Resonance Energies of Nonbenzenoid Hydrocarbons†

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Resonance energies of 30 conjugated hydrocarbons and their molecular ions have been calculated on the basis of the graph-theoretical theory of aromaticity. No difficulty was found in extending the aromaticity theory to ionic conjugated species. In general, the resonance energies obtained correlated well with typical chemical features of the compounds.

The chemistry of nonbenzenoid hydrocarbons has occupied the interest of many organic chemists to an increasing extent. The synthetic accessibility of a number of nonbenzenoid hydrocarbons has given rise to a new field of organic chemistry.[1,2] In parallel with this, a theoretical understanding of their electronic structures, centered on their aromaticity, has been attempted in a variety of sophisticated manners.[3]

The classical concept of aromaticity, based primarily upon the Hückel (4n+2) rule, has been adequately applied to benzenoid hydrocarbons.[4] However, it appears less effective in predicting aromaticities of nonbenzenoid hydrocarbons.[4] Recently, the classical concept of aromaticity has been replaced by a graph-theoretical theory of aromaticity.[5-8] This theory has proven quite suitable for describing aromaticities of nonbenzenoid hydrocarbons as well as those of the other kinds of conjugated compounds.[5] There has been a qualitative idea that aromatic compounds should be unusually stable.[9] In this paper, I would like to further examine the stabilities of typical nonbenzenoid hydrocarbons by means of the graph-theoretical theory of aromaticity.

Results and Discussion

Resonance energies of 30 conjugated hydrocarbons **1**—**30** and their molecular ions have been calculated. They are mostly non-alternant pyrene-like compounds of synthetic importance. For the other types of nonbenzenoid hydrocarbons, see Ref. 5. The method used for calculating resonance energies is the graph-theoretical one previously presented by the author.[5,8] The HMO theory used is the simplest one. Resonance energies obtained are all listed in Table 1. As shown in this table, a comparative study is made for the neutral and ionic species with an even number of π-electrons. Conjugated hydrocarbons with an even number of π-electrons have been of prime interest to synthetic organic chemists.[1,2] Free radicals are hence omitted from consideration. In fact, it is not easy to rationalize their stability in terms of an HMO model.

Table 1. Resonance energies of nonbenzenoid hydrocarbons in units of β

Compound (M)	Resonance energy[a)] M^{2+}	M^{+}	M	M^{-}	M^{2-}
1	0.199	—	0.598(0.81)	—	0.199
2	−0.116	—	0.398(0.554)	—	−0.116
3	0.111	—	0.372(0.508)	—	−0.041
4	−0.057	—	0.376(0.522)	—	0.201
5	0.167	—	0.247(0.293)	—	0.255
6	−0.074	—	0.122(0.251)	—	−0.082
7	−0.270	—	0.217(0.353)	—	−0.104
8	−0.252	—	0.214(0.332)	—	−0.252
9	−0.084	—	−0.146	—	−0.084
10	−0.173	—	−0.016	—	−0.173
11	−0.376	—	0.222(0.246)	—	0.536
12	−0.289	—	0.106(0.254)	—	0.539
13	—	0.072	—	0.554	—
14	—	0.250	—	0.509	—
15	—	0.519	—	0.101	—
16	—	0.498	—	0.302	—
17	0.464	—	0.133(0.299)	—	−0.110
18	0.470	—	0.230(0.301)	—	−0.132
19	0.139	—	0.035(0.167)	—	−0.024
20	—	−0.179	—	0.267	—
21	−0.180	—	0.578(0.77)	—	0.316
22	—	−0.247	—	0.520	—
23	—	0.507	—	0.048	—
24	−0.248	—	0.303	—	0.679
25	−0.339	—	0.491	—	0.661
26	—	0.410	—	0.410	—
27	0.396	—	0.725(0.98)	—	0.398
28	0.230	—	0.506	—	0.125
29	0.407	—	0.508	—	0.037
30	−0.047	—	0.522	—	0.464

a) Values in parentheses are the resonance energies of Hess and Schaad.[9]

