Pure & Appl.Chem. Vol.54, No.5, pp.1129-1142, 1982.
Printed in Great Britain.

0033-4545/82/051129-14$03.00/0
Pergamon Press Ltd.
©1982 IUPAC

Molecular Orbital Studies of the Hetero(A,B)polyenes and Hetero(A,B)annulenes [(A,B) = (C,C), (C,N), (B,N), (B,O)]

R. C. Haddon

Bell Laboratories
Murray Hill, New Jersey 07974

ABSTRACT

Ab initio molecular orbital theory has been used to compare the ability of the C-C, C-N, B-N and B-O linkages to develop π-electron conjugation in linear and monocyclic bonding configurations. The primary distinction occurs between the C,C and C,N group and the B,N and B,O group and it is concluded that the nature of the bonding in heteroconjugated systems is primarily determined by whether the doubly bonded form of the A,B pair involves a covalent (-A=B-) or ionic ($-\overset{-}{A}=\overset{+}{B}-$) form. Bond alternation is prevalent in the former category but bond equalization occurs exclusively in the latter group. Conjugation energies in the hetero(A,B)polyenes are positive for the C,C and C,N molecules but negative for the B,N and B,O molecules. The resonance energies of benzene, s-triazine, borazine and boroxine are calculated to be in the "ratio" of 3:2:1:0.

In contrast with the carbon-based molecules, the heteropolyenes and heteroannulenes have received comparatively little attention. We define the [2n]hetero(A,B)polyenes to be of the form $H(AB)_nH$ and the [2n]hetero(A,B)annulenes to be of the form $(AB)_n$ where each of the atoms A and B has a pπ-orbital available for conjugation within a coplanar framework and the A,B pair together contribute a total of two electrons to the π-system. In some cases, therefore A,B contain attached hydrogen atoms. Interest in the area of heteroaromatic chemistry may be traced to the recognition of borazine as an "inorganic benzene,"[1-3] although it had long been realized that s-triazine could also be classed as an aromatic compound. A firm theoretical foundation for such compounds was provided by Craig[4-6] in his discussion of homomorphic (pπ-pπ) and heteromorphic (pπ-dπ) bonding systems within the framework of the HMO theory (this work is limited to the former category). More complicated B,N networks were considered by Baird and Whitehead[7] and they surmised that many of the characteristics of organic molecules with carbon-carbon double bonds are present in conjugated B,X systems. However, on the basis of the Craig formulation, they concluded that the greater stability of conjugated monocyclic ring systems (annulenes) with 4n + 2 π-electrons is much less evident in rings with alternating B and N atoms than it is with carbon-carbon rings. In the linear B,N systems they found evidence for reduced bond length alternation and increased conjugation energy with respect to the polyenes.

The question of bond length alternation in the heteroannulenes was considered by Davies[8] and by Haigh and Salem.[9] The results of the treatment are less clear-cut than in the case of the carbon-based annulenes, and the occurrence of bond length alternation is critically dependent on the difference in the coulomb integrals of A and B. The enhanced diamagnetic susceptibilities of some of these systems have been attributed to induced ring currents.[6,10–12] Band structure calculations[13–19] have been reported for polyacetylene [$(CH)_x$] and polymethylenimine [$(CHN)_x$].

Taken together, this work provides strong qualitative evidence for conjugation in hetero(A,B)polyenes and aromatic character in [4n+2]hetero(A,B)annulenes. More recently some of the oligomeric hetero-chains and -rings have come within the reach of sophisticated theoretical techniques[20–40] but the effect of ring size and chain length on conjugation in these systems has not yet received high level systematic investigation. These questions are taken up in a quantitative manner in the present paper, and the results compared with the corresponding quantities for the analogous carbon-based molecules.

Method

Hartree-Fock (HF) ab initio calculations were carried out with the Gaussian 70,[41] Gaussian 80[42] and Hondo[43] programs using the STO-3G[44] and 4-31G[45] basis sets. Geometry optimization was performed with the STO-3G basis within the following simplifications. Planarity was enforced and bond angles were set to 120° with the exception of the four-membered rings where internal angles were fixed at 90° and the A-H bond direction was set to bisect the external angle. Standard bond lengths[46] to hydrogen were assumed: C-H, 1.08 Å; N-H, 1.01 Å (amino); N-H, 0.99 Å (imino); O-H, 0.96 Å; B-H, 1.25 Å.

Results

Geometries. The results for the heteropolyenes are collected in Table 1 and for the heteroannulenes in Table 2. A number of the smaller systems have received previous theoretical attention, but due to our focus of interest we have not included a detailed discussion of these results. Among this work are treatments of ethylene (*1*),[20,27] methylenimine (*2*);[28] aminoborane (*3*),[7,29,30,32,33] hydroxyborane (*4*),[30,31,33] butadiene (*5*),[22,23,27] *7*,[7] hexatriene (*9*),[24,27] *11*,[7] cyclobutadiene (*13*),[22,25] *14*,[37] *15*[7,38] (found to be nonplanar[38]), benzene (*17*),[26], s-triazine (*18*),[34] borazole (*19*),[4,7,32,33,35,36,39] boroxine (*20*)[33,36,39] and [18]annulene (*21*).[40] Particularly among ab initio studies employing the STO-3G basis set, there is good agreement with the present results, although small differences remain as a result of the geometrical simplifications adopted.

