Tetrahedron Vol. 44, No. 5, pp. 1351 to 1358, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00

AN AM1 STUDY OF THE COPE REARRANGEMENTS OF BULLVALENE, BARBARALANE, SEMIBULLVALENE, AND DERIVATIVES OF SEMIBULLVALENE

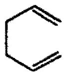
Michael J. S. Dewar* and Caoxian Jie[1]
Department of Chemistry,
The University of Texas at Austin,
Austin, Texas 78712

(*Received in USA* 15 *December* 1987)

Abstract: AM1 calculations are reported for the Cope rearrangements of $[3,3,2,0^{2,8}]$tricyclodeca-3,7,9-triene (bullvalene; 6), $[3,3,1,0^{2,8}]$tricyclonona-3,7-diene (barbaralane; 7), $[3,3,0,0^{2,8}]$tricyclonona-3,7-diene (semibullvalene; 8), and 12 derivatives of 8. All the reactions were predicted to take place via typical aromatic pericyclic transition states, unlike chair Cope rearrangements but like the boat rearrangement of 1,5-hexadiene. A second biradicaloid transition state of higher energy was found for 6 and 8. CN or F in 8 at C_2, C_4, C_6, or C_8 is predicted to accelerate the reaction.

Introduction

The mechanism of the Cope rearrangement[2] of 1,5-hexadiene (1) and its derivatives has aroused much interest recently because of its implications[3] concerning the theory of pericyclic reactions[4]. Cope himself formulated[2] it as what would now be called a synchronous pericyclic reaction and this interpretation was reinforced by the analysis of pericyclic reactions by Woodward and Hoffmann[5] and by the recognition[6] of the role of aromaticity in cyclic transition states (TS). The Cope rearrangement seemed indeed an archetypal example of an "allowed" pericyclic reaction taking place via an aromatic TS (2). The only remaining ambiguity, concerning the chair or boat conformation of the TS, was settled in favor of the chair by Doering and Roth[6].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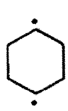
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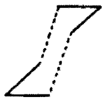
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In 1971 Doering *et al*[7] suggested an alternative nonsynchronous mechanism in which formation of the new (C_1C_8) bond precedes rupture of the old (C_3C_4) one, the TS being a species formally representable as the 1,4-cyclohexylene biradical (3). This mechanism was strongly supported by experimental[8] and theoretical[9] work here, to a point where there seemed little doubt concerning its correctness. Our calculations[9], and thermochemical considerations[7], indicated, however, that the symmetrical intermediate (SI) is not a genuine biradical. It is a *biradicaloid*, i.e. a closed shell "nonclassical" species derived from a biradical by a weak coupling between the radical centers. The coupling here involves through-bond[10,11] interactions which lead to a lengthening of the forming/breaking bonds (C_2C_8 and C_4C_6) in 3 and shortening of the others, their calculated[9] lengths in the SI being 1.61 and 1.44 Å, respectively. While this interpretation has been challenged on the basis of *ab initio* calculations[12] and studies of deuterium isotope effects[13], the arguments adduced are open to criticism[14], and a further detailed AM1 study [14] of the chair Cope rearrangements of 1 and of a number of its derivatives seems to have established that these reactions do in fact take place by the Doering mechanism.

If the chair and boat Cope rearrangements of 1 have similar mechanisms, they should have similar entropies of activation, as was indeed predicted by both our theoretical treatments[9,14]. The experimental value (-3.0 ± 3.6 e.u.) found by Goldstein and Benzon[15] for the boat rearrangement was, however, much less negative than that for the chair (-13.0 ± 0.1 e.u.). It has moreover been confirmed recently by Doering and Troise[17]. This discrepancy was disturbing because our procedures seem to reproduce entropies very effectively[17]. It seemed unlikely that the boat and chair rearrangements of 1 could in fact take place by the same mechanism.

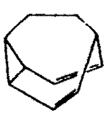
The aromatic and biradicaloid mechanisms for the rearrangement of 1 can be distinguished by the lengths (r) of the C_1C_8 and C_3C_4 bonds in the symmetrical (C_{2v}) intermediate (SI). If this is a typical aromatic pericyclic species, analogy suggests that r should be ca 2.0 Å. In the corresponding biradicaloid, r should be little greater than the length (1.54 Å) of a C-C single bond, the lengthening being due to the through-bond coupling between the radical centers (C_2 abd C_5). The value predicted by AM1 was 1.65 Å. While the value claimed in *ab initio* calculation[8] referred to above was 2.04 Å, this did not refer to a properly optimized geometry.

