Energetic properties of fluoranthenes

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Fluoranthenes form a class of polycyclic conjugated molecules, structurally very similar to benzenoid systems. They consist of two benzenoid units joined through a five-membered ring. The basic features of the structure dependence of the total \( \pi \)-electron energy of fluoranthenes have been established. The focus of the studies is on the joiner energy, i.e., the difference between the total \( \pi \)-electron energy of a fluoranthene and of its two benzenoid units.

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Fluorantheme (1) is a well-known tetracyclic conjugated hydrocarbon, present in large amounts in coal tar\(^1\). It consists of a benzene and a naphthalene unit, joined through a five-membered ring. Other polycyclic conjugated hydrocarbons, consisting of two benzenoid units joined through a five-membered ring are referred to as fluoranthenes (or fluoranthene-type benzenoids)\(^2\). A few examples of fluoranthenes are presented in Fig. 1.

Although the structures of fluoranthenes and benzenoid hydrocarbons are evidently similar, fluoranthenes were excluded from the chemical graph theoretical considerations of benzenoid systems because of the presence of the five-membered ring. As a result, while the topological theory of benzenoid molecules is nowadays one of the most thoroughly elaborated aspect of chemical graph theory\(^3-6\), the first attempts to develop an analogous theory of fluoranthenes started only very recently\(^2,7,8\).

In the present studies we report the results of a systematic study of the structure dependence of the total \( \pi \)-electron energy (\( E \)) of fluoranthenes. For details on total \( \pi \)-electron energy, as calculated within the simple Hückel molecular orbital (HMO) approximation, the reviews\(^9,10\), the recent papers\(^11-18\) and the references cited therein may be consulted. The general structure of a fluoranthene is shown in Fig. 2.

Theoretical

For the considerations that follow, we need to recall the concept of bay regions, well known in the theory of benzenoid molecules\(^4\), and to apply it to fluoranthenes\(^5\). On the boundary of fluoranthene molecules we distinguish between structural features called bays, coves, fjords, and lagoons. A few self-explanatory examples are given in Fig. 3.

Going along the boundary of a fluoranthene molecule, we encounter carbon-carbon bonds that have no attached hydrogen atoms. Such an isolated carbon-carbon bond forms a bay. Such two, three, and four consecutive carbon-carbon bonds form, respectively, a cove, fjord, and lagoon. In the case of planar fluoranthenes, no more than four consecutive hydrogen-free carbon-carbon bonds can occur on the boundary. If the number of bays, coves, fjords, and lagoons is denoted by \#B, \#C, \#F, and \#L, then the number of bay regions is:

\[
b = \#B + 2\#C + 3\#F + 4\#L
\]

Fig. 1 — Fluorantheme (1) and examples of fluoranthene-type benzenoid systems (2, 3, 4, 5). These species have 2, 7, 4, 9, and 10 bay regions, respectively, and their \( \Delta b \)-values are 2, 4, 2, 6, and 5, respectively. The bay regions of 4 are indicated by arrows. (For details see Fig. 3).
Fig. 2 — The general form of a fluoranthene-type benzenoid system (F), obtained by joining two benzenoid fragments (X and Y) through a five-membered ring. The fragment X may be referred as “female” and the fragment Y as “male”.

It is immediately clear that \( b \) is just the number of hydrogen-free carbon-carbon bonds on the boundary of the underlying fluoranthene (Figs 1 and 3).

The present study reports work done on the set of isomeric heptacyclic fluoranthenes (with one five- and six six-membered rings), having the formula \( \text{C}_{28}\text{H}_{16} \). This class of fluoranthenes has 96 members, some of which are depicted in Fig. 4. Eventually, the conclusions obtained for the \( \text{C}_{28}\text{H}_{16} \)-isomers were tested (and in all cases fully confirmed) on other sets of fluoranthenes, in particular on those with five and four hexagons.

**Results and discussion**

**Standard structure dependence relationships**

Because of the close structural similarity between fluoranthenes and benzenoid hydrocarbons, the obvious direction of this study was to examine if the relationships between total \( \pi \)-electron energy (\( E \)) and various molecular structural features, known to hold for benzenoids, are also obeyed by fluoranthenes. Two of the most important relationships (applicable to sets of isomers) are those involving the number of Kekulé structures (\( K \)) and with the number of bay regions (\( b \)).

For details on the \( E/K \)-dependence of benzenoid hydrocarbons see the reviews\(^{8,10} \) and the papers\(^{19-21} \). In nutshell, The \( E \)-values of isomeric benzenoids are strongly correlated with \( K \); this correlation is positive and is nearly linear.