Experimental structures are available for a subset of the molecules treated herein. The C-C bond length in ethylene (*1*) (1.330 Å);[47] the C-N bond length in methylenimine (*2*) (1.273 Å);[48] the B-N bond length in aminoborane (*3*) (1.403 Å);[49] the C-C bond lengths in butadiene (*5*) (A_1–B_2 = 1.341, B_2–A_3 = 1.463 Å),[50] hexatriene (*9*), (A_1–B_2 = 1.337, B_2–A_3 = 1.458, A_3–B_4 = 1.368 Å),[51] benzene (*17*) (1.397 Å)[52] and

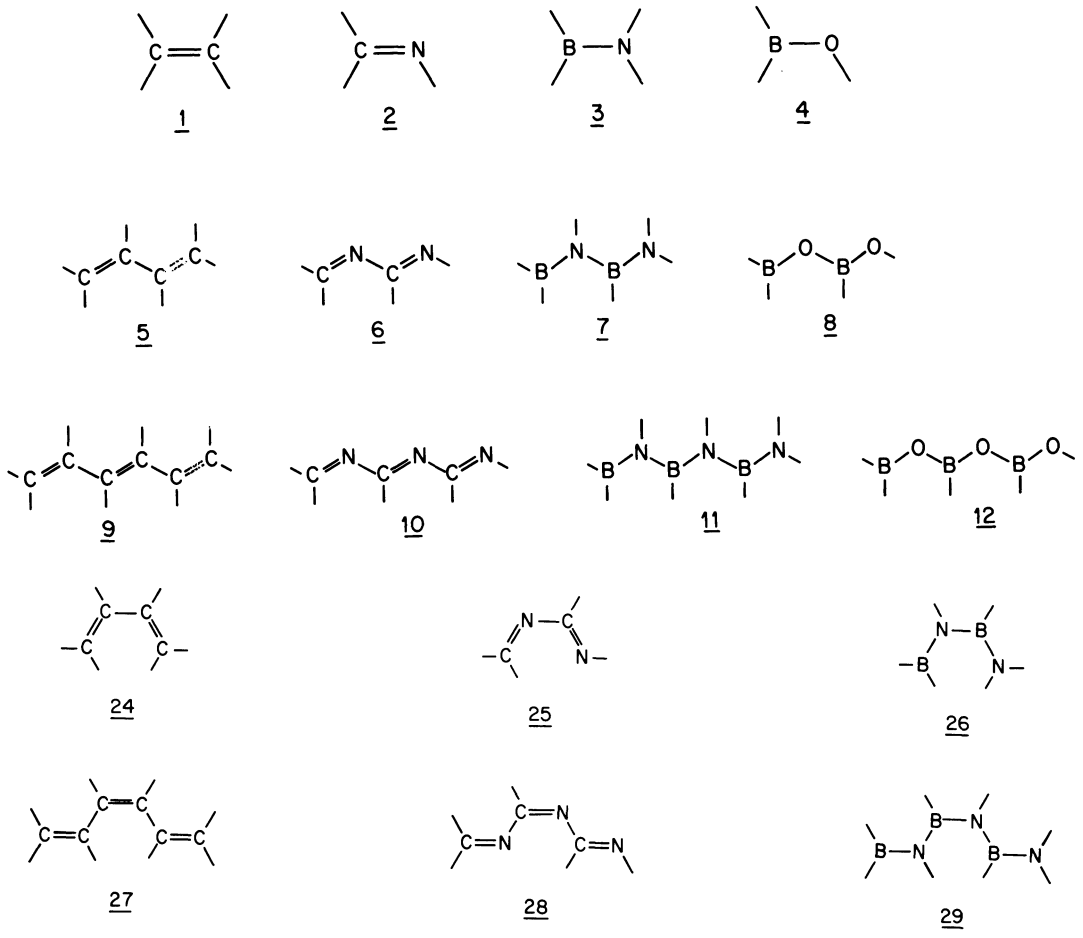
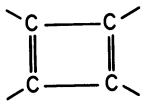
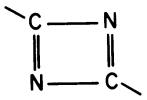


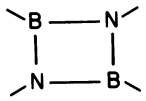
Table 1. STO-3G Calculated Bond Lengths for Linear [N]Hetero(A,B)polyenes (A°)

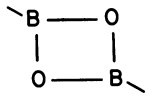
Mol	N	A,B	A_1–B_2	B_2–A_3	A_3–B_4	B_4–A_5	A_5–B_6	ΔR^a
1	2	C,C	1.309					
2	2	C,N	1.265					
3	2	B,N	1.375					
3p	2	B,N	1.457					
4	2	B,O	1.321					
4p	2	B,O	1.353					
5	4	C,C	1.313	1.488	1.313			0.175
6	4	C,N	1.274	1.449	1.267			0.179
7	4	B,N	1.396	1.446	1.391			0.053
8	4	B,O	1.341	1.376	1.328			0.042
9	6	C,C	1.319	1.488	1.327	1.488	1.319	0.161
10	6	C,N	1.275	1.444	1.277	1.444	1.267	0.167
11	6	B,N	1.398	1.443	1.414	1.437	1.394	0.026
12	6	B,O	1.344	1.372	1.347	1.368	1.329	0.023
24	4	C,C	1.318	1.516	1.318			0.198
25	4	C,N	1.274	1.457	1.270			0.185
26	4	B,N	1.395	1.467	1.386			0.077
27	6	C,C	1.319	1.494	1.338	1.494	1.319	0.156
28	6	C,N	1.275	1.457	1.278	1.449	1.268	0.175
29	6	B,N	1.398	1.439	1.431	1.440	1.393	0.009

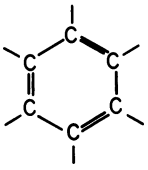
[a] $\Delta R = (B_2–A_3) - \frac{1}{2}[(A_1–B_2) + (A_3–B_4)]$, (N = 4); $\Delta R = \frac{1}{2}[(B_2–A_3) + (B_4–A_5)] - (A_3–B_4)$, (N = 6).

