Hückel Molecular Orbital π Resonance Energies. The Nonalternant Hydrocarbons

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The resonance energies and resonance energies per π electron (REPE) have been calculated for 92 nonalternant hydrocarbons. An excellent correlation between REPE and the chemical behavior of the known compounds has been found. A new class of aromatic nonalternant hydrocarbons is proposed, the azulenoids, which consist of two or more fused azulene units. Examples of the azulenoids are compounds **49**, **51**, and **65**.

We have recently introduced a new method of obtaining π resonance energies of cyclic conjugated hydrocarbons using the simple Hückel molecular orbital technique.[1] Empirical π-bond energies were obtained from a series of acyclic polyolefins (a total of eight π-bond energies), and these are used in an additive fashion to obtain the π energy of the hypothetical "localized"[2] structure of a cyclic polyolefin. The difference between the HMO π energy and the additive "localized" energy of a cyclic polyolefin is defined as the resonance energy. Dividing this by the number of π electrons gives the resonance energy per π electron (REPE), a quantity that correlates well with experimental aromaticity. Molecules with a positive REPE (in units of β) are aromatic; those with REPE = 0 are nonaromatic, that is they behave like polyolefins; and those with negative REPE are antiaromatic.[3] We have successfully applied this method to a wide variety of benzenoid hydrocarbons.[4] Unlike HMO delocalization energies, REPE appears to be equally successful in the prediction of aromaticity of both alternants and nonalternants.

In the above we have followed Dewar's definition of aromaticity,[2] except that we have computed energies by the simple HMO method rather than by the more elaborate Pariser–Parr–Pople technique. It is interesting that the simpler method appeared to give slightly better results.[4] In part to test the generality of this observation, we examine in the present paper 92 completely conjugated nonalternants containing four-, five-, six-, and seven-membered rings. The classification proposed by Zahradník has been followed.[5] Should the simpler method continue to perform as well as the more complex, it can be used exclusively with considerable savings in computer time and cost, but, more important, results of the simpler method should be more easily analyzable in any attempt to determine the physical basis of aromaticity.

Our statement that REPE correlates well with experimental aromaticity requires some comment. There is in fact no quantitative experimental measure of "aromaticity." There is only a qualitative idea that aromatic compounds should be unusually stable, and that typically they should undergo substitution rather than addition reactions. We observe that in fact compounds with positive REPE usually are stable and do react by electrophilic substitution; the greater the REPE, the more true this is. Compounds with REPE = 0 are like polyolefins; they are not especially stable; and they react by addition. Compounds with negative REPE usually have not been synthesized or exist only fleetingly. We have not shown why this correlation should exist; we have only noted that it does exist. When we find exceptions, such as a compound computed to have a large REPE but for which synthetic attempts have failed, there are usually found to be easy conversion routes to another with still higher REPE. Since our definition of aromaticity is only qualitative, we can have only a qualitative correlation of aromaticity and REPE, but the point is that even this qualitative correlation is much superior to anything achieved with such earlier theoretical parameters as delocalization energy.

Results and Discussion

Total π energies, additive "localized" energies, resonance energies (RE), and resonance energies per π electron (REPE) are tabulated for compounds **1**–**92** in Table I. In addition, those for which either the parent compound or simple derivatives have been isolated (i) or observed in solution (s) are indicated. In a number of cases more than one localized structure can be drawn for a compound. The average of these energies, which never differ significantly, was used.[4]

A. Bicyclic.—Of the three possible bicyclic nonalternants (excluding ions or radicals) only azulene (**2**) has appreciable resonance energy. In agreement with this is its chemical behavior which is well known to be that of an aromatic hydrocarbon. Heptalene (**3**) with a slightly negative resonance energy should behave as a reactive polyolefin as is found to be the case. Dauben has reported its preparation in solution but found it to be too reactive to be isolated.[6] Pentalene with a high negative resonance energy has never been prepared despite numerous attempts. The success of the correlation of REPE with the chemical stability of these three bicyclics might be contrasted to the lack of correlation between delocalization energy and stability. The delocalization energies per π electron (DEPE) for **1**–**3** are 0.307, 0.336, and 0.302 β, respectively. Note that pentalene has a higher DEPE than does heptalene which is just the opposite of their known chemical behavior and their REPE's.

