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criteria) appears to increase for the neutral ylides but to decrease for the charged ylidions.

Our calculations also reveal the importance of including electron correlation in calculating the structural features of some of the systems considered here, particularly those involving the more electronegative elements. The effect is most noticeable in the CH_2XH and $CH_3X^{\cdot+}$ species. On the whole, MP2/6-31G* optimizations tend to shorten the C–X bonds (relative to HF/6-31G*) with the largest reductions being 1.344 Å in CH_2ClH and 0.723 Å in $CH_3F^{\cdot+}$. On the other hand, the effects on the relative energies of using large basis sets and of using MP4 instead of MP3 are much less dramatic. Our highest level calculations reveal some significant discrepancies between theoretical and experimental relative energies.

Acknowledgment. We are pleased to acknowledge continuing, stimulating interaction with Professors F. W. McLafferty and J. L. Holmes.

Registry No. 1a, 74-89-5; **1b**, 67-56-1; **1c**, 593-53-3; **1d**, 593-54-4; **1e**, 74-93-1; **1f**, 74-87-3; **2d**, 36429-11-5; **5a**, 34516-31-9; **5b**, 12538-91-9; **5c**, 59122-96-2; **5d**, 91391-14-9; **5e**, 53369-41-8; **5f**, 12538-71-5; **6a**, 21444-88-2; **6b**, 25765-84-8; **6c**, 84609-27-8; **6d**, 56898-66-9; **6e**, 81255-83-6; **6f**, 81255-84-7; HF, 7664-39-3; HCl, 7647-01-0; H_2C:, 2465-56-7.

Supplementary Material Available: Total energies for the standard calculations for the first- and second-row systems (Tables VI and VII, respectively) (6 pages). Ordering information is given on any current masthead page.

Structure and Aromaticity of 14-Annulene and 18-Annulene[†]

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Abstract: The ground-state structures of 14- and 18-annulene were calculated for localized and delocalized geometries with the semiempirical MO method SINDO1 on the SCF and CI level. The results for geometry and energy are in agreement with other available theoretical and experimental data. The delocalized structures are obtained as most stable only if interpair correlation is included and the Davidson correction added. These structures can be called aromatic.

I. Introduction

The larger annulenes have been the subject of much discussion. Initially they served as objects of demonstration for the famous Hückel rule of aromaticity which classifies annulenes with $(4n + 2)$ π electrons as aromatic and with $(4n)$ π electrons as antiaromatic.[1] Since then it became clear that not only topology but also geometry has a decisive influence on the properties of such compounds. Dewar and Gleicher[2] suggested on the basis of PPP calculations a damped oscillation of resonance energies with increasing ring size. In their scheme the 22-annulene would present the limit for aromaticity with a positive resonance energy. All annulenes with more than 22 atoms were predicted to have negative resonance energies. Later Dewar[3] corrected this picture by suggesting that annulenes with an even number of 20 or more atoms would approach a common limit of resonance stabilization of about 2.8 kcal/mol. This small resonance energy implies bond alternation. Dewar estimated that an alternation of bond lengths would occur with limiting values for minimal bond lengths of 1.35 Å and maximal bond lengths of 1.46 Å under the assumption of an inverse linear relationship between bond order and bond length. Resonance energy methods advanced by Hess and Schaad[4] and Trinajstic et al.[5] on the Hückel electron level arrived at almost the same conclusions with respect to aromaticity as Dewar. More recently the structure of these compounds became the object of increased attention. Molecular mechanics calculation[6,7] on 14- and 18-annulenes and ab initio SCF calculations[8] on 10- and 18-annulenes determined the structures for alternative symmetries.

In this paper we wish to unify the view points of structure and aromaticity of annulenes. Here the question of bond alternation is most important. Experiments suggest that 14-annulene is nonplanar with very little bond alternation[9] and 18-annulene is planar also with very little bond alternation.[10] A summary of previous discussion on the structure of 18-annulene with particular reference to the electronic spectrum was given by Baumann and Oth.[11] Most previous calculations on the stability of 18-annulene are in disagreement with the experimental result. Using MINDO/3 Dewar[12] reported that a planar structure with D_{3h} symmetry and localized bonds is 26 kcal/mol more stable than the D_{6h} structure with delocalized bonds. But Binsch et al.[13] had already arrived qualitatively at a delocalized structure. More recently Baumann[14] predicted more definitively a delocalized structure by using MINDO/2 with correlation correction. In the following we wish to contribute to the discussion with the presentation of SINDO1[15] calculations on the structure of these two annulenes. The question of aromaticity is investigated with the bond order index recently introduced.[16]

Table I. Energy Lowering (kcal/mol) of Relevant Structures by CI Calculations with the Most Important Double Excitations

	14-annulene			18-annulene	
size of CI	D_2	C_{2h}	C_s	D_{3h}	D_{6h}
20	36.8	36.5			37.5
40	43.3	41.3			45.5
60	46.3	43.7	7.1	9.4	50.7

[†] Dedicated to Prof. R. G. Parr on the occasion of his 65th birthday.