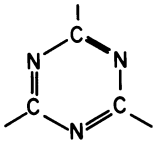

13

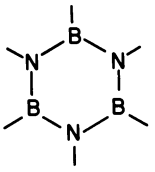

14

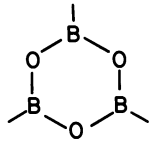

15

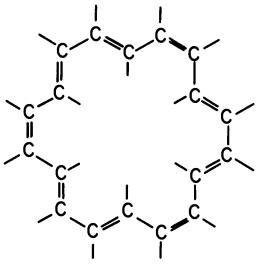

16

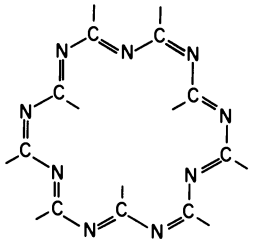

17


18


19


20


21


22

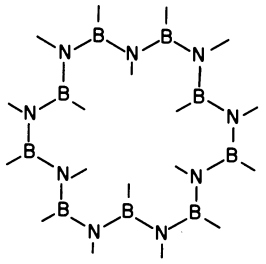

23

Table 2. STO-3G Calculated Bond Lengths for [N]Hetero(A,B)annulenes (A°)

Mol	Sym	N	A,B	A-B	B-A	ΔR^a
13	D_{2h}	4	C,C	1.313	1.569	0.256
14a	D_{2h}	4	C,N	1.424		
14b	C_{2h}	4	C,N	1.294	1.553	0.259
15	D_{2h}	4	B,N	1.441		
16	D_{2h}	4	B,O	1.409		
17	D_{6h}	6	C,C	1.387		
18	D_{3h}	6	C,N	1.348		
19	D_{3h}	6	B,N	1.417		
20	D_{3h}	6	B,O	1.361		
21a	D_{6h}	18	C,C	1.403		
21b	D_{3h}	18	C,C	1.336	1.490	0.154
22a	D_{3h}	18	C,N	1.351		
22b	C_{3h}	18	C,N	1.283	1.444	0.161
23	D_{3h}	18	B,N	1.431		

[a] $\Delta R = (B-A) - (A-B)$

[18]annulene (*21a*, D_{6h}) (inner, 1.382; outer, 1.419 Å).[53] The geometries of the [6]hetero(A,B)annulenes have also been obtained: s-triazine (*18*) (C-N = 1.319, 1.338 Å; N-C-N = 126.8, 127°);[54,55] borazine (*19*) (B-N = 1.436 Å, N-B-N = 117.7°);[56] boroxine (*20*) (B-O = 1.376 Å, O-B-O = 120°).[57] When the internal angles of the [6]hetero(A,B)annulenes were included in the STO-3G geometry optimization the following parameters were obtained: *18′* (C-N = 1.353 Å, N-C-N = 126.4°), *19′* (B-N = 1.418 Å, N-B-N = 117.5°), 20′ (B-O = 1.361 Å, O-B-O = 119.6°). In general the agreement with theory is reasonable and based on previous experience[58] it is to be expected that the STO-3G basis set will reproduce the chemical trends of interest. The overestimation of bond length alternation in the polyenes has been previously noted.[23,24,27]

It is clear from Tables 1 and 2 that the conjugated systems fall into two categories: (i) the C,C and C,N systems which show a marked degree of bond length alternation (with the exception of the six-membered rings, *17* and *18*), (ii) the B,N and B,O systems which show either bond equalization or weak bond alternation. The results for the B,N and B,O heteroannulenes suggest that bond equalization will prevail in these systems at long chain lengths. This is supported by the behavior of the B,N and B,O heteropolyenes where the center linkages of the chain may be seen to be approaching bond length equalization quite rapidly. The situation within the other category is not so clear cut. It is now well established that bond length alternation must eventually prevail in the carbon-based annulenes[15,18,19,59,60] although the critical ring size is still the subject of controversy. The status of [18]annulene (*21*) has been uncertain[40] almost from the time of its first synthesis[61] and even [10]annulene[62] has recently come under re-examination, although it seems that the planar *cis* configuration of [10]annulene is probably bond equalized.[62d] Nevertheless the margin

Table 3. Energies of [18]Hetero(A,B)annulenes

Mol	A,B	Basis Set	Sym	Bond Lengths(Å)	Rel (kcal/mol)	Energies HOMO (ev)	LUMO (ev)	ΔE (ev)
21a	C,C	STO-3G	D_{6h}	1.403	0.0	-3.64	3.15	6.79
21b	C,C	STO-3G	D_{3h}	1.336, 1.490	-39.0	-5.30	4.85	10.15
21a	C,C	4-31G	D_{6h}	1.403	0.0	-5.55	0.70	6.25
21b	C,C	4-31G	D_{3h}	1.336, 1.490	-18.7	-6.85	1.98	8.83
22a	C,N	STO-3G	D_{3h}	1.351	0.0	-6.09	1.51	7.60
22b	C,N	STO-3G	C_{3h}	1.283, 1.444	-41.7	-7.79	3.25	11.04
22a	C,N	4-31G	D_{3h}	1.351	0.0	-8.96	-0.48	8.49
22b	C,N	4-31G	C_{3h}	1.283, 1.444	-1.0	-9.81	0.37	10.18
23a	B,N	STO-3G	D_{3h}	1.431	0.0	-7.79	7.32	15.10
23b	B,N	STO-3G	C_{3h}	1.38, 1.56[a]	50.9	-7.90	7.46	15.37
23a	B,N	4-31G	D_{3h}	1.431	0.0	-10.00	4.16	14.15
23b	B,N	4-31G	C_{3h}	1.38, 1.56[a]	41.6	-10.07	4.12	14.20

