On the Development of Aromaticity in Cycloadditions: Ab Initio Transition Structures for the Trimerization of Acetylene and for the Addition of Ethylene and Acetylene to Formylketene

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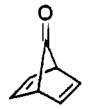
The trimerization of acetylene (**3**) and the cycloaddition of **3** with formylketene (**8**) are two examples of σ,π-aromatizations. The cycloaddition of ethylene and **8** completes the same σ-system as the latter, without the π-system. Transition structures (**4**, **9np**, and **11np**) and second-order saddle points (**9p** and **11p**) were calculated for these reactions using *ab initio* molecular orbital theory at the MP2/6-31G* level with MP4(SDTQ)/6-31G* + ZPE relative energies. It is argued that π-interactions may contribute to the planarity of the transition structure (**4**) for the trimerization of **3**. However, the very low frequency out-of-plane vibrations (MP2/6-31G*) indicates that any π-stabilization is weak. The transition structure **9np** for the addition of acetylene (**3**) with **8** is nonplanar, indicating that the closed shell π-repulsion is greater than any π-stabilization (aromatic or otherwise) in this cycloaddition. The potential energy surface for the addition of ethylene to **8** is closely balanced between the planar (**11p**) and nonplanar (**11np**) cycloaddition pathways, although at the MP4(SDTQ)/6-31G* + ZPE level the planar one is favored by 0.6 kcal/mol. Pseudopericyclic orbital interactions favor the planar pathway, but angle strain in the **8** moiety at the transition structure disfavors it.

The development of an aromatic π-system has often been invoked as contributing to the "driving force" of a reaction and thus to the low barriers often associated with such reactions. That subset of pericyclic reactions which form an aromatic product have been of particular interest.[1−4] For the purposes of this discussion, these pericyclic reactions may be divided into two general classes. The more common one is fragmentations, in which the σ-framework of the aromatic system already exists and the π-system is completed by the conversion of σ-bond(s) into π-bond(s). Several such reactions are known, including the decarbonylation of norbornadienone (**1**),[1b,c,f] to form benzene and the formation of two molecules of benzene from **2**.[1a,d,e] The low barriers ($\Delta G^{\ddagger}$ = 15 and 15.6 kcal/mol, respectively) to these allowed pericyclic reactions have been shown to be correlated with the overall exothermicity of the reactions, which in turn reflects the aromatic stabilization of the products.[1c,e,f]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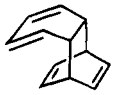
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In the second class of reactions (herein described as σ,π-aromatizations), both the σ- and π-systems of the aromatic ring are completed simultaneously. These reactions are uncommon, in part because the overlap of the appropriate p-orbitals to form the developing π-system requires an approximately planar transition state which is not commonly achieved in pericyclic reactions. The hypothetical trimerization of acetylene (**3**) via a planar transition state (**4**) to form benzene (**5**, Scheme 1A) which involves the formation of three new σ-bonds and three new π-overlaps is such a reaction.[2] Planar transition structures[6] have been calculated for this reaction at the RHF/STO-3G[2a] and 3-21G[2b] levels of theory. Although the aromatic stabilization of benzene contributes to the overall high exothermicity of this reaction, the reaction has a high calculated barrier[2a,b] and has not been experimentally observed[7] (although the reverse fragmentation may occur under special circumstances[8]). Houk[2a] and Bach[2b] have attributed the barrier to the very large closed shell electron repulsion between the out of plane π-bonds at the transition state. On the basis of a curve-crossing model, Ioffe and Shaik[2c] have suggested that in reactions such as this, there is an inherent energetic price (which they relate to the excitation energy of the fragments) to be paid for having three fragments combining instead of two, as in a Diels−Alder reaction, for example.[9] In view of the significance which this postulated reaction has had in discussions of the

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(4) The concept of aromaticity has been closely linked to pericyclic reactions ever since Dewar and Zimmerman[5] first suggested that the loop of interacting σ- and π-orbitals in the transition state of a pericyclic reaction could be considered to posses aromatic stabilization. The question of aromaticity addressed here is different in that it focuses on the stabilization afforded by the formation of a π-aromatic product.

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(6) Following Pople's usage, saddle points on the potential energy surface are referred to as transition structures.

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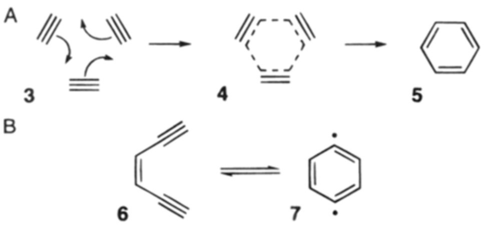
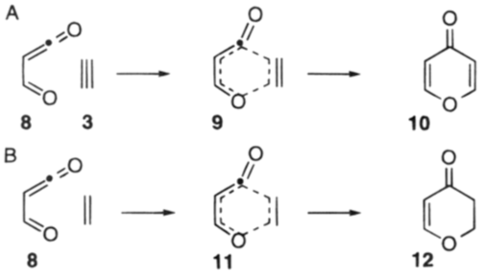
Scheme 1



Scheme 2



origins of barriers in pericyclic reactions, we have reexamined this system at higher levels of theory.

