Comparative Molecular Orbital Study of [6]-, [10]-, and [18]Annulenes and the Bridged [10]Annulenes

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Received May 16, 1984*

Abstract: Ab initio calculations have been carried out on representative free-standing annulenes (benzene, planar cis-[10]annulene, and [18]annulene) and the bridged [10]annulenes (1,6-methano[10]annulene, 1,5-methano[10]annulene, and 1,4,7-methino[10]annulene). Resonance energies and the tendency toward bond-length alternation are evaluated and compared for the free-standing annulenes which possess prefect orbital overlap as a result of coplanarity. These ideal annulenes are then used to provide a background for comparison of the much more common bridged annulenes in which delocalization is inhibited by nonplanarity and π-orbital misalignment. Attention is focused on the performance of nonempirical theoretical methods in the treatment of large conjugated π-electron systems, and the effects of basis set improvement and inclusion of electron correlation are considered in detail. The relevance of the annulene results to the nature of the electronic structure of conjugated polymers such as polyacetylene is also discussed.

The development of the Hückel $(4n + 2)$ π-electron rule placed the annulenes[1] at a focal point in the areas of synthetic, structural, physical, and theoretical organic chemistry. There is now vast literature on these compounds, and as a result of the ingenuity of experimentalists, a great deal has been learned about the properties of the higher annulenes. Work on the free-standing annulenes,[2] the bridged annulenes,[3,4] the dehydroannulenes,[2,5] the multicyclic annulenes,[5] the charged annulenes,[6] and the biradicaloid annulenes[7] represents a triumph in the area of synthetic organic chemistry and has contributed greatly to the diversity of available π-electron systems.

In some respects theory has lagged behind the synthetic advances in the field. In many cases where appeal is made to calculations, π-electron results are often cited.[8-25] Such methods

have provided excellent guidance to chemists, but it would also be desirable to have available more detailed calculations. In the main this void has been filled by semiempirical valence electron and molecular mechanics calculations which have been applied to reasonably large annulenes.[26-30] Apart from minimal[31] and extended[32] basis set Hartree–Fock (HF) calculations on [18]-annulene, nonempirical calculations have not been reported for conjugated systems with more than ten π-electrons.

In the present study we report the results of ab initio calculations on the free-standing annulenes (benzene (**1, 2**), planar cis-[10]-annulene (**3, 4**), and [18]annulene (**5, 6**)) and the bridged [10]annulenes (1,6-methano[10]annulene (**7-9**), 1,5-methano-

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[10]annulene (**10, 11**), and 1,4,7-methino[10]annulene (**12, 13**)).
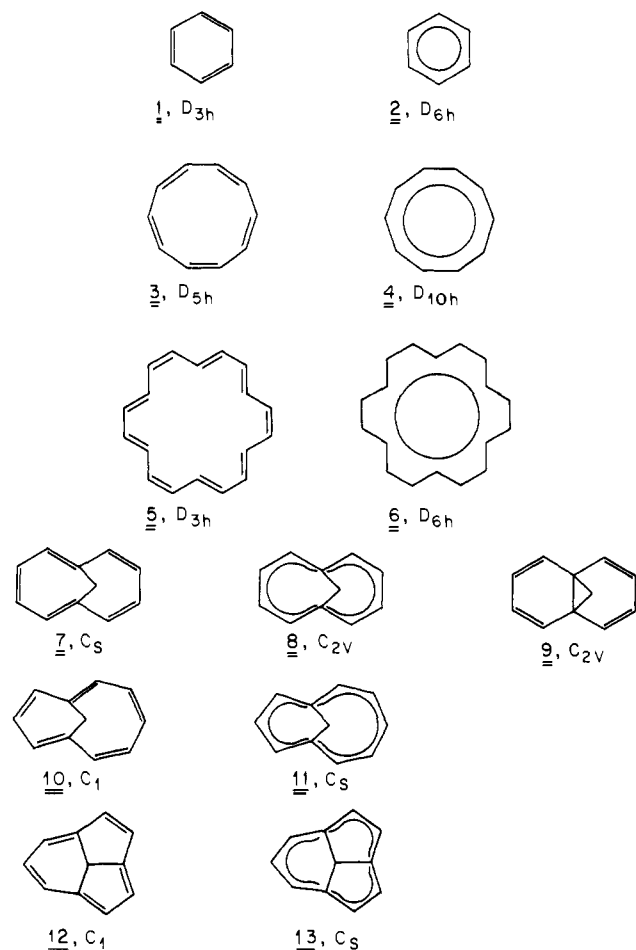
Our main purpose in this work is twofold: (i) to evaluate and compare the resonance energies and tendency toward bond-length alternation in representative free-standing annulenes with perfect orbital overlap as a result of coplanarity and (ii) to further compare these ideal annulenes with some of the much more common bridged annulenes in which delocalization is inhibited by non-planarity and π-orbital misalignment (**7–13**). Attention is also focused on the performance of nonempirical theoretical methods in the treatment of large conjugated π-electron systems. The effects of basis set improvement and inclusion of electron correlation are considered in detail. There is already compelling semi- and non-empirical theoretical evidence for the importance of these effects in achieving a balanced treatment of π-electron systems, and electron correlation is thought to play a crucial role in the transition from bond-length equilization to bond-length alternation in large annulenes.[28–30,33–36] The relevance of the annulene results to the nature of the electronic structure of conjugated polymers such as polyacetylene is also discussed.

As a result of the threefold disparity in molecular size which is spanned by the series of molecules chosen for study, the theoretical level of treatment is uneven. Nevertheless, for most molecules it has been possible to carry out a large basis set HF calculation and a small basis set calculation, including the effects of electron correlation. In this way an estimate is obtained of the result which might be obtained if it were actually possible to satisfactorily include basis set and electron correlation effects within a single calculation. Nevertheless, the calculation show large nonlinearities between molecules with different numbers of π electrons, and efforts to correct results on the annulenes by extrapolation must be viewed with some caution.
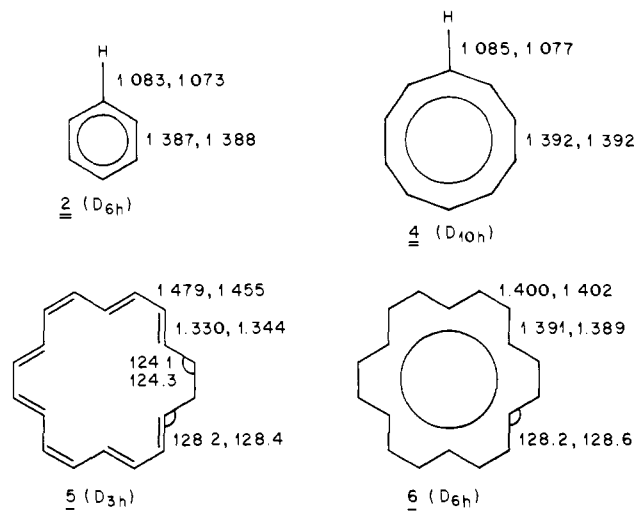
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Figure 1. HF/STO-3G and 6-31G calculated structures of the free-standing annulenes **2**, and **4–6** within specified symmetries.