[a] Assumed values, ref 39.

between bond alternation and bond equalization is quite small for this system and although electron correlation plays an important role in stabilizing the symmetrical structure, the magnitude of this effect is smaller than the earlier estimates. It is therefore possible that the HF result (Table 3) in favor of bond length alternation in [18]annulene will hold up even when electron correlation is included in the calculation. Clearly, however, the question of bond length alternation in [18]annulene will require further attention before a definitive answer is attained.

The C,N heteroconjugated systems show ostensibly similar behavior to that of the carbon-based compounds. Both the hetero(C,N)polyenes and hetero(C,N)annulenes show a very similar degree of bond alternation (ΔR) to that exhibited by the polyenes and annulenes themselves. At first glance it might therefore be expected that the tendency toward bond alternation in the two series would proceed in a parallel fashion, and the STO-3G result for the energy difference between *22a* and *22b* supports this idea. When this quantity is recalculated with the 4-31G basis set, however, it is apparent that the former result is probably a reflection of the poor description of the orbital energies which is provided by the STO-3G basis set. We have previously pointed out how such a deficiency can falsely accentuate the tendency toward bond length alternation.[62c] The 4-31G result therefore suggests that [18]hetero(C,N)annulene may be bond equalized. At the very least the tendency toward bond alternation is certainly less than in the analogous carbon compound and this is reflected in the calculated energy gaps (ΔE). The ΔE values in the symmetric structures provide a qualitative measure of the strength of the second-order Jahn-Teller effect which is ultimately responsible for distortion of the molecule to a bond alternate structure.[60,63,64] By way of contrast with *21* and *22*, it should be noted that the energy gap in [18]hetero(B,N)annulene is always large and this system shows no tendency toward bond alternation.

Within a single determinant treatment the antiaromatic *13* has a strong tendency toward distortion although the real situation is somewhat more complicated.[25] [4]Hetero(C,N)annulene (*14*) is also strongly distorted and at the STO-3G level, structure *14b* is preferred over *14a* by 22.1 kcal/mol. The remaining [4]hetero(A,B)annulenes (*15* and *16*) retain bond equalized perimeters, although it has been shown that *15* adopts a nonplanar structure[38] (we have not investigated deviations from planarity).

Resonance Energies. The conjugation energies are collected in Tables 4-7. The isodesmic reactions[65] are designed to conserve the number of bonds of a given formal type. The homodesmotic reactions[66] conserve the number of each type of carbon-carbon bond and the number of each type of carbon atom with a given number of attached hydrogen atoms. Clearly the latter category is more restrictive and it has been argued that in such reactions the extraneous energy contributions are minimized, allowing the identification of the underlying resonance energies.[66] It is a simple matter to extend this concept to the heteroconjugated species treated in this paper.

The isodesmic conjugation energies clearly fall into two groups, with the exception of the [4]hetero(A,B)annulenes which contain a ring strain component and are therefore not meaningful in the present context. As may be seen from Tables 4 and 5 the C,N conjugation energies are comparable to the

Table 4. Isodesmic Conjugation Energies for [N]Hetero(A,B)polyenes (kcal/mol)

N	A,B	Reaction	STO-3G	4-31G
4	C,C	*5* + $2CH_4$ → 2 *1* + C_2H_6[a]	12.3	11.2
4	C,N	*6* + CH_4 + NH_3 → 2 *2* + CH_3NH_2	15.4	15.2
4	B,N	*7* + BH_3 + NH_3 → 3 *3*	-8.3	-21.8
4	B,O	*8* + BH_3 + OH_2 → 3 *4*	-2.8	-6.1
6	C,C	*9* + $4CH_4$ → 3 *1* + $2C_2H_6$	25.2	21.1
6	C,N	*10* + $2CH_4$ + $2NH_3$ → 3 *2* + $2CH_3NH_2$	29.7	29.8
6	B,N	*11* + $2BH_3$ + $2NH_3$ → 5 *3*	-14.9	-41.7
6	B,O	*12* + $2BH_3$ + $2OH_2$ → 5 *4*	-3.3	-11.2
8	C,C	C_8H_{10}[b] + $6CH_4$ → 4 *1* + $3C_2H_6$	38.2[b]	
10	C,C	$C_{10}H_{12}$[c] + $8CH_4$ → 5 *1* + $4C_2H_6$	51.2[c]	

[a] Experimental value: 14.2 kcal/mol, see ref 27.
[b] *Trans*-octatetraene, ref 27.
[c] *Trans*-decapentaene, ref 27.