Somewhat more common are σ,π-aromatizations in which the creation of only one new σ-bond and one new π-overlap are necessary to complete an aromatic system. Of these, reactions related to the Bergman cyclization[3] have received considerable experimental[10] attention as well as theoretical attention[11] because of their proposed role in the mechanism of action of a number of antibiotics. In the parent system, the cyclization of 3-hexene-1,5-diyne (**6**) to 1,4-benzenediyl (**7**)[3b–d] (Scheme 1B), the aromaticity of **7** is not sufficient to offset the high energy of the biradical; the reaction is endothermic. However, when the enediyne is destablized by strain, as in the reactive intermediate from neocarzinostatin[10b] or in 1,6-didehydro[10]annulene,[10d] then ring closure is facile.[12]

Although not widely recognized, there are in principle σ,π-aromatizations in which two σ-bonds and two π-overlaps are formed. Such cycloadditions might be expected to be intermediate between the difficult, if not impossible, trimerization of acetylene and the known electrocyclizations.[2c] Specifically, the addition of acetylene (**3**) to formylketene (**8**) via a concerted pathway (**9**) to yield 4-pyranone (**10**, Scheme 2A) could be an example of such a process, which could meet the requirement for a planar transition state.[13] The reactions of formylketene (**8**) with water and formaldehyde have been calculated to have nearly planar transition structures.[14] These are best described as pseudopericyclic,[15] because there is a disconnection in the loop of orbitals undergoing bonding changes. There is a potential energetic benefit to a pseudopericyclic pathway because it lacks the electron−electron repulsions which are otherwise unavoidable when there is cyclic orbital overlap as is found in typical pericyclic transition states.[14] If the addition of acetylene to formylketene also had a planar transition state, the p-orbitals would be properly aligned to form the aromatic π-system in **10**, as shown in Figure 1. *Ab initio* calculations of this reaction were undertaken to explore this possibility. The addition of ethylene to **8** via a concerted cycloaddition transition structure (**11**) to form dihydropyran-4-one (**12**) (Scheme 2B) was also studied as a pseudopericyclic reaction in its own right and as one analogous to the addition of acetylene but lacking the potential for π-aromatic overlap.

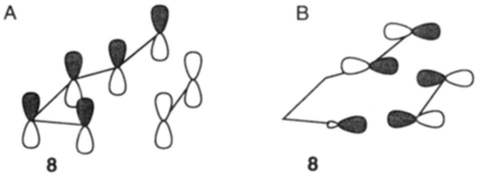


Figure 1. Basis orbitals which undergo bonding changes in the planar cycloadditions of **8** with ethylene and acetylene. (A) The out-of-plane orbitals. The unshaded orbitals represent the second π-bond of acetylene, absent in ethylene. (B) The in-plane orbitals.

Computational Methods

The *ab initio* calculations were carried out with GAUSSIAN 90 and 92,[16] using standard basis sets. Structures were optimized at the RHF/3-21G, RHF/6-31G*, and MP2/6-31G* (frozen core, fc) levels using standard gradient techniques. Selected structures (**4**, **8**, **9np**, **9p**, **11p**, **11np**, and **12**) are shown in Figure 2. The identities of all structures as minima, saddle points, or second-order saddle points were confirmed by frequency calculations at each level.[17] Single point energy calculations were performed on all the MP2/6-31G* optimized structures through the MP4(SDTQ)/6-31G* (fc) level. To explore the effects of diffuse functions on the energies, single point energies were calculated through the MP4(SDQ)(fc) level (MP4(SDTQ)(fc) for **3** and **4**) with the 6-31+G* basis set. This level of theory usually calculates activation energies of pericyclic reactions within a few kcal/mol of the experimental values.[18,19] In the discussion that follows all geometries are at the MP2/6-31G* level and all energies are MP4(SDTQ)/6-31G*(fc) with zero-point energy corrections based on the scaled[22] (0.9427) MP2/6-31G*(fc) frequencies, unless otherwise noted. Total energies as well at the imaginary or lowest real vibrations and the zero point vibrational energies are reported in Table 1. The relative energies are reported in Table 2. Heats of hydrogenation are reported in Table 3. The optimized *Z*-matrices for all previously unreported structures are provided in the supplementary material.

Results and Discussion

Trimerization of Acetylene. A planar transition structure with D_{3h} symmetry for this reaction has been

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(9) Because the HOMO and LUMO of a conjugated system are closer in energy than two nonconjugated ones, frontier molecular orbital theory would also predict this.

(10) (a) Meyers, A. G.; Proteau, P. J.; Handel, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 7212−7214. (b) Meyers, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 1146−1147. (c) Nicolaou, K. C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387. (d) Meyers, A. G.; Finney, N. S. *J. Am. Chem. Soc.* **1992**, *114*, 10986−10987.

(11) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1907−1911.

(12) This interpretation of the mode of action has been questioned.[3a]

(13) Experimentally, neither acetylenes nor unsubstituted alkenes are known to react with α-oxo ketenes, although vinyl ethers undergo [4 + 2] cycloadditions to form dihydropyranones. Coleman, R. S.; Fraser, J. R. *J. Org. Chem.* **1993**, *58*, 385−392.

(14) Birney, D. M.; Wagenseller, P. E. *J. Am. Chem. Soc.* **1994**, *116*, 6262−6270.

(15) Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325−4327.

(16) (a) GAUSSIAN 90: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc.: Pittsburgh PA, 1990. (b) GAUSSIAN 92: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh PA, 1992.

(17) We thank a reviewer for requesting the MP2/6-31G* frequencies, which provided illuminating results; *vide infra*.

(18) (a) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3412. (b) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 682−708. (c) Jorgensen, W. L.; Lim, D.; Blake, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 2936−2942.

