

Properties of Some Condensed Aromatic Systems

Kenneth B. Wiberg

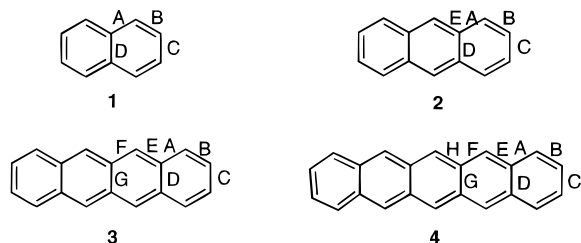
Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

Received September 24, 1996 (Revised Manuscript Received May 22, 1997[®])

The structures, energies, and other properties of a series of linearly annelated arenes, and of a corresponding series annelated in the fashion of phenanthrene, were examined at the B3LYP/6-311G** level of theory. The compounds in the latter series were uniformly found to have a lower energy than their isomers in the former series. In both series, the C–C bond lengths were found to be correlated with the charge density at the bond critical point, the ellipticity at that point, and with the π -bond order. This indicates that the π -electron distribution is the dominant factor in determining the bond lengths. The resonance energies were estimated and were found to increase linearly with the number of rings with the $[n]$ phenacenes, but at a slower rate with the linearly annelated benzenes. The ionization potentials were calculated, and the change in electron density on ionization was examined. It was found that the radical cations formed via ionization have the positive charge mainly located at the π -orbitals that had the highest bond order in the parent compounds and at the hydrogens. The carbons tended to increase their electron populations in the σ -bonds. The difference in the UV spectra of the two series of compounds also has been studied.

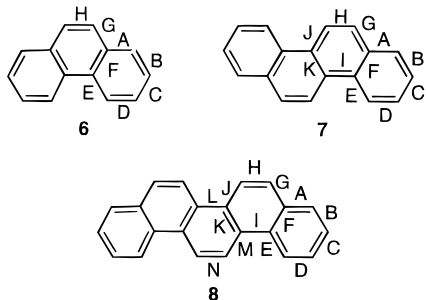
1. Introduction

Compounds with condensed benzene rings have received much study.¹ One series of these compounds is linearly annelated and includes naphthalene (**1**), anthracene (**2**), naphthacene (**3**), and pentacene (**4**). These



compounds are characterized by remarkably large shifts in their UV p-bands² (Figure 1) and increasing reactivity with increasing number of rings.¹ Thus, hexacene (**5**) is reported to be unstable to both light and air.³

Another series, recently named $[n]$ phenacenes,⁴ is based on the fusion found in phenanthrene (**6**) and includes chrysene (**7**) and picene (**8**). Here, the UV absorption band changes only slowly with increasing



number of rings (Figure 1), and at the same time, they

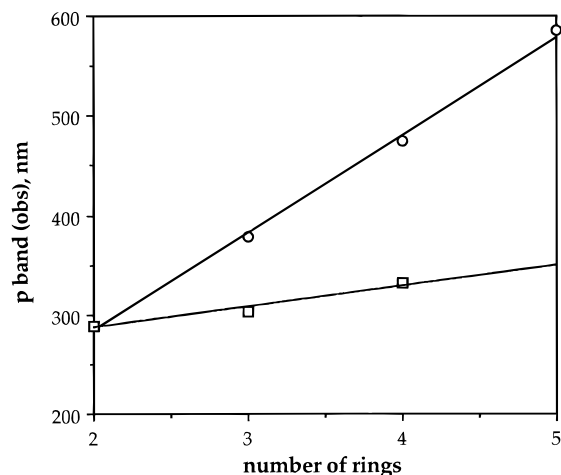


Figure 1. Position of p-band in the UV spectra of the arenes. The upper line is for the series **1**, **2**, **3**, and **4** and the lower line is for the series **1**, **6**, **7**, and **8**.

are less reactive than the linearly annelated compounds.⁵ The reactivity and the energy of the UV transition energies may be related. A low transition energy (long wavelength) implies a low HOMO–LUMO gap, and the latter frequently results in high reactivity. The question remaining is what is the origin of the differences between the two series of compounds? The properties of these compounds have been discussed by Clar⁶ in terms of “aromatic sextets” and by others in terms of Hückel π -MO theory.¹ It was of interest to explore the relationship between these results and those obtained using ab initio MO theory.

There have been two recent systematic studies of arenes using ab initio MO theory. Both Peck et al.⁷ and Herndon⁸ studied several of the above and related

[®] Abstract published in *Advance ACS Abstracts*, July 15, 1997.

(1) Cf. Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163, 3173 and references therein.

(2) (a) Clar, E. *Aromatische Kohlenwasserstoff*, 2nd ed.; Springer Verlag: Berlin, 1952. (b) Klevens, H. B.; Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 470. Platt, J. R. *Ann. Rev. Phys. Chem.* **1959**, *10*, 354. The band designations given herein are those of Clar. Platt has proposed a different and more systematic naming system.

(3) Clar, E. *Chem. Ber.* **1939**, *72*, 1817.

(4) Mallory, F. B.; Butler, K. E.; Evans, A. C.; Mallory, C. W. *Tetrahedron Lett.* **1996**, *37*, 7173. Mallory, F. B., Reaction Mechanisms Conference, June 1996.

(5) $[n]$ Phenacenes with n up to 11 have been prepared (ref 4) and are remarkably stable.

(6) Clar, E. *The Aromatic Sextet*; Wiley: New York, 1972.

(7) Peck, R. C.; Schulman, J. M.; Disch, R. L. *J. Phys. Chem.* **1990**, *94*, 6637.

(8) Herndon, W. *Chem. Phys. Lett.* **1995**, *234*, 82.

