A Theoretical Investigation of Through-space Interactions. Part 3.[1] A Semiempirical Study of the Cope Rearrangement in Singly Annellated Semibullvalenes

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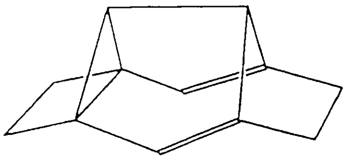
A series of singly annellated semibullvalenes has been studied by semiempirical (MNDO, AM1, PM3) calculations. The Cope rearrangement is examined in each case. In the ethano-annellated system **3** the groundstate for the molecule is predicted to be the symmetrical homoaromatic species **3c**. This provides another example of the elusive class of neutral homoaromatics.

There has been a considerable revival of interest in the concept of homoaromaticity particularly in searching for examples of neutral homoaromatic species.[2-7] On the basis of semiempirical results it was previously proposed that the bis-annellated semibullvalene **1** would be a neutral homoaromatic hydrocarbon.[1a] These studies were extended to establish 'semiempirical discriminators' for the existence of through-space (homoconjugative) interactions by studying a range of molecules in which the importance (or lack thereof) of homoconjugative interactions had been well established by alternative means.[1b] In summary, appreciable stabilizing homoconjugation (homoaromaticity) is indicated by a large drop in energy between the SCF and 2 orbital CI calculated energies and by negative two-centre energy partitioning terms between the appropriate centres.[1b] In the present study these discriminators are applied to examine the singly annellated semibullvalenes **2–6**. Also of interest is the effect of annellation upon the Cope equilibrium, **2a–6a** $\rightleftharpoons$ **2b–6b**, which, in the case of compounds **4–6** has been studied experimentally.[8,9] This allows for the calibration and verification of the computational methods involved in this work.



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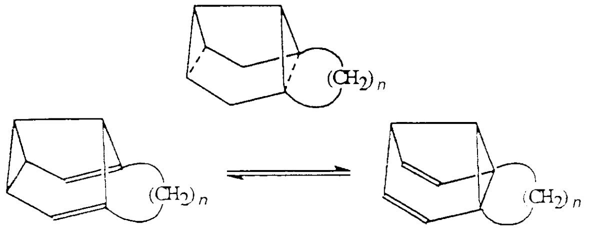


n=1	2a	2c	2b
n=2	3a	3c	3b
n=3	4a	4c	4b
n=4	5a	5c	5b
n=5	6a	6c	6b

Methods

The MOPAC semiempirical electronic structure program[10] was used to carry out MNDO,[11] AM1,[12] and PM3[13] calculations. Geometry optimizations were performed with each method to obtain the structures and energies reported. As semiempirical SCF theory is not capable of giving an accurate representation of the delocalized form,[1,14] simple 2 × 2 configuration interaction (CI) calculations, which have been shown to represent better such systems,[1,14] were also carried out. These calculations involve configuration interaction utilizing excitations from the highest occupied (HOMO) to the lowest unoccupied (LUMO) molecular orbitals and give rise to three singlet and one triplet states. In the remainder of the paper these will be referred to as CI2 calculations. To study further the effects of CI, calculations involving the next lower occupied and next higher unoccupied orbitals were also performed (referred to as CI4).

Discussion and Results

For the n = 2 and 3 systems only one conformation for each open (**3a**, **4a**), closed (**3b**, **4b**), and symmetric (**3c**, **4c**) form was found. The symmetric forms are the Cope rearrangement transition structures (TS). In both the n = 4 and 5 systems, however, local minima corresponding to different conformations of the annellating ring were located for each form. For n = 4, a pseudo-chair and two pseudo-boat (maintaining C_s symmetry) conformations are possible. In the pseudo-boat forms, the ring is puckered either toward or away from the ethano bridge of the semibullvalene moiety and these forms are designated as up-boat (UB) and down-boat (DB), respectively. For n = 5 there are four identifiable conformations and, following similar nomenclature to n = 4, these are referred to as up-boat (UB), down-boat (DB), up-chair (UC), and down-chain (DC). The calculated heats of formation (MNDO, AM1 and PM3) for all of these molecules are presented in Tables 1–4.