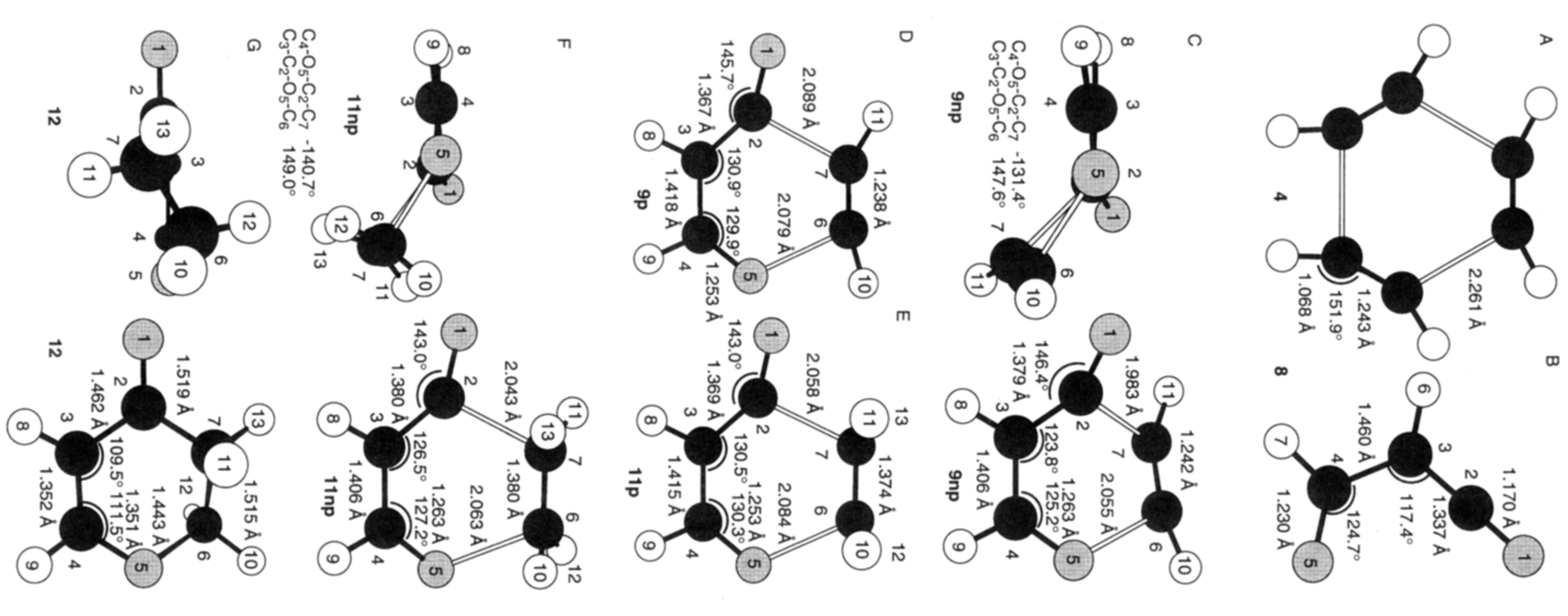

Figure 2. Views of the MP2/6-31G*-optimized structures **4**, **8**, **9np**, **9p**, **11p**, **11np**, and **12**. Structures are shown in top and side view, except for those that are planar, which are shown in top view only. Carbons are black, oxygens are shaded, and hydrogens are white. Atom numbering is consistent for all structures. Partial bonds are open. Distances are in angtroms, bond angles are in degrees. (A) Transition structure (**4**) for the trimerization of acetylene (**3**) to form benzene (**5**). (B) (*Z*)-Formylketene (**8**). (C) Nonplanar transition structure (**9np**) for the addition of acetylene (**3**) to formylketene (**8**). (D) Planar C_s second-order saddle point (**9p**) for the addition of acetylene (**3**) to formylketene (**8**). (E) Planar C_s second-order saddle point (**11p**) for the addition of ethylene to formylketene (**8**). (F) Nonplanar transition structure (**11np**) for the addition of ethylene to formylketene (**8**). (G) Dihydropyran-4-one (**12**).

Table 1. Absolute Energies, Imaginary and Low Frequencies, and Zero-Point Energies (ZPE) of Calculated Structures

		RHF/6-31G*[a,b]	low frequency[c,d]	ZPE[c,e]	MP2/6-31G*[b,f]	MP3/6-31G*[b,f]	MP4SDQ/6-31G*[b,f]	MP4SDTQ/6-31G*[b,f]	MP2/6-31+G*[b,f]	MP3/6-31+G*[b,f]	MP4SDQ/6-31+G*[b,f]
					Trimerization (**4**) of Acetylene, Relative to Three Acetylenes (**3**)						
3	$D_{\times b0}h$	−76.81 83	374.8	16.1	−77.066 79	−77.075 83	−77.081 54	−77.093 57	−77.073 24	−77.082 00	−77.087 43[g]
4	D_3h	−230.324 16	−541.7	52.9	−231.128 91	−231.136 90	−231.153 70	−231.205 96	−231.147 98	−231.154 23	−231.170 05[h]
					Addition of Ethylene to **8**, via **11p** or **11np**, Yielding **12**						
8	C_s	−264.457 35[i]	144.9	27.2	−265.177 85[i]	−265.175 07[i]	−265.195 55[i]	−265.230 16	−265.195 26	−265.190 53	−265.21 1 94
ethylene	D_2h	−78.031 72	849.6	32.7	−78.285 03	−78.305 97	−78.311 40	−78.319 83	−78.291 16	−78.311 73	−78.317 00
11p	C_s	−342.423 39	−587.3, −61.5	62.6	−343.425 03	−343.431 31	−343.458 75	−343.513 53	−343.448 90	−343.452 72	−343.481 17
11np	C_1	*j*	−608.3	62.5	−343.425 82	−343.432 61	−343.458 25	−343.512 58	−343.450 57	−343.454 68	−343.481 46
12	C_1	−342.538 04	129.2	66.3	−343.518 88	−343.542 72	−343.561 51	−343.601 92	−343.542 33	−343.563 80	−343.583 73
					Addition of **3** to **8**, via **9p** or **9np**, Yielding **10**						
9p	C_s	−341.211 81	−650.5, −114.3	46.0	−342.202 86	−342.200 75	−342.229 17	−342.287 01	−342.226 51	−342.221 90	−342.251 03
9np	C_1	−341.211 28	−647.7	46.2	−342.207 48	−342.205 23	−342.231 11	−342.288 73	−342.232 65	−342.227 55	−342.254 38
10	C_{2v}	−341.364 54	144.5	51.0	−342.337 13	−342.351 97	−342.369 22	−342.414 40	−342.360 14	−342.372 55	−342.390 61
					For Hydrogenation Reactions						
H_2	$D_\infty h$	−1.126 88	4539.0	6.5	−1.144 14	−1.149 33	−1.150 92	−1.150 92	−1.144 14	−1.149 33	−1.150 92
13	C_s	−343.714 40	99.6	81.7	−344.705 18	−344.737 86	−344.757 00	−344.792 94	−344.727 93	−344.758 43	−344.779 02