B. Tricyclic (Kata Condensed).—Only two of the 15 kata-condensed tricyclics **4**–**18** have significant resonance stabilization, cyclohept[*f*]indene (**15**) and cyclohept[*e*]indene (**16**). Neither has been prepared al-

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[2] (a) M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969); (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

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TABLE I

HÜCKEL π ENERGIES AND RESONANCE ENERGIES OF NONALTERNANT HYDROCARBONS IN UNITS OF β

Compd	Hückel	Additive	RE	REPE	Status[a]
1	10.456	10.596	−0.141	−0.018	—
2	13.364	13.132	0.231	0.023	i
3	15.618	15.668	−0.050	−0.004	s
4	13.309	13.612	−0.302	−0.030	—
5	13.416	13.640	−0.224	−0.022	—
6	15.872	16.148	−0.276	−0.023	—
7	15.889	16.120	−0.231	−0.019	—
8	15.870	16.148	−0.277	−0.023	—
9	16.203	16.176	0.027	0.002	—
10	16.231	16.121	0.110	0.009	i
11	15.899	16.148	−0.249	−0.021	—
12	18.413	18.656	−0.243	−0.017	—
13	18.395	18.684	−0.289	−0.021	—
14	18.533	18.711	−0.178	−0.013	—
15	18.894	18.657	0.237	0.017	—
16	19.038	18.684	0.354	0.025	—
17	21.338	21.193	0.145	0.009	—
18	21.097	21.220	−0.123	−0.008	—
19	12.995	13.610	−0.615	−0.062	—
20	16.366	16.146	0.220	0.018	i
21	16.619	16.146	0.473	0.039	i
22	18.911	18.682	0.229	0.016	i
23	19.145	18.682	0.463	0.033	i
24	20.913	21.218	−0.305	−0.019	—
25	18.749	19.164	−0.415	−0.030	—
26	19.097	19.164	−0.067	−0.005	—
27	21.890	21.646	0.244	0.015	—
28	21.749	21.673	0.076	0.005	—
29	21.745	21.700	0.045	0.003	—
30	21.757	21.700	0.057	0.004	—
31	29.144	29.252	−0.108	−0.005	—
32	29.336	29.252	0.084	0.004	—
33	29.151	29.280	−0.129	−0.006	—
34	29.343	29.280	0.063	0.003	—
35	29.122	29.308	−0.186	−0.008	—
36	29.347	29.308	0.039	0.002	—
37	24.220	24.208	0.012	0.001	—
38	24.381	24.208	0.173	0.010	—
39	24.402	24.236	0.166	0.009	—
40	24.238	24.236	0.002	0.000	—
41	24.553	24.236	0.317	0.018	—
42	24.473	24.208	0.265	0.015	—
43	24.503	24.180	0.323	0.018	—
44	24.445	24.180	0.265	0.015	—
45	24.528	24.208	0.320	0.018	—
46	24.502	24.236	0.266	0.015	—
47	24.455	24.236	0.219	0.012	—
48	24.511	24.236	0.275	0.015	—
49	24.595	24.236	0.359	0.020	—
50	24.522	24.208	0.314	0.017	—
51	24.583	24.208	0.375	0.021	—
52	24.529	24.236	0.293	0.016	—
53	22.210	21.700	0.510	0.032	—
54	24.745	24.236	0.509	0.028	—
55	21.959	21.697	0.262	0.016	—
56	22.036	21.699	0.337	0.021	—
57	22.063	21.725	0.338	0.021	—
58	24.595	24.233	0.362	0.020	—
59	24.396	24.235	0.161	0.009	—
60	24.525	24.261	0.264	0.015	—
61	16.194	16.626	−0.432	−0.036	—
62	19.128	19.162	−0.034	−0.002	—
63	19.280	19.162	0.118	0.008	—
64	22.030	21.698	0.332	0.021	—
65	22.051	21.698	0.353	0.022	i
66	21.949	21.698	0.251	0.016	i
67	24.401	24.234	0.167	0.009	i
68	24.298	24.234	0.064	0.004	—
69	26.552	26.770	−0.218	−0.011	—
70	19.426	19.162	0.254	0.018	s
71	19.410	19.164	0.246	0.018	—
72	19.494	19.162	0.332	0.024	—
73	22.252	21.698	0.554	0.035	i
74	21.993	21.700	0.293	0.018	—
75	22.206	21.698	0.508	0.032	i
76	22.220	21.698	0.522	0.033	i
77	24.533	24.234	0.299	0.017	—
78	24.537	24.236	0.301	0.017	—
79	24.608	24.234	0.374	0.021	—
80	35.666	35.285	0.381	0.015	—
81	46.807	46.361	0.446	0.013	—
82	57.948	57.437	0.511	0.012	—
83	69.089	68.514	0.574	0.011	—
84	35.782	35.285	0.497	0.019	—
85	46.982	46.361	0.621	0.018	—
86	58.180	57.437	0.743	0.018	—
87	69.378	68.514	0.864	0.017	—
88	35.822	35.284	0.538	0.021	—
89	47.064	46.360	0.704	0.021	—
90	58.305	57.435	0.870	0.021	—
91	69.547	68.511	1.036	0.021	—
92	67.455	66.454	1.001	0.021	—