Fig. 3 — Structural features on the boundary of fluoranthenes. Bays, coves, fjords, and lagoons pertain respectively to 1, 2, 3, and 4 carbon-carbon bonds without hydrogen atoms. The total number of these carbon-carbon bonds is called the number of bay regions. (For examples see Fig. 1, molecule 4).

Fig. 4 — Examples of fluoranthenes with six hexagons. There exists a total of 96 species of this type, all of which are isomers with formula \( \text{C}_{28}\text{H}_{16} \). Molecule 6 has minimal (\( = 39.4059 \)) whereas 7 has maximal (\( = 39.7941 \)) HMO total \( \pi \)-electron energy. Molecule 8 has minimal (\( = 0.8134 \)) whereas 9 has maximal (\( = 0.9346 \)) joinder energy.

In the case of fluoranthenes the \( E/K \)-dependence is essentially the same, as seen in Fig. 5. The spread of the data points is somewhat greater than that in the case of benzenoid systems and, as expected\(^{22} \), mainly due to difference in the number of bay regions.

For isomeric benzenoid molecules with equal number of Kekulé structures, the total \( \pi \)-electron energy, increases in an almost linear manner, with the number \( b \) of bay regions\(^{22,23} \). In the case of fluoranthenes precisely the same regularity has been found, as illustrated in Fig. 6.
Non-standard structure dependence relationships

The structure dependence relationships outlined in the preceding section imply that, as far as the total \( \pi \)-electron energy is concerned, the fluoranthenes behave almost identical to benzenoids. In order to find some energetic property of fluoranthenes that would significantly distinguish them from benzenoids, we considered the quantity \( \Delta E \), defined as the difference between the total \( \pi \)-electron energy of the fluoranthene \( F \) and the total \( \pi \)-electron energies of its two benzenoid units \( X \) and \( Y \), (cf. Fig. 2). Thus,

\[
\Delta E = \Delta E(F) = E(F) - [E(X) + E(Y)]
\]

We propose that this quantity be called “joinder energy”. Needless to say that the joinder energy has no counterpart in the theory of benzenoid molecules, and is thus a genuine energetic characteristic of fluoranthenes.

The joinder energies were computed for all members of the \( C_{28}H_{16} \) fluoranthene family. Plot of joinder energy versus the number of Kekulé structures \( K \) and that versus the total \( \pi \)-electron energy \( E \) are shown in Figs 7 and 8.

At first sight it appears that the data points in Figs 7 and 8 are distributed in a completely irregular manner.
However, a more careful inspection reveals two regularities:

(a) The data points are clustered in several (four) mutually disjoint groups.

(b) Within each such cluster, the energy released by joining two benzenoid units (that is the joinder energy, $\Delta E$) is correlated with the parameters $K$ and $E$. This correlation, although weak, is negative. It implies that the joinder energy $\Delta E(F)$ has a tendency to decrease with the increasing stability of the fluoranthene, i.e., with the increasing stability of the respective benzenoid units $X$ and $Y$.

In Fig. 4 are depicted the $C_{28}H_{16}$ fluoranthene isomers with minimal (8) and maximal (9) joinder energy. As seen from Fig. 4, these differ from the species with maximal (7) and minimal (6) total $\pi$-electron energy, respectively. This detail shows that Rule (b) above is only a rough approximation.

In connection with Rule (a) above, the obvious question is, which is the structural parameter of a fluoranthene that determines to which cluster the corresponding data point belongs to. By a trial-and-error examination we arrived at the following conclusion:

(c) The parameter that determines the cluster to which the ($\Delta E/K$)- and ($\Delta E/E$)-data points belong to is $\Delta b$, defined in analogy to $\Delta E$ as follows:

$$\Delta b = \Delta b(F) = b(F) - [b(X) + b(Y)]$$

The validity of Rule (c) in the case of the $C_{28}H_{16}$ fluoranthene isomers is evident from Fig. 8.

The parameter $\Delta b$ counts the hydrogen-free carbon-carbon bonds at and around the five-membered ring of the underlying fluoranthene. Its value is at least 2 and at most 6 (In the case of the $C_{28}H_{16}$ isomers, $\Delta b$ assumes the values 2, 3, 4, and 5, which is in harmony with the fact that the data points in Figs 7 and 8 form four clusters).

The true physical meaning of Rule (c) is not clear, but it is clear that $\Delta b$ somehow represents the structural details at the immediate vicinity of the five-membered ring of fluoranthene.

The results outlined in this article do not provide a complete solution of the structure dependence problem for the energy of fluoranthenes, but establish its basic features, and shall serve as a useful starting point for further research.

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