Table 1. Calculated Energies, B3LYP/6-311G**

compd	energy	ΔE^a	ΔH_f^b	$\Delta\Delta H_f$
benzene	-232.308 55		19.7 \pm 0.2	
naphthalene	-385.984 93		35.9 \pm 0.3	
anthracene	-539.655 18		55.2 \pm 0.5	
naphthacene	-693.322 94		69.9 \pm 2.2	
pentacene	-846.989 53			
phenanthrene	-539.663 20	-5.0	49.6 \pm 0.4	5.9 \pm 0.7
chrysene	-693.339 05	-10.1	64.5 \pm 1.6	5.4 \pm 2.7
picene	-847.015 81	-16.5		

^a Relative energy with respect to the isomeric linearly annelated hydrocarbon. ^b Reference 10.

compounds at the HF/6-31G* level in order to obtain estimates of heats of formation of the compounds for which experimental were not available. Some of these compounds also were studied at the B3LYP/6-311G* level by Cioslowski et al. in connection with estimates of their C–H bond dissociation energies.⁹ However, the full set of the above compounds was not examined, and the properties of the compounds, other than their energies, were not studied.

Therefore we have carried out geometry optimizations at the B3LYP/6-311G** level for the above compounds. It uses a reasonably flexible basis set and includes correction for electron correlation. This was the highest practical level for the larger molecules. The differences in structure were examined with the aid of calculated π -bond orders and information on the properties of the C–C bond critical points. The relative energies were examined, and resonance energies were derived. The radical cations formed on ionization were studied, as well as the electronically excited states.

2. Energies

The calculated energies are summarized in Table 1. Since the zero-point energies of isomeric compounds in this series are essentially the same,⁸ the energy differences may be compared with the experimental values.¹⁰ The observed energy difference between anthracene and phenanthrene is well reproduced. The difference in energy between naphthacene and chrysene is not well established because of the difficulty in measuring the heats of sublimation at 25 °C for compounds that are relatively high melting and have negligible vapor pressure at room temperature. The calculated energy difference is significantly higher than the reported experimental value, but the former may prove to be the more accurate value. The heats of formation of pentacene and picene have not been determined, but the calculated energies suggest that the difference in energy continues to increase by about 5 kcal/mol per ring as the number of rings increases.

It is important to recognize that the thermochemical stability and the reactivity are not necessarily related in a series such as this. The fact that anthracene and phenanthrene undergo facile reactions with many reagents¹ does not necessarily indicate that they have a lower degree of thermochemical stabilization per carbon than benzene or naphthalene. The stabilization of these

Table 2. Delocalization Energies, kcal/mol

compd	deloc per C=C		compd	deloc per C=C	
	E	bond		E	bond
benzene	36	12.0	pentacene	117	10.6
naphthalene	60	12.0	phenanthrene	85	12.1
anthracene	80	11.4	chrysene	109	12.1
naphthacene	99	11.0	picene	133	12.1

compounds is usually given as the delocalization energy. There has been much controversy over how this should be calculated.¹¹ The simplest approach is to use the thermochemically derived stabilization energies, i.e., 36 kcal/mol for benzene and 60 kcal/mol for naphthalene.¹² The compounds of interest are formed from benzene by successive additions of four carbon units, and if each of the compounds were equally stabilized, the energy change on going from one to another should be the same throughout. On this basis, the thermochemical delocalization energies may be derived from the calculated energies by:¹³

$$\text{deloc. energy} = 627.5(E_{\text{calc}} + 232.251 18 + (n - 1)153.638 13)$$

where 627.5 is the conversion factor from hartrees to kcal/mol, E_{calc} is the calculated energy (Table 1), 232.251 18 is the energy of benzene corrected for its delocalization energy, n is the number of rings, and 153.638 13 is the difference in energy between benzene and naphthalene, corrected for the difference in delocalization energy. The values thus derived are given in Table 2. It can be seen that in the series benzene, **1**, **6**, **7**, and **8** the delocalization energy per double bond is essentially constant and in the series **1**, **2**, **3**, and **4** it decreases somewhat with increasing number of rings. However, despite the high reactivity of compounds such as **4**, the delocalization energy remains high.

Addition readily occurs across the 9,10 positions of anthracene and across the **H** bond in phenanthrene, whereas these reactions are difficult for benzene and naphthalene. Addition across a double bond of benzene would result in a loss of 33 kcal/mol of stabilization (i.e., 36 less the stabilization energy of butadiene, 3 kcal/mol), and with naphthalene, addition across bond **B** would result in a loss of 22 kcal/mol of stabilization (60 less the stabilization energy of styrene, 38 kcal/mol). Both of these numbers are large. On the other hand, addition across the 9,10 positions of anthracene would only result in an 8 kcal/mol loss in stabilization energy (80 less 2×36 kcal/mol), and with phenanthrene it is 11 kcal/mol (85 less 2×36 kcal/mol less the extra stabilization of biphenyl (2 kcal/mol)). Both of these numbers are relatively small and could lead to rapid reactions. With

(11) Cf. Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305, 2413. Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 2404. Herndon, W. C.; Ellzey, M. L. *J. Am. Chem. Soc.* **1974**, *96*, 6631. Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750; **1977**, *99*, 2048. Chestnut, D. B.; Davis, K. M. *J. Comput. Chem.* **1997**, *18*, 584.

(12) Cf. Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994; pp 36–37. They recommend the HSE method which gives a resonance energy for naphthalene of 57 kcal/mol if benzene is taken as 36 kcal/mol. The HRE method would lead to a somewhat larger value of 66 kcal/mol. Wheland [Wheland, G. W. *Resonance in Organic Chemistry*, Wiley: New York, 1955] derived a resonance energy for naphthalene of 61 kcal/mol from thermochemical data. A value of 60 appears to be a reasonable average.

(13) This is equivalent to using $-38.708 53$ per CH and $-38.110 54$ per C in defining the unstabilized counterparts. It represents a simple scaling scheme for extrapolating the thermochemical delocalization energies starting with those for benzene and naphthalene.