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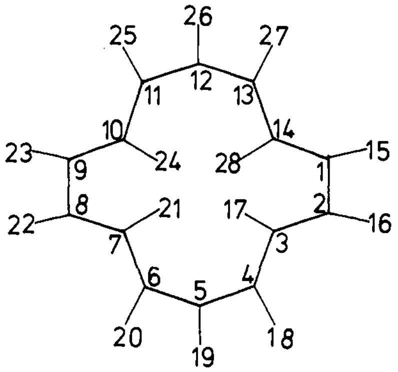

Figure 1. Structure and labeling of 14-annulene.

II. Method of Calculation

The geometries were calculated by optimizing the symmetry structures of D_2, C_{2h}, and C_s point groups for 14-annulene and D_{3h} and D_{6h} for 18-annulene on the SCF level with the semiempirical MO method SINDO1. In the ab initio calculation[8] the D_{3h} structure of 18-annulene was constrained to alternating single and double bonds with only one distinct bond length for each type of bond. We allowed an independent optimization of bond lengths for those bonds which are not equal by symmetry so that two different single and double bond lengths appear. For the optimized structures various levels of CI were applied. We started with double excitations of intrapair type $\psi_k\bar{\psi}_k \rightarrow \psi_p\bar{\psi}_p$, where k labels an occupied MO of the SCF wave function and p a virtual orbital and the bar indicates β spin. We selected those configurations which gave significant energy lowering and ordered them in decreasing contributions. However, when it became apparent that all these contributions were not going to change the relative energy compared to the SCF calculation, we included also interpair correlation. This correlation consists of double excitation of the type $\psi_k\psi_l \rightarrow \psi_p\psi_q$ or $\psi_k\bar{\psi}_l \rightarrow \psi_p\bar{\psi}_q$. Both types of correlation correction were already used by Baumann.[14] The number of interpair excitations increases approximately quadratically compared to the number of intrapair type. In a system like 14-annulene there would be about one thousand intrapair excitations in a minimal basis set and on the order of one million interpair excitations. By selective search we have determined those double excitations of both types which correlate most strongly with the ground state SCF configuration. We have then ordered these contributions from each double excitation in decreasing order and have selected the 20, 40, and 60 largest contributions for a CI calculation. In this fashion we could see the trend of stabilization of certain symmetry structures compared to others (Table I). As a result we found that the correlation was much larger for the delocalized structures than for the localized structures. From the correlation energy of a 60 × 60 CI approximately one-third was due to intrapair correlation and to each of the two types of interpair correlation. Finally we calculated the correction suggested by Davidson[17] for quadruple excitations. This energy correction is $\Delta E = (1 - c_0^2)\,E_{\mathrm{corr}}(\mathrm{DCI})$, where the correlation energy of the double excitation configuration interaction (DCI) wave functions is multiplied with the complementary weighting factor of the square of the coefficient c_0 of the SCF configuration in the DCI wave function.[18]

III. 14-Annulene

The 14-annulene was studied experimentally by Sondheimer.[19-21] These studies led to the conclusion that two conformational isomers exist differing essentially only in the hydrogen arrangement. From the four inner hydrogens depicted in Figure 1 two are above and the other two below the plane of the carbon ring. For H_{17} and H_{28} above the plane we obtain C_{2h} symmetry. If H_{17} and H_{24} are above the plane, the molecule has D_2 symmetry. We calculated the optimal structures for the two delocalized forms with D_2 and C_{2h} symmetry and also for the localized form with C_s symmetry with SINDO1. The results are given in Table II. The geometries refer to the SCF calculations. The CI energy was determined by a 60 configuration CI with the most important intra- and interpair double excitations. The total energy includes the Davidson correction. For the final total energy we find the C_{2h} symmetry as the most stable form, followed by the C_s symmetry and the D_2 symmetry. For the 60 configuration CI the stabilities of C_{2h} and C_s forms are approximately equal. It is now important to address the question of relative stability of delocalized and localized form. On the basis of MINDO/2 calculations without and with CI, Baumann[14] found the enthalpy of formation of the C_s form by about 11 kcal/mol more stable than the C_{2h} form, whereas a CI calculation with 52650 doubly excited configurations switched the stability to favor the C_{2h} form by about 27 kcal/mol. We had doubts about this result for two reasons: First MINDO/2 geometries and energies are not very accurate. Second the huge number of configurations is not easily justifiable in a semiempirical method. However, we are now convinced that the major portion of correlation energy in ring systems of this size cannot be parametrized empirically. In particular, the effect of interpair correlation is not included in our parametrization of SINDO1.

