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The $C_{10}H_8$ Potential Energy Surface: The Azulene-to-Naphthalene Rearrangement

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Abstract: The azulene-to-naphthalene rearrangement (AN rearrangement) has been studied, using MNDO and MINDO/3. All of the proposed unimolecular pathways have been examined in detail and found wanting. The results presented here agree with the first step of a mechanism proposed by Becker et al. A new mechanism is proposed for the rest of the reaction.

We recently reported[1] a preliminary study of the azulene-to-naphthalene **(1 → 2)** rearrangement (AN reaction) which eliminated from consideration several of the mechanisms that had been previously proposed and we also suggested a new alternative. Here we present the results of a systematic study of the $C_{10}H_8$ potential energy (PE) surface, carried out in the hope of finally solving the problem. We will not discuss its historical developement because an excellent review has recently appeared.[2]

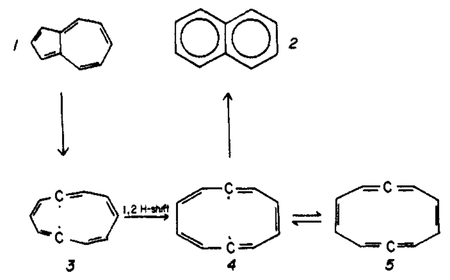
Experimental Procedure

MNDO[3] was used for closed-shell species and the spin-unrestricted version of MNDO[4] (UMNDO) for biradical or open-shell species. All geometries were fully optimized, using the DFP method.[5] In certain cases where MNDO is known to give large errors (e.g., hydrogen transfers), MINDO/3[6] (or UMINDO/3) calculations were also carried out for comparison. All transition states (TS) were located by using the reaction coordinate method,[7] refined by minimizing the norm of the gradient,[8] and characterized by establishing that the Hessian (force constant) matrix had one, and only one, negative eigenvalue.[8] Options for all these procedures are included in the MOPAC package of computer programs.[9]

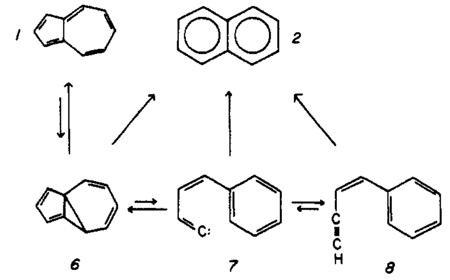
Results and Discussion

Schemes I and II show the unimolecular mechanisms proposed, respectively, by Scott[10] and Becker,[11] while Scheme III shows the mechanism proposed here on the basis of our calculations. First we will explain why our results eliminate the Scott and Becker mechanisms as possible major contributors to the AN rearrangement. Unfortunately, no mechanism yet proposed, not even the one suggested here, can explain *all* of the results obtained from labeling studies.[12] We have therefore also studied various possible pathways for the scrambling of the labels in azulene and naphthalene in the hope of resolving the remaining discrepancies. This work is presented in the following paper.

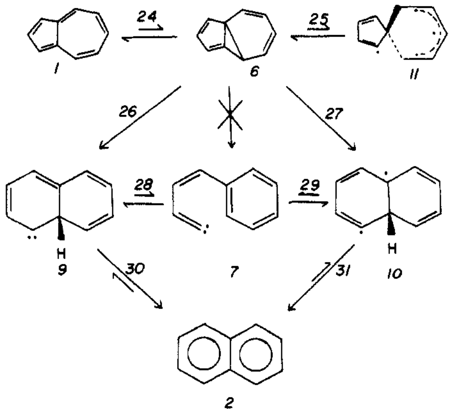
Scheme I. The Scott Mechanism



Scheme II. The Becker et al. Mechanism



Scheme III. The MNDO Mechanism



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(12) (a) Alder, R. W.; Whittaker, G. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 714. (b) Alder, R. W.; Whilshire, C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1464. (c) Alder, R. W.; Whiteside, R. W.; Whittaker, G. J.; Whilshire, C. *J. Am. Chem. Soc.* **1979**, *101*, 629. (d) Zeller, K. P.; Wentrup, C. *Z. Naturforsch. B* **1981**, *36*, 852. (e) Scott, L. T.; Kirms, M. A.; Earl, B. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1373. (f) See ref 2, 10, 11, 16.