(9) Cioslowski, J.; Liu, G.; Martinov, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1996**, *118*, 5261. They state that the calculations were carried out at the B3LYP/6-311G** level, but the energies reported suggest that B3LYP/6-311G* was used.

(10) Pedley, J. D. *Thermochemical Data and Structures of Organic Compounds*, Vol. I; Thermodynamics Research Center: College Station, TX, 1994.

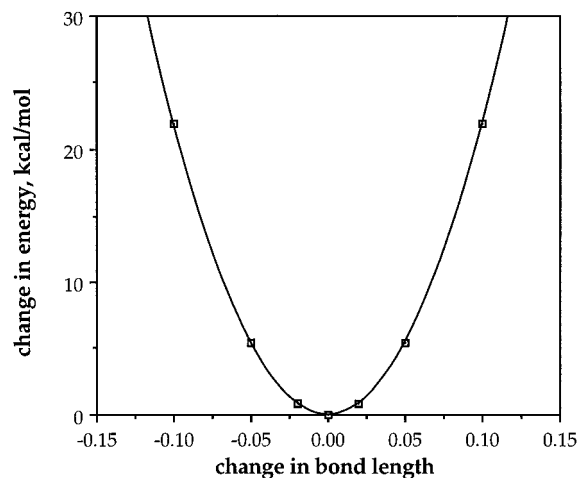


Figure 2. Change in energy with distance for the antisymmetric C–C stretching mode of benzene.

pentacene, 1,4 addition across the central ring would increase the delocalization energy from 117 kcal/mol to 120 kcal/mol (two naphthalene rings) and this can account for its high reactivity. On the other hand, with chrysene, the energy change on adding across a C–C bond would be about the same as for phenanthrene.

Simpson has proposed a model for benzene which leads to the conclusion that the vertical resonance energy (i.e., the stabilization resulting from mixing two Kekule structures having the bond length found in benzene) is given by one-half of the energy of the first electronic transition of benzene (206 nm = 110 kcal/mol) or 55 kcal/mol.¹⁴ The difference between this and the thermochemical resonance energy is the compression energy for changing the bond lengths in a Kekule structure to that found in benzene. The $B_{2u} \nu_{14}$ vibrational mode¹⁵ is the antisymmetric C–C stretching mode that effectively couples Kekule structures and the symmetrical ground state structure. The energy change associated with this vibration was obtained at the B3LYP/6-311G** level (Figure 2) via a series of calculations in which the bond lengths were varied.

For a change in bond length of 0.168 Å (i.e., from 1.394 to 1.310 and 1.478 Å) the energy increases by 15 kcal/mol, and for a change of 0.188 Å (to 1.300 and 1.488 Å) it increases by 19 kcal/mol.¹⁶ Therefore, the compression energy is on the order of 15 kcal/mol. This is in remarkably good agreement with the difference (19 kcal/mol) between the thermochemical delocalization energy (36 kcal/mol) and the spectroscopic value (55 kcal/mol).

3. Bond Lengths

The calculated and observed bond lengths are compared in Table 3. For naphthalene and anthracene there are both electron diffraction and X-ray structural data. The two sets of data are fairly consistent, and the X-ray data are in somewhat better agreement with the calculated structures. The electron diffraction studies have the disadvantage that the individual C–C bond lengths

cannot be resolved separately, but must be inferred from the nonbonded C–C distances. The X-ray data are also not ideal since they may be influenced by crystal forces.

The IR data for benzene and the X-ray data for naphthalene and anthracene are compared with the calculated bond lengths in Figure 3. The slope is close to unity (0.99) and the intercept is small ($r^2 = 0.97$). The data for the remaining compounds are not as precise, with uncertainties on the order of 0.01–0.02 Å. A plot making use of all of the data gave a slope of 1.09 ($r^2 = 0.90$). In view of the very good agreement between the more precise experimental data and the calculated bond lengths, it seems reasonable to make use of the latter in the following discussion.

One of the striking features of these compounds is the range of C–C bond lengths (1.339–1.457 Å). Are the lengths controlled by the π -bonds, the σ -bonds, or both? In the case of benzene, the origin of the observed hexagonally symmetrical structure has been the subject of considerable controversy. One group of investigators concluded that the structure is determined by the σ -bonds and that the π -bonds would prefer a structure with alternating bond lengths.¹⁷ Another more recent study concluded that both the σ - and π -bonds preferred the symmetrical structure.¹⁸

It should be possible to obtain further information on the importance of the π -electrons by examining the origin of the variation in bond lengths in the annelated benzenes. First, the electron densities at the bond critical points were determined and they were found to be linearly dependent on the bond lengths (Figure 4). One measure of the π -character of a bond in a planar unsaturated system is the ellipticity (ϵ) which is defined as¹⁹

$$\epsilon = [\lambda_1/\lambda_2 - 1]$$

where λ_1 and λ_2 are the curvatures in the electron density, ρ , at the bond critical point in the directions perpendicular to the bond and $\lambda_1 > \lambda_2$. The ellipticity will increase with increasing π -character, since the latter will lead to a smaller drop-off of electron density with distance in the direction of the π -bond and a smaller value of λ_2 . The relationship between the ellipticity and the bond length is shown in Figure 5, and it is clear that the shorter bonds are characterized by a higher ellipticity and a greater π -character.

A more direct way of obtaining information on the subject is to calculate the σ - and π -components of the bond orders. Two methods for calculating the bond orders from the electron density distribution have been developed, the covalent bond orders of Cioslowski and Mixon²⁰ and the sharing indices of Fulton.²¹ With most

(14) Simpson, W. T. *J. Am. Chem. Soc.* **1953**, *75*, 597.

(15) Cf. Goodman, L.; Ozkabak, A. G.; Thakur, S. N. *J. Phys. Chem.* **1991**, *95*, 9044.