Calculation Section

Computational. Most of the calculations were carried out with a version of the GAUSSIAN 80 program[37] modified for use on the CRAY-1 computer. HF calculations on highly symmetrical molecules possessing a threefold axis were carried out with a modified version of the HONDO 76 program.[38] The standard STO-3G,[39] 6-31G,[40] 6-31G*,[41] and 6-31G+5D basis sets were employed, and electron correlation effects were included by Moller–Plesset perturbation theory.[42,43]

Geometries. The molecular structures were optimized at the HF/6-31G theoretical level. In calculations on π-electron systems, the extended 6-31G basis set has been shown to perform reasonably well although it is clear that the extent of bond-length alternation is overestimated—a deficiency which is common to HF methods.[28-36] For comparison purposes, structural optimizations were also carried out with the minimal STO-3G basis set. The final calculated atomic coordinates of **5–13** are available as supplementary material.

Energies (Table I). The energies were calculated at widely different theoretical levels as a result of the variation in formula weight of the compounds studied (from 78 to 234 amu). Thus, while benzene energies were obtained up to MP4/6-31G+5D, it was only possible to examine [18]annulene at relatively modest theoretical levels. As noted earlier, the extrapolated energy values which are included in parentheses should be viewed with some caution. This is particularly true of the results obtained with the minimal STO-3G basis set which is normally not satisfactory for use in electron correlation calculations. Nevertheless, the values which may be checked against better quality calculations suggest that the trends are correctly reproduced.

Structural Models for Distortional Energies. Benzene retains a bond-equalized perimeter at all theoretical levels, and in order to provide a comparison with the higher annulenes at a uniform level, we adopted model[36,43] bond-alternate (BA; C—C = 1.46, C=C = 1.34, C—H = 1.08 Å) and bond-equalized (BE; C—C = 1.40, C—H = 1.08 Å) structures (C—C—C = 120° (**1, 2, 5, 6**); 144° (**3, 4**); C—C—H set to bisect C—C—C angle). In this way it was possible to obtain a comparison of the calculational tendency of the free-standing annulenes to adopt a bond-alternate perimeter, both as a function of ring size and of theoretical level.

Structural Models for Resonance Energies. As a starting point, we adopted the homodesmotic reaction scheme[44] for the resonance

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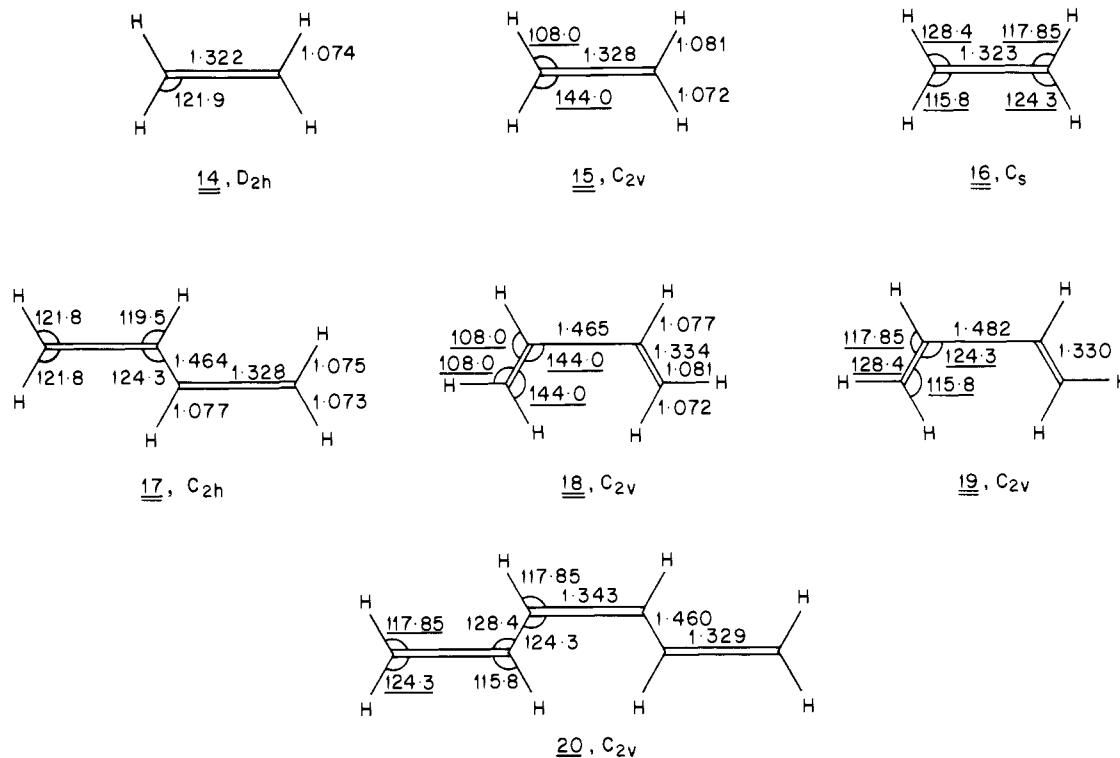
Figure 2. HF/6-31G calculated structures of the reference molecules **14–20** within specified symmetries. Underlined values were taken from (and constrained to) analogous annulene parameters for modeling purposes (see text).

energies—this allows for conservation of bond and hybridization types in the thermocycle. From this standpoint the benzene resonance energy is straightforward and may readily be obtained from the negative of the thermocycle 3 **17** → **2** + 3 **14** (Figures 1 and 2).

The resonance energy analysis of the higher annulenes is considerably more complicated due to the presence of angle strain and nonbonded interactions which are not included in the standard reference compounds (**14, 17**) used in the homodesmotic model. In planar *cis*-[10]annulene (**4**) the C–C–C bond angles are constrained to lie at 144° with the C–C–H bond angles (108°) set to bisect the carbon bond angles. Allowance must be made for the angle strain inherent in such a structure if a meaningful resonance energy is to be obtained. This may be accomplished by incorporating the deformation into the reference compounds (while optimizing all other parameters) and thus providing a mechanism for the cancellation of angle strain in the RE scheme which becomes the negative of the thermocycle 5 **18** → **4** + 5 **15** (Figures 1 and 2).

The situation with [18]annulene (**6**) is even more complex as allowance must be made for the internal nonbonded interactions as well as the angle strain. Although it is not immediately obvious, this may be accomplished by choosing the negative of the thermocycle 3(**19** + **20**) → (**5** or **6**) + 6 **16** (Figures 1 and 2). The substitution of a hexatriene for a butadiene fragment is permissible in the present instance as it has been shown that the bond energies in the linear polyenes are independent of chain length.[9,12,45,46] With the resonance energies defined in this way, a fairly uniform comparison of the three free-standing annulenes (**1–6**) is possible. Nevertheless, it must be remembered that benzene is slightly disadvantaged on this scale as the bond angles in the reference compounds (**14** and **17**) are fully optimized rather than being set to the values calculated for the annulene (120°) as in the case of **4** and **6** (Figures 1 and 2). Calculations to assess the magnitude of this effect find a maximum deviation of 3 kcal/mol from the REs which would be calculated with 120° bond angles in the reference compounds. The present approach, however, allows experimental contact with the theoretical thermocycle.