Table 5. Isodesmic Conjugation Energies for [N]Hetero(A,B)annulenes (N = 2,3) (kcal/mol)

N	A,B	Reaction	STO-3G	4-31G
4	C,C	*13* + $4CH_4$ → 2 *1* + $2C_2H_6$	-64.2	-66.5
4	C,N	*14* + $2CH_4$ + $2NH_3$ → 2 *2* + $2CH_3NH_2$	-48.1	-64.5
4	B,N	*15* + $2BH_3$ + $2NH_3$ → 4 *3*	-74.8	-95.6
4	B,O	*16* + $2BH_3$ + $2OH_2$ → 4 *4*	-69.8	-73.7
6	C,C	*17* + $6CH_4$ → 3 *1* + $3C_2H_6$	72.8	66.5
6	C,N	*18* + $3CH_4$ + $3NH_3$ → 3 *2* + $3CH_3NH_2$	76.1	74.1
6	B,N	*19* + $3BH_3$ + $3NH_3$ → 6 *3*	-9.4	-54.4
6	B,O	*20* + $3BH_3$ + $3OH_2$ → 6 *4*	1.6	-20.6

carbon-based systems for both the linear chains and s-triazine (*18*). On the isodesmic reaction scale all of the B,N and B,O systems have a negative energy of conjugation. This comes about because the reference molecules (*3* and *4*) allow for conjugation but do not include the singly bonded component which arises in the other schemes. This problem can be circumvented to some extent by including the appropriate number of perpendicular forms *3p* and *4p* in the reference but then the conjugation energies become very large [STO-3G: *7* (32.6), *8* (17.2), *11* (66.9), *12* (36.7), *19* (113.3), *20* (61.6 kcal/mol)].

Table 6. Homodesmotic Conjugation Energies for [N]Hetero(A,B)annulenes (N = 2,3) (kcal/mol)

N	A,B	Reaction	STO-3G	4-31G
4	C,C	*13* + 2 *1* → 2 *5*	-92.6	-88.6
4	C,N	*14* + 2 *2* → 2 *6*	-78.9	-95.0
4	B,N	*15* + 2 *3* → 2 *7*	-58.1	-51.9
4	B,O	*16* + 2 *4* → 2 *8*	-64.3	-61.5
6	C,C	*17* + 3 *1* → 3 *5* [a]	30.3	33.3
6	C,N	*18* + 3 *2* → 3 *6*	30.1	28.3
6	C,N	*18* + 3 *2* → 3 *25*	25.3	20.5
6	B,N	*19* + 3 *3* → 3 *7*	15.7	11.0
6	B,O	*20* + 3 *4* → 3 *8*	9.9	-2.2

[a] Experimental value: 21.2 kcal/mol, see ref 66.

Table 7. Homodesmotic Conjugation Energies for [18]Hetero(A,B)annulenes (kcal/mol)

				Corrected[a]	
A,B	Reaction	STO-3G	4-31G	STO-3G	4-31G
C,C	*21* + 9 *1* → 9 *5* [b]	-43.3	-30.6	-6.1	6.7
C,N	*22* + 9 *2* → 9 *6*	14.1	16.5	4.1	-1.2
B,N	*23* + 9 *3* → 9 *7*	-0.4	2.0	16.3	18.2
B,N	*23* + 9 *3* → 3 *7* + 6 *26*	14.9	18.0		

[a] For *21* includes energy correction for 3(*5* + *9*) → 3(*24* + *27*); for *22*, 3(*6* + *10*) → 3(*25* + *28*); for *23*, 3(*7* + *11*) → 3(*26* + *29*).
[b] Experimental value: 4.9 ± 5.8 kcal/mol, see ref 63.

The homodesmotic conjugation energies given in Table 6 provide a more balanced picture of the [6]hetero(A,B)annulenes. Within this scheme the C,N and C,C resonance energies are comparable, whereas the B-N and B-O values are considerably reduced. Based on the best level of theory and using the analysis of Table 6, the aromatic character is roughly, benzene: s-triazine: borazine: boroxine in the "ratio" of 3:2:1:0 (see, however, the discussion below regarding [18]hetero(B,N)annulene).

In order to obtain a correct reference structure for the [18]hetero(A,B)annulenes, a correction must be applied for the internal nonbonded interactions. This can be accomplished by the procedure shown in the footnotes of Table 7. For the *trans* -> *cis* isomerization reactions the following values (STO-3G, 4-31G, kcal/mol) were calculated: *5* -> *24* (7.0, 7.0), *9* -> *27* (5.4, 5.5), *6* -> *25* (-0.5, -2.6), *10* -> *28* (-2.8, -3.3), *7* -> *26* (2.6, 2.7) and *11* -> *29* (3.0, 2.7). It is interesting to note that the C-N conformers prefer the *cis* structures *25* and *28* over the *trans* isomers *6* and *10*, respectively. This finding contrasts with the results obtained by band structure calculations on polymethylenimine.[16,19]

The homodesmotic conjugation energies for the C,C and C,N [18]hetero(A,B)annulenes are both effectively zero, at least within the accuracy of the model systems. It has been previously pointed out[63] that the resonance energy of *21* is expected to be negligibly small and this is in accord with the experimental result. The result for [18]hetero(B,N)annulene is surprising at first sight, and given the good models which are available, is probably reliable in suggesting a resonance energy for *23* within the scheme of Table 7. Nevertheless it is important to bear in mind that the model compounds *7* and *26* are themselves conjugatively *destabilized* (Table 4).

Conclusion. In the present study we have compared the ability of the C-C, C-N, B-N and B-O linkages to develop π-electron conjugation in linear and monocyclic bonding configurations.

