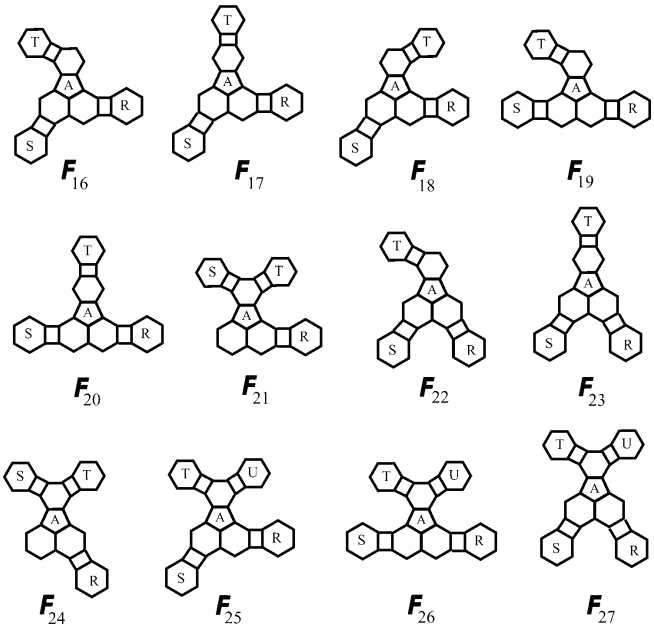
Rule 4*. The effect of an angular BCBD-annelation on the intensity of cyclic conjugation in the five-membered ring is significantly weaker than the analogous effect of linear BCBD-annelation.

Rule 5*. The same difference between "male" and "female" effects, as stated in Rule 5, exists also in the case of BCBD-annelation.

Rules 2* and 3* are convincingly illustrated by the following data: *ef*(**F_1**,A) = = 0.0031 (no BCBD-annelation); *ef*(**F_3**,A) = 0.0047, *ef*(**F_5**,A) = 0.0036 (one BCBD-



(a)



(b)

Fig. 3. a) Mono- and di-benzocyclobutadieno-annelated fluoranthenes, and b) tri- and tetra-benzocyclobutadieno-annelated fluoranthenes and the labeling of the attached benzene rings.

annelation); *ef*(**F**$_{11}$,A) = 0.0081 , *ef*(**F**$_{13}$,A) = 0.0060 (two BCBD-annelations); *ef*(**F**$_{23}$,A) = 0.0110 (three BCBD-annelations, maximum possible). Thus, due to Rule 2*, the cyclic conjugation in the five-membered ring of **F**$_{23}$ is roughly three times greater than in fluoranthene (**F**$_1$).

TABLE I. The energy effects (in β units) of the five- and six-membered rings of fluoranthene and its benzocyclobutadieno-annelated congeners (depicted in Figs. 2, 3a and 3b)

Molecule	*ef*(**F**,A)	*ef*(**F**,R)	*ef*(**F**,S)	*ef*(**F**,T)	*ef*(**F**,U)
F$_1$	0.0031				
F$_2$	0.0031	0.3439			
F$_3$	0.0047	0.5086			
F$_4$	0.0023	0.4459			
F$_5$	0.0036	0.4356			
F$_6$	0.0042	0.3183	0.5524		
F$_7$	0.0028	0.3705	0.3705		
F$_8$	0.0023	0.3433	0.4451		
F$_9$	0.0036	0.3431	0.4344		
F$_{10}$	0.0023	0.3438	0.4458		
F$_{11}$	0.0081	0.4287	0.4287		
F$_{12}$	0.0033	0.5225	0.4407		
F$_{13}$	0.0060	0.4903	0.4247		
F$_{14}$	0.0033	0.5245	0.4432		
F$_{15}$	0.0020	0.3375	0.3375		
F$_{16}$	0.0030	0.3180	0.5667	0.4434	
F$_{17}$	0.0052	0.3188	0.6316	0.4262	
F$_{18}$	0.0030	0.3184	0.5636	0.4416	
F$_{19}$	0.0022	0.3701	0.3705	0.4453	
F$_{20}$	0.0031	0.3703	0.3703	0.4343	
F$_{21}$	0.0020	0.3434	0.3371	0.3376	
F$_{22}$	0.0049	0.4463	0.4477	0.4371	
F$_{23}$	0.0110	0.4143	0.4143	0.4078	
F$_{24}$	0.0025	0.5359	0.3355	0.3370	
F$_{25}$	0.0023	0.3182	0.5759	0.3369	0.3358
F$_{26}$	0.0018	0.3702	0.3702	0.3373	0.3373
F$_{27}$	0.0034	0.4626	0.4626	0.3352	0.3352

Analogously, Rules 1* and 3* are illustrated by the following data: *ef*(**F**$_1$,A) = = 0.0031 (no BCBD-annelation); *ef*(**F**$_2$,A) = 0.0031, *ef*(**F**$_4$,A) = 0.0023 (one BCBD-annelation); *ef*(**F**$_7$,A) = 0.0028, *ef*(**F**$_8$,A) = 0.0023, *ef*(**F**$_{10}$,A) = 0.0023, *ef*(**F**$_{15}$, A) = 0.0020 (two BCBD-annelations); *ef*(**F**$_{19}$,A) = 0.0022, *ef*(**F**$_{21}$,A) = = 0.0020 (three BCBD-annelations); *ef*(**F**$_{26}$,A) = 0.018 (four BCBD-annelations, maximum possible). Thus, due to Rule 1*, the cyclic conjugation in the five-membered ring of **F**$_{26}$ is roughly two thirds that in fluoranthene (**F**$_1$).