Pyrene-like tetracycles constitute the most attractive group of non-alternant hydrocarbons. It is interesting to see how these compounds are like or unlike the parent compound pyrene (**1**). Figure 1 shows the relative resonance energies of pyrene and its eight isomers (**2**—**9**) with the same formula of $C_{16}H_{10}$. First of all, pyrene (**1**) is quite a stable compound. Its resonance energy is almost twice as large as that of benzene ($0.273\,\beta$).[5] Most compounds cited in Fig. 1 have the largest resonance energy in the neutral 16-π-electronic state. They are Compounds **2**, **3**, **4**, **6**, **7**, and **8**. Stabilities of these compounds can roughly be justified by the fact that they have so far been synthesized.[10-15] One should here note that in general the easiness of synthesis is one of the most realistic measures of stability (or aromaticity) of a conjugated compound.[9,16]

Compound **5** has not been prepared yet. For this

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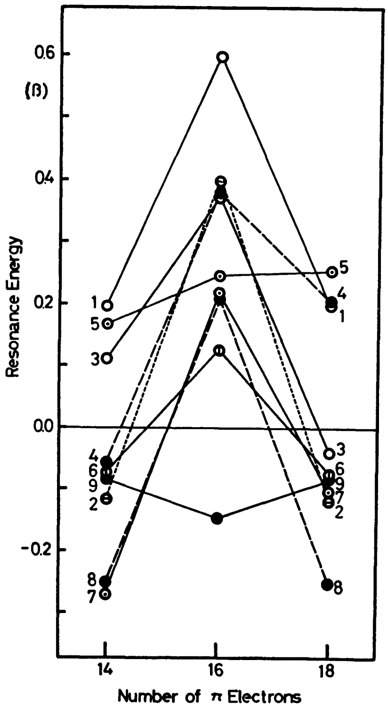
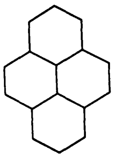


Fig. 1. Resonance energies of pyrene and its structural isomers.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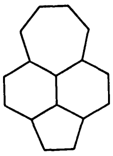
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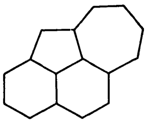
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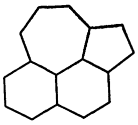
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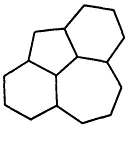
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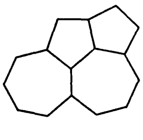
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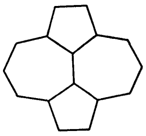
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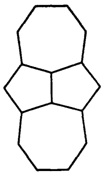
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compound, the resonance energy of the neutral species is not so large and is comparable to that of the dianion. Such a situation may be less favorable to the exclusive existence of either species. Aromaticity of this compound may be depicted by means of a perimeter model,[17] since a central double bond in the canonical structure is fixed there. The resonance energy of Compound **6** is small even in the neutral state. This compound appears to gain additional stability by locally introducing bond alternation.[18] The resulting system is an azulene conjugated with a triene unit. The resonance energy is comparable to that of azulene (0.151 β).[5]

An alternant isomer of pyrene (**9**) is antiaromatic because of its negative resonance energy. This compound, however, has been synthesized by Wilcox *et al.*,[19] but the NMR spectrum shows it to be paratropic, in accord with the resonance energy. Compound **10** is essentially nonaromatic, since a conjugated system of Compound **9** is stabilized by the third benzene ring. It has also been synthesized by Wilcox *et al.*[20]

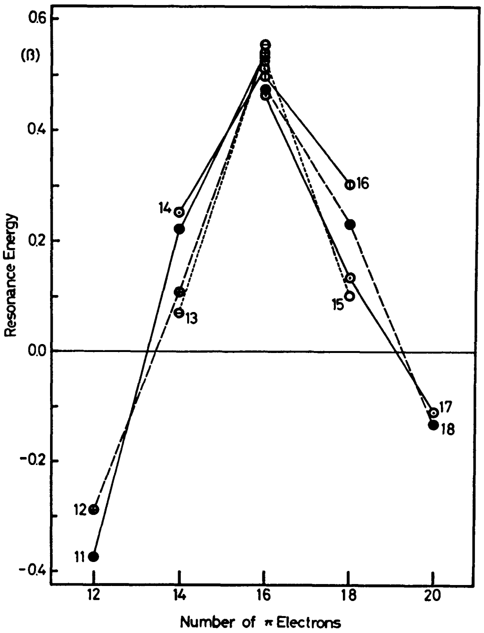
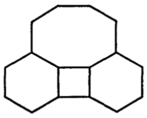


Fig. 2. Resonance energies of pyrene-like hydrocarbons.