The calculated bond lengths of the reference molecules (**14–20**) are in good agreement with the available experimental evidence; **14**, C=C = 1.330;[47] **17**, C=C = 1.341, and C–C = 1.463 Å;[48] *trans*-hexatriene,

C=C(outer) = 1.337, C–C = 1.458, and C=C(inner) = 1.368 Å.[49] Previous HF theoretical geometries obtained with standard basis sets include the following: **14**, C=C = 1.306 (STO-3G),[50] 1.315 (3-21G),[51] 1.316 (4-31G),[50] and 1.317 Å (6-31G*);[52] **17**, C=C and C–C = 1.313 and 1.488 (STO-3G),[53] 1.321 and 1.467 (3-21G),[46] 1.318 and 1.490 (4-31G),[54] 1.323 and 1.468 Å (6-31G*);[46] *trans*-hexatriene, C=C(outer), C–C, and C=C(inner) = 1.319, 1.488, and 1.327 (STO-3G),[45] 1.322, 1.462, and 1.327 (3-21G),[46] 1.324, 1.463, and 1.329 Å (6-31G*).[46] As previously noted, the 6-31G basis set seems best suited for the calculation of polyene geometries within the HF approximation even though the degree of bond-length alternation is slightly overestimated in the absence of electron correlation effects. The bond angle constraints applied to **15**, **16**, and **18–20** exert a relatively minor effect on the other geometrical parameters.

Results and Discussion

1. Free-standing Annulenes. (1.1) Benzene (1, 2). Benzene is a particularly well-studied aromatic molecule, and the primary purpose for its inclusion in this study is to serve as a reference point for the higher annulenes. The 6-31G structure (Figure 1) is in good agreement with both previous theoretical studies[32,44,46,55,56] and recent experimental results (C–C = 1.396, C–H = 1.085 Å).[57]

The calculated resonance energies (Table II) are generally in fair agreement with the experimental value (21.2 kcal/mol)[44] and earlier theoretical estimates[32,46] although the STO-3G results are uniformly too high. Previous theoretical calculations of the benzene resonance energy have given rise to values of 30.3

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Table I. Total Energies

molecule	geometry	basis set	energy, hartrees			
			HF	MP2	MP3	MP4
1	BA	STO-3G	−227.882 30	−228.227 65	−228.277 91	−228.299 01
2	BE	STO-3G	−227.890 07	−228.239 05	−228.287 76	−228.309 65
2	6-31G	STO-3G	−227.890 86	−228.234 07	−228.282 30	−228.303 66
1	BA	6-31G	−230.613 44	−231.126 65	−231.154 34	−231.187 85
2	BE	6-31G	−230.623 43	−231.139 37	−231.165 36	−231.199 88
2	6-31G	6-31G	−230.624 47	−231.135 99	−231.162 27	−231.195 83
1	BA	6-31G+5D	−230.692 61	−231.436 25	−231.468 86	−231.511 27
2	BE	6-31G+5D	−230.701 25	−231.448 85	−231.479 15	−231.522 93
2	6-31G	6-31G+5D	−230.702 45	−231.447 67	−231.478 17	−231.520 90
2	6-31G	6-31G*	−230.703 09	−231.456 43		
3	BA	STO-3G	−379.615 26	−380.208 88	−380.294 99	−380.332 56
4	BE	STO-3G	−379.610 23	−380.222 11	−380.297 96	−380.340 27
4	6-31G	STO-3G	−379.610 70	−380.216 37	−380.291 87	−380.333 52
3	BA	6-31G	−384.187 87	−385.065 59	−385.110 75	
4	BE	6-31G	−384.193 41	−385.088 64	−385.122 18	
4	6-31G	6-31G	−384.194 26	−385.084 78	−385.118 76	
3	BA	6-31G+5D	−384.326 71	−385.577 99		
4	BE	6-31G+5D	−384.327 78	−385.603 03		
4	6-31G	6-31G+5D	−384.328 68	−385.601 28		
5	BA	STO-3G	−683.453 91	−684.516 52	−684.676 90	
6	BE	STO-3G	−683.398 01	−684.512 57	−684.646 28	
5	STO-3G	STO-3G	−683.495 38	−684.548 83	−684.710 70	
6	STO-3G	STO-3G	−683.438 55	−684.544 90	−684.675 75	
5	6-31G	STO-3G	−683.491 72	−684.554 44	−684.714 07	
6	6-31G	STO-3G	−683.438 38	−684.544 14	−684.674 80	
5	BA	6-31G	−691.644 98			
6	BE	6-31G	−691.636 46			
5	STO-3G	6-31G	−691.702 62			
6	STO-3G	6-31G	−691.680 68			
5	6-31G	6-31G	−691.706 97			
6	6-31G	6-31G	−691.680 89			
5	BA	6-31G*	−691.913 88			
6	BE	6-31G*	−691.878 10			
5	STO-3G	6-31G*	−691.951 31			
6	STO-3G	6-31G*	−691.919 66			
5	6-31G	6-31G*	−691.953 24			
6	6-31G	6-31G*	−691.919 85			
7	STO-3G	STO-3G	−417.144 81	−417.782 71	−417.876 79	−417.915 35
8	STO-3G	STO-3G	−417.135 50	−417.785 30	−417.868 93	−417.910 65
9	STO-3G	STO-3G	−417.172 60	−417.793 92	−417.890 03	−417.926 88
7	6-31G	STO-3G	−417.136 68	−417.781 41	−417.866 99	−417.907 54
8	6-31G	STO-3G	−417.134 16	−417.780 89	−417.864 00	−417.905 45
9	6-31G	STO-3G	−417.167 01	−417.791 21	−417.884 62	−417.921 52
7	6-31G	6-31G	−422.135 24	−423.112 30		
8	6-31G	6-31G	−422.135 22	−423.114 72		
9	6-31G	6-31G	−422.126 51	−423.089 83		
10	STO-3G	STO-3G	−417.120 10	−417.757 83	−417.855 62	−417.894 27
11	STO-3G	STO-3G	−417.093 85	−417.753 07	−417.836 30	−417.880 49
10	6-31G	STO-3G	−417.114 92	−417.756 31	−417.850 99	−417.889 85
11	6-31G	STO-3G	−417.092 58	−417.748 69	−417.831 70	−417.875 48
10	6-31G	6-31G	−422.105 92	−423.076 33		
11	6-31G	6-31G	−422.098 56	−423.085 77		
12	STO-3G	STO-3G	−415.982 50	−416.623 20	−416.712 37	−416.750 11
13	STO-3G	STO-3G	−415.972 40	−416.628 19	−416.705 02	−416.747 71
12	6-31G	STO-3G	−415.976 48	−416.624 05	−416.706 58	−416.746 03
13	6-31G	STO-3G	−415.970 98	−416.624 11	−416.700 79	−416.743 03
12	6-31G	6-31G	−420.954 99	−421.924 78		
13	6-31G	6-31G	−420.954 57	−421.930 30		
14	6-31G	STO-3G	−77.073 33	−77.192 83	−77.217 11	−77.225 64
14	6-31G	6-31G	−78.004 46	−78.182 57	−78.200 33	−78.211 13
14	6-31G	6-31G+5D	−78.031 32	−78.281 60	−78.303 19	−78.316 02
14	6-31G	6-31G*	−78.031 67	−78.284 43	−78.305 42	−78.318 82
15	M,6-31G	STO-3G	−77.042 61	−77.164 91	−77.189 71	−77.198 51
15	M,6-31G	6-31G	−77.975 81	−78.156 29	−78.174 32	−78.185 47
15	M,6-31G	6-31G+5D	−78.003 93	−78.256 47	−78.278 09	−78.291 32
16	M,6-31G	STO-3G	−77.070 49	−77.190 95	−77.215 36	
16	M,6-31G	6-31G	−78.001 64			
16	M,6-31G	6-31G+5D	−78.029 04			
17	6-31G	STO-3G	−153.019 02	−153.253 88	−153.296 83	−153.312 46
17	6-31G	6-31G	−154.864 58	−155.213 69	−155.242 43	−155.264 24
17	6-31G	6-31G+5D	−154.918 96	−155.415 65	−155.450 14	−155.476 76
17	6-31G	6-31G*	−154.919 56	−155.421 44	−155.454 75	−155.482 52
18	M,6-31G	STO-3G	−152.961 03	−153.200 86	−153.244 03	−153.260 47
18	M,6-31G	6-31G	−154.809 16	−155.162 83	−155.191 43	−155.214 23
18	M,6-31G	6-31G+5D	−154.865 39	−155.365 38	−155.399 72	−155.427 42