In the C,C case bond length alternation prevails, with the exception of the lower annulenes. At the present theoretical level [18]annulene is found to be bond alternate. Strong bond alternation is also found in the C,N compounds, although the weak energy gain on distortion of [18]hetero(C,N)annulene suggests that bond equalization should persist in the hetero(C,N)annulenes to larger ring sizes than in the annulenes themselves. The B,N and B,O structures were found to be quite different from those adopted by the C,C and C,N systems. In particular the B,N and B,O hetero(A,B)annulenes were all found to be bond equalized, including the "antiaromatic" four-membered rings. The B,N and B,O hetero(A,B)polyenes, also showed evidence of a trend toward bond equalization at the center of the chain as "end effects" were minimized.

The division of the bonding A,B pairs into the C,C and C,N group and the B,N and B,O group was also evident in the consideration of the resonance energies. The former group of hetero(A,B)polyenes showed positive isodesmic conjugation energies whereas the latter group exhibited negative values. The resonance energies (aromatic character) of benzene, s-triazine, borazine and boroxine were found to be in the "ratio" of 3:2:1:0. In the [18]hetero(A,B)annulenes the C,C and C,N cases exhibit effectively zero resonance energy, whereas the B,N molecule appears to possess a finite resonance energy.

It is therefore concluded that the primary differences in these systems does not arise from whether A and B are different, but on whether the multiply bonded form is covalent (-A = B-) or ionic ($-\overset{-}{A} = \overset{+}{B}-$). This classification is consistent with the idea that the extent of delocalization in hetero(A,B)conjugated systems is dependent on the differences in Coulomb integrals of the A,B pairs;[4–10] thus $|\alpha_A - \alpha_B| =$ 0.0 (C,C), 0.51 (C,N), 1.82 (B,N), 2.54β (B,O).[67]

Appendix

	Total Energy (h)			Total Energy (h)	
Mol	STO-3G	4-31G	Mol	STO-3G	4-31G
BH_3[a]	-26.07070	-26.34845	*17*	-227.89132	-230.37745
CH_4[b]	-39.72686	-40.13976	*18*	-275.12368	-278.23266
NH_3[c]	-55.43767	-56.10482	*19*	-238.13207	-240.81322
OH_2[b]	-74.96590	-75.90324	*20*	-296.74304	-300.24063
CH_3CH_3[b]	-78.30618	-79.11582	*21a*	-683.39820	-690.89464
CH_3NH_2	-94.01617	-95.06873	*21b*	-683.46032	-690.92437
1[d]	-77.07265	-77.92088	*22a*	-825.18343	-834.58723
2	-92.81582	-93.88069	*22b*	-825.24981	-834.58888
3	-80.45423	-81.37337	*23a*	-714.32064	-722.39002
4	-99.97506	-101.17141	*23b*	-714.23958	-722.32375
5[d]	-153.02036	-154.69568	*24*	-153.00920	-154.68460
6	-184.50775	-186.60987	*25*	-184.50857	-186.61395
7	-159.82326	-161.63857	*26*	-159.81918	-161.63432
8	-198.88417	-201.25277	*27*	-228.95335	-231.46284
9[d]	-228.96198	-231.47160	*28*	-276.20245	-279.34320
10	-276.19795	-279.33787	*29*	-239.19036	-241.90255
11	-239.19517	-241.90688	*3p*[e]	-80.38900	
12	-297.79687	-301.33583	*4p*[e]	-99.94322	
13b	-151.74792	-153.40837	*18'*[f]	-275.13767	
14a	-183.22293		*19'*[f]	-238.13397	
14b	-183.25817	-183.30695	*20'*[f]	-296.74309	
15	-158.64550	-160.44765	C_8H_{10}[g]	-304.90753	
16	-197.71580	-200.06478	$C_{10}H_{12}$[h]	-380.85290	

[a] Ref 30a.
[b] Ref 21.
[c] W. A. Lathan, W. J. Hehre, L. A. Curtiss and J. A. Pople, *J. Am. Chem. Soc. 93, 6377 (1971).*
[d] Ref 27.
[e] Perpendicular form.
[f] Optimized ring bond angles.
[g] *Trans*-octatetraene, ref 27.
[h] *Trans*-decapentaene, ref 27.

References

1. A. Stock and R. Wierl, *Z. Anorg. Allgem. Chem., 203,* 228 (1931).
2. S. H. Bauer, *J. Am. Chem. Soc. 60,* 524 (1938).
3. E. Wiberg, *Naturwiss. 35,* 182, 212 (1948).
4. D. P. Craig, *J. Chem. Soc.* 997 (1959).
5. D. P. Craig in "Theoretical Organic Chemistry," Butterworths, London, 1959, p 20.
6. D. P. Craig, M. L. Heffernan, R. Mason and N. L. Paddock, *J. Chem. Soc.* 263 (1961).
7. N. C. Baird and M. A. Whitehead, *Can. J. Chem. 45,* 2059 (1967).
8. D. W. Davies, *Nature 194,* 82 (1962); *196,* 1309 (1962).
9. C. W. Haigh and L. Salem, *Nature 196,* 1307 (1962).
10. H. Watanabe, K. Ito and M. Kubo, *J. Am. Chem. Soc. 82,* 3294 (1960).
11. H. J. Dauben, Jr., J. D. Wilson and J. L. Laity in "Nonbenzenoid Aromatics," Ed. J. P. Snyder, Academic Press, NY, 1971, p 167.
12. P. H. Blustin, *Mol. Phys. 36,* 279 (1978).
13. C. A. Coulson and G. S. Rushbrooke, *Proc. Camb. Phil. Soc. 44,* 272 (1948).
14. A. A. Ovchinnikov, I. I. Ukrainskii and G. V. Kventsel, *Soviet Physics Uspekhi 15,* 575 (1973).
15. (a) A. Karpfen and J. Petkov, *Solid State Commun. 29,* 251 (1979)
    (b) M. Kertesz, J. Koller and A. Azman, *Int. J. Quant. Chem. 18,* 645 (1980).
16. (a) A. Karpfen, *Chem. Phys. Lett. 64,* 299 (1979).
    (b) M. Kertesz, J. Koller and A. Azman, *Chem. Phys. Lett. 69,* 225 (1980).
17. M. Kertesz, J. Koller and A. Azman *Int. J. Quant. Chem., Quant. Chem. Symp. 14,* 463 (1980).
18. P. M. Grant and I. P. Batra, *Syn. Metals 1,* 193 (1979/80).
19. M. -H. Whangbo, R. Hoffmann and R. B. Woodward, *Proc. Roy. Soc. 366A,* 23 (1979).
20. W. A. Lathan, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc. 92,* 4796 (1970).
21. W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle and J. A. Pople, *Prog. Phys. Org. Chem. 11,* 175 (1974).
22. W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc. 97,* 6941 (1975).