From these examples, it can be seen that linear BCBD-annelation has a much stronger effect on cyclic conjugation in the five-membered ring than angular BCBD-annelation, as claimed by Rule 4*.

If both linear and angular BCBD-annelations are present, then their effect is a delicate combination of the effects described by Rules 1 and 2; for details see Table I. In all studied cases, the (magnifying) effect of linear annelation dominates over the (attenuating) effect of angular annelation. A characteristic example is **F$_6$** (one linear and one angular annelation), in which the cyclic conjugation in the five-membered ring is by some 33 % more intense than in fluoranthene itself.

There exist three pairs of isomers that differ in the position of an annelation at the sites a_3 and a_4 (Fig. 2). These are **F$_8$**–**F$_{10}$**, **F$_{12}$**–**F$_{14}$**, and **F$_{16}$**–**F$_{18}$**. These isomers of *cis*-like and *trans*-like types have almost identical modes of cyclic conjugation, which is just another manifestation of isoarithmicity.[2,24,25] For instance, for **F$_{16}$**, one has *ef*(A) = 0.0063, *ef*(R) = 0.1157, *ef*(S) = 0.1652 and *ef*(T) = 0.1308, whereas for **F$_{18}$**, they are *ef*(A) = 0.0062, *ef*(R) = 0.1169, *ef*(S) = = 0.1653 and *ef*(T) = 0.1321.

On comparing Rules 1–4 with Rules 1*–4*, it was immediately recognize that BCBD-annelation and benzo-annelation affect cyclic conjugation in exactly the opposite ways. In order to show the quantitative aspects of this opposite tendency, the correlation between the *ef*-values of the five-membered rings of benzo-annelated fluoranthenes and the *ef*-values in the analogous BCBD-annelated species is presented in Fig. 4.

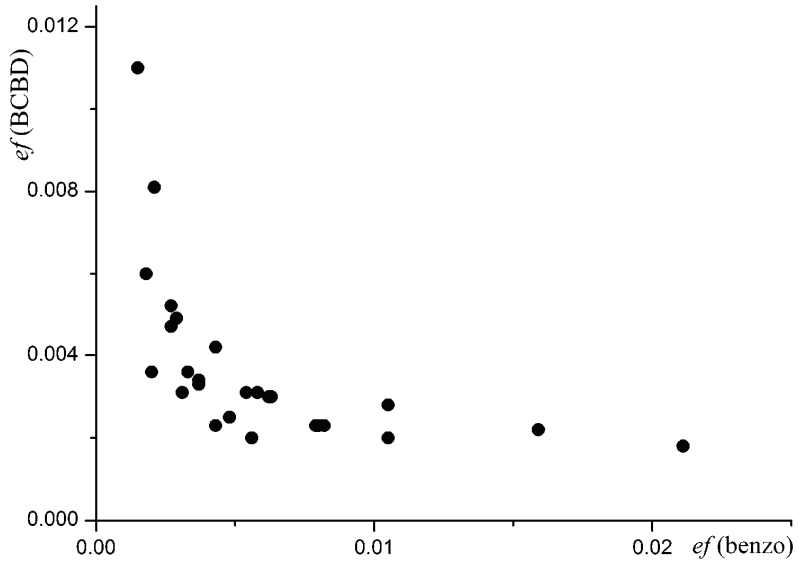


Fig. 4. The energy effects (*ef*) of the five-membered rings of BCBD-annelated fluoranthenes plotted *versus* the corresponding *ef*-values of the benzo-annelated species.

Plots of the energy effects of the benzene rings in BCBD-annelated fluoranthenes *versus* the analogous *ef*-values of the benzo-annelated species are shown in Figs. 5 and 6.