[a] i, isolated; s, observed in solution; —, unknown.

though attempts at the synthesis of **15** have been made.[7] Bertelli[7b] thought that the failure of his attempted synthesis of a simple derivative of **15** was due either to the high reactivity of **15** because of its potential facile conversion to a benzenoid aromatic system by reaction with its environment or to the fact that it possessed essentially no π-electron delocalization. Our calculations suggest that the inability to isolate **15** is due to the former reason.

Compounds **9**, **10**, and **17** all possess relatively little resonance energy and should behave as polyolefins. The synthesis of *s*-indacene (**10**) has been reported by Hafner and its behavior is that of a polyene.[8] The remainder of the kata-condensed tricyclics have substantially negative REPE's; none have been prepared; and it would appear that further attempts at synthesis would be futile. Examination of the REPE's of **4** and **5** (−0.030 and −0.022 β) which are both π isoelectronic with azulene and which might be conceived of as having cyclic ten-π peripherial systems indicates the danger of applying the Hückel $4n + 2$ rule to other than monocyclic systems.[9]

C. Tricyclic (Peri Condensed).—Compounds **20–23** possess a significant amount of resonance energy as indicated by their high REPE's. The parent hydrocarbons **21** and **23**[10] and a dimethyl derivative of **22**[11] are known and exhibit normal aromatic behavior. A dimethyl derivative of **20** has been reported.[12] Com-