(16) The B3LYP/6-311G** bond lengths for the C=C bond and the central C–C bond of cisoid-butadiene are 1.336 and 1.470 Å, respectively, or a difference of 0.134 Å. The conventional bond lengths for C=C double bonds and for C–C single bonds between sp^2 -hybridized carbons are 1.33 and 1.50 Å, respectively, for a difference of 0.17 Å.

(17) Berry, R. S. *J. Chem. Phys.* **1961**, *35*, 29. Shaik, S. S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 411. Hiberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657. Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Phys. Chem.* **1988**, *92*, 5086. Hiberty, P. C. In *Topics in Current Chemistry*; Gutman, I., Cyrin, S. J., Eds.; Springer: New York, 1990; Vol. 153, p 27. Jug, K.; Koster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772.

(18) Glendening, E. D.; Faust, R.; Streitwieser, A.; Vollhardt, K. P. C.; Weinhold, F. *J. Am. Chem. Soc.* **1993**, *115*, 10952. Cf. Hiberty, P. C.; Ohanessian, G.; Shaik, S. S.; Flament, J. P. *Pure Appl. Chem.* **1993**, *65*, 35.

(19) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990; p 78.

(20) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

(21) Fulton, R. L. *J. Phys. Chem.* **1993**, *97*, 7516. Fulton, R. L.; Mixon, S. T. *J. Phys. Chem.* **1993**, *97*, 7530.

Table 3. Calculated and Observed Structures

compd	method	A	B	C	D	E	F	G	H	I	J	K
benzene	theor	1.394										
	IR ^a	1.390										
	π -index	0.425										
naphthalene	theor	1.420	1.375	1.415	1.431							
	X-ray ^b	1.425(1)	1.378(1)	1.421(1)	1.426(1)							
	ED ^c	1.422(3)	1.381(2)	1.417(4)	1.412(8)							
	π -index	0.302	0.519	0.325	0.287							
anthracene	theor	1.429	1.367	1.424	1.443	1.398						
	X-ray ^b	1.434(1)	1.369(1)	1.431(1)	1.441(1)	1.403(1)						
	ED ^d	1.437(4)	1.397(4)	1.422(16)	1.437(4)	1.392(6)						
	π -index	0.268	0.557	0.286	0.245	0.380						
naphthacene	theor	1.433	1.364	1.429	1.450	1.390	1.409	1.450				
	π -index	0.253	0.573	0.269	0.224	0.416	0.336	0.222				
pentacene	theor	1.437	1.361	1.434	1.454	1.385	1.415	1.453	1.401			
	π -index	0.245	0.585	0.257	0.213	0.436	0.314	0.210	0.370			
phenanthrene	theor	1.413	1.378	1.406	1.380	1.413	1.424	1.434	1.356	1.457		
	X-ray ^e	1.428(9)	1.374(17)	1.386(14)	1.399(15)	1.412(8)	1.416(8)	1.450(7)	1.341(10)	1.468(10)		
	π -index	0.330	0.486	0.336	0.484	0.341	0.316	0.241	0.592	0.213		
	theor	1.415	1.376	1.407	1.378	1.416	1.425	1.425	1.361	1.452	1.430	1.415
chrysene	X-ray ^f	1.428	1.363	1.394	1.381	1.409	1.409	1.421	1.368	1.468	1.428	1.401
	π -index	0.320	0.497	0.325	0.495	0.329	0.308	0.260	0.564	0.231	0.267	0.362
	Theor	1.414	1.376	1.414	1.379	1.415	1.424	1.427	1.360	1.452	1.433	1.418 ^g
picene	Theor	1.414	1.376	1.414	1.379	1.415	1.424	1.427	1.360	1.452	1.433	1.418 ^g
	π -index	0.323	0.494	0.349	0.491	0.332	0.310	0.254	0.572	0.225	0.260	0.347

^a Pliva, J.; Johns, J. W. C.; Goodman, L. *J. Mol. Spectrosc.* **1991**, *148*, 427. ^b Brock, C. P.; Dunitz, J. D.; Hirshfeld, F. L. *Acta Crystallogr.* **1991**, *B47*, 789. ^c Ketkar, S. N.; Fink, M. *J. Mol. Struct.* **1981**, *77*, 139. ^d Ketkar, S. N.; Kelley, M.; Fink, M.; Ivey, R. C. *J. Mol. Struct.* **1981**, *77*, 127. ^e Kay, M. I.; Okaya, Y.; Cox, D. E. *Acta Crystallogr.* **1971**, *B27*, 26. ^f Cruickshank, D. W. J.; Sparks, R. A. *Proc. R. Soc. (London)* **1960**, *A258*, 270. ^g L = 1.446 (0.253), M = 1.420 (0.290), N = 1.366 (0.535).

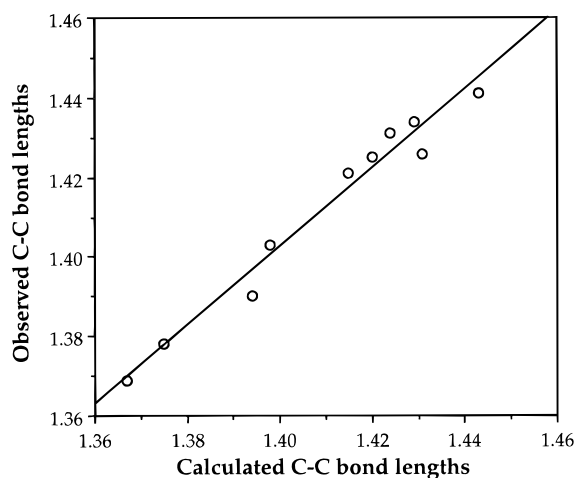


Figure 3. Comparison of calculated and observed bond lengths.

compounds, the two methods give essentially the same results. In the former method, the bonds are localized prior to the calculation of the bond orders. This may lead to difficulties with conjugated π -systems. As an example, with benzene it leads to alternating high and low π -bond orders (i.e., a Kekule-like arrangement). Similar problems were found with the present compounds. The Fulton sharing indices, on the other hand, do not involve a bond localization, and they correctly give the same bond order for all of the bonds in benzene. These bond indices, and their σ - and π -components, are available in the Supporting Information. The π -components are also included in Table 3.