[a] At the RHF/6-31G*-optimized geometry. [b] In hartrees. 1 hartree/particle = 627.51 kcal/mol. [c] Calculated using the MP2/6-31G* analytical second derivatives, unscaled. [d] In cm^{-1}. [e] In kcal/mol, unscaled. [f] At the MP2/6-31G*-optimized geometry. [g] At the MP4(SDTQ)/6-31+G* level, the energy is −77.099 88 hartree. [h] At the MP4(SDTQ)/6-31+G* level, the energy is −231.224 42 Hartree. [i] From ref 14. [j] Not a stationary point at the RHF/6-31G* level.

Table 2. Relative Energies of Calculated Structures in kcal/mol

	RHF 6-31G*[a]	MP2 6-31G*[b]	MP3 6-31G*[b]	MP4SDQ 6-31G*[b]	MP4SDTQ 6-31G*[b]	MP4SDTQ 6-31G* + ZPE[b,c]	MP2 6-31+G*[b]	MP3 6-31+G*[b]	MP4SDQ 6-31+G*[b]	MP4SDTQ 6-31+G* + ZPE[b,c]
Trimerization (**4**) of Acetylene, Relative to Three Acetylenes (**3**)										
4	81.2	44.8	56.9	57.1	46.9	51.1	45.0	57.6	57.9	51.4
Addition of ethylene to **8**, via **11p** or **11np**, yielding **12**										
ethylene + **8**	30.7	35.1	38.7	34.2	32.6	26.5	35.1	38.6	34.4	
11p	71.9	58.9	69.9	64.5	55.5	51.9	58.6	69.7	64.4	
11np	*d*	58.4	69.1	64.8	56.1	52.5	57.6	68.5	64.2	
12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
E, ethylene+**8** to **11p**	41.2	23.8	31.2	30.3	22.9	25.4	23.5	31.1	30.0	
E,ethylene+**8** to **11np**	*d*	23.3	30.4	30.6	23.5	26.0	22.5	29.9	29.8	
Addition of **3** to **8**, via **9p** or **9np**, yielding **10**										
3 + **8**	56.1	58.0	63.4	57.8	56.9	49.7	57.5	62.8	57.3	
9p	96.3	84.3	94.9	87.9	79.9	75.3	83.9	94.5	87.6	
9np	96.2	81.4	92.1	86.7	78.9	74.4	80.0	91.0	85.5	
10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
E, **3** + **8** to **9np**	40.1	23.4	28.7	28.9	22.0	24.7	22.5	28.2	28.2	

[a] At the RHF/6-31G*-optimized geometry. [b] At the MP2/6-31G*-optimized geometry. [c] From the MP2/6-31G* frequencies, scaled by 0.9427. (ref 22). [d] Not a stationary point at the RHF/6-31G* level.

Table 3. Calculated Energies of Hydrogenation in kcal/mol

	MP4SDTQ 6-31G*[a]	MP4SDTQ 6-31G*[a] + ΔZPE[b]
10 + H_2 yielding **12**	23.0	14.6
12 + H_2 yielding **13**	25.2	16.8
ΔΔ energy	2.2	2.2
3 + H_2 yielding ethylene	47.3	37.8

[a] At the MP2/6-31G*-optimized geometry. [b] From MP2/6-31G* frequencies, scaled by 0.9427, ref 22.

previously located at the RHF/STO-3G[2a] and RHF/3-21G[2b] levels of theory. However, in view of the importance of electron correlation for accurately describing transition structures,[23] it seemed appropriate to reinvestigate this reaction at a higher level of theory. Beginning with the RHF/3−21G geometry of Bach et al.,[2b] the transition structure (**4**) was optimized at the RHF/6-31G* and MP2/6-31G* levels. Frequency calculations at both levels showed a single imaginary frequency corresponding to the reaction coordinate, calculated to be 1063 cm^{-1} at the RHF/6-31G* level but only 542 cm^{-1} at the MP2/6-31G* level. This rather dramatic difference in magnitude parallels the lowering of the barrier from 81.2 kcal/mol at the RHF/6-31G* level to 44.8 kcal/mol at the MP2/6-31G* level. It is reassuring that both RHF and MP2 methods agree that the D_{3h} structure is a saddle point. Distortions away from planarity are extremely facile at the MP2/6-31G* level; however, there are three other real, but extremely low frequency, out-of-plane vibrations calculated for this structure, 29 cm^{-1} (E'', bending toward a Diels−Alder-like transition structure),[24] 29 cm^{-1} (E'', bending), and 162 cm^{-1} (A_1'', twisting of each acetylene).

Both σ- and π-interactions might contribute to this small preference for a planar transition structure. In previous discussions, it has been pointed out that the energy of the π-orbitals increase upon going from three acetylenes to the transition state **4**, and based on this, it was argued that there was no π-aromatic stabilization of the transition state.[2a,b] The separation of σ and π bonding effects on molecular geometries has been controversial.[25] Although a detailed analysis of these points is beyond the scope of this paper, a brief discussion is worthwhile. A nonplanar transition structure was found for the trimerization of ethylene[2c] (RHF/3-21G, D_3 symmetry), and one (**11np**) is also possible for the addition of ethylene to formylketene (**8**, *vide infra*). In these cases, which involve only the formation of σ-bonds between the reactants, there is not a strong preference for a planar transition structure. Because of the lack of cyclic orbital overlap in a pseudopericyclic reaction there may be an energetic preference for a planar transition structure; however, the trimerization of acetylene is not pseudopericyclic. On the basis of these considerations, in the transition structure (**4**) for the trimerization of acetylene, any σ-contribution to planarity appears to be small.