Table I (Continued)

molecule	geometry	basis set	energy, hartrees			
			HF	MP2	MP3	MP4
19	M,6-31G	STO-3G	-153.01025	-153.24824	-153.29101	
19	M,6-31G	6-31G	-154.85221			
19	M,6-31G	6-31G+5D	-154.90684			
20	M,6-31G	STO-3G	-228.95774	-229.31156	-229.37266	
20	M,6-31G	6-31G	-231.71709			
20	M,6-31G	6-31G+5D	-231.79968			

Table II. Resonance Energies (Referenced to Finite Polyenes)

scheme	mol	basis set	energy, kcal/mol[a]			
			HF	MP2	MP3	MP4
3(17-14) → 2	2	STO-3G	33.7	32.0	27.1	27.1
	2	6-31G	27.7	26.8	22.6	22.9
	2	6-31G+5D	23.7	28.6	23.4	24.3
5(18-15) → 4	4	STO-3G	11.7	23.0	12.7	14.9
	4	6-31G	17.3	32.7	20.8	(23)
	4	6-31G+5D	13.4	35.6	(24)	(26)
3(19 + 20 - 2 16) → 5	5	STO-3G	6.7	13.0	9.6	(12)
	5	6-31G	5.6			
	5	6-31G+5D	5.0			

[a] Values in parentheses were estimated by extrapolation.

Table III. Distortional Energies (Bond Equalized to Bond Alternate)

mols	geom	basis set	energy, kcal/mol[a]			
			HF	MP2	MP3	MP4
2 → 1	std	STO-3G	4.9	7.2	6.2	6.7
2 → 1	std	6-31G	6.3	8.0	6.9	7.5
2 → 1	std	6-31G+5D	5.4	7.9	6.5	7.3
4 → 3	std	STO-3G	-3.2	8.3	1.9	4.8
4 → 3	std	6-31G	3.5	14.5	7.2	(10)
4 → 3	std	6-31G+5D	0.7	15.7	(8)	(11)
4 → 3	6-31G	6-31G	-0.01	1.2		
6 → 5	std	STO-3G	-35.0	-2.5	-19.2	(-10)
6 → 5	std	6-31G	-17.9	(14)	(-3)	(7)
6 → 5	std	6-31G*	-22.5	(10)	(-7)	(3)
6 → 5	STO-3G	STO-3G	-35.7	-2.5	-21.9	
6 → 5	6-31G	STO-3G	-33.5	-6.5	-24.6	
6 → 5	6-31G	6-31G	-16.4			
6 → 5	6-31G	6-31G*	-21.0			
8 → 7	STO-3G	STO-3G	-5.8	1.6	-4.9	-2.9
8 → 7	6-31G	6-31G	-0.02	1.5		
11 → 10	STO-3G	STO-3G	-16.5	-3.0	-12.1	-8.6
11 → 10	6-31G	6-31G	-4.6	5.9		
13 → 12	STO-3G	STO-3G	-6.3	3.1	-4.6	-1.5
13 → 12	6-31G	6-31G	-0.3	3.5		

[a] Values in parentheses were obtained by extrapolation.

(STO-3G),[32] 33.3 (4-31G),[32] 26 (3-21G),[46] and 23 kcal/mol (6-31G*)[46] at the HF level. A nonempirical calculation of the resonance energy of benzene utilizing a model wave function without conjugation for the reference energy obtained a value of 26 kcal/mol.[58]

In the case of the distortional energies (Table III) it is the HF results which are apparently in error (low). HF calculations usually give rise to force constants which are about 10–30% too stiff,[59] but in this case, the results obtained for benzene are a manifestation of the tendency of HF methods to overestimate the tendency toward bond alternation in conjugated systems.

(1.2) **Planar** *cis*-**[10]Annulene (3, 4).** Previous experimental[60-62] and theoretical[63,64] work has established that the planar *cis*-

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[10]annulene structures (3 and 4) are not local minima on the potential surface and are unlikely to be observable. Nevertheless, these structures provide a useful reference point in any comparative survey of the free-standing annulenes. Previous theoretical treatments have shown that planar *cis*-[10]annulene adopts the bond alternate structure (3) when optimized at the HF level with the STO-2G,[64] STO-3G,[64] 4-31G,[64] 6-31G,[33] and 6-31G*[36] basis sets although the extent of bond-length alternation [ΔR = (C—C) - (C=C) (Å)] is small with the more detailed basis sets [ΔR = 0.116 (STO-3G),[64] 0.032 (6-31G),[33] and 0.065 Å (6-31G*)].[36] It is for this latter reason that, when the standard geometries are used, **4** is preferred over the highly bond alternate **3** (ΔR = 0.12 Å) at the HF level (Table III). Nevertheless an optimization including the effects of electron correlation (MP2/6-31G) found structure **4** (C–C = 1.417 Å) to be the outright minimum within the D_{5h} point group.[33] The calculations on the standard geometries (Table III) suggest that inclusion of electron correlation at the MP2 level favors the bond-equalized structure by about 11 kcal/mol but that this effect is somewhat moderated by the higher order terms to give an electron correlation contribution in the vicinity of 8 kcal/mol in favor of **4**. Nevertheless, the assignment of a fully delocalized aromatic structure (**4**) to planar *cis*-[10]-annulene seems fairly secure.

The resonance energies show qualitatively the same behavior, although the electron correlation contribution at the MP2 level increases monotonically with the size of the basis set: 11 (STO-3G), 15 (6-31G), and 22 kcal/mol (6-31G+5D). This large contribution to the RE is considerably moderated by inclusion of the higher order terms. Values obtained by calculations with simpler basis sets have been used to obtain the extrapolated results in parentheses in Table II.

(1.3) **[18]Annulene (5, 6).** The bulk of the discussion of these results is reserved for to the next sections, but we note that in common with all previous HF-based theoretical treatments, the 6-31G (limited) geometry optimization gives rise to the bond-alternate **5** as the minimum on the D_{3h} potential surface.[26-32] Although far from complete, the electron correlation results show the importance of this effect on the relative energies of the bond-alternate and bond-equalized forms of the molecule (**5**, **6**). An X-ray crystallographic study[65] found no evidence for the bond alternation implied by **5** but rather a structure approximating **6** with ring bond lengths of 1.382 (inner) and 1.419 Å (outer).

Because the localized structure **5** is found to be the minimum at all theoretical levels employed in this study (and is therefore used in the RE themocycle), the REs do not show the same sensitivity to electron correlation and basis set effects.