The bond indices are related to the bond lengths as shown in Figure 6. The π -components are of special interest, and their relation to the bond length is shown in Figure 7. The σ -components of the bond index change relatively little and are not well correlated with the bond lengths (Figure 8). In addition, one should note that the range of π -indices is large (0.21–0.59) whereas the range of σ -indices is small (0.92–0.98). These results make it

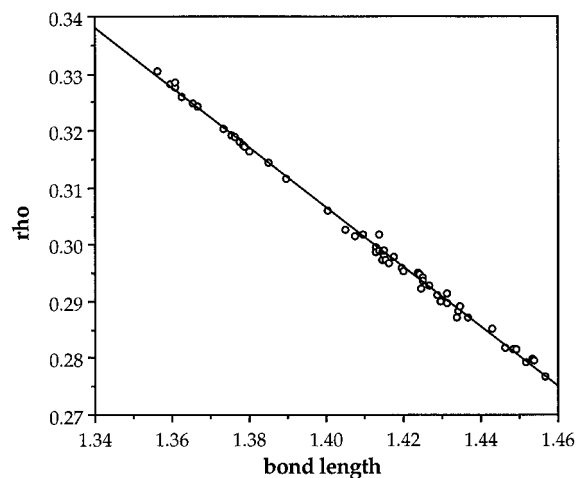


Figure 4. Relationship between the electron density at the bond critical point and the C–C bond length.

clear that the bond lengths for these compounds are largely determined by the degree of π -character in the bond.

Are the Fulton π -bond indices related to the bond orders obtained in the Hückel π -electron calculations? The two are not directly comparable since the Hückel bond orders at a given atom do not sum to the valence of that atom, whereas in the absence of ionic contributions to the bonds the Fulton indices do sum properly. We have noted that the Hückel bond orders (as well as those derived from other zero-differential overlap calculations) may be converted to bond indices by squaring them,²² and then the latter will sum properly. The relation between the Fulton and Hückel type bond indices is shown in Figure 9. They are remarkably well correlated with an intercept close to zero (0.02), and a slope (0.95) close to unity ($r^2 = 0.95$). One might not have expected such a good relationship between the ab initio derived π -bond

(22) Wiberg, K. B. *Tetrahedron* **1967**, *24*, 1083.

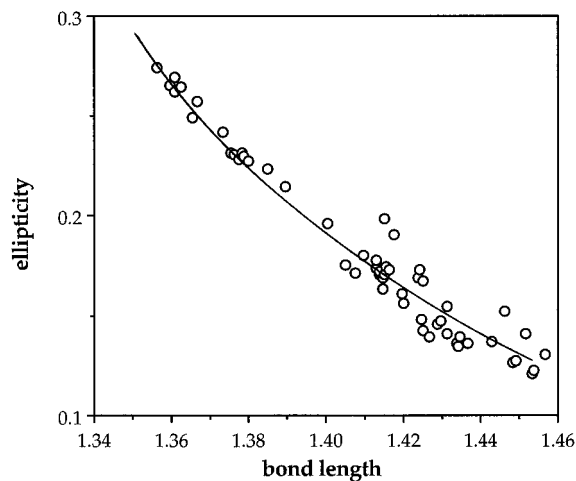


Figure 5. Relationship between the ellipticity at the bond critical point and the C–C bond length.

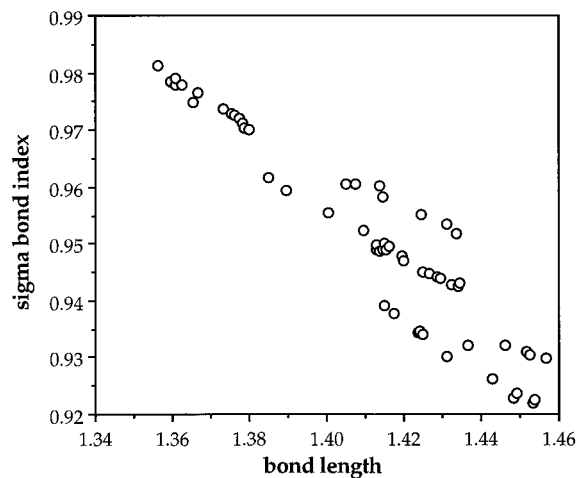


Figure 8. Relationship between the σ -component of the bond index and the C–C bond length.

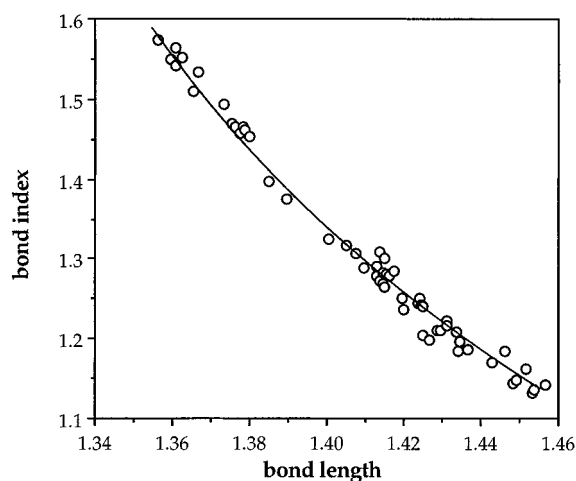


Figure 6. Relationship between the Fulton bond index and the C–C bond length.