Table II. Geometries (Å and deg) and Total Energies (kcal/mol) of 14-Annulene

	SINDO1			MM[a]		exptl[b]
	D_2	C_{2h}	C_s	D_2	C_{2h}	$C_i(C_{2h})$
bond lengths						
C_1C_2	1.420	1.422	1.509	1.407	1.410	1.395
C_2C_3	1.423	1.424	1.368	1.409	1.408	1.382
C_3C_4	1.418	1.418	1.484	1.403	1.405	1.350
C_4C_5	1.426	1.423	1.368	1.413	1.411	1.407
bond angles						
$C_1C_2C_3$	122.7	127.5	127.0	120.4	124.2	123.3
$C_2C_3C_4$	137.7	133.6	132.5	130.3	126.9	130.3
$C_3C_4C_5$	127.1	126.4	125.5	125.2	123.7	125.5
$C_4C_5C_6$	132.0	130.0	128.5	129.7	126.9	128.4
dihedral angles						
$C_1C_2C_3C_4$	174.3	158.6	161.1	158.2	158.5	162.5
$C_2C_3C_4C_5$	177.9	−156.5	−139.6	174.5	163.4	−162.7
$C_3C_4C_5C_6$	14.7	15.2	−2.5	15.1	18.7	13.1
$C_4C_5C_6C_7$			39.1			15.4
$C_{14}C_1C_2C_3$	−21.0			23.5		
energy						
SCF	62.9	50.5	13.8			
CI	16.6	6.8	6.7			
total	9.5[c]	0[c]	6.6[c]	2.5	0	

[a] Reference 6. [b] Reference 9. [c] With Davidson correction.

Allinger[7] calculated with molecular mechanics (MM) only the C_{2h} and D_2 forms. He finds the same sequence, but a smaller difference between these two forms. Our bond length variation is similar to the molecular mechanics results and smaller than the crystal data.[9] Our angles are on the average larger than the MM or experimental data. We assume that the agreement would be better if geometry optimization would be performed on a CI surface. However, this task was too time consuming on our computer. Finally there is an almost uniform distribution of bond orders in the delocalized forms ranging from 1.70 to 1.74. With the criterion[13] that the lowest ring bond order determines the ring current, the C_{2h} structure has an aromaticity index of 1.71 and the D_2 structure an index of 1.70. Since benzene with an aromaticity index of 1.75 is the prototype of an aromatic system, these two structures must be called aromatic. The C_s structure, however, has an aromaticity index of 1.34 and would be called moderately aromatic close to nonaromatic.

IV. 18-Annulene

The X-ray structure[10] of the crystal study of 18-annulene suggested that the carbon skeleton conforms to the delocalized D_{6h} symmetry rather than to the localized D_{3h} symmetry. Two slightly different C–C bond lengths were observed, both different from the normal single and double bond lengths. These bond lengths are C_1–C_2, which is equal to C_4–C_5, and C_2–C_3, which

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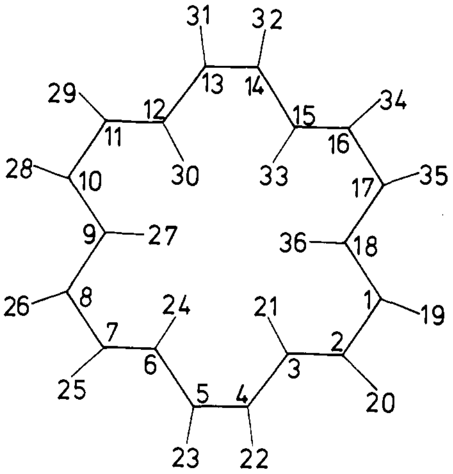

Figure 2. Structure and labeling of 18-annulene.