Table 1 Heats of formation for the $(CH_2)_2$ bridged compounds **3**

Method		Open **3a**	Closed **3b**	Symmetric **3c**
MNDO	SCF	92.675	88.944	101.827
	CI2	91.215	88.476	83.767
	CI4	81.310	81.151	76.669
AM1	SCF	109.620	115.364	117.363
	CI2	108.373	114.900	99.461
	CI4	99.895	108.873	93.075
PM3	SCF	95.283	97.119	105.639
	CI2	93.841	96.739	89.385
	CI4	85.560	90.580	83.355

The Cope equilibrium between the closed and open derivatives, **3a**–**6a** $\rightleftharpoons$ **3b**–**6b**, is finely balanced and can be rationalized in simplified fashion by assuming that the additional ring strain in the closed forms (**3a**–**6a**) or the anti-Bredt destabilization in the open forms (**3b**–**6b**) is dominant. Intuitively one might expect that the smaller the annellating ring (smaller *n*) the greater the anti-Bredt destabilization. Consequently for small *n* the closed form should predominate and for larger *n* the open form might be expected to be favoured. This simple model is in reasonable agreement with our calculated results. These results reveal little difference between the relative SCF and CI2 energies for the localized species and there is good agreement between the MNDO, AM1 and PM3 methods. The heats of reactions and activation energies (*E*) for the Cope rearrangements are shown in Tables 5 and 6, respectively. This rearrangement is assumed to proceed through a homoaromatic TS (**3c**–**6c**). Therefore, consideration of the *E* gives a clear indication, not only of the ease of the Cope process in each system, but also the degree of relative stabilization imparted to the TS by homoaromatic interactions. As can be seen, compound **3** (*n* = 2) is an exception as the 'activation energy' has become negative. This strongly implies that the

Table 2 Heats of formation for the $(CH_2)_3$ bridged compounds **4**

Method		Open **4a**	Closed **4b**	TS **4c**
MNDO	SCF	64.340	62.021	84.093
	CI2	63.042	61.644	76.470
	CI4	54.078	53.283	67.302
AM1	SCF	78.119	77.109	92.852
	CI2	76.907	76.809	88.776
	CI4	69.752	70.384	80.726
PM3	SCF	69.001	65.362	85.203
	CI2	67.788	65.057	79.546
	CI4	60.486	58.244	71.866

Table 3 Heats of formation for the $(CH_2)_4$ bridged compounds **5**

		Up-boat		Down-boat		Chair	
Method		Open	Closed	Open	Closed	Open	Closed
MNDO	SCF	61.599	59.630	57.264	59.912	53.659	58.448
	CI2	58.565	59.261	55.863	59.530	48.941	53.074
	CI4	49.572	50.460	47.023	50.651	47.721	51.516
AM1	SCF	70.516	70.376	69.323	70.177	63.500	68.150
	CI2	69.317	69.523	68.034	69.214	60.477	67.255
	CI4	62.078	63.758	60.873	62.289	55.099	61.222
PM3	SCF	64.399	61.883	61.757	61.507	56.192	58.945
	CI2	62.618	60.990	68.084	69.214	53.478	57.274
	CI4	55.293	54.761	53.160	54.137	47.721	51.516

Table 4 Heats of formation for the $(CH_2)_5$ bridged compounds **6**

		Up-boat		Down-boat		Up-chair		Down-chair	
Method		Open	Closed	Open	Closed	Open	Closed	Open	Closed
MNDO	SCF	61.910	65.483	53.628	60.188	50.005	57.917	52.863	59.925
	CI2	60.690	64.529	53.195	59.862	46.375	54.190	49.491	56.277
	CI4	51.533	56.143	43.457	50.805	39.809	48.398	42.623	50.370
AM1	SCF	70.564	72.520	61.898	66.468	58.314	63.257	59.594	64.588
	CI2	62.299	71.667	60.673	65.550	57.162	62.329	58.525	62.908
	CI4	62.222	65.689	53.600	59.678	50.187	56.325	51.456	57.530
PM3	SCF	62.161	63.882	55.782	59.437	52.186	55.475	53.854	56.918
	CI2	60.881	62.982	54.536	58.442	51.774	54.460	52.644	55.976
	CI4	53.852	56.605	47.314	52.144	43.784	47.960	45.560	49.343