Next, let us consider the aromaticities of eight conjugated hydrocarbons which are iso-π-electronic with pyrene (**1**); these are necessarily ionic species. The resonance energies are compared with each other in Fig. 2. One may notice at once that each of these compounds has the largest resonance energy when it has 16 π-electrons. Furthermore, it is noteworthy that the resonance energies of these 16-π-electronic species lie within a relatively narrow energy range of 0.46—0.56 β.

Compound **11** in its neutral state has not been prepared yet, although its dianion has been prepared by Trost *et al.*[21] This fact is quite consistent with the resonance energy of the dianion, which is twice as large as that of the neutral species. Compound **12** has also been prepared by Trost *et al.*[22] Its half-wave reduction potential is anomalously low, suggesting that this compound is not obviously aromatic. It readily reacts with butyllithium to form a dianion.[23] These aspects of the compound suggest reasons for the increased resonance energy of the dianion.

The anion of Compound **13** has been prepared by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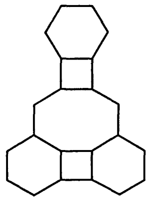
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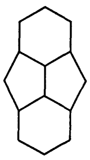
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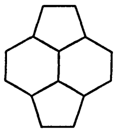
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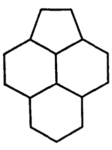
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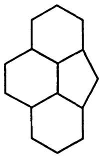
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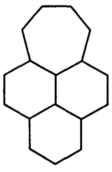
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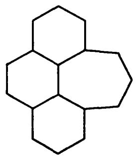
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Murata *et al.*[24] The NMR spectrum indicates that the charge is delocalized over the entire conjugated system. This result is in marked contrast to the anion of Compound **14**, which has been prepared by Cox *et al.*,[25] in that the latter ion appears from an NMR viewpoint to be a phenanthrene derivative. The two anions likewise have resonance energies as large as pyrene (**1**). The cationic species of these compounds have not been prepared. Cationic species of Compounds **15** and **16** have so far been synthesized by Murata *et al.*[26,27] It should be stressed that the synthetic accessibility thus correlates very well with the large resonance energies. Two compounds (**17** and **18**) have not been prepared, nor have their ions.

The methyl derivative of Compound **19** has been prepared by Hafner *et al.*[28] It is thermally unstable, protonates easily, and has a relatively high-field proton. These facts evidently reflect the olefinic character shown by the small resonance energy. A mononegative anion of Compound **20** has been synthesized by Wilner and Ravinovitz.[29] The positive resonance energy is again in line with its synthesis.

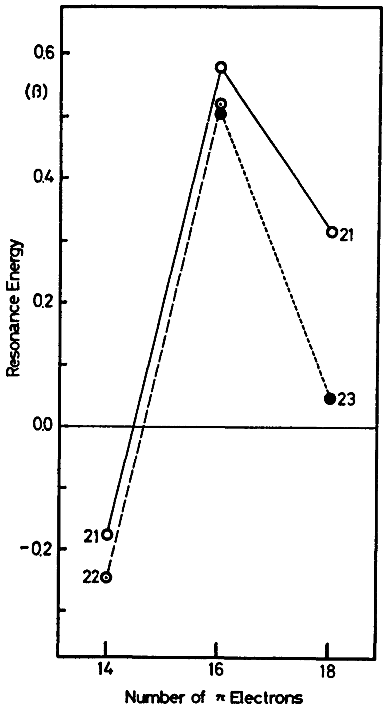
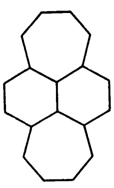


Fig. 3. Resonance energies of fluoranthene-like hydrocarbons.

Fluoranthene (**21**) is a structural isomer of pyrene (**1**). It is a stable nonbenzenoid hydrocarbon composed of two benzenoid units. The two iso-π-electronic species **22** and **23** have been synthesized by Murata and his coworkers.[30,31] In each of the 16-π-electronic ions, the charge is delocalized over the entire conjugated system. As shown in Fig. 3, these compounds likewise have the largest resonance energy in the 16-π-electronic state.