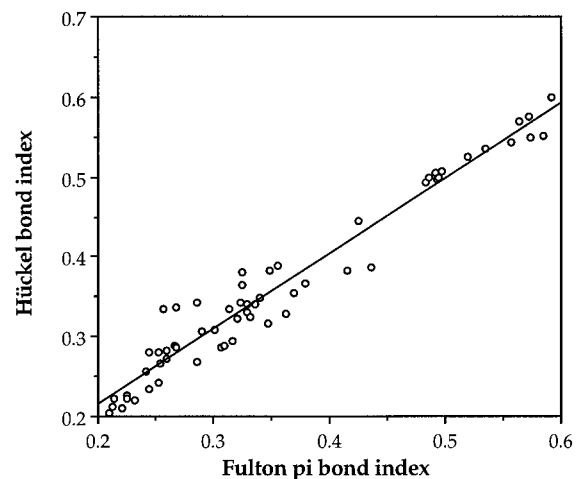


Figure 9. Comparison of the Fulton and Hückel bond indices.

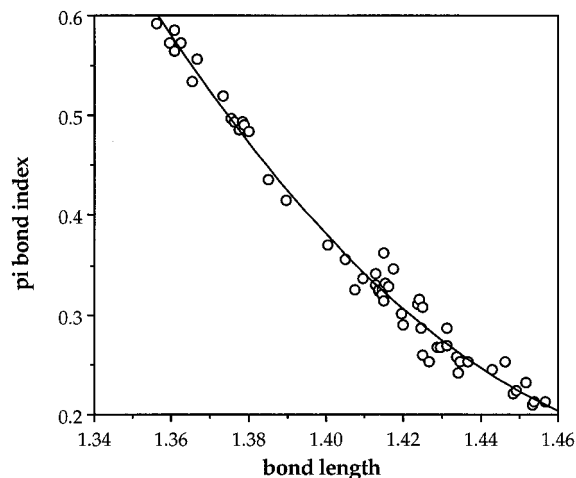


Figure 7. Relationship between the π -component of the bond index and the C–C bond length.

indices, and those obtained via the very simple semi-empirical Hückel method that neglects both overlap and electron repulsion.

4. Ionization Potentials

One of the important properties of benzene derivatives is their ionization potentials. It is known that they

Table 4. Ionization Potentials

radical cation	energy (hartree)	IP (eV)	
		calcd	obsd ^a
benzene	-231.969 19	9.2	9.2
naphthalene	-385.693 99	7.9	8.2
anthracene	-539.393 93	7.1	7.4
naphthacene	-693.081 67	6.6	7.0
phenanthrene	-539.382 05	7.7	7.9
chrysene	-693.072 08	7.3	7.6

^a Reference 22.

change more rapidly in the series **1–4** than in the series **1, 6, 7, and 8**.²³ The energies of the radical cations formed via photoionization were calculated, and the changes in energy with respect to the corresponding hydrocarbons are compared with the experimental values in Table 4. Although there are small differences between the observed and calculated ionization potentials, the observed trends are reproduced, and the changes in the ionization potentials with number of rings is greater for the linearly annelated compounds than for the other series. The correlation between the observed and calculated ionization potential is shown in Figure 10. The observed ionization potentials are fairly well correlated with the energies of the highest occupied MO's, but the

(23) Clark, P. A.; Brogli, F.; Heilbronner, E. *Helv. Chim. Acta* **1972**, *55*, 1415. Biemann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163.

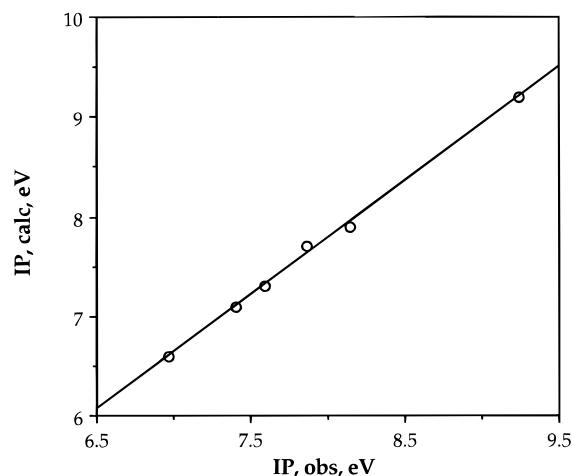


Figure 10. Relationship between the observed and calculated ionization potentials.

latter are about 2 eV smaller than the observed IP's. The HOMO energies are available in the Supporting Information.

It was of interest to examine where the positive charge was located in the radical cations. Three-dimensional arrays of electron density about each molecule and ion were calculated from the density matrices, and that for the radical cations was subtracted from that for the parent hydrocarbons. Plots of the difference in electron densities are shown in Figure 11. Solid contours indicate regions that lose electron density on ionization, and dashed contours indicate regions that gain electron density. The electron is generally taken from the π -or-

bitals that have the greatest bond orders. In addition, some electron density is taken from the hydrogens that are in the nodal planes of the molecules, but there is generally increased electron density at the carbons and some of their bonds in the σ -planes. We have noted that this is a general trend.²⁴ When an electron is taken from the π -system of the carbons, the electronegativity of the carbons is increased. As a result, there will be an increased attraction for the σ -electrons in the vicinity of the carbons, and some of this electron density is taken from the hydrogens.

As a first approximation, it is commonly assumed that the first ionization potential corresponds to the loss of an electron from the highest occupied molecular orbital. If that were true, the difference densities seen in Figure 11 would correspond to the electron density distribution in the highest occupied MO's. They are shown in Figure 12, and for the first set of compounds (naphthalene through naphthacene) this is approximately true, except for the effects in the σ -plane noted above.