(1.4) **Comparative Aspects of the Distortional Energies (1-6).** Symmetry has always held a particular fascination for chemists, and the trio of symmetry-related problems in (static) structural physical organic chemistry[66-69] seems about to be reduced to a

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(66) Hydrogen bonding in compounds such as the enol of acetylacetone (unsymmetrical);[67] bridging in the nonsolution state of the 2-norbonyl cation (symmetrical);[68] bond-length alternation in the annulenes. Among the lower annulenes, only cyclobutadiene remains questionable and even here a resolution has been put forward.[69]
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Table IV. Electron Correlation Energy Contributions to the Distortional Energies (Bond Equalized to Bond Alternate) at Standard Geometries

mols	basis set	no. of π electrons	HF → MP4, kcal/mol[a] total	per π electron
2 → 1	STO-3G	6	1.8	0.3
2 → 1	6-31G	6	1.2	0.2
2 → 1	6-31G+5D	6	1.9	0.3
4 → 3	STO-3G	10	8.0	0.8
4 → 3	6-31G	10	(6.5)	(0.6)
4 → 3	6-31G+5D	10	(10)	(1)
6 → 5	STO-3G	18	(25)	(1.4)

[a] Values in parentheses were estimated by extrapolation.

Table V. Relative Energies

mols	geom	basis set	energy, kcal/mol HF	MP2	MP3	MP4
3 2 → 5	6-31G	STO-3G	113.5	92.7	83.4	
3 2 → 5	6-31G	6-31G	104.4			
3 2 → 5	6-31G	6-31G*	97.9			
8 → 9	STO-3G	STO-3G	−23.3	−5.4	−13.2	−10.2
8 → 9	6-31G	6-31G	5.5	15.6		
7 → 10	STO-3G	STO-3G	15.5	15.6	13.3	13.2
7 → 10	6-31G	6-31G	18.4	22.6		
8 → 11	STO-3G	STO-3G	26.1	20.2	20.5	18.9
8 → 11	6-31G	6-31G	23.0	18.2		

single outstanding question: the ring size for the onset of bond-length alternation in the aromatic $[4n + 2]$annulenes.[70,71] For some time attention has been focused on [18]annulene in the belief that this molecule lay near the demarcation point. Although the molecule was first synthesized[72] in 1962, the structure has remained in doubt despite the best efforts of experimentalists and theoreticians. A recent series of particularly elegant studies by Oth and co-workers has swung the balance of the experimental evidence in favor of **6**, and these authors have included a detailed review of work on the structure of the compound.[73]

Virtually all of the previous SCF MO calculations which were carried out in the absence of electron correlation effects concur in finding the bond-alternate form of [18]annulene (**5**) to be more stable than the bond-equalized structure (**6**).[26–32] In the more recent calculations, this energy difference amounts to about 20–30 kcal/mol. The HF calculations with the more detailed basis sets (Table III) are in good agreement with this value although the STO-3G result is seen to represent an overestimate.

However, a number of workers have drawn attention to the importance of electron correlation effects in stabilizing delocalized aromatic structures over their localized counterparts.[26–35] A CNDO-based configuration interaction (CI) treatment found electron correlation contributions to favor the delocalized structures of benzene (**2**) and [18]annulene (**6**) by 24.2 and 53.9 kcal/mol, respectively, for relative total energies of 30.7 (**2** → **1**) and 31.8 kcal/mol (**6** → **5**).[28] Correspondingly, a UHF/MNDO study favors the delocalized form of [18]annulene.[29] In the same vein, a MNDOC calculation with electron correlation effects introduced via perturbation theory (PT) found a final relative energy of 1.1 kcal/mol (**6** → **5**) with electron correlation effects contributing 28.1 kcal/mol to the stability of the delocalized structure (**6**).[30]

The natures of the relative electron correlation contributions to the localized and delocalized structures of benzene, [10]-annulene, and [18]annulene are summarized in Tables III and IV. The values become sketchy as the size of the molecule and the detail of the calculations increase—in the case of [18]annulene, the results are particularly sparse, and it is clear from the other results that the preferential electron correlation contribution to the stability of the delocalized structure obtained with the STO-3G basis set may well represent an underestimate. It is also clear from Table IV that the preferential electron correlation contribution to the delocalized structure of the aromatic annulenes increases quite rapidly with ring size in a nonlinear manner, even on a per π-electron basis. As noted earlier, the situation with planar cis-[10]annulene seems fairly clear with the fully delocalized aromatic structure favored over the localized geometry (by about 10 kcal/mol). While our calculations on [18]annulene are very far from definitive, it is clear that the results are not

inconsistent with a delocalized aromatic structure (**6**) for the molecule. The available calculations on [18]annulene (Table III) are in quite good agreement with the results obtained with the MNDOC/PT treatment.[30]

The highest occupied molecular orbital energies of [18]annulene are calculated to lie at −6.83 (**5**) and −5.77 eV (**6**) at the HF/6-31G* level, which on correction[74] lead to estimated ionization potentials of 7.71 (**5**) and 6.90 eV (**6**), and similar values have been obtained by other authors.[30,31] A photoelectron spectroscopic study of [18]annulene gave rise to an experimental ionization potential of 7.23 eV, and in a companion theoretical study, the authors concluded that Koopmans' theorem (utilization of orbital energies) does not allow a detailed interpretation of the spectrum.[75]

(1.5) Comparative Aspects of the Resonance Energies (1–6). The resonance energies of [10]- and [18]annulene are found to be considerably larger than expected (Table II) on the basis of previous estimates. If the projected results are accepted, [10]-annulene (**4**) is calculated to possess a larger total resonance energy than benzene, although this does not hold on a per π-electron basis. Even the bond-alternate [18]annulene (**5**) is found to be significantly resonance stabilized. Previous HF calculations of the resonance energy of [18]annulene utilizing a different reference structure gave rise to values of −6.1 (STO-3G)[32] and 6.7 kcal/mol (4-31G).[32]

The π-electron treatments have generally found [10]annulene and [18]annulene to possess 40–70% and 30–55%, respectively, of the resonance energy of benzene.[8–25] The present calculations suggest that these values may represent a slight underestimate, at least in the case of [10]annulene. The available results in Table II provide the best estimates for the resonance energies as follow: benzene, 24; [10]annulene, 26; [18]annulene, 12, kcal/mol.

The best experimental estimate of the resonance energy of [18]annulene comes from an analysis of the enthalpy of conformational exchange which occurs in the solution state of the molecule. With the assumption that all the aromatic stabilization is lost in the transition state of this process, a resonance energy of ≤19 kcal/mol was derived.[76] From the available results in Table II it is not difficult to imagine that a high-level calculation of the resonance energy of [18]annulene could be consonant with this value.

An interesting comparison is provided by the relative energies of benzene and [18]annulene[77] as expressed by the eq 3 **2** → **5**. It may be seen in Table V that the calculated energy of this reaction is particularly sensitive to the size of the basis set and the electron correlation level. The best results are still far from the experimental value of 65 ± 6 kcal/mol[77] but clearly tending toward lower values as the calculational level is improved.