Derivatives of Compounds **24** and **25** have been prepared in their neutral state.[32,33] Every proton NMR signal of Compound **25** exhibits a downfield shift of 1—2 ppm compared with the corresponding signal of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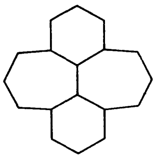
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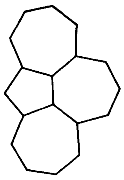
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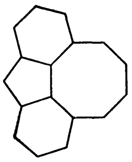
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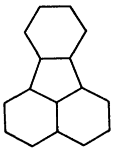
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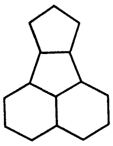
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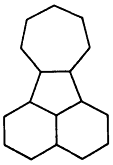
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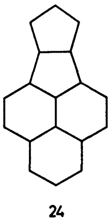
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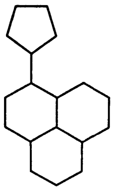
Compound **24**. This trend is in parallel with the order of magnitude of their resonance energies. In relation to these compounds, phenalene (**26**) is remakable in that it gives rise to a relatively stable anion and cation.[34] These mononegative and monopositive ions have the same resonance energies, which are seemingly large enough to justify the stability.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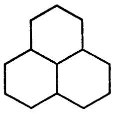
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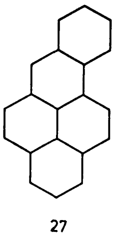
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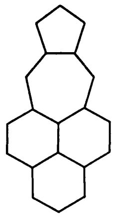
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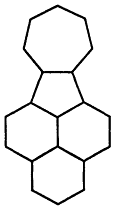
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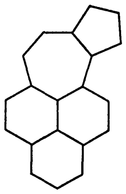
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Compounds **28**—**30** are a set of benzo[*a*]pyrene isomers, benzo[*a*]pyrene (**27**) being famous for its carcinogenicity. Benzo[*a*]pyrene is stable in our chemical sense. All the isomers considered here have been prepared.[2,35,36] Our resonance energies predict these isomers to be fairly stable in the neutral state, in accord with their chemical properties.[2] Figure 4 shows this aspect of the benzo[*a*]pyrene isomers.

As has been seen above, our definition of resonance energy has proven very effective in predicting the stability of a non-alternant hydrocarbon with or without electric charges. This supports a view that the same approach can be used for designing novel conjugated systems. For example, appropriate attempts to prepare dications of Compounds **17** and **18** are quite promising because of their large resonance energies.

It goes without saying that some other effects must be considered at the same time when one attempts to design a new conjugated system. The strain of a molecular framework is of course a destabilizing factor. When

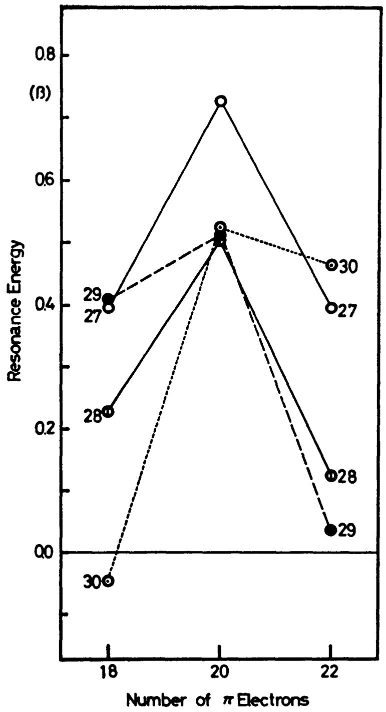

Fig. 4. Resonance energies of benzo[*a*]pyrene and its structural isomers.

a conjugated system is polycyclic, the resonance energy distribution is non-uniform in the system.[7] This may diversify the reactivity of the conjugated system. The least aromatic sites in the compound might be preferentially attacked by reagents even if the entire conjugated system has a large resonance energy.

The use of facilities of the Hokkaido University Computing Center is gratefully acknowledged. This work was motivated by a comprehensive review of Profs. I. Murata and K. Yamamoto on the condensed polycyclic conjugated systems (Ref. 2).

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