The corresponding plots for phenanthrene and chrysene also are shown in Figures 11 and 12. With phenanthrene, there is a significant difference between the electron density difference plot and the electron density for the highest occupied MO, and a difference is also found with chrysene. It is interesting to note that these two compounds deviate somewhat from the observed IP vs HOMO energy plot derived from benzene and the linearly annelated arenes.

5. Electronic Transitions

The first strong band in the UV spectra of these compounds is known as the p-band,^{2a} and it is polarized

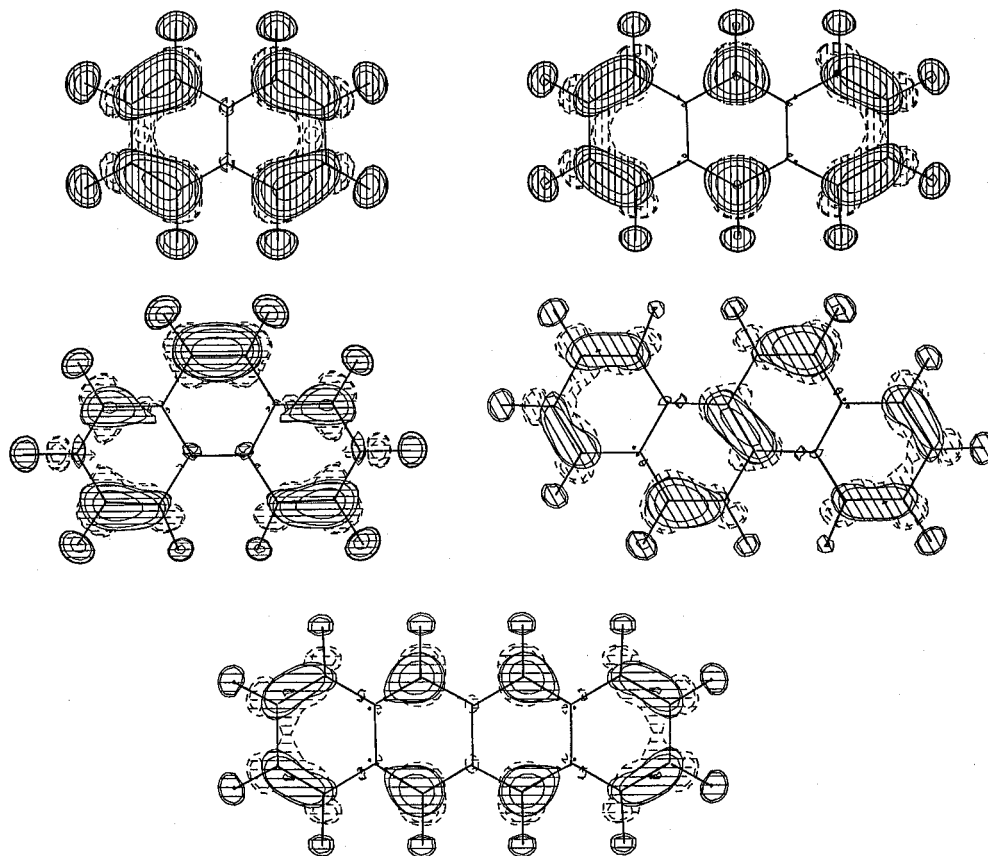


Figure 11. Electron density difference plots for the conversion of the arenes to their radical cations. Solid lines indicate regions that have lost electron density, and dashed lines indicate an increase in electron density.

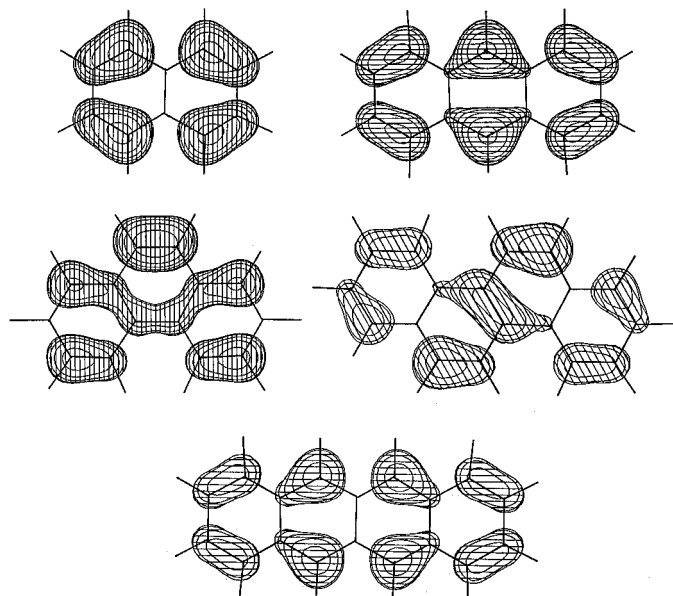


Figure 12. Electron density contours for the HOMO of the arenes.

Table 5. Calculated and Observed UV Transitions

compd	calcd		obsd ^a	
	p	β	p	β
naphthalene	276	213	289	220
anthracene	350	242	379	256
naphthacene	424	265	473	273
pentacene	488	281	585	310
phenanthrene	286	237	303	254
chrysene	318	250	331	269
picene	330	259		

^a Reference 2.

along the short axis of these molecules.²⁵ At a higher energy is found the β -band that is polarized along the long axis. The positions of the p-bands are shown in Figure 1, and it is seen that whereas the changes in transition energy^{2b} are large with the linearly annelated compounds, it is relatively small for the [*n*]phenacenes.

It would be interesting to examine these compounds via ab initio calculations. However, only the CIS procedure²⁶ is practical for the present compounds, and it does not reproduce the transition energy of naphthalene in a satisfactory fashion. Thus, the semiempirical Pariser–Pople–Parr (PPP)²⁷ procedure which includes electron correlation was used. The calculated transition energies are compared with the observed values in Table 5. Although the calculated and observed values differ somewhat, they are linearly related with a slope of 1.38 (Figure 13). Thus, the PPP procedure reproduces the difference in the first electronic transition between the linearly annelated arenes and the [*n*]phenacenes.

