

Comparative molecular orbital study of the lower annulenes

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Abstract – Ab initio calculations have been carried out on the lower antiaromatic annulenes: cyclobutadiene, planar cyclooctatetraene and planar *cis*-[12]annulene. Resonance energies for the singlet and triplet states are evaluated and compared with results obtained previously for the aromatic annulenes. Cyclobutadiene is the only annulene to exhibit strong resonance destabilization. Planar singlet cyclooctatetraene shows a very small negative resonance energy. The most surprising result is provided by planar *cis*-[12]annulene which exhibits a small *positive* resonance energy.

The assignment of resonance energies in conjugated molecules is a problem of longstanding interest. The idea that the π -electrons in certain bonds should be (de)stabilized as a function of ring size, chain length or topological connectivity is a relatively straightforward concept. The qualitative aspects of this viewpoint (in particular the $(4n + 2)$ rule), have been appreciated for some time.^{1–37} Nevertheless, it has only been during the last twenty years that truly quantitative measures of the resonance energy have been advanced. This development was initiated by the work of Dewar, in which he redefined the reference energy for calculation of the energy of aromatic stabilization.^{7–12} His method employs the appropriate number of localized single and double bond energies (taken from a series of polyenes) for the estimation of a reference energy which is defined to be the nonaromatic energy of the particular system. With this definition the annulenes were found to possess a wide and continuous spectrum of resonance energies which included both positive (aromatic) and negative (antiaromatic) values. This approach has been successfully implemented by a number of other authors using a variety of π -electron procedures.^{13–25,30,31}

Quantitative assessments of resonance energies by all-electron calculations are of a much more recent advent.^{32–37} Particular problems arise in such treatments due to the necessity of correctly matching the σ -system of the reference structure to the conjugated molecule under consideration. In order to provide an accurate reflection of π electron (de)stabilization it is often necessary to allow for angle strain and nonbonded interactions; otherwise the computed resonance energies contain contributions from extraneous effects and the heuristic value of the concept is lost.

In a nonempirical study of the resonance energies of cyclobutadiene and benzene, Hess and Schaad³⁷ were able to allow for the σ -bond effects in cyclobutadiene by utilization of an empirical strain energy correction (32 kcal/mol). In previous studies of benzene, planar *cis*-[10]annulene and [18]annulene, we obtained nonempirical resonance energies by incorporating the effects of angle strain and nonbonded interactions directly into the structure of the reference molecules.³⁴ In the present study we report an extension of this work to the lower antiaromatic annulenes, planar cyclooctatetraene and planar *cis*-[12]annulene. Also included are results for cyclobutadiene, using the strain energy correction derived by Hess and Schaad.³⁷ The benzene resonance energies reported herein are slightly higher than the previous values.³⁴ This is because we have utilized a set of reference structures for benzene which are exactly analogous to those employed for the other annulenes, whereas the previous study³⁴ utilized fully optimized structures for ethylene and butadiene to allow experimental comparison with the theoretical values.

A comparison of the present resonance energies to those derived by other authors is also included.

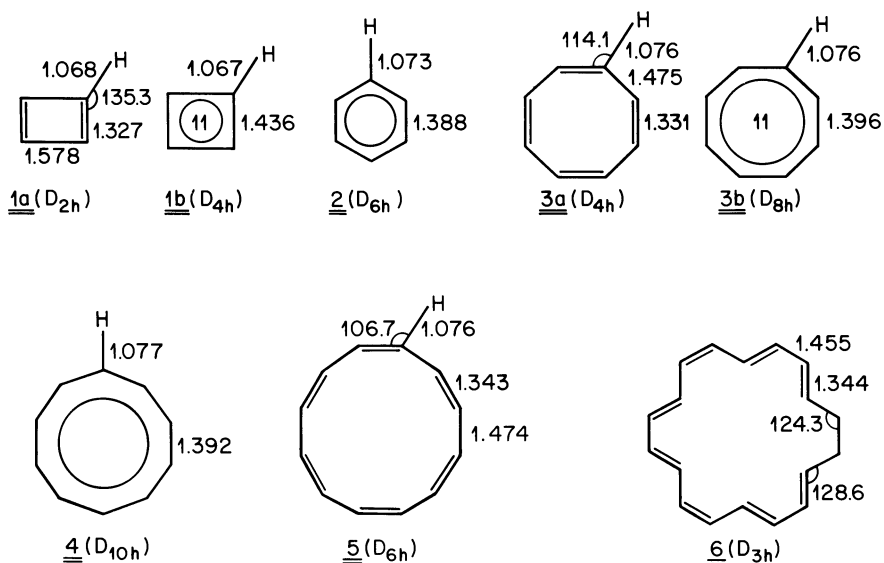
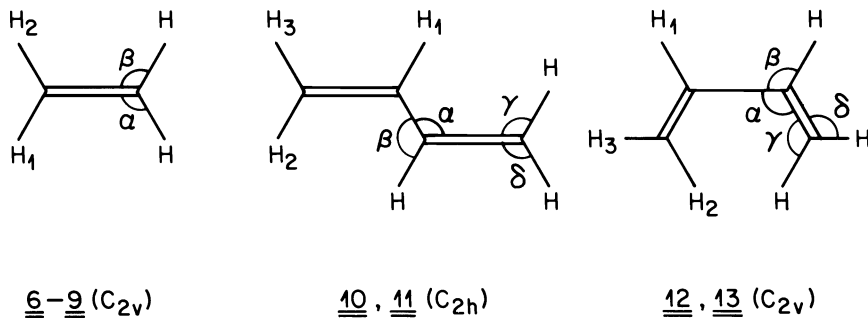