23. (a) S. Skaarup, J. E. Boggs and P. N. Skancke *Tetrahedron 32,* 1179 (1976).

(b) J. P. Daudey, G. Trinquier, J. C. Barthelat and J. P. Malrieu *Tetrahedron 36,* 3399 (1980).

24. (a) G. J. Mains, P. George, C. W. Bock, M. Trachtman and A. M. Brett, *J. Mol. Struct. 41,* 87 (1977).

(b) A. Banks, G. J. Mains, C. W. Bock, M. Trachtman and P. George, *J. Mol. Struct. 56,* 267 (1979).

25. (a) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys. 48,* 354 (1968).

(b) R. C. Haddon and G. R. J. Williams, *J. Am. Chem. Soc. 97,* 6582 (1975).

(c) H. Kollmar and V. Staemmler, *J. Am. Chem. Soc. 99,* 3583 (1977).

(d) W. T. Borden and E. R. Davidson *J. Am. Chem. Soc. 99,* 4587 (1977).

(e) W. T. Borden, E. R. Davidson and D. Hart, *J. Am. Chem. Soc. 100,* 388 (1978).

(f) J. A. Jafri and M. D. Newton, *J. Am. Chem. Soc. 100,* 5012 (1978).

(g) R. C. Haddon, *Nouv. J. Chim. 3,* 719 (1979).

(h) T. Bally and S. Masamune, *Tetrahedron 36,* 343 (1980).

(i) W. T. Borden and E. R. Davidson, *Acc. Chem. Res. 14,* 69 (1981).

26. L. Radom and H. F. Schaefer, III, *J. Am. Chem. Soc. 99,* 7522 (1977).

27. R. C. Haddon and W. H. Starnes, Jr. *Adv. Chem. Ser. 169,* 333 (1978).

28. (a) J. M. Lehn, B. Munsch, and P. Mille, *Theor. Chim. Acta, 12,* 91 (1968); (b) J. M. Lehn, B. Munsch, and P. Millie, *Theor. Chim. Acta., 16,* 351 (1970); (c) B. Levy, P. Millie, J. M. Lehn, and B. Munsch, *Theor. Chim. Acta., 18,* 143 (1970); (d) E. Kochanski, J. M. Lehn, and B. Levy, *Theor. Chim. Acta., 22,* 111 (1971); (e) J. Vinh, B. Levy, and P. Millie, *Mol. Phys., 21,* 345 (1971); (f) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc., 93,* 289 (1971); (g) R. Ditchfield and J. E. Del Bene, *J. Am. Chem. Soc., 94,* 703 (1972); (h) P. Botschwina, *Chem. Phys. Lett., 29,* 580 (1974); (i) S. Wolf, H. B. Schlegel, and M. -H. Whangbo, *Can. J. Chem., 54,* 795 (1976); (j) N. D. Epiotis, R. L. Yates, J. R. Larson, C. R. Kirmaier, F. Bernardi, *J. Am. Chem. Soc. 99,* 8379 (1977). (k) D. J. DeFrees and W. J. Hehre, *J. Am. Chem. Soc. 82,* 391 (1978); (l) Y. Osamura, K. Kitaura, K. Nishimoto and S. Yamabe, *Chem. Phys. Lett. 63,* 406 (1979); (m) T. J. Lang, G. J. Wolber and R. D. Bach, *J. Am. Chem. Soc., 103,* 3275 (1981).

29. (a) H. Bock and W. Fuss, *Chem. Ber. 104,* 1687 (1971).

(b) M. -H. Whangbo and S. Wolfe, *Can. J. Chem. 54,* 949 (1976).

(c) D. R. Armstrong, B. J. Duke and P. G. Perkins, *J. Chem. Soc. A,* 2566 (1969).

(d) D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. A,* 2748 (1970).

(e) O. Gropen and H. M. Seip, *Chem. Phys. Lett. 25,* 206 (1974).

30. (a) J. D. Dill, P. v. R. Schleyer and J. A. Pople, *J. Am. Chem. Soc. 97,* 3402 (1975).

(b) T. Fjeldberg, G. Gundersen, T. Jonvik, H. M. Seip, S. Saebo, *Acta Chem. Scand. 34A,* 547 (1980).

31. (a) O. Gropen and R. Johansen, *J. Mol. Struct. 25,* 161 (1975).

(b) F. Bernardi, A. Bottoni and N. D. Epiotis, *J. Am. Chem. Soc. 100,* 7205 (1978).