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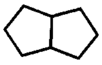
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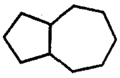
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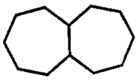
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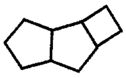
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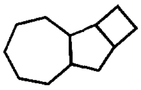
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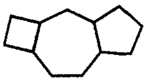
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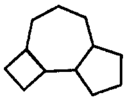
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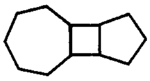
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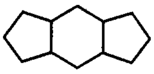
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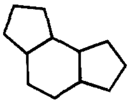
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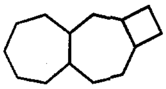
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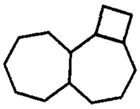
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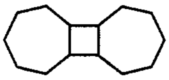
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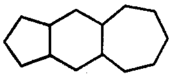
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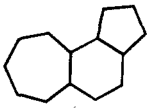
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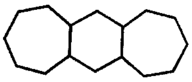
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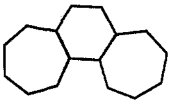
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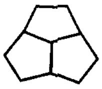
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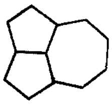
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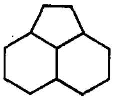
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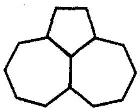
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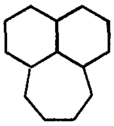
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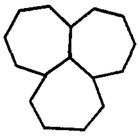
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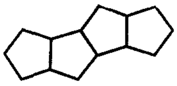
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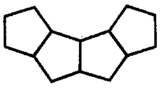
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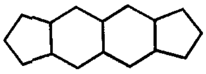
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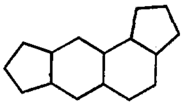
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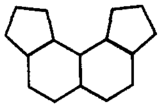
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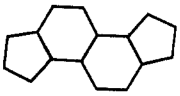
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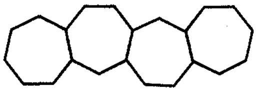
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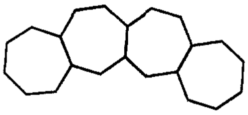
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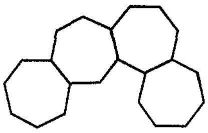
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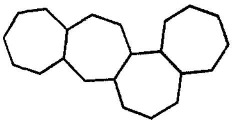
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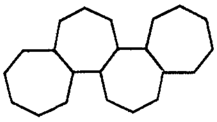
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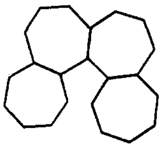
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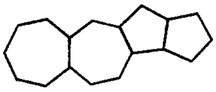
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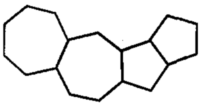
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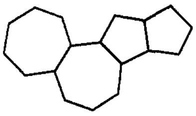
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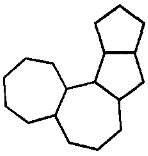
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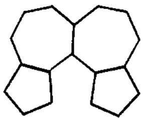
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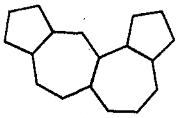
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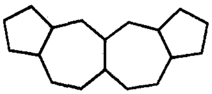
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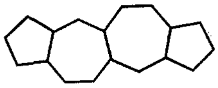
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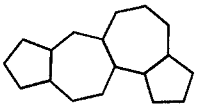
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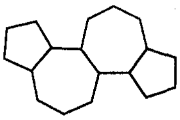
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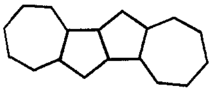
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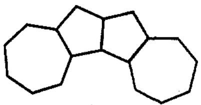
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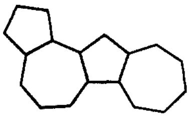
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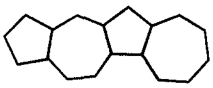
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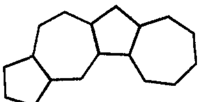
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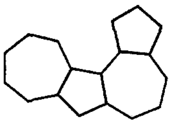
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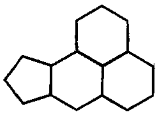