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Table I. Heats of Formation (kcal/mol) Calculated for **1–7**

compd	MNDO	UMNDO	UMINDO/3
1	77.1 (73.5[a])	56.7	
2	38.1 (36.1[a])	30.9	
3		131.5	124.7
4		116.4	
5	116.6	108.0	
6	134.0	124.7	
7	158.1	155.0	
8	91.5 (95.6[b])		
9	140.5		
10		104.3	
11		128.5	
12		131.9	
13		131.5	
14		121.0	
15		126.4	
16		181.3	152.7
17		114.9	
19	136.3		
20	116.1	113.4	
24	135.3		
25		145.6	
26	153.0		
27		131.5	
28	169.8		
29		163.0	
30	155.6		
31		144.7	

[a] Experimental values from the following: Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970. [b] Estimated from thermochemical data[a] assuming first that the following pair of reactions have similar heats of reaction PhH + $CH_2CH_2 \rightarrow PhCHCH_2 + H_2$ and PhH + $CH_2CHCCH \rightarrow$ **8** + H and secondly that the same is true for the following pair: $CH_2CH_2 + HCCH \rightarrow CH_2CHCCH + H_2$ and $PhCHCH_2 + HCCH \rightarrow$ **8** + H. The two corresponding values for the heat of formation of **8** were identical.

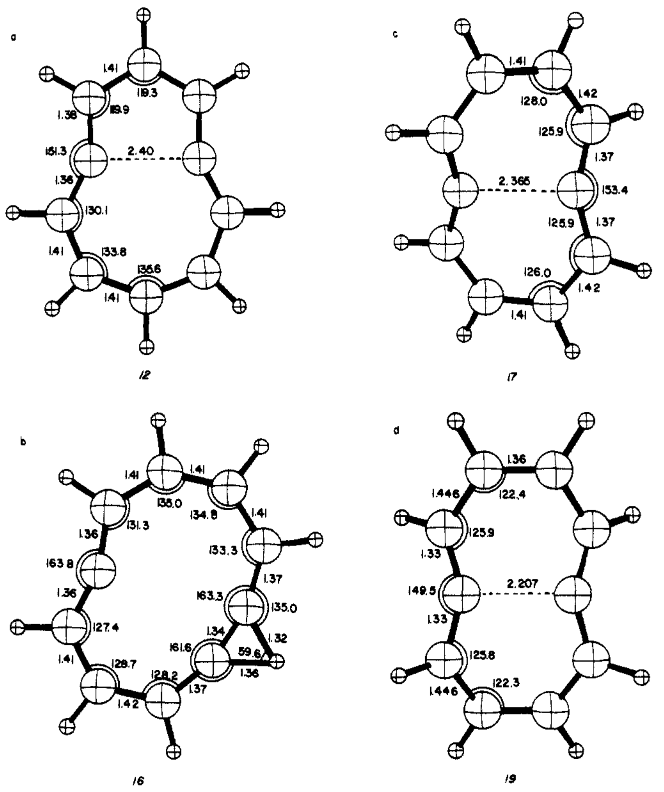


Figure 1. Calculated geometries for the TSs **12** (UMNDO), **16** (UMNDO), **17** (UMNDO), and **19** (MNDO/RHF).

The heats for formation (ΔH_f) of all the species located in this study are listed in Table I. Pertinent geometries are given in Figures 1–4.