If this is so, then neither can there be a strong π-repulsion in **4**, since this would lead to a nonplanar distortion, as illustrated by the nonplanar transition structure (**9np**) for the addition of acetylene (**3**) to **8** (*vide infra*). However, the net π-interactions in **4** must be very weak, since the out-of-plane bending is so facile.[28] The calculated bond distances in **4** (Figure 2A) are close to

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(19) Although multiconfiguration SCF calculations would be of value in estimating the importance of alternative open shell pathways, the size of the system here makes such calculations difficult. Furthermore, when MCSCF calculations have been carried out on pericyclic reactions,[20] the qualitative results are in agreement with MP calculations.[18,21]

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(21) (a) Wang, Z.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 1754−1756. (b) Houk, K. N.; Gustafson, S. M.; Black, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 8565−8572.

(22) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(23) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986.

(24) This is similar to the C_2 distortion observed in the central aromatic ring of the sterically congested molecule, perchlorotriphenylene. Shibata, K.; Kulkarni, A. A.; Ho, D. A.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 5983−5984

(25) Although it is commonly assumed that the equal bond lengths in benzene are due to the π-framework, it has been argued that this is due instead to the σ-framework.[26] The conventional view has been vigorously defended.[27]

(26) (a) Hibberty, P. C.; Shaik, S. S.; Lefour, J.-M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4657−4659. (b) Shaik, S. S.; Hibberty, P. C.; Ohanessian, G.; Lefour, J.-M. *Nouv. J. Chim.* **1985**, *9*, 395−388. (c) Heilbronner, E. *J. Chem. Educ.* **1989**, *66*, 471−478. (d) Hibberty, P. C.; Shaik, S. S.; Ohanessian, G.; Lefour, J.-M. *J. Org. Chem.* **1986**, *51*, 3908−3909.

(27) (a) Baird, N. C. *J. Org. Chem.* **1986**, *51*, 3907−3908. (b) Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4178−4190.

(28) For comparison, the lowest frequency (nonimaginary) mode in **11np** is 105.5 cm^{-1} at the MP2/6-31G* level. A reviewer pointed out that a strong nonplanar σ-interaction and a strong planar π-interaction would also lead to weak out of plane vibrations. Although our other results do not support this interpretation, it is consistent with at least some stabilizing π-interactions.

the 2.2 Å upper limit suggested for homoaromatic overlap,[29] also suggesting weak π-bonding. In conclusion, however, since the transition structure is indeed planar, and in the absence of apparent σ-contributions to planarity, we would suggest that the π-interactions, although closely balanced, are weakly stabilizing overall.

The geometry of the transition structure (**4**) calculated at the MP2/6-31G* level (Figure 2A) is similar to that previously found at lower levels. The forming bonds are calculated to be 2.261 Å long, which is only 0.048 Å longer that at the RHF/3-21G level,[2b] and the CCH angles differ by only 0.1° at these levels. The forming bonds are calculated to be almost the same length as the forming bonds in the Diels–Alder reaction between ethylene and butadiene, which are 2.285 Å at the MP2/6-31G* level.[18b]

The best calculated value for the activation energy for this reaction is 51.4 kcal/mol (MP4(SDTQ)/6-31+G*//MP2/6-31G* + ZPE). This is still a very high barrier for a pericyclic reaction, but it is significantly lower than the 61.6 kcal/mol estimated by Bach et al.[2b] at the MP3/6-31G* level (from RHF/6-31G* and MP2/3–21G energies). Their estimate was itself high, approximately 5 kcal/mol higher than calculated here; the MP3/6-31G*//MP2/6-31G* activation energy is 56.9 kcal/mol. Additionally, diffuse functions do not appear to be necessary to represent the system; their inclusion raises the calculated barrier by only 0.3 kcal/mol at the MP4(SDTQ) level.

The significantly higher level calculations reported herein support the conclusions from previous work that, first, although the trimerization of acetylene is orbital symmetry allowed, the barrier (51.4 kcal/mol) is too high for the reaction to be observable and second, that π-aromaticity does not significantly stabilize the transition state. In contrast to previous discussions, however, we would argue that the planarity of the transition structure, when compared to nonplanar ones found for similar reactions which do not form aromatic rings, suggests that π-stabilization, though small, is real and significant.

Addition of Ethylene to Formylketene. Although there is clearly not significant π-stabilization at the transition state of the acetylene trimerization; *a priori* it is not clear whether π-stabilization or repulsion would dominate at the transition state of a two-fragment cycloaddition which forms an aromatic ring. The addition of ethylene to **8** to form dihydro-4-pyranone (**12**, Scheme 2B) was first studied, both to establish whether a pseudopericyclic mechanism could indeed be operative and also to serve as a control, separating the effects of the pseudopericyclic mechanism from those of the π-aromaticity and/or repulsion. Furthermore, in previous studies on the addition of **8** to water and formaldehyde, lone pairs of electrons on the latter had complicated the orbital analysis of the pseudopericyclic reactions.[14] It was anticipated that their absence in ethylene would provide a clearer picture of the underlying electronic factors in the reaction.