A further AM1 study[18] of the boat and chair rearrangements of 1 led to an unexpected resolution of this anomaly. In each case we found a second genuine TS with the structure expected for the aromatic mechanism, the lengths of the relevant CC bonds being 1.98 Å (boat) and 1.99 Å (chair). The calculated entropy of activation for the aromatic boat mechanism (-6.3 e.u.) agreed with experiment[15,16] to within the claimed error limits. While the activation energy for the aromatic chair rearrangement was greater by 6.5 kcal/mol than that for the preferred biradicaloid path, the difference for the boat was much less (2.8 kcal/mol). Given the difference in entropy of activation, the aromatic path is predicted to be favored at the temperature used in the kinetic study. Given the limited accuracy of AM1 energies and the situation concerning the entropies, it seems clear that the boat and chair rearrangements of 1 must indeed take place by different routes, the former by a synchronous pericyclic mechanism and the latter by a nonsynchronous biradicaloid one.

The prediction, that the Cope rearrangement of 1 can take place by two distinct paths, involving different mechanisms and yet having TSs with such similar geometries, was very surprizing and has important mechanistic implications. Many other pericyclic reactions offer a similar choice between alternative synchronous and nonsynchronous mechanisms, involving, respectively, aromatic and biradicaloid TSs. It has been commonly assumed that such reactions in fact take place by a spectrum of mechanisms involving a continuous gradation of TSs from one extreme to the other[13]. Our results suggest that this is not the case. If the Cope rearrangement takes place by one or other of two distinct mechanisms, rather than by a graded series of intermediate mechanisms, it seems likely that the same will prove true in all cases of this kind, given that the pairs of TSs are usually much less alike than they are for the Cope. Dewar *et al.* have indeed presented arguments[19] to this effect in the case of the Diels--Alder reaction.

The Cope rearrangements of bullvalene (6), barbaralane (7), and semibullvalene (8) have aroused much attention, partly because of their extraordinary facility and partly because of the remarkable way in which 6 undergoes complete scrambling by multiple Cope rearrangements[20]. Their low activation energies are especially noteworthy since they necessarily take place by the normally less favored boat mechanism.

Further interest was aroused by early MINDO/2 calculations[21] which suggested that certain derivatives of 8 might exist as "nonclassical" bishomobenzenes (11), the TS for the normal aromatic rearrangement of 8 becoming more stable than 8 itself. MINDO/2 was, however, far from reliable and a calculation using MNDO[22] led to an activation energy for 8 that was far too large. Errors of this kind commonly occur in cases where the TS contains unusually long bonds, due to the tendency of MNDO to overestimate interatomic repulsions between atoms separated by more than ca 1.5 times the corresponding covalent bond distance[23]. The calculated[22] lengths of the forming/breaking CC bonds in the TS for rearrangement of 8 fell in this area.



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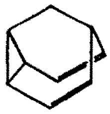

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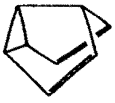

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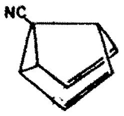

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Recently Miller et al[24] have reported a MNDO-CI study of the rearrangements of 8 and a number of its derivatives which supported the earlier conclusions[21] and also led to a good estimate of the activation energy for 8 itself. However, these calculations are also subject to uncertainty because open shell versions of MNDO tend[25] to overestimate the stabilities of biradical-like species[26]. The two errors might have cancelled in the case of 8, leading to a fortuitous agreement with experiment. The geometry calculated for the SI does indeed indicate a biradical structure with little or no bonding between C_2 and C_8 or C_4 and C_6. As noted above, the thermochemical evidence contradicts this conclusion.