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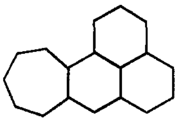
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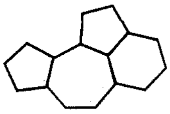
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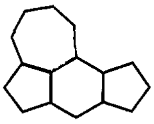
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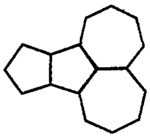
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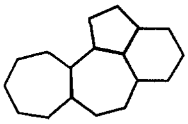
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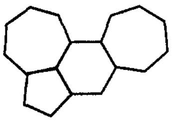
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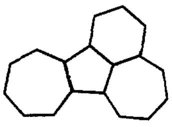
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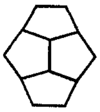
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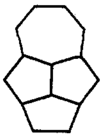
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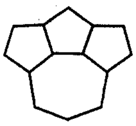
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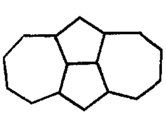
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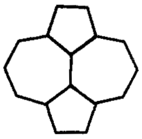
pound **20** does not behave as an aromatic hydrocarbon but as a polyolefin since it readily undergoes reaction with dienes and dienophiles. Hafner attributes its reactivity to angle strain and its ability to form the azulene system. The remaining two tricyclics **19** and **24** are predicted to be antiaromatic. Neither has been isolated.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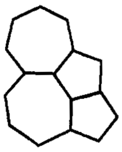
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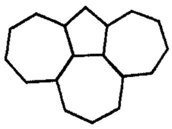
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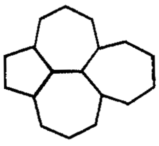
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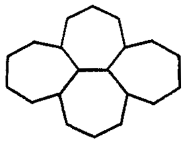
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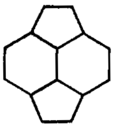
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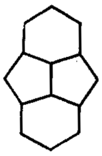
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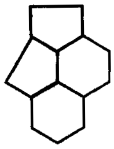
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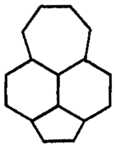
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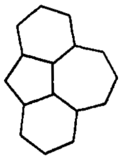
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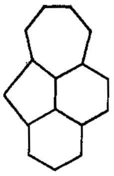
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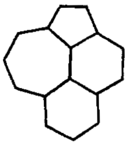
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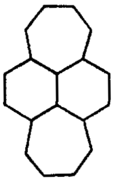
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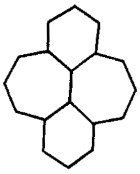
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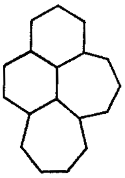
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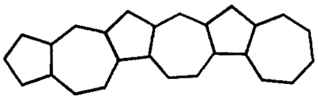
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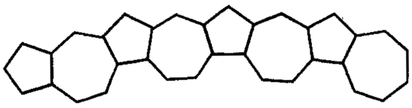
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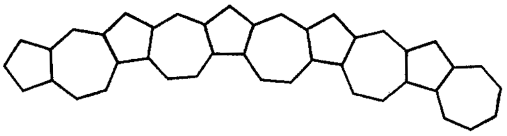
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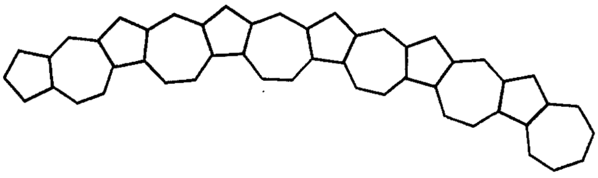
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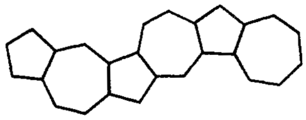
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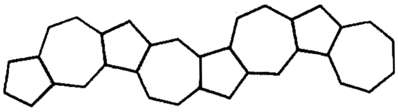
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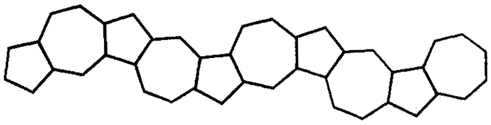
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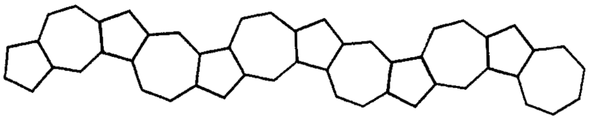
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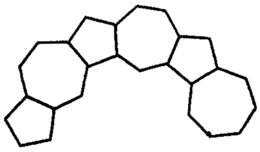
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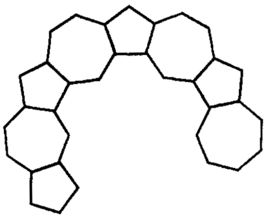
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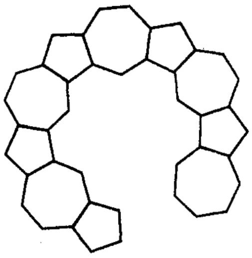
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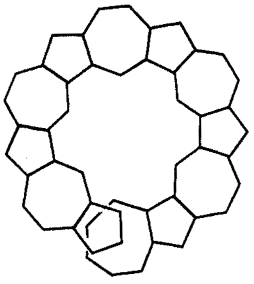
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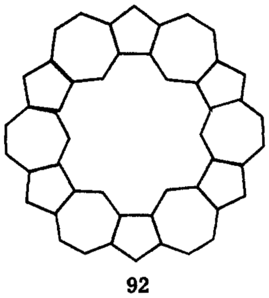
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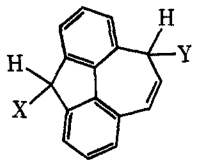
D. Tetracyclic (Kata Condensed).—One conclusion may be immediately made about the kata-condensed tetracyclics. Usually only those compounds which consist of two fused azulene units (**41–52**) appear to be potentially aromatic and therefore isolable. Compound **27** is not of this type but also is predicted to have significant resonance stabilization. However, potential conversion to a benzenoid system makes its isolation questionable. There is a remarkable constancy in the REPE's of **41–52**. They all fall between +0.015 and +0.021 β with the exception of **48**. Furthermore, all potential conversion products would be simple azulene derivatives. Since azulene has only a slightly higher REPE, these compounds all appear to be potentially stable aromatic systems (see further discussion below). None have yet been prepared.