Dihydropyran-4-one (**12**) optimized to a nonplanar structure, twisted about the C_6-C_7 bond to relieve eclipsing (Figure 2G). The search for a transition structure was therefore begun without symmetry constraints but converged to a planar structure (**11p**) at the RHF/3-21G and RHF/6-31G* levels. This was confirmed as a transition structure at these levels by frequency calculations. The MP2/6-31G* optimization of this structure was initially carried out in C_s symmetry and gave the structure **11p** shown in Figure 2E. However, the frequency calculation[17] showed two imaginary vibrations, indicating that it is a second-order saddle point at this level. Such a qualitative change in the potential energy surface is unexpected for pericyclic reactions.[18]

A true transition state (**11np**) was subsequently located in C_1 symmetry, having a single imaginary frequency (Figure 2F). This geometry optimization was difficult because the potential energy surface was quite flat in the vicinity of the two structures **11p** and **11np**; the nonplanar transition structure (**11np**) is only 0.5 kcal/mol below the planar second-order saddle point (**11p**) at the MP2/6-31G* level. The relative energies of these two structures changes again with higher levels of theory. At the MP3/6-31G*, MP3/6-31+G*, and MP4(SDQ)/6-31+G* levels, the nonplanar structure (**11np**) remains lower in energy than the planar one (**11p**) by 0.8, 1.2, and 0.2 kcal/mol, respectively. However, at the MP4(SDQ) level with the 6-31G* basis set, the planar structure **11p** is 0.3 kcal/mol lower in energy than the nonplanar one (**11np**). Significantly, the inclusion of the triple excitations (MP4(SDTQ)/6-31G*) provides an additional 0.3 kcal/mol stabilization of the planar structure (**11p**) relative to the nonplanar one (**11np**). Thus, assuming additivity, the two structures (**11p** and **11np**) would be isoenergetic at the MP4(SDTQ)/6-31+G* level. Although it would be desirable to carry out this and even higher level calculations, these were prevented by the constraints of available CPU time and disk space. Nonetheless, at all levels of MP theory explored here, the planar and nonplanar structures are within approximately 1 kcal/mol of each other. There is a relatively flat potential ridge separating reactants and products, with a wide range of reaction trajectories accessible to the system.

In view of the qualitative differences between the RHF and MP2 potential energy surfaces, it is worth noting that an extensive search at the RHF/6-31G* level was carried out for an alternative nonplanar transition structure. This culminated in an optimization of the entire structure with the constraint that the ethylene was held 65° above the plane of the formylketene (**8**). This structure was 10.9 kcal/mol above transition structure **11p** at the RHF/6-31G* level and had significant forces on the constrained angles. There is not a nonplanar transition structure for this cycloaddition at the RHF/6-31G* level.

In the nonplanar transition structure (**11np**), ethylene approaches formylketene (**8**) at an angle of approximately 145° to the plane of **8** (Figure 2G).[30] This is significantly flatter than the angle of 118.8° (RHF/6-31G*) calculated for the addition of ethylene to butadiene, the prototypical Diels–Alder cycloaddition.[31] Thus, this transition structure (**11np**) appears to represent a compromise between a planar, pseudopericyclic pathway (*vide supra*) and a more conventional, nonplanar overlap between the diene and dienophile π-systems found in both all-carbon and hetero-Diels–Alder reactions.[32]

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[29] McEwen, A. B.; Schleyer, P. v. R. *J. Org. Chem.* **1986**, *51*, 4357.

[30] The C4–O5–C2–C7 and C3–C2–O5–C6 dihedral angles in **11np** are 140.7° and –149.0°, respectively.

[31] Bach, R. D.; Joseph J. W. McDouall, H. B. S.; Wolber, G. J. *J. Org. Chem.* **1989**, *54*, 2931–2935.

[32] For calculations involving the all-carbon Diels–Alder reaction see refs 18b, 19a, 31, and 33. For semiempirical calculations on acrolein hetero-Diels–Alders reactions see refs 34. For experimental evidence on the transition state geometry of acrolein hetero-Diels–Alders reactions see ref 35. For RHF/3-21G(*) calculations of related hetero-Diels–Alder reactions see ref 36.

[33] (a) Coxon, J. M.; Grice, S. T.; Maclagan, R. G. A. R.; McDonald, D. Q. *J. Org. Chem.* **1990**, *55*, 3804–3807. (b) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127–4133. (c) McCarrick, M. A.; Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1499–1500.

The trends in the bond angles are somewhat unusual, but are consistent with the above explanation. In a non-least-motion trajectory, the $C_2-C_3-C_4$ and $C_3-C_4-O_5$ bond angles are wider in the transition structure **11np**, as compared to both formylketene (**8**) and dihydropyranone (**12**). The $C_2-C_3-C_4$ angles are 117.4°, 126.5°, and 109.5° in **8**, **11np**, and **12**, respectively, while the $C_3-C_4-O_5$ bond angles are 124.7°, 127.2°, and 111.5°, respectively. The opening of these angles appears to be necessary to accommodate an otherwise energetically favorable pseudopericyclic trajectory, so that the preferred angles of attack on the ketene carbon (C_2) and the carbonyl oxygen (O_5) point to the ends of the ethylene (see Figure 3). This destabilizing angle strain is greater in **11p** (the $C_2-C_3-C_4$ and $C_3-C_4-O_5$ angles are 130.5 and 130.3°, respectively, in **11p**). The nonplanar distortion in **11np** reduces the angle strain, at the expense of the otherwise stabilizing pseudopericyclic nature of the transition structure.

The forming C_2-C_7 bond is slightly shorter than the O_5-C_6 bond in both **11p** and **11np**, despite the fact that the former is longer in the product **12**. This suggests that it is the addition of the electron rich ethylene π-system to the ketene in-plane π^* which leads the reaction. In the planar, pseudopericyclic system, the electron flow may be understood as follows. As electron density flows from the ethylene π-system toward O_1, the out-of-plane π-system of **8** can shift electron density toward O_5 as may be seen in Figure 1. This increases the nucleophilicity of O_5 as it adds a lone pair of electrons back to the ethylene π^*. Since the nucleophilic and electrophilic sites on ethylene are coplanar, the ethylene is not twisted, in contrast to the twisting in the transition structures with water and formaldehyde calculated in earlier work.[14] If, as the MP4(SDTQ)/6-31G* single point calculations suggest, the true transition state is planar, then this is the most straightforward example of a pseudopericyclic reaction discussed to date. In the planar system, the symmetry of the transition structure ensures separation of the σ and π orbitals. Thus, there cannot be orbital overlap around the ring of breaking and forming bonds, although an orbital symmetry analysis predicts the reaction is allowed.

