

$$\Delta\lambda_s = 7.63 \left( \frac{1}{R_0} - \frac{1}{R} \right) \quad (3)$$

Alternatively, based on the values for  $\Delta\lambda_s$ ,  $V$  and  $V_0$  of 1.05 eV, 11 cm<sup>-1</sup>, and 200 cm<sup>-1</sup>, and assuming a value of  $1.5 \pm 0.2$  Å<sup>-1</sup> for  $\beta$ , eq 2 and 3 can be used to determine the two unknown distances  $R_0$  and  $R$  directly. In this manner, values for  $R_0$  and  $R$  of  $3.7 \pm 0.2$  and  $7.6 \pm 0.7$  Å are obtained.

The present results demonstrate that the efficiency with which excited complexes undergo solvation to solvent-penetrated pairs and then to free-radical ions and products thereof is highly influenced by a wide range of  $(k_{-et})_{ct}$  and that the factors which control this rate are consistent with recent electron-transfer theories. The quantum yield of formation of solvent-penetrated ion pairs from the excited complexes could be negligible, as  $(k_{-et})_{ct}$  exceeds  $10^{11}$  s<sup>-1</sup>, or approach unity, when  $(k_{-et})_{ct}$  drops below  $10^8$  s<sup>-1</sup>. In addition, the different dependencies of  $(\Phi_{ions})_{ct}$  and  $(\Phi_{ions})_{rip}$  upon  $-\Delta G$  strongly suggest that electron-transfer quenching of the free acceptors does not proceed via the intermediacy of a contact ion pair but results in the formation of the solvent-separated ion pair directly.

### Homoaromaticity in a Cyclic Polyacetylene<sup>1</sup>

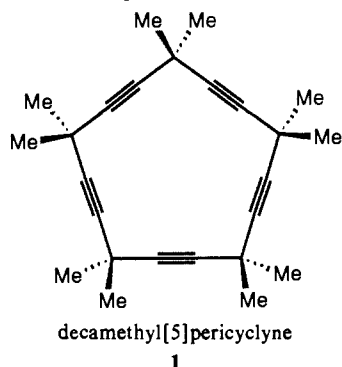
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We have previously reported on the synthesis of decamethyl-[5]pericyclyne (**1**) and have cited evidence for a strong electronic interaction among the five acetylenic units therein.<sup>3,4</sup> In particular, the photoelectron spectrum of **1** shows a splitting of the



degeneracy of filled  $\pi$  orbitals by more than 1.0 eV, and electron transmission spectroscopy shows a lowering of the LUMO in **1** by more than 1.0 eV compared to that in an isolated alkyne.<sup>4</sup> Thus, the electronic properties of **1** appear to be strongly influenced by cyclic homoconjugation. We now address the separate question, is this molecule homoaromatic, and offer an answer in the affirmative. Homoaromaticity in cationic systems was first identified many years ago,<sup>5,6</sup> but the evidence for homoaromaticity in neutral organic molecules is sparse,<sup>6,7</sup> and much controversy surrounds

(1) Part 6 in the series "Cyclines". For parts 4 and 5, see ref 3 and 4.

(2) (a) University of Nevada. (b) Long Island University.

(3) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, *107*, 6546-6555.

(4) Houk, K. N.; Scott, L. T.; Rondon, N. G.; Spellmeyer, D. C.; Reinhardt, G.; Hyun, J. L.; DeCicco, G. J.; Weiss, R.; Chen, M. H. M.; Bass, L. S.; Clardy, J.; Jørgensen, F. S.; Eaton, T. A.; Sarkozi, V.; Petit, C. M.; Ng, L.; Jordan, K. D. *J. Am. Chem. Soc.* **1985**, *107*, 6556-6562.

(5) Scott, L. T.; Hashemi, M. M. *Tetrahedron* **1986**, *42*, 1823.

(6) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106-117, and references cited therein.