An interesting feature of the spectral data is that the β -bands do not show the large difference between the

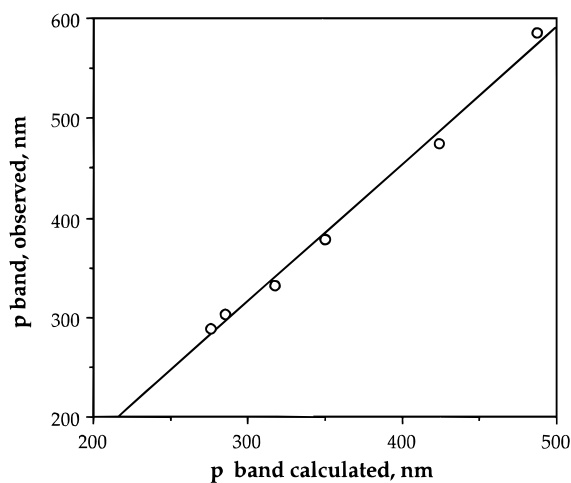


Figure 13. Comparison of the calculated and observed p-band positions for the arenes.

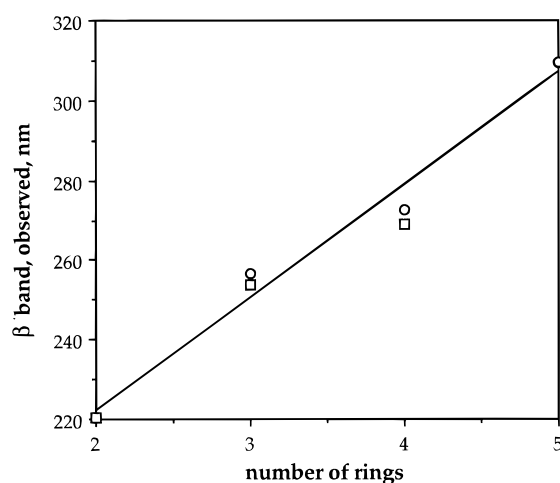


Figure 14. Comparison of the calculated and observed β -band positions of the arenes. The circles are for the linearly annelated arenes, and the squares are for the [*n*]phenacenes.

series of compounds as found with the p-bands (Figure 14). A further analysis of the UV bands will require a detailed comparison between the ab initio and PPP p-MO energies and an analysis of the structural effects on the higher occupied and lower virtual orbitals. This is beyond the scope of the present work and will be examined at a later time.

6. Discussion

The B3LYP/6-311G** calculations reproduce the available experimental data for the arenes in this study. They also extend the available data. In addition, they provide calculated σ - and π -bond indices. The Hückel bond indices are in remarkably good agreement with those derived from the ab initio density matrices. The calculations for the radical cations provide information on the change in electron density associated with the first ionization potential of the arenes.

It may be noted that the positions that have the highest π bond orders and the shortest C–C bond lengths are those for which the canonical resonance structures most frequently place a double bond.²⁸ Thus, the bond lengths are determined by the π -system and not by the σ -system. However, despite the considerable differences

(24) Wiberg, K. B.; Hadad, C. M.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820. Wiberg, K. B.; Schleyer, P. v. R.; Streitwieser, A. *Can J. Chem.* **1995**, *74*, 892.

(25) McClure, D. S. *J. Chem. Phys.* **1954**, *22*, 1256, 1668. Sidman, J. W. *J. Chem. Phys.* **1956**, *25*, 115, 122.

(26) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135.

(27) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466, 767. Parr, R. G.; Pariser, R. *J. Chem. Phys.* **1955**, *23*, 711. Pariser, R. *J. Chem. Phys.* **1956**, *25*, 1112. Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375; *Proc. Phys. Soc.* **1955**, *68A*, 81.

in the bond order and bond lengths, the resonance energy per double bond has only a small dependence on the structure.

The linearly annelated systems may be thought of as being formed by adding a four-carbon diene fragment across a C–C bond that has a low π -bond order, leading to relatively little stabilization. On the other hand, with the [*n*]phenacenes, where the fragment is added across a C–C bond that has high π -bond character, there is a greater opportunity to gain electron delocalization leading to a more stable compound.

In the ionization of the hydrocarbons, the electron is taken from the C–C bonds that have the highest π -character. With the linearly annelated benzenes, this does correspond to the highest occupied MO. However, with the [*n*]phenacenes, there are differences, and they also show up in a plot of the observed IP vs the HOMO energy.

Calculations

The ab initio calculations were carried out using Gaussian-95 and standard basis sets.²⁹ The bond properties and the bond indices were calculated using AIM-

(28) Pauling, L.; Brockway, L. O.; Beach, J. Y. *J. Am. Chem. Soc.* **1935**, *57*, 2705. Pauling, L.; Brockway, L. O. *J. Am. Chem. Soc.* **1937**, *59*, 1223.

ALL.³⁰ The PPP calculations were carried out using QCPE program 641.³¹ The electron density plots were made using CASGEN.³²

Acknowledgment. This investigation was supported by a grant from the National Science Foundation. I thank Todd Keith for providing a copy of AIMALL.

Supporting Information Available: Tables of bond properties and σ - and π -bond indices and of HOMO and LUMO energies (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO961831J

(29) M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople. Gaussian 95, Development Version (Rev. D) Gaussian, Inc., Pittsburgh, PA 1995.

(30) Keith, T. A., Yale University. This is based on PROAIM: Biegler-König, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.

(31) Griffiths, J.; Lasch, J. G. QCPE program 641.

(32) Rablen, P. R.; Hadad, C. M. Yale University.