2. Bridged [10]Annulenes. (2.1) 1,6-Methano[10]annulene System (7–9). 1,6-Methano[10]annulene is probably the most heavily investigated annulene beyond benzene in terms of the derivatives prepared and properties studied.[4] Although the

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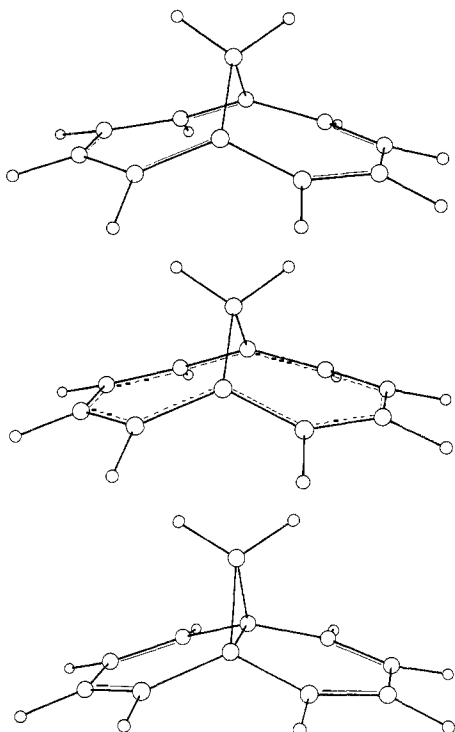(77) Oth, J. F. M.; Bünzli, J.-C.; de Zelicourt, Y. de J. *Helv. Chim. Acta* **1974**, *57*, 2276.

Figure 3. Plots of the HF/6-31G calculated structures of **7–9** within specified symmetries.

molecule was synthesized some 20 years ago,[78] there is little diminution in the attention that these compounds command. The 1,6-methano[10]annulenes,[4] together with the dihydropyrenes,[3] did much to usher in the fruitful era of bridged-annulene chemistry.

As befits its status in the field of annulene chemistry, 1,6-methano[10]annulene has been thoroughly investigated by experimentalists and theoreticians alike. The structural[79] and spectroscopic[4,80] studies leave little doubt that 1,6-methano-[10]annulene is an aromatic compound possessing the fully delocalized ground state implied by formula **8**. Nevertheless, it has been shown that the norcaradienic form **9** can be observed in the presence of suitable bridgehead substitution.[80,81]

The calculational studies of **8** include the application of extended Huckel theory,[82] force-field methods,[27,83–85] CNDO/INDO techniques,[86] and nonempirical HF theory;[86–88] apart from a UMNDO study,[29] none of the calculations have attempted to assess the importance of electron correlation effects in this system. Much of the previous theoretical work on **7–9** is summarized in the recent publication by Farnell and Radom[87] on this subject. In their study,[87] completely optimized structures (HF/STO-2G) and energies (HF/STO-2G, STO-3G, and 4-31G) were reported for **7–9** and a number of derivatives.[87] The previous STO-2G calculations[87] and the STO-3G results reported herein both favor the bond-alternate (**7**) over the bond-equalized structure (**8**) by about 5 kcal/mol. This energy difference is very much reduced in the extended 6-31G basis set optimizations, and the resulting structures (**7** and **8**) are very similar; nevertheless, we find **7** to
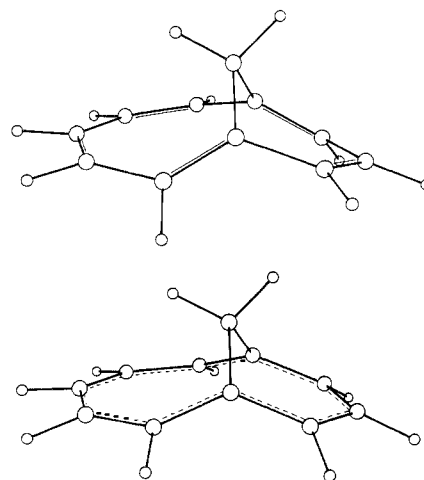
Figure 4. Plots of the HF/6-31G calculated structures of **10** and **11** within specified symmetries.

be favored at all levels of HF theory. The structure calculated for **8** (Figure 3) at the 6-31G level is in excellent agreement with a recent structural study,[79] and most of the theoretical parameters lie within the limits of the experimental estimated standard deviations. This basis set seems to provide a particularly good description of the geometries of conjugated organic molecules.[35]

The inclusion of electron correlation in the calculation at the MP2 level swings the energy balance in favor of **8** with both basis sets, although this trend is not maintained with the minimal basis set on inclusion of the higher order terms (MP3 and MP4).

The calculated relative energies of the annulenic (**7, 8**) and norcaradienic (**9**) structures are very sensitive to the size of the basis set and the inclusion of electron correlation (Tables III and V). The former effect stems primarily from the tendency of minimal basis sets to artifically favor three-membered rings at the expense of their olefinic counterparts, whereas extended basis sets exhibit exactly the opposite tendency.[89] The electron correlation contribution to the stability of the annulenic **8** as against the norcaradienic isomer **9** arises from the presence of an extended, delocalized π-electron system in the former compound in contrast with the localized, polyolefinic character of **9**.

(2.2) 1,5-Methano[10]annulene System (10, 11). The second of the bridged [10]annulenes to be synthesized, 1,5-methano-[10]annulene, was first reported by Masamune[90] in 1976, and since that time its chemistry has been extensively developed by Scott and co-workers.[91] In contradistinction to 1,6-methano[10]-annulene where the transannular homoaromatic interaction (to produce homonaphthalene character) does not interfere with the alternant character of the hydrocarbon, 1,5-methano[10]annulene (**11**) is rendered nonalternant by the transannular interaction, and this perturbation of the peripheral configuration is sufficiently well developed for the compound to be referred to as homoazulene.[91] Nevertheless, **11** seems to have been established as a bona fide aromatic bridged annulene, and while it is not as stable as its isomer **8**, the compound is comparable in many respects (Figure 4).

Apart from a molecular mechanics study,[27] there have been few theoretical investigations of this system. In agreement with this work, we also find large dihedral angles at the bridgehead carbon atoms. The misalignment of the pπ atomic orbitals in the conjugated system and the resultant strain are presumably responsible for the stabilization of the localized structure **10** at the expense of the aromatic **11** at the HF level. Nevertheless, at the

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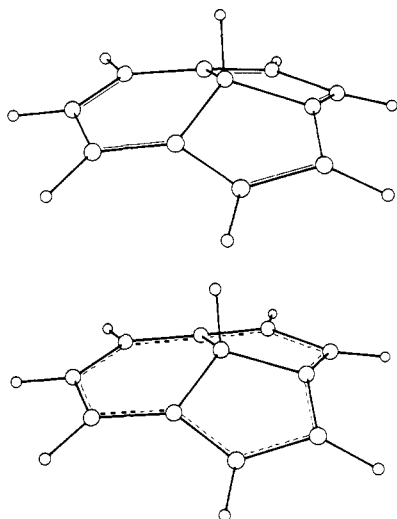
Figure 5. Plots of the HF/6-31G calculated structures of **12** and **13** within specified symmetries.

Table VI. Calculated Dipole Moments

| | dipole moment, D | |
mol	STO-3G	6-31G
7	0.34	0.62
8	0.41	0.61
9	0.01	0.10
10	0.25	0.68
11	0.47	0.89
12	0.48	0.59
13	0.29	0.46

extended basis set level, the second-order electron correlation term (MP2) makes a large contribution in favor of the aromatic **11**.