Other details of the structure of **11np** suggest an early transition structure, as expected for an exothermic reaction. The lack of twisting about the C_6-C_7 bond (the $H_{10}-C_6-C_7-H_{11}$ dihedral angle is only 3.9°) implies that the ethylene π bond remains strong. The bond lengths are also consistent with an early transition structure. For example, the C_2-C_3 bond in **8** has lengthened by only 0.043 Å in **11np** while in **12** it is 0.082 Å longer than in **11np**. Similar changes are observed in the other bond lengths (Figure 2).

The activation energy for this cycloaddition (Scheme 2B) is calculated to be 25.4 kcal/mol. This is a significant barrier but it is slightly lower than that calculated for the [2 + 2] addition of ethylene to ketene when compared at the MP2/6-31G* level (ethylene + ketene, 26.7 kcal/mol,[21] ethylene + **8**, 23.8 kcal/mol). This suggests that the [4 + 2] pathway could be experimentally observed for the reaction of an α-oxo ketene with an unactivated alkene if dimerization of the α-oxoketene could be suppressed.[13,37] A comparison of the barrier heights and exothermicities for the addition of ethylene to butadiene (experimental) and to **8** (calculated) is also instructive. The Diels–Alder reaction is 40.5 kcal/mol exothermic[38] and the barrier is 27.5 kcal/mol.[39] The pseudopericyclic addition of ethylene to **8** is calculated to be much less exothermic, only 26.5 kcal/mol, yet the barrier is similar to the Diels–Alder, 25.4 kcal/mol. This suggests that there is some energetic benefit for the addition of ethylene to **8**, due not only to the exothermicity of the reaction but also to the pseudopericyclic pathway. However, this is by no means comparable to the remarkably low barrier calculated for either water or formaldehyde (6.3 and 10.6 kcal/mol respectively).[14] The exothermicity of the addition of ethylene to **8** is comparable to the calculated exothermicities of the additions of water and formaldehyde to **8**.[14]

In summary, the addition of ethylene to formylketene (**8**) is calculated to be 26.5 kcal/mol exothermic, with an activation barrier of 25.4 kcal/mol. Two trajectories are possible, a planar (**11p**) and a nonplanar (**11np**) one, in contrast to most pericyclic reactions. However, the energetic benefit of the planar, pseudopericyclic pathway is available only at the cost of widening the bond angles of **8** in the transition structure **11p**.

Addition of Acetylene to Formylketene. In anticipation of some degree of aromatic stabilization, a search in C_s symmetry for a planar transition structure for the addition of acetylene to formylketene (**8**) was carried out. Structure **9p** was thus located (Figure 2D), but frequency calculations at both the RHF/6-31G* and MP2/6-31G* levels showed it to be a second-order saddle point, with one imaginary frequency corresponding to formation of the two σ-bonds and a second (-49.2 cm^{-1}, RHF/6-31G*; −114.3 cm^{-1}, MP2/6-31G*) corresponding to an out-of-plane deformation toward a transition structure more like a conventional Diels–Alder reaction. A true transition structure (**9np**) for this addition was located and is shown in Figure 2E. It is lower than **9p** at all levels of theory, but only 0.9 kcal/mol below the planar structure **9p** at the MP4(SDTQ)/6-31G* + Δ ZPE level. Again, the relative flatness of this potential energy surface implies that actual reactions would follow trajectories with a broad range of geometries between the calculated transition structure **9np** and the planar structure **9p** but that nonplanar trajectories would be favored.

With this caveat, the out-of-plane folding of **9np** makes it slightly closer to the usual transition structures calculated for Diels–Alder and hetero-Diels–Alder reactions than is **11np**.[32] With $C_4-O_5-C_2-C_7$ and $C_3-C_2-O_5-C_6$ dihedral angles of 131.4° and −147.6°, respectively, transition structure **9np** has a somewhat more open geometry than found for butadiene plus ethylene (118.8°, RHF/6-31G*), but less open than for **8** plus ethylene (*vide supra*).

Other trends in the geometry of **9np** are unremarkable. In cycloadditions to butadiene, the forming bonds

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(34) (a) Lee, I.; Han, E. S.; Choi, J. Y. *J. Comput. Chem.* **1984**, *5*, 606. (b) Martin, S. F.; Benage, B.; Geraci, L. S.; Hunter, J. E.; Mortimore, M. *J. Am. Chem. Soc.* **1991**, *113*, 6161–6171. (c) Tietze, L. F.; Geissler, H.; Fennen, J.; Brumby, T.; Brand, S.; Schulz, G. *J. Org. Chem.* **1994**, *59*, 182–191.

(35) Tietze, L. F.; Beifuss, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 131–163.

(36) (a) Dau, M. E. T. H.; Flament, J.; Lefour, J.; Riche, C.; Grierson, D. S. *Tetrahedron Lett.* **1992**, *33*, 2343–2346. (b) Yamabe, S.; Kawajiri, S.; Minato, T.; Machiguchi, T. *J. Org. Chem.* **1993**, *58*, 1122–1127.

(37) Additions to α-(alkoxycarbonyl) ketenes proceed via [2 + 2] pathways. (Stevens, R. V.; Bisacchi, G. S.; Goldsmith, L.; Strouse, C. E. *J. Org. Chem.* **1980**, *45*, 2708–2709.) It may be that the ester resonance in α-(alkoxycarbonyl) ketenes reduces their reactivity in [4 + 2] cycloadditions.

(38) Tardy, D. C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508–1514.