E. Tetracyclic (Kata–Peri Condensed).—Compounds **53–60** all have significant positive REPE's with the exception of **59** and hence appear to be good candidates for aromatic systems. None have been reported, but a benz derivative of **53** has been reported to possess aromatic properties much like azulene.[13] Zahradník has previously examined the potential aromaticity of these compounds and has arrived at similar conclusions.[14] His conclusions were based mainly on specific delocalization energies (DE$_{sp}$); these are obtained by dividing delocalization energy by the number of C–C bonds. Although DE$_{sp}$ correlates quite well with REPE and therefore aromaticity for compounds of similar structure and size (*e.g.*, a good linear relation is found between DE$_{sp}$ and REPE of the 14-π tetracyclic systems in Table I), the correlation when systems of differing size and structure are considered is quite poor. For example, while hexatriene, trimethylenecyclopropane, fulvene, heptafulvene, and heptalene all have essentially the same HMO REPE[1] (all are predicted to be nonaromatic), their DE$_{sp}$ vary from 0.198 β for hexatriene to 0.278 β for heptalene, which is a considerably greater variation than is found between benzene (DE$_{sp}$ = 0.333 β) and azulene (DE$_{sp}$ = 0.306 β).

F. Tetracyclic (Peri Condensed).—Three compounds in this group have an REPE greater than +0.030 β: **73, 75,** and **76.** Their high REPE may be due partially to the presence of the naphthalene system in all three. All have been prepared and possess typical aromatic properties.[11,15,16] Of the remaining compounds a large number possess significant REPE (**64–66, 70–72, 74, 77–79**). The parent hydrocarbons **65** and **70** and methyl derivatives of **66** and **67** have been prepared.[17–20] Several attempted syntheses of **74** have failed.[21] Although **74** does possess significant REPE (0.018 β), its potential conversion to the biphenyl (**93**) by addition across the azulene system may make it a rather reactive system. It has also been noted that **74** may possess a triplet ground state.[22]



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Trost has recently reported the synthesis and properties of pyracyclene (**70**).[20] Although pyracyclene is stable in solution it cannot be isolated and, in general, exhibits a rather low stability. We suggest that its low stability may be due to its potential conversion to the more highly aromatic acenaphthylene system (+0.039 β). Trost's argument for the antiaromaticity of pyracyclene may be incorrect since he bases it mainly on the nmr spectrum of **70.** The use of nmr chemical shifts as a criterion for aromaticity has been seriously questioned.[23]

Both **61** and **69** are significantly antiaromatic, and neither has been prepared. Garratt and Sargent have suggested that since **61** has a $4n + 2$ periphery, it might be a good candidate for attempted synthesis.[24] Again we see the danger of applying Hückel's rule to polycyclic systems. For **61** we calculate an REPE of −0.036 β, which certainly will make this system antiaromatic.

Zahradník has computed a "stability index" for compounds **61–79.**[25] This index correlates reasonably well with REPE. However, it is based partially on DE$_{sp}$ and therefore its use is limited to a series of similar compounds such as the tetracyclic–peri-condensed systems.

H. Larger Systems.—The very similar REPE's of **41–52** suggested to us the possibility that larger ring systems containing three or more fused azulene units might produce stable aromatic nonalternant hydrocarbons. We therefore examined several series of alternating five- and seven-membered rings, **80–83, 84–87,** and **88–91.** The REPE's of the first series **80–83** drop well below the value of azulene (+0.023 β) as the number of rings increases, suggesting increased reactivity as the number of rings increases. This behavior is similar to that of the linear polyacenes where REPE falls quite drastically as the number of rings is increased in the naphthalene, anthracene .... series.[4] However, in the case of the second series, **84–87,** the REPE falls only slightly with increase in the number of rings. These potentially form a new series of stable aromatic nonalternants. The behavior of REPE in this series is again similar to that of a polyacene series, naphthalene, phenanthrene, chrysene .... in which the REPE falls off only slightly as the number of rings increases.[4] Even more striking is the constancy of the REPE in the third series **88–91.**

These observations suggested to us that nonalternants composed of two or more fused azulene units may well represent a new class of nonalternant aromatics for which we suggest the name azulenoids. For example, we predict that compounds **49, 51,** and **88** should possess aromatic properties very much like those of azulene.