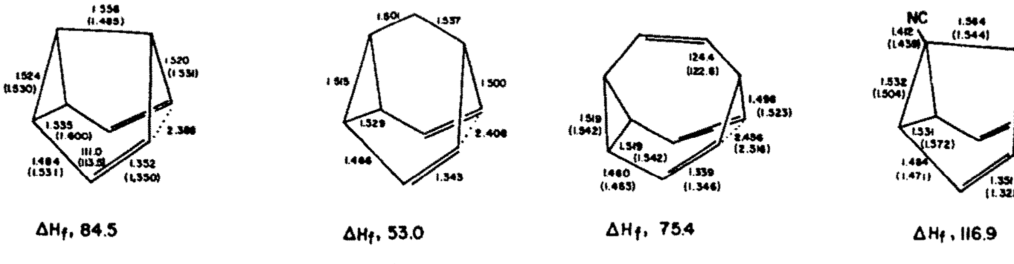
Since these reactions were of interest to us as further examples of boat Cope rearrangements, we decided to carry out AM1 calculations for them.

Procedure

The calculations were carried out using the standard AM1[27] procedure as implemented in the AMPAC program[28]. All geometries were completely optimized without making any assumptions. TSs were located by the reaction coordinate method[29] and refined by minimizing the scalar gradient of the energy[30]. Stationary points were characterized by calculating force constants[30]. Open shell calculations were carried out using the "half electron" version of AM1 with 3x3 CI (AM1-HE-CI). Options for all these procedures are included in AMPAC.

Results and Discussion

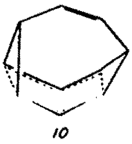
Calculations were carried out first for 6, 7, and 8. Their calculated heats of formation and geometries are shown in Figure 1a-c, available experimental values being listed in parentheses. The agreement between the calculated and observed CC bond lengths in 6 is satisfactory, except for C_2C_8 where the experimental value (1.600 Å) seems unreasonably large. As a check, calculations were also carried out for 1-cyanosemibullvalene (9) for which an experimental geometry is also available[31]. As Figure 1d shows, the agreement here is better, except for the C=C bonds where the experimental value (1.321 Å) seems improbably small.



(a) (b) (c) (d)

Figure 1

Figure 1. Calculated (observed) bond lengths (Å) and heats of formation (ΔH_f; kcal/mol) for (a) semibullvalene; (b) barbaralane; (c) bullvalene; (d) 1-cyanosemibullvalene. Experimental values: (a) Y. C. Wang and S. F. Bauer, *J. Am. Chem. Soc.* 94, 5651 (1972); (c) B. Anderson and A. Marstrander, *Acta Chem. Scand.* 25, 1271 (1971); (d) L. A. Paquette, W. E. Bano, M. A. Volz, and G. G. Christoff, *J. Am. Chem. Soc.* 97, 2562 (1975).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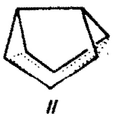
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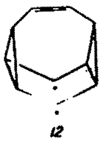
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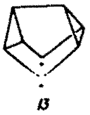
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The Cope rearrangements of 6 and 8 were each found to take place by two distinct alternative reaction paths involving different SIs and TSs, one SI being a bishomobenzene (10 or 11) and the other a biradicaloid (12 or 13). In the case of 7, only the aromatic SI (*cf.* 10) was located. The heats of formation (ΔH_f) of the SIs and TSs are listed in Table I. Since the differences in energy between corresponding SIs and TSs were negligible (<<0.1 kcal/mol), the results show only that each of the minimum energy reaction paths (MERP) is very flat in the vicinity of the SI. For all practical purposes, the SIs can be regarded as the overall TSs. Table I shows the lengths in them of the CC bonds directly involved in the reactions. Single point HE-CI calculations for the stationary points led to a lowering of 10-15 kcal/mol in the energy. This indicates that none of these species has a high degree of biradical character and that the RHF energies should be accepted[26]. The intermediates in the Doering mechanism are thus predicted to be closed shell species, i.e. biradicaloids rather than biradicals, in agreement with the thermochemical arguments[7]. Similar comments apply to the aromatic SIs. Their calculated geometries (Table I) indicate that the C_2C_8 and C_4C_6 bonds in them are quite strong. They do not contain pairs of weakly interacting allyl radicals.

In the boat rearrangement of 1, the aromatic TS was higher in energy than the biradicaloid TS by 2.1 kcal/mol. In that of 6 or 8, it was lower, by 12.7 and 15.9 kcal/mol, respectively; see Table I. This difference is not surprizing in view of the accompanying changes in strain energy. Conversion of 6 to 10, or of 8 to 11, leads to relief of most of the ring strain in 6 or 8 whereas formation of 12 or 13 involves the formation of an additional cyclopropane ring. The strain in the cyclopropane ring(s) is reflected by the lengths of the forming/breaking bonds in the SIs, those in 12 (1.77 Å) and 13 (1.74 Å) being greater than that in the biradicaloid boat SI from 1 (1.65 Å) while those in 10 (2.19 Å) and 11 (2.24 Å) are likewise greater than that in the aromatic boat SI from 1 (1.99 Å).