Table 5 Heats of reaction (open ⟶ closed)

	MNDO			AM1			PM3		
	SCF	CI2	CI4	SCF	CI2	CI4	SCF	CI2	CI4
3	−3.73	−2.74	−0.16	5.74	6.53	8.98	1.84	2.90	5.02
4	−2.32	−1.40	−0.80	−1.01	−0.10	0.63	−3.64	−2.73	−2.24
5 UB	−1.97	0.70	0.89	−0.14	0.21	1.68	−2.52	−1.63	−0.53
5 DB	2.65	3.67	3.63	0.85	1.13	1.42	−0.25	−0.03	0.98
5 CH	4.79	4.13	5.76	4.65	6.78	6.12	2.75	3.80	3.79
6 UB	3.57	3.84	4.61	1.96	9.37	3.47	1.72	2.10	2.75
6 DB	6.56	6.67	7.35	4.57	4.88	6.08	3.66	3.90	4.83
6 UC	7.91	7.81	8.59	4.94	5.52	6.14	3.29	2.69	4.18
6 DC	7.06	6.78	7.75	4.99	4.38	6.07	3.06	3.33	3.78

Table 6 Cope rearrangement activation energies[a]

	Open ⟶ TS			Closed ⟶ TS		
Species	SCF	CI2	CI4	SCF	CI2	CI4
MNDO						
3	9.15	−7.45	−4.64	12.88	−4.71	−4.48
4	19.75	13.43	13.26	22.07	14.83	14.06
5 UB	19.96	3.96	4.30	21.93	3.27	3.42
5 DB	22.81	7.25	9.15	20.16	5.59	5.52
5 CH	21.19	21.15	18.71	16.40	17.02	12.95
AM1						
3	7.74	−8.91	−6.82	2.00	−15.44	−15.80
4	14.73	11.87	10.98	15.74	11.97	10.34
5 UB	15.83	2.53	2.24	15.97	2.33	0.56
5 DB	16.08	12.47	11.41	15.22	11.34	9.99
5 CH	19.66	18.28	15.90	15.01	11.50	9.77
PM3						
3	10.36	−4.46	−2.20	8.52	−7.35	−7.22
4	16.20	11.76	11.38	19.84	14.49	13.62
5 UB	17.71	5.70	6.14	20.23	7.33	6.67
5 DB	18.60	11.87	10.34	18.85	11.90	9.36
5 CH	16.99	16.83	15.57	14.23	13.03	11.78

[a] For the compounds **2** negative energies actually correspond to heats of reaction from localized to symmetric forms.

lowest energy form for this system is the homoaromatic molecule **3c** and that the localized semibullvalenes, **3a** and **3b** are higher energy forms that are a minimum of the PE surface corresponding to the localized form. Applying our discriminators to this compound is most illuminating. The energy change for **3c** between the SCF and CI2 heats of formation is large and the key atoms at the semibullvalene termini display negative (stabilizing) two-centre energy partitioning terms. On this basis we proposed that compound **3** is another example of a neutral homoaromatic groundstate hydrocarbon.

Compounds **4** and **6** behave much as might be expected. The closed and open forms are relatively close in energy and the activation barrier for the Cope process is moderate in each case. This leads to the expectation of facile Cope rearrangements with similar concentrations of the closed and open geometries. Experimental (NMR) studies[8,9] of these systems led to similar conclusions, and are in good agreement with our results. In each case the heat of reaction (for the Cope rearrangement) was determined to be small. Compounds **4** and **6** display a significant temperature dependence in their Cope equilibria that is attributed to competition between slight enthalpic control and slight entropic control.