(2.3) 1,4,7-Methino[10]annulene System (12, 13). The most recent entry into the fold of bridged [10]annulenes, 1,4,7-methino[10]annulene, was first reported (as a methyl derivative) by Rees and co-workers in 1981.[92] Compelling evidence is already available for the pronounced aromatic character of this compound and its derivatives including the first isolable higher annulenol.[93] This latter synthetic study[93] seems to have been motivated by a MNDO theoretical investigation of keto–annulenol equilibria in this system.[94] The MNDO study[94] also included calculated structures for the centrally methylated derivative of **13** which was actually synthesized,[92] and the bond-equalized structure (**13**) is in good agreement with the 6-31G geometry shown in Figure 5, but the bond deformation found for **12** is more pronounced in the MNDO study. Thus, the single configuration MNDO calculation favors **12** by 6.4 kcal/mol, but with the addition of a 9 × 9 configuration interaction treatment, the bond-equalized **13** is preferred by a margin of 0.6 kcal/mol.[94] The present results are qualitatively similar but lean more toward the aromatic **13** both before and after the inclusion of electron correlation effects (Table III).

(2.4) Comparative Aspects of the [10]Annulenes (3, 4, 7–13). The [10]annulenes present a particularly interesting series of compounds, and although there is a strong structural relationship between the three bridged compounds, contrasts abound (Figures 6–10).

Of the bond-equalized structures, **11** and **13** exhibit a smaller range of calculated peripheral bond lengths (1.386–1.414 Å) than **8** (1.380–1.423 Å). The larger variations in bond lengths in **8** probably result from the transannular homoaromatic interaction.[22–24,85,95–102] The transannular distances in **13** are large, the pπ bridgehead orbitals are not so well directed for this type of

interaction, and this compound seems likely to most closely approximate a free-standing [10]annulene.[93] It is known from a PMO theory analysis[24] that unlike the 1,6 interaction in **8**, the 1,5 interaction in **11** does not produce a first-order change in peripheral bond lengths in [10]annulene, and this seems to be reflected in the high degree of uniformity calculated for the bond lengths of **11**.

In comparing the peripheral pπ-orbital misalignment (ring dihedral angles), it is apparent that the 1,5-bridged compound **11** suffers most from this inhibition of resonance (Figures 8 and 9). The bridgehead dihedral angles in **11** are particularly large, and although there is a comparable value in the periphery of **13**, this only occurs at one bridgehead.

Relaxation of the bond-equalized structures brings about the largest changes in the geometry of **13** (**12**) and particularly **11** (**10**). The transition to a semilocalized π-electron system allows relief of strain through twisting about the weakly conjugated bonds, and this is particularly important in those compounds with large dihedral angles. The effect of electron correlation on the relative energies of the delocalized and localized structures is largest in the case of 1,5-methano[10]annulene for the same reason. The 6-31G distortional energies of 1,6-methano[10]annulene and 1,4,7-methano[10]annulene are very similar to the values found for planar *cis*-[10]annulene, suggesting that the bridged annulenes can serve as excellent models for the hypothetical ideal free-standing annulenes (Table III).

The results of the best calculations on the relative energy of 1,6- and 1,5-methano[10]annulene (Table V) are in excellent agreement with very recent thermochemical measurements which gave rise to values of 18.4 and 20.3 kcal/mol (**8 → 11**).[103]

The inclusion of electron correlation in the extended basis set calculation favors **7** over **10**, presumably because **10** is a more localized structure. On the other hand, electron correlation effects enhance the stability of **11** at the expense of **8** (to the extent of 4.8 kcal/mol at MP2/6-31G), perhaps reflecting the importance of the homoaromatic transannular interaction in these compounds. At the same theoretical level, electron correlation effects favor azulene over naphthalene by 9.6 kcal/mol.[33,35]

In support of the homoazulene title,[91] 1,5-methano[10]annulene is calculated to possess the largest dipole moment (Table VI). Whereas the dipole moment in 1,6-methano[10]annulene is necessarily directed out of the mean plane of the π-electron system, the moment in **11** possesses a large in-plane component with a positive pole in the homoconjugated seven-membered ring and a negative pole in the homoconjugated five-membered ring. Furthermore, 1,5-methano[10]annulene is the only bridged [10]annulene to show a substantial increase in dipole moment on passing from the bond-alternate to the bond-equalized structure, again paralleling the results obtained for azulene.[33,35]

3. Polyacetylene ([∞]Annulene/Polyene). It has often been pointed out that [∞]annulene and [∞]polyene (polyacetylene)[104–107]

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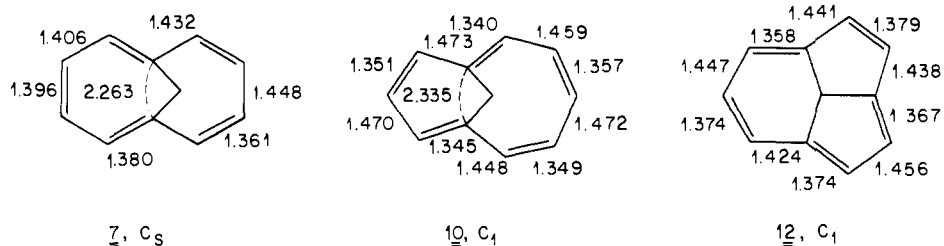
Figure 6. Comparison of the HF/6-31G calculated bond lengths of **7**, **10**, and **12**.
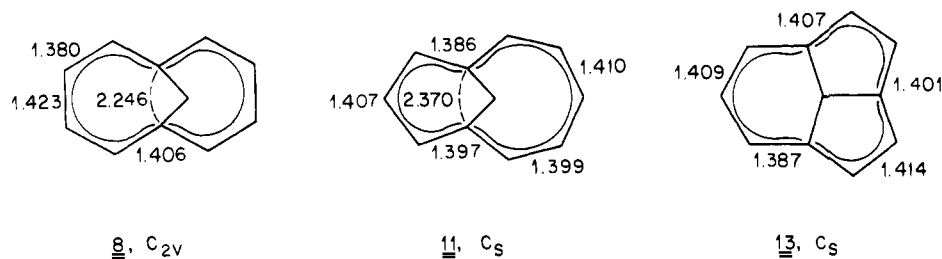
Figure 7. Comparison of the HF/6-31G calculated bond lengths of **8**, **11**, and **13**.
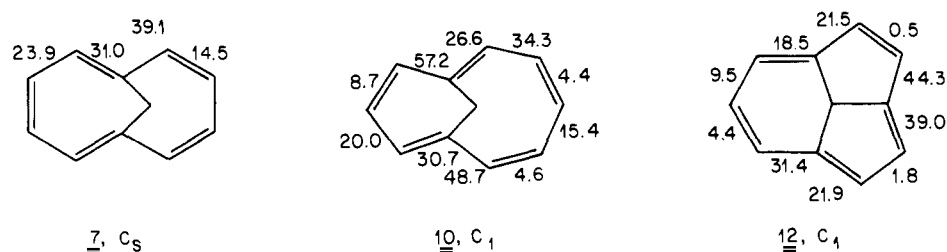
Figure 8. Comparison of the HF/6-31G calculated dihedral angles of **7**, **10**, and **12**.
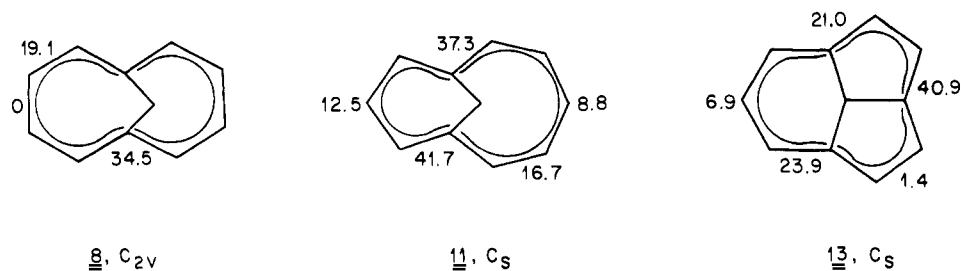
Figure 9. Comparison of the HF/6-31G calculated dihedral angles of **8**, **11**, and **13**.
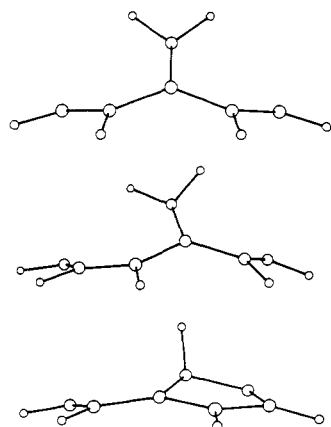
Figure 10. Cross sections on the major symmetry planes of the HF/6-31G calculated structures of **8**, **11**, and **13**. Cross-sectional (folding) angles to the π-electron skeleton (above the plane) from left to right: 194.0°, 163.1°, and 110.2° (**8**); 190.0°, 173.1°, 160.7°, 96.0°, 125.2°, 168.8°, and 195.2° (**11**); 187.7°, 173.9°, 148.6°, 52.4°, 165.4°, 47.2°, and 150.9° (**13**).