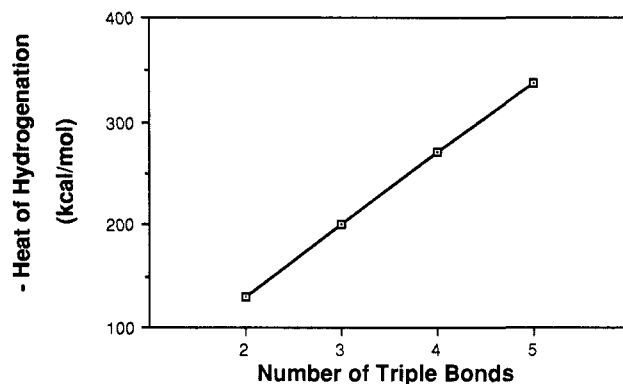
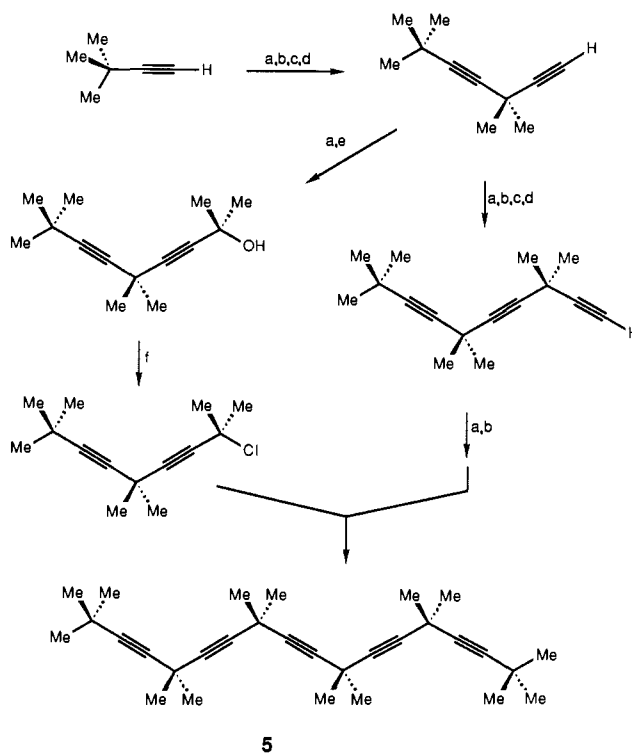


Figure 1. Heats of hydrogenation of polyacetylenes **2**, **3**, **4**, and **5**.

#### Scheme I<sup>a</sup>



<sup>a</sup> (a) EtMgBr; (b) CuCl catalyst; (c) Me<sub>2</sub>C(Cl)-C≡C-TMS; (d) KOH, MeOH; (e) CH<sub>3</sub>COCH<sub>3</sub>; (f) HCl, CaCl<sub>2</sub>, Cu powder.

the question of homoaromaticity in anions.<sup>6,8</sup>

The concept of aromaticity, though somewhat ill-defined, is normally associated with the special consequences arising from electron delocalization around a closed cycle of conjugated  $\pi$  bonds.<sup>9</sup> One dramatic consequence of cyclic electron delocalization is the exceptionally large thermodynamic stabilization of benzene relative to acyclic conjugated  $\pi$  systems. From heats of hydrogenation measurements, an experimental value of the 36 kcal/mol has been determined for the resonance stabilization of benzene.<sup>10</sup> By using this same classical technique, we have now determined the extent to which the closed cycle of homoconjugation in decamethyl[5]pericyclyne (**1**) imparts a thermodynamic stabilization to this unusual molecule.

Such a study required that we carefully determine the heat of hydrogenation expected for compound **1** in the absence of any

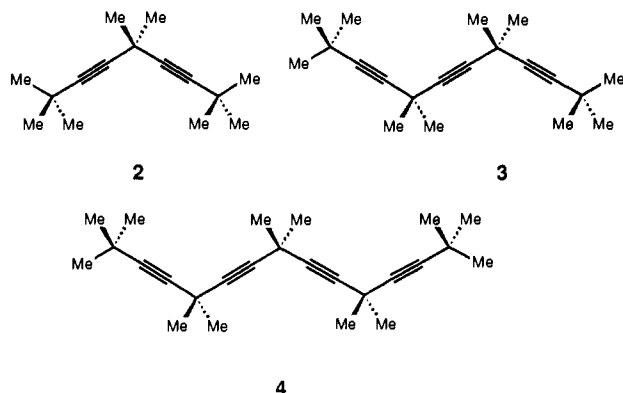
(7) Liebman, J. F.; Paquette, L. A.; Peterson, J. R.; Rogers, D. W. *J. Am. Chem. Soc.* **1986**, *108*, 8267-8268, and references cited therein.

(8) Lee, R. E.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 5078-5086, and references cited therein.

(9) Garratt, P. J. *Aromaticity*; John Wiley and Sons: New York, 1986.