For **5** the differences in energy for the various forms are again calculated to be small. In all our calculations on **5**, the open form **5b** has the lowest energy and the open form with a pseudochair conformation of the annellating group represents our global minimum. Experimentally[9] the equilibrium **5a** $\rightleftharpoons$ **5b** was found to be essentially independent of temperature. This was taken to indicate that the heat of reaction was approximately zero and that the very strong predominance of **5b** at equilibrium resulted from entropic control. The slight increase in concentrations of **5b** relative to **5a** with decreasing temperature can be taken as an indication that **5b** is indeed the lower energy species. This of course assumes that ΔH and ΔS are relatively temperature independent. In each case, for **4**, **5** and **6**, the species found experimentally to increase in concentration with decreasing temperature corresponds to our AM1 calculated low energy geometry.

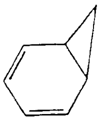
As already mentioned for **3**, the lowest energy form is expected to be the highly delocalized homoaromatic species **3c**. Consideration of **4c**–**6c** supports the assertion that for the Cope process in semibullvalenes the reaction is concerted and synchronous with a homoaromatic transition state. In each case there is a considerable decrease in energy for the TS in proceeding from SCF to CI2 calculations. Negative (stabilizing) two centre terms across the semibullvalene termini are also observed. Together this evidence supports the concept of a homoaromatic TS. The mechanism of the simple Cope rearrangement in hexa-1,5-diene has been the subject of extensive recent study.[15,16] There are two proposals for this simple reaction: (1) a process proceeding through a biradicaloid transition state/intermediate and (2) a concerted synchronous rearrangement through a homoaromatic transition state. Dewar has extended his studies to the Cope process in semibullvalene itself and was able to locate a biradicaloid TS/intermediate that was higher in energy than the corresponding homoaromatic TS.[17] The current study and our own investigation of the semibullvalene potential energy surface[18] strongly favour a concerted synchronous process for these rearrangements. Similarly Dupuis *et al.* showed that the biradicaloid species were not located on the lowest energy reaction coordinate.[19]

The key interatomic distances for **3**–**6** meet with our expectations. In the localized closed (**3a**–**6a**) and open (**3b**–**6b**) forms there is bond alternation corresponding with the double and single bonds and the distances across the semibullvalene termini are widely disparate (bonded and no bond). In the delocalized 'TSs' (**3c**–**6c**) there is a bond equalization both across the termini and around the periphery of the semibullvalene nucleus.

We also studied the methano-annellated species **2**. However, the results are probably spurious as a consequence of the inadequate parametrization for this highly unusual molecule.

Conclusions

In all of our calculations there is a general trend that the MNDO heats of formation are the lowest, followed by the PM3, and finally the AM1 energies which are the highest. Qualitatively these differences are of little consequence as the relative energy ordering and energy differences are comparable. However in systems where the energy gap between the various tautomers is slight, *e.g.*, **4a** and **4b**, then the precision of each method is low enough to lead to reversals in the predicted low energy form. This is not a problem as for these systems the experimentally determined heat of reaction is also small and similar errors in precision are likely. Previously we found that the AM1 method gave more accurate results.[1a] In contrast with the MNDO method which gave the incorrect energy ordering for the norcaradiene **7** and 1,6-methano-bridged [10]annulene **8** system, the AM1 method agreed with experiment in these systems. In the current study where there are discrepancies between the methods, the AM1 method is always closest to the experimental results. As already mentioned these discrepancies are relatively unimportant as they occur only when the energy differences between the various forms are insignificant compared with the likely errors in the calculated absolute energies.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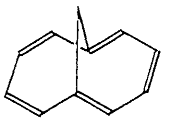
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Our calculations lead to the fascinating prediction that the symmetrical species **3c** will be another example of a neutral homoaromatic groundstate hydrocarbon. We plan to test this prediction by synthesis.

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