Table 1. Reference Molecule Geometries

Molecule	Bond Lengths (Å)					Bond Angles (deg) ^a			
	C=C	C-C	C-H ₁	C-H ₂	C-H ₃	α	β	γ	δ
6	1.322		1.074	1.074		121.9	121.9		
7	1.326		1.073	1.073		(120)	(120)		
8	1.324		1.072	1.078		(135)	(112.5)		
9	1.333		1.072	1.083		(150)	(105)		
10	1.328	1.464	1.077	1.075	1.073	124.3	116.2	121.8	121.8
11	1.333	1.469	1.074	1.073	1.073	(120)	(120)	(120)	(120)
12	1.324	1.447	1.088	1.086	1.067	(135)	(112.5)	(135)	(112.5)
13	1.333	1.471	1.076	1.072	1.082	(150)	(105)	(150)	(105)

^a Parenthesized values were taken from (and constrained to) analogous annulene parameters for modeling purposes (see text and ref 34).



CALCULATIONAL

Computational. The calculations were carried out with a version of the GAUSSIAN 80 program³⁸ modified for use on the CRAY-1 computer. The triplet state calculations employed unrestricted Hartree-Fock (UHF) theory. 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

Geometries (Table 1). The molecular structures were optimized at the (U)HF/6-31G theoretical level within the specified symmetries (Table 1). In calculations on π -electron systems the extended 6-31G basic set has been shown to perform reasonably well although it is clear that the extent of bond-length alternation is overestimated. This deficiency is common to HF methods.⁴³⁻⁵⁷

Table 2. Total Energies

Molecule	Basis Set	Energy (hartree)			
		HF	MP2	MP3	MP4
1a	STO-3G	-151.74666	-151.99621	-152.03637	-152.05185
	6-31G	-153.57530	-153.92599	-153.95039	-153.97326
	6-31G+5D	-153.64015	-154.13841	-154.16598	-154.19448
1b	STO-3G	-151.75332	-151.96759	-152.00690	-152.01978
	6-31G	-153.58527	-153.90778	-153.93381	-153.95272
	6-31G+5D	-153.64961	-154.12450	-154.15235	-154.17739
3a	STO-3G	-303.74001	-304.20699	-304.28058	-304.30995
	6-31G	-307.39148	-308.08008	-308.12329	-308.16866
	6-31G+5D	-307.50186	-308.48864	-308.54042	
3b	STO-3G	-303.70881	-304.17232	-304.23801	-304.26872
	6-31G	-307.37683	-308.06771	-308.10135	-308.14977
	6-31G+5D	-307.48390	-308.48176	-308.52047	
5	STO-3G	-455.41443	-456.13578	-456.24479	-456.29113
	6-31G	-460.90608	-461.96205		
	6-31G+5D	-461.08040			
7	STO-3G	-77.07199	-77.19205	-77.21624	-77.22474
	6-31G	-78.00357	-78.18177	-78.19941	-78.21025
	6-31G+5D	-78.03054	-78.28102	-78.30250	-78.31538
8	STO-3G	-77.06215	-77.18264	-77.20712	-77.21575
	6-31G	-77.99387	-78.17292	-78.19078	-78.20171
	6-31G+5D	-78.02123	-78.27235	-78.29394	-78.30693
9	STO-3G	-77.02352	-77.14768	-77.17276	-77.18173
	6-31G	-77.95853	-78.14025	-78.15843	-78.16980
	6-31G+5D	-77.98733	-78.24124	-78.26285	-78.27634
11	STO-3G	-153.01541	-153.25165	-153.29453	-153.31008
	6-31G	-153.86142	-155.21114	-155.23979	-155.26162
	6-31G+5D	-154.91616	-155.41362	-155.44795	-155.47463
12	STO-3G	-152.99816	-153.23446	-153.27727	-153.29335
	6-31G	-154.84337	-155.19400	-155.22260	-155.24483
	6-31G+5D	-154.89796	-155.39557	-155.43011	-155.45713
13	STO-3G	-152.92418	-153.16778	-153.21128	-153.22804
	6-31G	-154.77523	-155.13183	-155.16044	-155.18378
	6-31G+5D	-154.83309	-155.33571	-155.36981	-155.39818