The fact that 12 and 13 are predicted to be stationary points on the PE surfaces is interesting. It strongly supports our earlier[18] conclusion, that Cope rearrangements take place by one or other of two distinct paths rather than by a graded series of "merging" mechanisms. Even here, where the biradicaloid mechanism is very unfavorable, it nevertheless corresponds to a distinct reaction path with an independent TS.

Table I. Cope Rearrangement of Bullvalene, Barbaralane, and Semibullvalene

Reactant	(type)[a]	ΔH_f[b]	ΔE[c]	Calc. bond lengths (Å)		
				C_2C_8	C_2C_3	C_1C_2
6	(aro)	104.5	12.8[d]	2.194	1.381	1.488
	(birad)	117.1	-	1.766	1.395	1.493
7	(aro)	76.9	8.6[e]	2.186	1.385	1.491
8	(aro)	104.2	4.8[f]	2.242	1.395	1.500
	(birad)	120.1	-	1.743	1.413	1.519

(a) Calculations for aromatic (aro) and biradicaloid (birad) symmetrical intermediates.
(b) Calculated heat of formation of the SI (kcal/mol).
(c) Observed activation energy (kcal/mol).
(d) A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc.* 87, 4092 (1965).
(e) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders *Tetrahedron* 23, 3943 (1967).
(f) Ref. 33.

Table II. Enthalpies of Activation (kcal/mol) for Cope Rearrangement of Bullvalene, Barbaralane, and Semibullvalene.

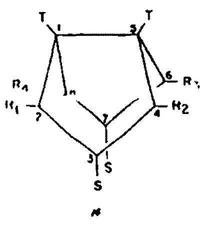
Compound	Enthalpy of Activation Calc.	 Obs.	error
6	29.1	12.8[a]	16.3
7	23.9	8.6[b]	15.3
8	19.7	4.8[c]	14.9

(a) A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc. 87*, 4092 (1965). (b) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron 23*, 3943 (1967). (c) Ref. (33).

Table II compares with experiment the enthalpies of activation calculated for the three aromatic Cope rearrangements. The errors are much larger than those so far encountered in AM1 studies of pericyclic reactions. Thus the errors in the AM1 $\Delta H^\ddagger$ for the Cope rearrangements of 1 and several of its derivatives were all *ca* 3 kcal/mol and similar agreement with experiment was obtained for several Diels-Alder reactions[26] and for the electrocyclic conversion of cyclobutene to butadiene[27]. An analogous situation was encountered in earlier MINDO/3 and MNDO calculations where the errors in the calculated $\Delta H^\ddagger$ were indeed even larger. While the reason for this is not known, the errors for 6 (16.3 kcal/mol), 7 (15.3 kcal/mol), and 8 (14.9 kcal/mol), are almost identical, suggesting that they are due to some factor inherent in the ring system present in the SIs. Similar errors have been found in the heats of formation calculated[27] by AM1 for some other unsaturated ring compounds, e.g. fulvene (15.2 kcal/mol) and maleic anhydride (19 kcal/mol). It therefore seems likely that a similar systematic error (+15 kcal/mol) will occur in AM1 calculations for such tricyclic hexadienes.

Early MINDO/2 calculations[21] suggested that the Cope rearrangement of 8 should be facilitated by replacing the even numbered (see 8) carbon atoms by heteroatoms or by attaching π acceptor (+E) substituents (e.g. CN) to them. Hoffmann and Stohrer[32] arrived at similar conclusions on the basis of EH calculations and qualitative arguments. Since the activation energy for the rearrangement of 6 itself is only 4.8 kcal/mol[33], there is a clear implication that appropriate substitution might make it *negative*, the corresponding derivative of 11 existing as a stable "nonclassical" *bis*homobenzene. Hoffmann and Stohrer also concluded that electron releasing conjugative (-E) substituents, in particular fluorine, at the even numbered positions in 4 should have the opposite effect, leading to an increase in the activation energy for rearrangement.