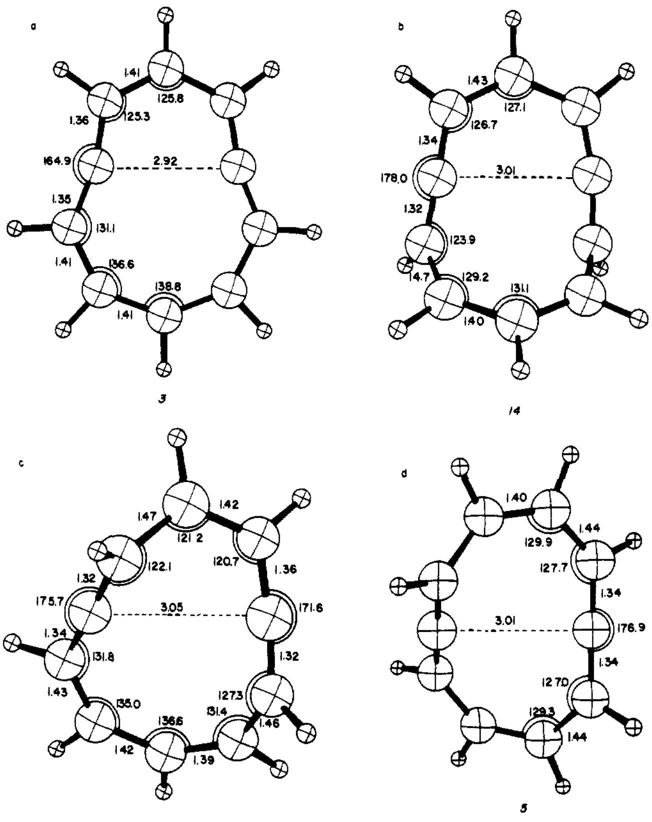
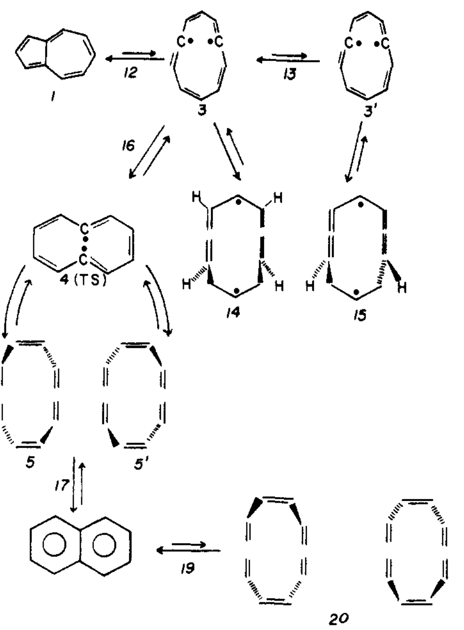


Figure 2. Calculated geometries for the GSs **3** (UMNDO), **14** (UMNDO), **15** (UMNDO), and **5** (MNDO/RHF).

Scheme IV. The MNDO PE Surface for the Scott Mechanism



The EA for the AN rearrangement was originally reported[13] to be ca. 49 kcal/mol.[12] Subsequent studies[12] have, however, suggested that this value is probably too low and that the real EA could well be 60–65 kcal/mol.

(A) The Scott Mechanism. Scheme IV indicates the calculations reported here for the interconversions of species involved in the Scott mechanism. According to the latter (see Scheme I), the first step is breaking of the transannular bond in azulene (**1**)

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[13] Heilbronner, E. In *Nonbenzenoid Aromatic Compounds*; Ginsburg, D., Ed.; Interscience: New York, 1959; p 263.