Energies (Table 2). 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 156 amu). Cyclobutadiene energies were obtained up to MP4/6-31G+5D but it was only possible to examine [12]annulene at relatively modest theoretical levels. As noted previously,³⁴ 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.

Resonance Energies. As before we adopted the homodesmotic reaction scheme⁵⁸ as a starting point for the resonance energies — this allows for conservation of bond and hybridization type in the thermocycle. The resonance energy analysis of the annulenes (apart from benzene), is complicated by the presence of angle strain and non-bonded interactions which are not included in the standard reference compounds used in the homodesmotic model.³⁴

It is difficult to generate reference structures for cyclobutadiene which compensate for the strain energy of the four-membered ring and we found it preferable to utilize fully optimized structures for the reference molecules (**6** and **10**), with subsequent application of an empirical ring strain correction factor (32 kcal/mol).³⁷

The benzene reference structures (**7** and **11**) were based on 120° bond angles (rather than fully optimized geometries), so as to provide a direct comparison with the calculated resonance energies of the other annulenes (rather than experiment).³⁴

The reference structures (**8**, **12** and **9**, **13**) for planar [8]annulene and planar *cis*-[12]annulene were based on the symmetry constrained internal bond angles of 135° and 150° for the two molecules, respectively. The C-C-H bond angles were set to bisect the carbon bond angles. Optimization of these latter angles (as in **3a** and **5a**), produced changes in the final resonance energies of less than 1 kcal/mol and these effects were not included in the final analysis.

The planar *cis*-[10]annulene and [18]annulene structures were obtained with the same approach, and the calculated resonance energies were taken directly from our previous study.³⁴

RESULTS AND DISCUSSION

The dependence of the resonance energies (Table 3) of the antiaromatic annulenes on the effects of basis set improvement and the inclusion of electron correlation do not present a consistent picture. The results for cyclobutadiene (**1**) show variations comparable in magnitude to those found for benzene, but the deviations occur in the opposite sense in so far as the electron correlation effects on the singlet state (**1a**) are concerned. As expected, basis set improvement lowers the energy of the four-membered ring relative to the reference structures for both **1a** and **1b**. In the estimation of the resonance energy of **1b** it is apparent that the UHF calculations favor the triplet state (**1b**) against the singlet reference structures but that this effect is moderated at higher orders of perturbation theory. The final resonance energies for cyclobutadiene were obtained by inclusion of an empirical ring strain correction (RSC) factor as outlined by Hess and Schaad.³⁷

The benzene resonance energies obtained in the present treatment (with model geometries) are 3-5 kcal/mol higher than those found previously with fully optimized reference structures.³⁴ The values given herein are suitable for comparison with the theoretical resonance energies of the other annulenes.

The planar cyclooctatetraene singlet state (**3a**) results are quite insensitive to the calculational level. The triplet state (**3b**)