We accordingly studied the Cope rearrangements of twelve derivatives (14) of 8. Table III summarizes the results. The values reported in each case are the heat of formation (ΔH_f) of the parent molecule, the enthalpy of activation ($\Delta H^\ddagger$), the heat of reaction for formation of the corresponding SI (ΔH_{SI}), values of ΔH_{SI} relative to that for 8, and the lengths of the relevant CC bonds in the SI.



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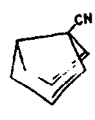
(all substituents H except as indicated)
a, R_{1-4} = CN
b, R_1 = R_4 = CN
c, R_1 = R_2 = CN
d, S = CN
e, R_{1-4} = F
f, S = F
g, R_{1-4} = CN; S = F
h, R_{1-4} = F; T = CN
i, R_{1-4} = CN; T = F
j, T = F
k, R_{1-4} = OCH_3
l, R_2 = R_4 = OCH_3; R_1 = R_3 = CN



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Our calculated enthalpies of activation both confirm and quantify our earlier[21] conclusion, that +E substituents in the even numbered positions of 8 should accelerate its Cope rearrangement. Thus the $\Delta H^{\ddagger}$ calculated for the 2,4,6,8-tetracyano derivative (14a) is less than that for 6 by 8.0 kcal/mol and there is a similar difference (9.0 kcal/mol) between the corresponding pair of 1,5-difluoro derivatives, 14g and 14f. While the $\Delta H^{\ddagger}$ for 2,4- (14c) and 2,6- (14d) dicyanosemibullvalenes are likewise less than that for 6, the differences are, as expected, smaller (4.6 and 5.9 kcal/mol, respectively).

The species of major interest are of course the SIs. For reasons indicated earlier, the errors in the corresponding ΔH_{SI} are expected to be the same for all reactions of this kind, being ca 15 kcal/mol. Correspondingly corrected values (ΔH^{*}_{SI}) are shown in the fifth column of Table III. Those for 14a and 14g are predicted to be negative, implying that the parent molecules are higher in energy than the corresponding "nonclassical" species derived from 11.

Table III. Cope Rearrangements of Semibullvalene Derivatives

Compound	ΔH_f^{a}	$\Delta H^{\ddagger b}$	ΔH_{SI}^{c}	ΔH_{SI}^{*d}	r_{28}^{e}	
8	84.5	$(19.7)^{f}$	19.7	(4.8)	2.242	1.395
14a	220.9	11.7	9.9	-5.0	2.329	1.400
14b	149.4	15.1	14.6	-0.3	2.283	$1.392(1.404)^{g}$
14c	149.7	13.8	12.8	-2.1	2.298	$1.396(1.399)^{g}$
14d	146.3	$(20.8)^{f}$	20.8	+5.9	2.238	1.401
14e	-89.5	11.7	9.0	-5.9	2.368	1.402
14f	-7.8	$(22.3)^{f}$	22.3	+7.4	2.237	1.405
14g	137.6	13.3	12.1	-2.8	2.325	1.412
14h	-9.9	13.4	11.6	-3.3	2.357	1.400
14i	145.2	12.7	12.4	-2.5	2.339	1.401
14j	-0.8	$(21.5)^{f}$	21.5	+6.6	2.230	1.394
14k	-60.5	12.9	10.5	-4.4	2.374	1.402
14l	78.3	11.0	7.0	-7.9	2.365	1.400

(a) Heat of formation; (b) Enthalpy of activation; (c) Heat of reaction for formation of symmetrical intermediate (SI); (d) ΔH_{SI}^{c} corrected (see text) (and) kcal/mol; (e) Bond lengths (Å) in SI; (f) SI is the transition state. (g) Value in parentheses for bond adjacent to CN.

In the case of the tetracyano derivative (14a), this result agrees with our earlier prediction[21] and with that of Hoffmann and Stohrer[32]. Hoffmann and Stohrer[32] also predicted that π donor substituents, in particular fluorine, at the even numbered positions in 4 should retard its rearrangement. Our calculations lead, however, to the opposite conclusion, predicting 14e to be another "nonclassical" bishomobenzene. Indeed, the ΔH^{*}_{SI} predicted for 14e is even more negative than that for 14a. Similar remarks apply to the 2,4,6,8-tetramethoxy derivative (14k), though here the predicted difference in energy between the classical and nonclassical structures is less than for the cyano and fluoro analogs.