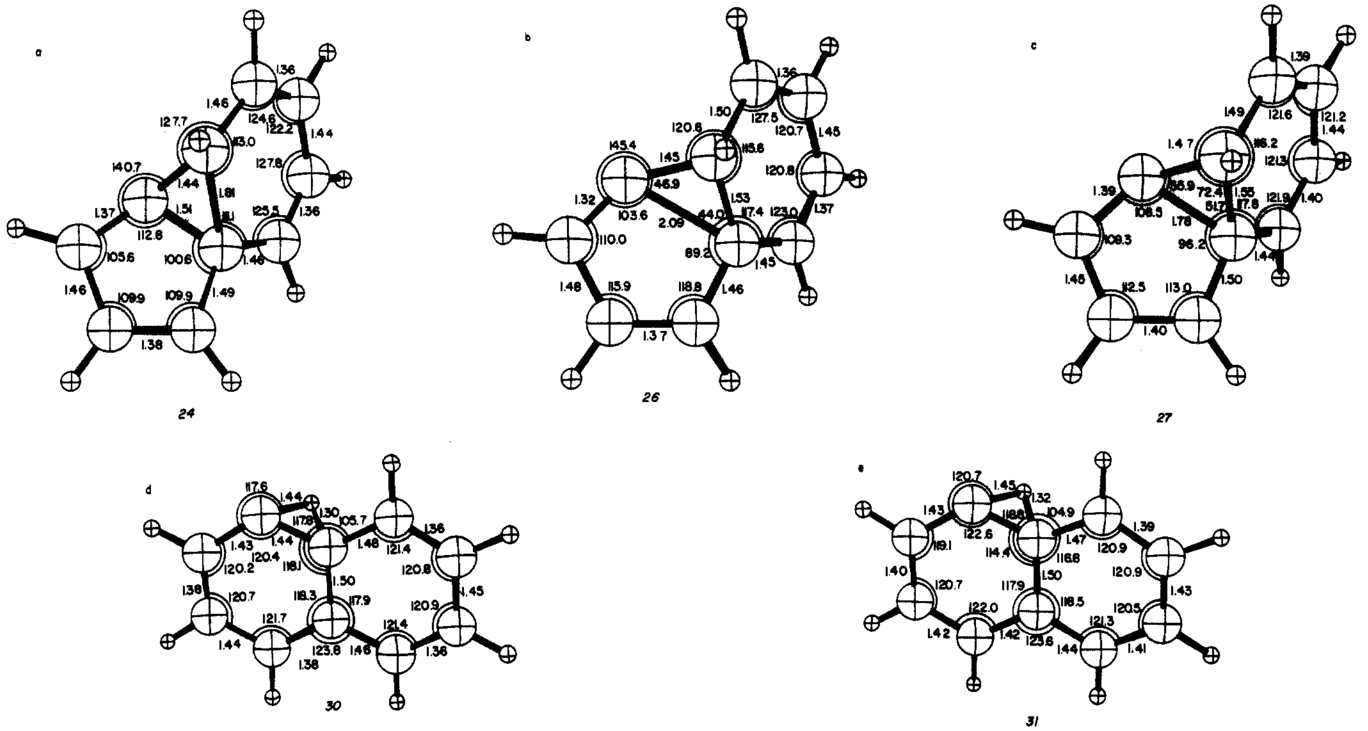

Figure 3. Calculated geometries for the TSs **24** (MNDO/RHF), **26** (MNDO/RHF), **27** (UMNDO), **30** (MNDO/RHF), and **31** (UMNDO).

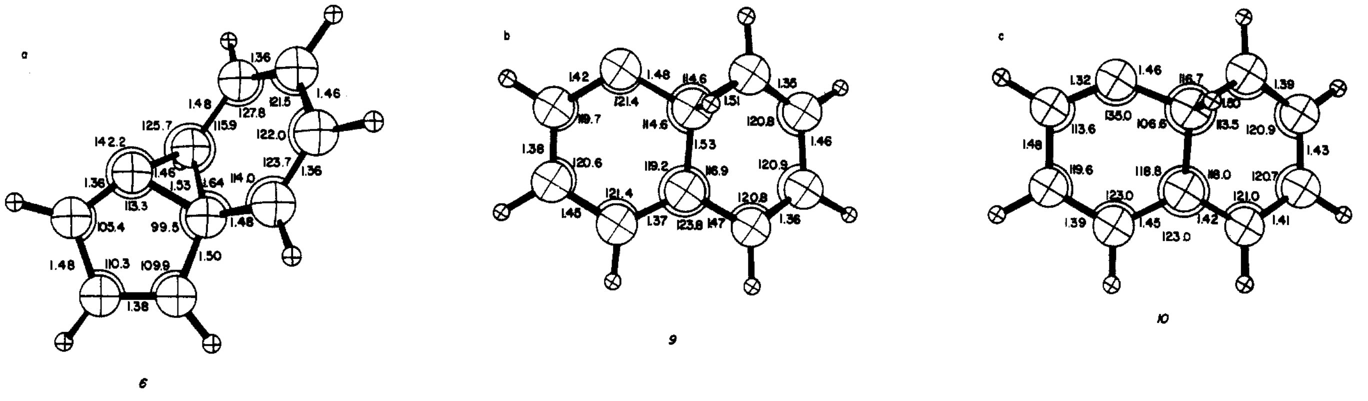

Figure 4. Calculated geometries for the GSs **6** (MNDO/RHF), **9** (MNDO/RHF), and **10** (UMNDO).

to form an intermediate biradical (**3**). This then rearranges via a 1,2-hydrogen shift to another diradical (**4**), which collapses to naphthalene.

The calcuated (UMNDO) activation energy (EA) for the homolytic cleavage of the transannular bond in **1** is 75.2 kcal/mol. Since UMNDO is known to overstabilize biradical species by about 20–25 kcal/mol, it would seem appropriate to apply a corresponding correction to the EA calculated for the formation of **12**. Here, however, the ground state **1** is also overstabilized by UMNDO (see Table I) so no correction should be needed. The activation energy for this process is probably close to 75 kcal/mol. The UMNDO geometry for this TS (**12**) is given in Figure 1a.