Table III. Geometries (Å and deg) and Total Energies (kcal/mol) of 18-Annulene

	SINDO1		MM[a]	ab initio[b]		exptl[c]
	D_{3h}	D_{6h}	D_3	D_{3h}	D_{6h}	$C_i(D_{6h})$
bond lengths						
C_1C_2	1.358	1.423	1.357	1.344	1.402	1.412
C_2C_3	1.495	1.418	1.465	1.455	1.389	1.377
C_3C_4	1.361	1.418	1.361	1.344	1.389	1.380
C_4C_5	1.502	1.423	1.465	1.455	1.402	1.429
bond angles						
$C_1C_2C_3$	125.5	126.7	126.0	124.1	124.2	123.6
$C_2C_3C_4$	130.6	133.4	123.2	128.3	128.4	127.8
$C_3C_4C_5$	125.1	126.7	123.2	124.3	124.2	122.9
$C_4C_5C_6$	125.1	126.7	126.0	124.3	124.2	124.0
energy						
SCF	21.1	59.4		139.5[e]	173.0[e]	
CI	11.7	8.7		100.2[e,f]	106.5[e,g]	
total	11.5[d]	0[d]		0[e,g]	24.9[e,g]	

[a] Reference 7. [b] Reference 8. [c] Reference 10. [d] With Davidson correction. [e] 6-31G* geometry, STO-3G basis. [f] With MP2. [g] With MP3.

is equal to C_3–C_4 in Figure 2. Later experimental studies support the delocalized form.[22] We have performed calculations for 18-annulene with SINDO1 similar to those for 14-annulene. The results are contained in Table III. The D_{3h} symmetry is much more stable on the SCF surface. The 60 configuration CI results in almost equal stability and the Davidson correction favors the D_{6h} structure. Again interpair type correlation is essential to lower the D_{6h} structure compared to the D_{3h} structure. Molecular mechanics results[7] favor a D_3 structure which is localized and slightly nonplanar. Ab initio calculations on the STO-3G level result always in a more stable D_{3h} structure even with perturbation correction of second and third order. However, 6-31G* calculations on the SCF level reduce the difference between the two structures to 16.4 kcal/mol compared to the 33.5 kcal/mol of the STO-3G calculation, both based on 6-31G* geometry. There is a chance that correlation will change the order of stability for the 18-annulene also on the ab initio level. Thiel[23] obtained similar results to ours in MNDOC calculations. With Davidson correction his D_{6h} structure is 1.1 kcal/mol below the D_{3h} structure.

A justification for the extensive use of CI in SINDO1 is given by comparison of calculated and experimental values of heat of formation. Oth et al.[22] deduce a value of 124 ± 6 kcal/mol from their measurement, which is close to the MM value[24] of 128.3 kcal/mol by Allinger. Dewar's MINDO/3 results in 129.1 kcal/mol for the D_{3h} structure and 154.8 kcal/mol for the D_{6h} structure. With the 60 configuration CI plus Davidson correction and with explicit calculation of zero-point energy we obtain a value of 147.5 kcal/mol for the D_{6h} structure and 158.9 kcal/mol for the D_{3h} structure. Since it is apparent from Table I that the absolute energy of the D_{6h} structure has not converged with a 60 × 60 CI, we expect from a larger CI a further lowering by more than 10 kcal/mol, which brings us closer to the experimental value. Without CI the SINDO1 heat of formation of 18-annulene would not be acceptable.

The classification of aromaticity according to the ring current criterion[13] yields results for 18-annulene similar to those for 14-annulene. The D_{6h} structure with an index of 1.72 would be termed aromatic, the D_{3h} structure with an index of 1.35 moderately aromatic close to nonaromatic.

V. Conclusion

It is gratifying to see that the geometries of the various symmetry types of structures of 14-annulene and 18-annulene are very close regardless of the theoretical method used. The stability of the structures depends on the level of accuracy of the calculation. Configuration interaction favors the delocalized form much more than the partially localized form on the semiempirical and the ab initio level. Interpair correlation and Davidson correction are essential to favor the stability of the delocalized structures. These structures can be called aromatic.

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A Triplet Ground State for the Planar Conformation of $(\mu\text{-NO})_2[Co(\eta^5\text{-}C_5H_5)]_2$?

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Abstract: Ab initio MO–SCF and multiconfiguration SCF calculations carried out on the d^9–d^9 complex $(\mu\text{-NO})_2[Co(\eta^5\text{-}C_5H_5)]_2$ indicate that the ground state of this molecule might be a triplet separated by 280 cm^{-1} from the associated covalent singlet. This conclusion is in agreement with the similarity of the metal–metal bond lengths observed for various d^8–d^8 and d^9–d^9 complexes. A careful reinvestigation of the magnetic susceptibility of the title compound is suggested.

The electronic structure of dibridged binuclear complexes of the type $(\eta^5\text{-}C_5H_5)_2M_2(NO)_{2-x}(CO)_x$ (x = 0, 1, 2; M = Fe, Co, Ni) has been the subject of continuing interest in the last 10 years.[1-8] This interest has been mainly focused on (a) the relation

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