In conclusion we again emphasize that a positive REPE of a compound is not necessarily the only requirement for chemical stability but possible conversion paths to more stable products must also be considered (*e.g.*, compound **70** as discussed above).[26]

Registry No.—**1,** 250-25-9; **2,** 275-51-4; **3,** 257-24-9; **4,** 26223-08-5; **5,** 253-01-0; **6,** 31151-50-5; **7,** 31151-51-6; **8,** 31151-52-7; **9,** 7001-11-8; **10,** 267-21-0; **11,** 210-65-1; **12,** 13375-70-7; **13,** 13375-69-4; **14,** 257-53-4; **15,** 270-19-9; **16,** 235-43-8; **17,** 259-63-2; **18,** 229-21-0;

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Cobalt-60 Radiation-Initiated Oxidation of Hydrocarbons in Emulsion[1]

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Aqueous emulsions of a variety of hydrocarbons under cobalt-60 irradiation have been allowed to react with molecular oxygen at pressures of 1–4 atm at 50°. Unlike the effect observed in polymerization, emulsification of styrene had no significant effect on the oxidation rate or products as compared to that observed in hydrocarbon solution. With emulsions of styrene and α-methylstyrene, dependency on the rate of initiation and temperature is consistent with the bulk mechanism, and the product distribution qualitatively parallels bulk oxidations. Other hydrocarbons investigated include cyclohexene, cyclopentene, tetramethylethylene, tetralin, and cumene. The efficiency of initiation by radiation varied from 10 to 40%.

The effect of emulsification on the oxidation of hydrocarbons has received attention from a number of researchers, largely in the hope of finding an increase in the kinetic chain length or variation in products. The information available at the start of our program was inadequate to tell what the effect of emulsification was on any oxidation process. For example, studies have been made on methyl oleate,[3] methyl linoleate,[4] aldehydes,[5] cumene,[6] and 1,1-diphenylethylene,[6] but in these cases all experiments were performed without controlled initiation. Thus a comparison of rate with that in solution is not possible. The literature also contains many other articles reported in a phenomenological manner which contribute little to the understanding of emulsion oxidation.

Recently Hyde and Verdin[7] have reported on the effect of emulsification on the radiation-induced oxidation of methyl oleate under controlled conditions. Although hydroperoxide is formed quantitatively in the initial stages of the reaction in both emulsion and bulk, the yield of the hydroperoxide decreases more rapidly with conversion in the emulsion system than in bulk. The rate of emulsion oxidation, based on the amount of methyl oleate present, is increased up to a factor of 5.8 over the bulk rate. This increase is attributed to an increase in initiation rate and not to an enhancement in chain length. Apart from this small enhancement of rate, the reaction kinetics seem similar to those of the homogeneous system.

Using emulsion polymerization[8-12] as a model for emulsion oxidation one might expect that emulsification should cause rate enhancement. Briefly, the theory of emulsion polymerization[13,14] has utilized the concept of isolation of the chain carriers in the soap micelle or polymer particle, thereby preventing termination. Further rate enhancement occurs due to the high viscosity of the growing particle,[12] which retards diffusion-controlled termination within the particle even after another chain carrier enters the particle. Since the oxidation of hydrocarbons also follows a free-radical mechanism,[15,16] emulsification is expected to have an effect if the concept of isolation of the growing chain carriers is important. If the high viscosity of growing particles is the main factor which causes enhancement of rate in emulsion polymerization, then enhancement would be expected to be small in cases where the product is of a low molecular weight such that there is little change in the viscosity of the particle with conversion. In the oxidation of olefins which form alternating copolymers with oxygen, there may be sufficient changes in viscosity so that some rate enhancement might be expected to occur. There is only a limited amount of data on the emulsion oxida-

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