The intermediate biradical **3** is only marginally stable, being predicted by UMNDO to collapse to **1** with an EA of 0.4 kcal/mol. Two other nonplanar diradical intermediates (**14** and **15**) were also found to exist on the UMNDO PE surface. The UMNDO geometries of **3**, **14**, and **15** are given in Figure 2a–c. Note that **3** is slightly nonplanar, the corresponding planar species **13** being the TS for interconversion of **3** and its mirror image, **3′**. The EA calculated for this process was only 0.13 kcal/mol. While the TSs for the rearrangement of **3** to **14** or **15** were not located, we expect the barriers to these processes to be low. These bisallene biradicals are more stable than **3** by 10.43 and 5.05 kcal/mol, respectively. Their geometries are interesting. The meso isomer **14** has a "half-chair" (C_s) conformation whereas the *d,l* isomer **15** has a "twist" (C_2) geometry.[14] As a result of this conformational difference, the way in which the radical centers are stabilized differs. In **14**, one radical center interacts with the 2p AOs of the adjacent methine groups to form an allyl system, isolated from the adjacent cumulene units, while the other interacts with double bonds of both the adjacent cumulene units to form a pentadienyl system. This is indicated by its geometry; see Figure 2b. The "twist" structure of **15**, on the other hand, allows an effective π interaction between each radical center and only one of the adjacent cumulene systems; see Figure 2c.

Rearrangements involving hydrogen migration were next studied. While the conversion of **3** to **4** presented no unusual features, the reaction paths for the corresponding conversions of **14** or **15** to **4** were found to have discontinuities, large changes in ΔH_f, and the gradient occurring between closely adjacent points. The corresponding energy barriers were also very high. The only way in which the 1,2-hydrogen shift can occur is therefore by conversion of **3** to **4**, the corresponding UMNDO EA being 49.8 kcal/mol. Since MNDO is known[15] to overestimate activation energies for hydrogen migrations by ca. 20 kcal/mol, and since MINDO/3 is known[15] to give better results, the reaction was re-

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[14] Similar structural types have been encountered in the allowed and forbidden ring opening of benzocyclobutadiene. See: Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6175.

[15] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

investigated with MINDO/3. The EA obtained in this way was 28 kcal/mol, which is indeed ca. 20 kcal/mol less than the UMNDO estimate. All subsequent MNDO activation energies for hydrogen migrations were therefore corrected by subtracting 20 kcal/mol. The TS **16** for **3** → **4** is the highest point on this portion of the $C_{10}H_8$ PE surface and therefore corresponds to the overall TS for the Scott mechanism. The corresponding (corrected) EA is 104.5 kcal/mol. The UMNDO geometry for **16** is shown in Figure 1b. The UMINDO/3 geometry of **16** resembled it closely.

No minimum corresponding to **4** could be found on the UMNDO PE surface. Indeed, UMNDO predicts **4** to be the TS for interconversion of the two enantiomers **5**. The structure **5** (twist; C_2) corresponds to the product formed from the forbidden ring opening (conrotatory) of naphthalene.[16] The ring closure of **5** therefore needs to be investigated with a method which can treat biradicals correctly. UMNDO was chosen for this purpose. The calculated UMNDO EA for the ring closure of **5** was 6.9 kcal/mol. However, since UMNDO overstabilizes biradicals by ca. 20 kcal/mol, the true EA is probably much greater. This suggests that **5** could be generated and observed at low temperatures, especially if the cyclization to **2** could be further inhibited. The MNDO geometries for **5**, and for its conrotatory ring closure to naphthalene, are interesting. They are shown in Figures 2d and 1c, respectively.

The allowed ring opening of **2** was also investigated. The EA for this process is predicted by MNDO to be 98 kcal/mol. However, since MNDO tends to give EA for pericyclic reactions which are too high by ca. 15 kcal/mol,[17] this EA should be considered as an upper limit. The sturcture calculated for the corresponding TS (**19**) is given in Figure 1d. The product of this reaction is another interesting bisallene (**20**) with a tublike (C_{2h}) geometry. It is interesting to note that MNDO predicts the heat of formation of **20** to be similar to that of **5**. It should be possible to observe its formation from **2** if it is appropriately stabilized.

No direct path could be found from **4** to **20**. The PE surface was searched in sufficient detail for it to be certain that no TS corresponding to such a reaction exists, at least according to the MNDO model.