are effectively equivalent in their electronic structure.[71] It is, therefore, of interest to compare our results on the larger annulenes

such as **5** and **6** with the nonempirical crystal orbital band structure calculations on (*trans-*) polyacetylene.[108-113]

For bond-alternate *trans*-polyacetylene, the calculated[111] bond lengths are C=C and C—C = 1.325 and 1.481 (HF/STO-3G), 1.349 and 1.461 (MP2/STO-3G), 1.347 and 1.456 (HF/6-31G), and 1.365 and 1.450 Å (MP2/6-31G), whereas the bond-equalized bond lengths are C≂C = 1.391 (HF/STO-3G), 1.396 (MP2/STO-3G), 1.386 (HF/6-31G), and 1.393 Å (MP2/6-31G). The HF/STO-3G and 6-31G bond lengths calculated for polyacetylene[111] are very close to those obtained in the present geometry optimization of [18]annulene (Figure 1). Experimentally, *trans*-polyacetylene is known to be bond-alternate with lengths

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Table VII. Resonance Energies for Benzene (Referenced to [∞]Annulene/Polyene)

| | energy, kcal/mol | | | |
| | BA ref | | BE ref | |
basis set	HF	MP2	HF	MP2
STO-3G	31.1	23.8	52.4	35.1
6-31G	29.3	17.2	40.5	24.2
6-31G*	26.6	27.6	37.1	33.5

of about C=C and C—C = 1.36 ± 0.02 and 1.44 ± 0.02 Å.[106,107]

The distortional energies in *trans*-polyacetylene (bond equalized to bond alternate) on a per π-electron basis have been reported[111] as 3.56 (HF/STO-3G), 1.89 (MP2/STO-3G), 1.96 (HF/6-31G), 1.16 (MP2/6-31G), and 1.75 kcal/mol (HF/6-31G*). Although the geometrical treatment is somewhat different,[111] these values may be compared with our results for [18]annulene: 1.98 (HF/STO-3G), 0.14 (MP2/STO-3G), 0.91 (HF/6-31G), and 1.17 kcal/mol (HF/6-31G*). These values are significantly smaller than those given for *trans*-polyacetylene, and it therefore appears that while the bond lengths in the [$N = 4n + 2$]annulenes are close to the limiting value, the distortional energies have not converged to the result for $N \rightarrow \infty$ at [18]annulene, which therefore suggests a more delocalized electronic structure for [18]annulene than for *trans*-polyacetylene.

The resonance energies discussed in an earlier section were reference to finite polyenes (Table II), but in fact HMO schemes have been developed which effectively utilize an [∞]annulene/polyene for the reference energy. By making use of the total energy per unit cell obtained in the crystal orbital calculations on polyacetylene, it is possible to develop an [∞]annulene/polyene reference energy for use in more detailed resonance energy calculations.[114] While such a scheme cannot be used with molecules not based on $(C_2H_2)_n$ structures or on annulenes which suffer from angle strain or the presence of nonbonded interactions without correction factors, it is directly applicable to benzene, and the results are summarized in Table VII. The values obtained using BA *trans*-polyacetylene for the reference energy may be most

appropriately compared with the resonance energies based on finite polyenes as these latter reference molecules are also bond-alternate. It may be seen that the HF results are comparable but the MP2 values are much reduced in the [∞]annulene/polyene scheme—with the exception of the results obtained with the 6-31G* basis set, which show little sensitivity to the inclusion of electron correlation effects. This latter result is surprising, as the HF/6-31G* energy for the reaction 3 benzene → [18]annulene was noted to be in error by about 30 kcal/mol, and this discrepancy was previously ascribed to the neglect of electron correlation effects.

4. Origin of Basis Set and Electron Correlation Effects in Extended Conjugated Systems. The origin of these effects (discussed above and previously) has been considered by a number of authors.[26–36,111,112] It is generally agreed that these deficiencies operate in concert to favor localized over delocalized structures, particularly in extended systems.

From a consideration of the Viral theorem,[115] it becomes clear that the kinetic energy (KE) and the potential energy (PE) are too low in magnitude in the delocalized structure when a comparison is made with its localized counterpart in the presence of deficiencies in the basis set and neglect of electron correlation effects. As the electrons are more mobile in the delocalized structure, it is not surprising to find that they should execute a more complicated motion with higher KE to avoid one another than is necessary in the localized structure. Clearly a flexible basis set with additional nodes in the atomic functions and correlation of the motions of the electrons will serve to facilitate the necessary increase in KE in the delocalized structure. On the other hand, the PE suffers in the structure with the more mobile electrons because its orbitals are less localized, and thus the necessity for the electrons to occupy different regions of space and instantaneously correlate their motions becomes crucial. The PE of the localized structure will not be as sensitive to these effects, and in order to correctly treat the two cases in a balanced manner, it is clear that detailed basis sets and the inclusion of electron correlation effects will be critical.

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Magnetotropism of Biphenylene and Related Hydrocarbons. A Circuit Current Analysis

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Abstract: A general formula for ring currents induced in a polycyclic conjugated system was derived graph-theoretically. This formula is applicable to all planar carbocyclic and heterocyclic conjugated systems. Ring currents (i.e., bond currents in our terminology) are therein expressed as a superposition of currents induced in all possible π-electron circuits. Here, π-electron circuits signify ring components defined in Sachs' graph theory. It was proved that [$4n + 2$]-membered and [$4n$]-membered circuits in a polycyclic system are always diatropic and paratropic, respectively. Biphenylene and related hydrocarbons illustrate this magnetotropic behavior well. Benzenoid atopism in dicyclooocta[1,2,3,4-*def*:1′,2′,3′,4′-*jkl*]biphenylene was found to arise from the cancellation of currents induced in numerous [$4n + 2$]-membered and [$4n$]-membered circuits. London susceptibility can likewise be partitioned among the π-electron circuits.

Our interest in aromaticity and antiaromaticity has centered on the associated magnetotropism.[1–10] Monocyclic aromatic and

antiaromatic systems give rise to diamagnetic and paramagnetic ring currents, respectively.[3,6,7,11–13] Systems formed by the fusion

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