Our calculations predict cyano and fluoro groups at the odd numbered positions in 6 to hinder its Cope rearrangement; compare 14d, 14f, and 14j with 6; 14g and 14i with 14a; and 14h with 14e. Here again the predictions for CN agree with those of Hoffmann and Stohrer while those for F do not. The equilibrium between 1- and 5-monosubstituted semibullvalenes is of interest in this connection. Table IV shows the heats of formation calculated for three such pairs of "Cope isomers" (e. g. 10, 15). The results predict the favored isomer in each case to be the one where the substituent is attached to the cyclopropane ring, in agreement with experiment in the case of CN and CH_3. While no data are available for the fluoro derivative, the available evidence[34] seems to suggest that fluorine normally has a destabilizing effect on cyclopropane. A study of the equilibrium for the 1(5)-fluorosemibullvalenes would clearly be of interest.

Table IV. Energies of Isomeric Semibullvalenes

Substituent	Heat of formation (kcal/mol) 1-X	5-X	Obs. equilibrium constant[a] (temp)
CN	116.9	118.8	95 (25)[b]
CH_3	78.5	79.9	3 (36)[c]
F	40.4	41.6	-

(a) Equilibrium constant for 5-X-8 → 1-X-8.
(b) L. A. Paquette, W. E. Volz, M. A. Beno, and C. G. Christoff, *J. Am. Chem. Soc.* 97, 2562 (1975).
(c) D. R. James, G. H. Birnberg, and L. A. Paquette, *J. Am. Chem. Soc.* 98, 2562 (1976).


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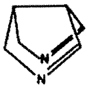
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As noted above, early MINDO/2 calculations[21] led to the prediction that the nonclassical isomer (11) of 8 should be stabilized relative to 8 by replacing carbon atoms in the aromatic ring of 11 by nitrogen. We therefore carried out calculations for 2,4,6,8-tetraazasemibullvalene (16) and 3,5-diazasemibullvalene (17) and for their Cope rearrangements. The results are shown in Table V.

Table V. Cope Rearrangements of Azasemibullvalenes.

Compound	ΔH_f^a	$\Delta H^{\ddagger a}$	ΔH_{SI}^a	Bond lengths[b] (Å) r_{28}	r_{23}	r_{34}	r_{28}	
16	175.1	33.1	25.9	1.428	1.487	1.304	2.558	1.364
17	105.0	15.1	15.0	1.556	1.447	1.303	2.234	1.349

(a) For notation, see Table II.
(b) Bond lengths in reactant (r_{ij}) and SI (r^*_{ij}).

Table VI. Atomic Charges in Rearrangement of Semibullvalene.

Species	Formal Charges at Atoms: C_1	C_2	C_3	C_4	C_5
8	-0.172	-0.125	-0.144	-0.165	-0.047
SI	-0.053	-0.182	-0.136	-0.177	-0.053
TS	-0.053	-0.180	-0.137	-0.180	-0.053

The basis of the original prediction[21] was that the even numbered carbon atoms in 8 become more negative in the corresponding SI. As Table VI shows, the atomic charges predicted by AM1 follow the same pattern, both in the TS and in the SI. Other things being equal, this should certainly imply, according to PMO theory, that replacement of these atoms by nitrogen should stabilize 11 relative to 8. However, the ΔH_{SI} calculated by AM1 for the 2,4,6,8-tetra-aza derivative (16) is *greater* than that for 8 by no less than 13.4 kcal/mol. The effect of the change in electronegativity is presumably outweighed by the differences in bond energy between the bonds that are formed and broken during the reaction (CN and NN bonds in 16 *vs*. CC in 8) and the different strain energies of the three-membered rings (diazane in 16 *vs*. cyclopropane in 8). It seems in any case very unlikely that 16 can exist as a nonclassical bishomoaromatic species.

Strangely enough, the situation is exactly reversed in the case of the 3,5-diaza derivative, 17. Here the relevant atoms (C_3 and C_5) are predicted to be *less* negative in the SI (11) than in 8 itself; yet the calculated ΔH_{SI} for 17 is *less* than that for 8.

Acknowledgements: This work was supported by the Air Force Office of Scientific Research (AF86-0022) and the Robert A. Welch Foundation (F-126).

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