The Scott mechanism therefore seems to be excluded from consideration because the calculated activation energy is far too large (104.5 kcal/mol). It is extremely unlikely that the MNDO calculations could be in error to this extent; see below.

(B) The Becker and MNDO Mechanisms. Both of these mechanisms involve the generation of the intermediate **6**. They differ in their interpretations of the way in which **6** collapses to form **2**. In the Becker mechanism (Scheme II), **6** undergoes a two-bond cleavage to give the carbene **7** which then rearranges to naphthalene. In the MNDO mechanism (Scheme III) **7** is not an important intermediate. Its place is taken by a carbene (**9**) or a biradical (**10**). These intermediates undergo 1,2-hydrogen migrations to give **2**. Scheme III shows all the species and reactions studied on this portion of the $C_{10}H_8$ PE surface.

The EA calcuated for the "allowed" cyclization of **1** to **6** was 63.1 kcal/mol. The intermediate **6** can undergo ring opening in several different ways, the most important being to **7**, **9**, or **10**. *No* TS could be found for the direct conversion of **6** to **7**, postulated by Becker et al.[11] While a stationary point was found that could have corresponded to such a TS, it proved to be a hill top, not a saddle point, its Hessian (force constant) matrix having two negative eigenvalues. It proved in fact to be a high point in the ridge separating **6** from **7**, between the two saddle points, the latter being the TSs (**28** and **29**) for breaking of *one* CC bond in **6** to form **9** or **10**. It is therefore certain that there is *no* TS on the MNDO surface corresponding to the direct conversion of **6** to **7**. **7** can be formed from **6** *only* via **9** or **10**, by successive cleavage of the two CC bonds. Note also that the heat of formation calculated for **7** is much higher than that for **9** or **10**. It seems clear that the only role that **7** could play would be as an intermediate in a different reaction manifold leading into the AN rearrangement proper. Becker et al.[11] have indeed shown that generation of **7**, by flash vacuum thermolysis of a suitable precursor, led to a mixture of **1**, **2**, and **8**. The MNDO geometry of the TS for the electrocyclization of **1** is given in Figure 3a and the geometries of **6**, **9**, and **10** in Figure 4a–c.

The formation of **9** from **6** via the TS **26** has an EA of 19.1 kcal/mol. Formation of **2** from **9** involves a hydrogen migration. MNDO predicts the EA for this process to be 15.1 kcal/mol. However, as noted previously, MNDO overestimates activation energies for hydrogen migrations. Formation of **9** is therefore probably the rate-determining step for this reaction. If so, the EA for the overall process is 75.9 kcal/mol. The alternative route involves formation of the biradical **10**, via the TS **27**, followed by rearrangement to **2**, via the TS **31**. Since the second step involves a hydrogen migration, the rate-determining step is probably again the formation of **10**. The corresponding predicted E_a for the overall reaction is then 74.8 kcal/mol. Both pathways are therefore predicted to occur with comparable ease. The geometries for **26**, **27**, **30**, and **31** are given in Figure 3b–e.

Another possible intermediate that can be generated from **6** is **11**. The EA (ca. 89 kcal/mol) calculated for this process is, however, much higher than for the other two alternatives. It therefore seems unlikely to play a significant role.

As noted above, our calcualted EA (ca. 75 kcal/mol) is 26 kcal/mol greater than the reported[12] experimental value. However, as also noted above, this is probably too small, possibly by 15 kcal/mol, and the rest of the difference could well be due to the known propensity of MNDO to overestimate activation energies.[17]

Conclusions

While the studies reported here cover only a small part of the $C_{10}H_8$ PE surface, they seem, in conjunction with experiment, to have established the reactions responsible for the major part of the AN rearrangement. The mechanism proposed here accounts for 80–90% of the products observed in isotopic labeling experiments, as indeed do all three of the mechanisms considered above (Schemes I–III). Equally, all three fail to account for the remaining 10–20%. Possible routes to these are examined in the following paper, in conjunction with the related automerization of naphthalene.

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Registry No. 1, 275-51-4; **2**, 91-20-3.

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[16] For further discussion on these species see: Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie International: Deerfield Beach, FL; p 63.

[17] For example MNDO gives an E_a for the conversion of cyclobutene to butadiene that is too high by 16.88 kcal/mol. See: Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1420.