(39) Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198.

with acetylene are shorter than those with ethylene (2.198 Å[33a] vs 2.201 Å,[31] respectively, at the RHF/6-31G* level.) The same trend is found in the additions to formylketene (**8**) as seen in Figure 2C,F. Transition structure **9np** shows more asynchronicity than **11np**, with the C_2C_7 forming bond 0.08 Å shorter than the O_5C_6 forming bond in the former, while in the latter, the bonds differ by only 0.02 Å. This would be consistent with the nucleophilic addition at C_2 (*vide supra*) being somewhat more advanced with the more electron rich acetylene than with ethylene.

The addition of acetylene to **8** is calculated to be a very exothermic reaction (49.7 kcal/mol), much more so than the addition of ethylene to **8** (26.5 kcal/mol). This exothermicity is primarily due to the high energy of acetylene rather than any aromatic stabilization of **10**. The heat of hydrogenation of **10** to **12** is calculated to be only 2.2 kcal/mol less than that of **12** to tetrahydropyran-4-one (**13**) (Table 3). Although this analysis neglects strain and other factors which complicate the quantification of aromaticity,[40] the aromatic stabilization of **10** is clearly fairly small. The significantly greater (23.2 kcal/mol) exothermicity for the addition of acetylene versus ethylene to **8** may be reflected in what is only a slightly lower activation energy for the former addition (25.9 vs 24.7 kcal/mol). Alternatively, the lower barrier for the addition of acetylene could be attributed to its greater nucleophilicity rather than the exothermicity of the reaction.[41]

The extremely similar energies for the planar (**11p**) and nonplanar (**11np**) transition structures for the addition of ethylene to **8** demonstrates not only that a planar geometry is possible, but indeed that it may favored by the developing σ-bonds in this pseudopericyclic reaction. Since the only difference between **11p** and **9p** is the out-of-plane π-system from the acetylene, the greater preference for nonplanarity of the transition structure **9np** necessarily means that a factor associated with this π-system disfavors the planar structure. The most reasonable explanation is that the π-electron repulsion at the transition state is stronger than the developing π-bonding or aromaticity. The difference between the two effects must be at least the 0.9 kcal/mol which favors **9np** over **9p** because **11p** and **11np** are so closely balanced and **9np** is more distorted from the pseudopericyclic geometry (*vide supra*). The difference between the activation energies and the energies required to distort the reactants to their geometries in the transition structures has been previously used to provide a measure of the electron repulsion in a transition structure.[2a,b] An energy of 1.6 kcal/mol is thus calculated for **9np** (at the MP4(SDQ)/6-31G* level) and of 2.3 kcal/mol for **9p**. Although this is consistent with the proposal that the distortion out of plane occurs to reduce the closed-shell electron repulsion it is also consistent with the proposal that the formylketene moiety bends to allow a better angle of attack on the ketene carbon and carbonyl oxygen (Figure 3, *vide supra*). A similar calculation gives a repulsion energy of 3.0 kcal/mol for **11p**, larger than for **9p** because the angle bending is larger in **11p**.

In summary, the transition structure (**9np**) for the addition of acetylene to **8** is distinctly nonplanar, resembling that for a typical Diels–Alder reaction. This nonplanarity is due to π-repulsions in the transition structure which are at least 0.9 kcal/mol greater than any π-aromatic stabilization. The barrier is calculated to be 24.7 kcal/mol, which is slightly lower than the barrier calculated for the addition of ethylene to **8**.

8

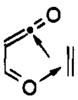

Figure 3. Proposed angles for in-plane nucleophilic and electrophilic attack on formylketene (**8**).

Conclusion. Pericyclic reactions which form aromatic systems may be grouped into two classes, those in which only the aromatic π-system is completed during the reaction and those for which the σ-system is completed concurrently. The latter are termed σ,π-aromatizations. Transition structures (**4** and **9np**) have been located at the MP2/6-31G* level for two examples of this class. The planarity of the transition structure for the trimerization of acetylene (**4**) reflects a small degree of either σ- and/or π-stabilization. Although not substantial, it is sufficient to overcome any closed-shell repulsions in the out-of-plane π-system which might tend to lower the symmetry of the transition structure. The planar (**11p**) and nonplanar (**11np**) pathways for the addition of ethylene to formylketene (**8**, in which a π-aromatic system is not formed) have similar energies, although at the best level (MP4(SDTQ)/6-31G*//MP2/6-31G* + ZPE) the planar structure (**11p**) is slightly favored, by just 0.6 kcal/mol. Achieving the planar transition structure requires significant and non-least-motion angle bending of **8**. The planar, pseudopericyclic mechanism must have an inherently lower barrier since the nonplanar, pericyclic transition structure (**11np**) has less angle strain. When the analogous planar structure is calculated for the addition of acetylene to **8**, in which a π-aromatic system is formed, it is a second-order saddle point (**9p**) at all levels of theory. The true transition structure (**9np**) for this reaction is nonplanar and resembles those usually found for Diels–Alder cycloadditions. The higher energy of planar the second-order saddle point **9p** (0.9 kcal/mol above **9np**) demonstrates that at least for this example of a two-fragment cycloaddition, the closed-shell repulsions in the π-system are greater than any developing aromaticity (which admittedly provides an only fairly small additional stabilization to the product **10**.) Further studies of pseudopericyclic reactions (including electrocyclizations) which form aromatic rings are in progress and will be reported in due course.

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Supplementary Material Available: Tables of optimized *Z*-matrices for structures **4**, **8**, **9np**, **9p**, **11p**, **11np**, **12**, and **13** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[40] Garratt, P. J. *Aromaticity*; Wiley: New York, 1986.

[41] The calculated barrier for the addition of acetylene to butadiene is higher than that for ethylene (14.6 kcal/33a vs 13.6 kcal/mol,[31] MP2/6-31G*//RHF/6-31G* relative to *cis*-butadiene).