Table 3. Resonance Energies

Molecule	Scheme	Basis Set	Energy (kcal/mol)			
			HF	MP2	MP3	MP4
1a	2(10-6)→1a	STO-3G	-90.8	-79.0	-77.2	-76.4
		6-31G	-91.0	-85.5	-84.0	-83.4
		6-31G+5D	-84.8	-81.4	-80.3	-79.7
		+ RSC 6-31G+5D	-53	-49	-48	-48
1b	2(10-6)→1b	STO-3G	-86.6	-97.0	-95.7	-96.6
		6-31G	-84.7	-96.9	-94.4	-96.3
		6-31G+5D	-78.9	-90.1	-88.8	-90.4
		+RSC 6-31G+5D	-47	-58	-57	-58
2	3(11-7)→2	STO-3G	38.0	34.7	29.8	29.9
		6-31G	32.0	30.1	25.8	26.2
		6-31G+5D	28.6	31.3	26.2	27.1
3a	4(12-8)→3a	STO-3G	-2.5	-0.2	-0.02	-0.3
		6-31G	-4.1	-2.6	-2.5	-2.4
		6-31G+5D	-3.2	-2.7	-2.7	(-2.5)
3b	4(12-8)→3b	STO-3G	-22.1	-22.0	-26.7	-26.1
		6-31G	-13.3	-10.4	-16.3	-14.3
		6-31G+5D	-14.4	-7.0	-15.2	(-14)
4	a	STO-3G	11.7	23.0	12.7	14.9
		6-31G	17.3	32.7	20.8	(23)
		6-31G+5D	13.4	35.6	(24)	(26)
5	6(13-9)→5	STO-3G	6.6	9.5	8.6	8.3
		6-31G	3.7	7.9	(7)	(7)
		6-31G+5D	3.7	(8)	(7)	(7)
6	a	STO-3G	6.7	13.0	9.6	(12)
		6-31G	5.6			
		6-31G+5D	5.0			

^a An analogous scheme was applied (see ref 34).

Table 4. Calculated Resonance Energies as a Ratio to the Benzene Value.

Molecule	MO ^a	Dewar ⁹	A-II ²⁰	HS ^{13,15}	UT ^{30,33}	HCS ^{33,35}
		π -SCF	GMT ²¹			
1a	-1.85	-0.94	-4.49	-2.74	-2.25	
1b	-2.21					-11.3
2	1	1	1	1	1	1
3a	-0.09	-0.16	-2.18	-1.23	-1.36	
3b	-0.52					-7.74
4	0.96	0.45	0.58	0.67	0.58	1.30
5	0.18	0.08	-1.44	-0.74	-0.93	-5.41
6	0.44	0.15	0.33	0.56	0.32	

^a This work and ref 34.

results also show surprisingly little dependence on the inclusion of electron correlation effects although there is some dependence on the size of the basis set. The available resonance energies for planar *cis*-[12]annulene (**5**) parallel the computational dependence of the results obtained for singlet planar [8]annulene (**3a**).

In a previous study of cyclobutadiene and benzene, Hess and Schaad³⁷ obtained resonance energies of -54.7 and 23.4 kcal/mol at the HF/6-31G* theoretical level (cf Table 3). Our best values for the resonance energies are as follows: cyclobutadiene, -48 kcal/mol (**1a**) and -58 (**1b**); benzene, 27; planar cyclooctatetraene, -2.5 (**3a**) and -14 (**3b**); planar *cis*-[10]annulene, 26; planar *cis*-[12]annulene, 10; [18]annulene, 12.

The resonance energies of the aromatic annulenes, have been discussed elsewhere;³⁴ there is a small increase in the benzene value due to the modification of the reference structure. Cyclobutadiene⁵⁹ is the only annulene to exhibit strong resonance destabilization. Planar singlet cyclooctatetraene⁶⁰ shows a very small negative resonance energy. The most surprising result is provided by planar *cis*-[12]annulene which exhibits a small *positive* resonance energy.

The calculated resonance energies reported herein are compared with the results obtained with π -electron procedures in Table 4, in the form of ratios to the benzene value. Our finding that [10]annulene possesses a resonance energy comparable to benzene, contrasts with the lower values of the π -electron procedures. The resonance destabilization calculated for [8]- and [12]-annulene is considerably lower than that found by all but the Dewar π -SCF treatment.

The relative energies calculated for the singlet and triplet states of cyclobutadiene^{61,62} and planar cyclooctatetraene are given in Table 5. As expected, the inclusion of electron correlation effects favors the singlet state of cyclobutadiene over the triplet state, but this dependence on theoretical level is much less for the two states of cyclooctatetraene.

Table 5. Singlet and Triplet State Relative Energies.

Reaction	Basis Set	Energy (kcal/mol)			
		HF	MP2	MP3	MP4
1a \rightarrow 1b	STO-3G	-4.2	18.0	18.5	20.1
	6-31G	-6.2	11.4	10.4	12.9
	6-31G+5D	-5.9	8.7	8.6	10.7
3a \rightarrow 3b	STO-3G	19.6	21.8	26.7	25.9
	6-31G	9.2	7.8	13.8	11.9
	6-3G+5D	11.3	4.3	12.5	(11)

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