32. R. Hoffmann, *J. Chem. Phys. 40,* 2474 (1964).

33. M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc. 99,* 5231 (1977).

34. (a) R. Gleiter, E. Helbronner and V. Hornung, *Helv. Chim. Acta 55,* 255 (1972).

(b) J. Almlöf, B. Roos, U. Wahlgren and H. Johansen, *J. Electron Spect., Rel. Phenom. 2,* 51 (1973).

(c) F. Mulder, G. v. Dijk, C. Hiuszoon, *Mol. Phys. 38,* 577 (1979).

35. (a) M. F. Guest, I. H. Hillier and I. C. Shenton, *Tetrahedron, 31,* 1943 (1975).

(b) P. H. Blustin, *Mol. Phys. 36,* 279 (1978).

36. A. Serafini and J. F. Labarre, *J. Mol. Struct. 26,* 129 (1975).

37. W. Yang, R. Minard and C. Matthews, *J. Theoret. Biol. 56,* 111 (1976).

38. M. J. S. Dewar and M. L. McKee, *J. Mol. Struct. 68,* 105 (1980).

39. B. M. Gimarc and N. Trinajstic, *Pure Appl. Chem. 52,* 1443 (1980).

40. (a) M. J. S. Dewar, R. C. Haddon and P. J. Student, *J. Chem. Soc., Chem. Commun.* 569 (1974).

(b) H. Baumann, *J. Am. Chem. Soc. 100,* 7196 (1978).

(c) R. C. Haddon, *Chem. Phys. Lett. 70,* 210 (1980).

(d) M. J. S. Dewar and M. L. McKee, *Pure Appl. Chem. 52,* 1431 (1980).

(e) W. Thiel, *J. Am. Chem. Soc. 103, 1420 (1981).*

41. W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton and J. A. Pople, *QCPE 11,* 236 (1973).

42. J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn and J. A. Pople, *QCPE 13,* 406 (1981).

43. M. Dupuis, J. Rys and H. King, *QCPE 11,* 338 (1977).

44. W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys. 51,* 2657 (1969).

45. R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys. 54,* 724 (1971).

46. J. A. Pople and D. L. Beveridge," Approximate Molecular Orbital Theory," McGraw-Hill, NY, 1970, p 110.

47. K. Kuchitsu, *J. Chem. Phys. 44,* 906 (1966).

48. R. Pearson, Jr. and F. L. Lovas, *J. Chem. Phys. 66,* 4149 (1977).

49. M. Sugie, H. Takeo and C. Matsumara, *Chem. Phys. Lett. 64,* 573 (1979).

50. K. Kuchitsu, T. Fukuyama, Y. Morino, *J. Mol. Struct. 1,* 463 (1967/68).

51. M. Traetteberg, *Acta Chem. Scand. 22,* 628 (1968).

52. A. Langseth and B. P. Stoicheff, *Can. J. Phys. 34,* 350 (1956).

53. (a) J. Bregman, F. L. Hirshfeld, D. Rabinovitch and G. M. J. Schmidt, *Acta Cryst. 19,* 227 (1965).
(b) F. L. Hirshfeld and D. Rabinovitch, *Acta Cryst. 19,* 235 (1965).

54. P. J. Wheatley, *Acta Cryst. 8,* 224 (1955).

55. J. E. Lancaster and B. P. Stoicheff, *Can. J. Phys. 34,* 1016 (1956).

56. W. Harshbarger, G. Lee, R. F. Porter and S. H. Bauer, *Inorg. Chem. 8,* 1683 (1969).

57. C. H. Chang, R. F. Porter and S. H. Bauer, *Inorg. Chem. 8,* 1689 (1969).

58. J. A. Pople in "Applications of Electronic Structure Theory," Vol. 4, Ed. H. F. Schaefer, Plenum, NY, 1977, p 1.

59. H. C. Longuet-Higgins and L. Salem. *Proc. Roy. Soc. 251A,* 172 (1959).

60. L. Salem, "Molecular Orbital Theory of Conjugated Systems," Benjamin, NY, 1966, Chap 8.

61. (a) F. Sondheimer, R. Wolovsky and Y. Amiel, *J. Am. Chem. Soc. 84,* 274 (1962).
(b) F. Sondheimer, *Acc. Chem. Res. 5,* 81 (1972).

62. (a) J. Leska and D. Loos, *J. Mol. Struct. 21,* 245 (1974).
(b) L. Farnell, J. Kao, L. Radom and H. F. Schaefer, III, *J. Am. Chem. Soc. 103,* 2145 (1981).
(c) R. C. Haddon and Z. Wasserman, *Nouv. J. Chim.,* in press.
(d) R. C. Haddon and K. Raghavachari, to be published.

63. R. C. Haddon, *J. Am. Chem. Soc. 101,* 1722 (1979).

64. R. C. Haddon, *J. Am. Chem. Soc. 102,* 1807 (1980).

65. (a) W. J. Hehre, R. Ditchfield and L. Radom, *J. Am. Chem. Soc. 92,* 4796 (1970).
(b) L. Radom, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc. 93,* 289 (1971).

66. (a) P. George, M. Trachtman, C. W. Bock and A. M. Brett, *Theor. Chim. Acta 38,* 121 (1975).
(b) P. George, M. Trachtman, C. W. Bock and A. M. Brett, *J. C. S., Perkin 2,* 1222 (1976).

67. F. A. Van-Catledge, *J. Org. Chem. 45,* 4801 (1980).