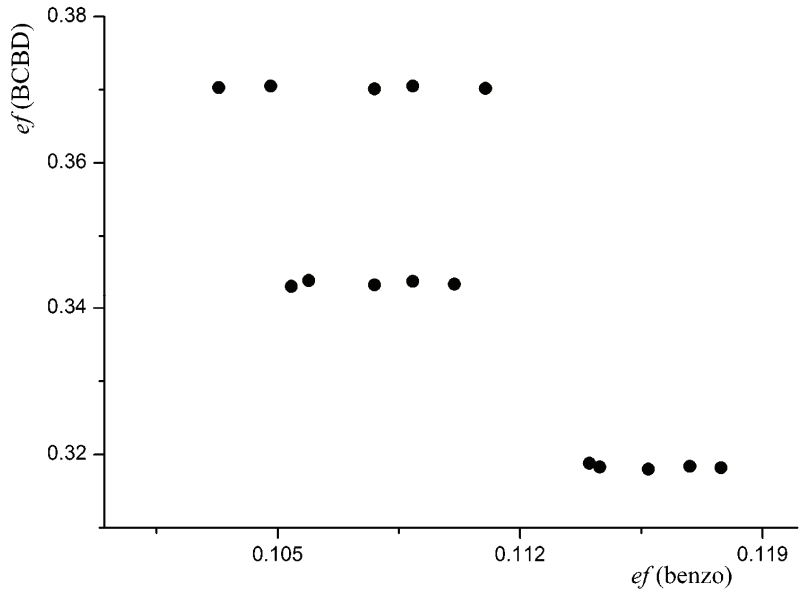


Fig. 5. The energy effects (*ef*) of the benzene rings of BCBD-annelated fluoranthenes in positions a_1 and/or a_2 (*cf.* Fig. 2), plotted *versus* the corresponding *ef*-values of the benzo-annelated species. For details see text.

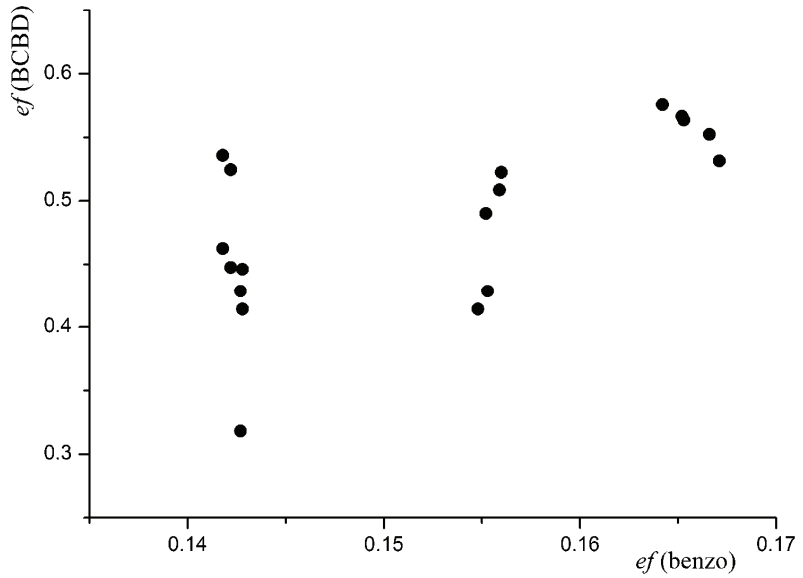


Fig. 6. The energy effects (*ef*) of benzene rings of BCBD-annelated fluoranthenes in positions l_1 and/or l_2 (*cf.* Fig. 2), plotted *versus* the corresponding *ef*-values of the benzo-annelated species. For details see text.

Figure 5 pertains to the angularly annelated benzene rings. Only annelation in the "female" positions, a_1 and/or a_2, are considered because of Rules 5 and 5^*. In harmony with Rules 1 and 1^*, it can be seen that benzo-annelation has a much stronger structure-dependency than BCBD-annelation. The data points are grouped into three clusters, depending on whether in the "female" part of the respective molecule there are two angular annelations (bottom), an angular and a linear annelation (top), or just a single angular annelation (middle).

Figure 6 pertains to the linearly annelated benzene rings. Again, in view of Rules 5 and 5^*, only annelation in the "female" positions, l_1 and/or l_2, are considered. In harmony with Rules 2 and 2^*, this time BCBD-annelation has a much stronger structure-dependency than benzo-annelation. The data points are grouped into three clusters, depending on whether in the "female" part of the respective molecule there are two linear annelations (right), a linear and an angular annelation (left), or just a single linear annelation (middle).

The data in Figs. 4–6 may be viewed as illustrations of the previously established Rules 1–4, the presently established Rules 1^*–4^*, and the fundamental differences between benzo- and benzocyclcobutadiene-annelations.

Acknowledgement. I. G. and B. F. thank the Ministry of Science and Technological Development of the Republic of Serbia for partial support of this work, through Grant No. 144015G.

ИЗВОД

УТИЦАЈ БЕНЗОЦИКЛОБУТАДИЕНСКЕ АНЕЛАЦИЈЕ НА ЦИКЛИЧНУ КОЊУГАЦИЈУ У ЈЕДИЊЕЊИМА ФЛУОРАНТЕНСКОГ ТИПА

ИВАН ГУТМАН[1], БОРИС ФУРТУЛА[1] и ALEXANDRU T. BALABAN[2]

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Ранија истраживања показала су да бензоанелација на специфични начин утиче на интензитет цикличне конјугације у петочланом прстену једињења флуорантенског типа. У овом ради проучен је аналогни утицај бензоциклобутадиенске анелације, и показано је да је он супротан утицају бензоанелације: бензоциклобутадиенски фрагмент у ангуларном (одн. линеарном) положају у односу на петочлани прстен, умањује (одн. увећава) интензитет цикличне конјугације у петочланом прстену.

(Примљено 1. децембра 2010)

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