(10) Conant, J. B.; Kistiakowsky, G. B. *Chem. Rev.* **1937**, *20*, 181. This frequently quoted value of 36 kcal/mol is based on a comparison of benzene to completely unconjugated alkenes; for just the cyclic contribution to the stabilization of benzene, a slightly lower value would be more accurate.

cyclic contribution to homoconjugation. Toward this end we synthesized the homoconjugated acyclic pentayne **5** by the route summarized in Scheme 1. Completely analogous reactions likewise provided the lower homologues in this new family of reference compounds, i.e., the acyclic diyne **2**, triyne **3**, and tetrayne **4**.<sup>11</sup>



By using the calorimeter and methods we have previously described,<sup>7</sup> we found the heats of hydrogenation for acyclic homoconjugated polyacetylenes **2**, **3**, **4**, and **5** to be  $-130 \pm 1$ ,  $-201 \pm 1$ ,  $-271 \pm 1$ , and  $-339 \pm 2$  kcal/mol, respectively (duplicate runs on each).<sup>12</sup> A plot of these values versus the number of triple bonds gives a remarkably good straight line (Figure 1). Linear least-squares treatment of the eight independent experimental results shows the standard deviation of all points about the linear function to be only 0.8 kcal/mol. These data provide an additivity value for the enthalpy increment per homoconjugated triple bond of  $-69.8$  kcal/mol. Consequently, the heat of hydrogenation predicted for compound **1** in the absence of any special effects associated with closing the cycle of homoconjugation is  $-69.8 \times 5$  or  $-349.0 \pm 0.8$  kcal/mol.

The experimental heat of hydrogenation for decamethyl[5]-pericycylene (**1**) was found to be  $-340.7$  kcal/mol with a standard deviation of the mean of 2.2 kcal/mol from the pooled experimental data.<sup>13</sup> This value is significantly smaller ( $\Delta\Delta H = 8.3$  kcal/mol), though not dramatically so, than the value predicted on the basis of acyclic model compounds which have an equivalent degree of homoconjugation but lack the cyclic component.

Before attributing this entire  $\Delta\Delta H$  to homoaromaticity in **1**, one must first consider the possible presence of *extra* strain in the cyclic hydrogenation product derived from **1** relative to that in the saturated acyclic models. Any *destabilization* in the cyclic hydrogenation product would have the same effect on  $\Delta\Delta H$  as would an electronic stabilization of the cyclic pentayne. To probe this aspect of the problem, we carried out molecular mechanics calculations<sup>14</sup> on the hydrogenation products of all the polyacetylenes **1-5** and found that the reduced 15-membered ring suffers from no more than 2 kcal/mol of extra strain over that present in the saturated acyclics. After correcting for the strain increase on hydrogenation, enthalpy lowering relative to the model remains statistically significant at the 0.99 confidence level. We attribute this enthalpy lowering to stabilization of the cyclic pentayne, i.e., to homoaromaticity.

The recent discovery<sup>7</sup> of a 4.5 kcal/mol stabilization energy in triquinacene (a *trishomobenzene*) has been interpreted as the first evidence that cyclic homoconjugation can actually have thermodynamic consequences in neutral systems. Our results with

decamethyl[5]pericycylene(**1**) reinforce this conclusion. The fact that the thermodynamic effects are small in magnitude reflects, we believe, the highly "bond-alternate" character of these homoconjugated cycles.

Finally, it should be emphasized that the absence of a large thermodynamic stabilization (homoaromaticity) does *not* necessarily imply that orbital interactions (homoconjugation) must also be small. Triquinacene and decamethyl[5]pericycylene are characterized by strong homoconjugative orbital interactions, as revealed by PES and other spectroscopic measurements, yet they exhibit only a modest degree of homoaromaticity, by the thermodynamic criterion. Cyclic homoconjugation is a necessary condition for homoaromaticity but does not guarantee that the effects of homoaromaticity will be large.<sup>15</sup>

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**Registry No.** **1**, 88057-40-3; **2**, 116503-39-0; **3**, 116503-40-3; **4**, 116503-41-4; **5**, 116503-42-5.

(15) For further examples of cyclic homoconjugation in neutral organic molecules, see: Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 105.

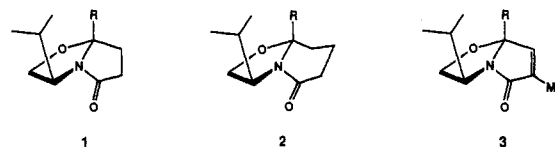
## A Novel Asymmetric Synthesis of Substituted Cyclopropanes<sup>†</sup>

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During the past several years, we have been studying the synthetic utility of chiral nonracemic bicyclic lactams such as **1-3**.



These readily accessible materials have led to efficient syntheses of enantiomerically pure compounds containing a quaternary stereocenter.<sup>1</sup> Thus, routes to chiral 4,4-disubstituted cyclopentenones, 4,4-disubstituted cyclohexenones, 2,2-disubstituted-4-keto acids, and various natural products were achieved. For instance, photoaddition of ethylene to **3** led to a chiral cyclobutane synthesis and the pheromone, grandisol.

We now describe how these versatile chiral bicyclic lactams may be utilized as a starting point to various chiral, nonracemic cyclopropanes, an area with rather few general synthetic approaches.<sup>2</sup> The wide variety of important natural products<sup>3</sup> and currently employed insecticides (e.g., permethrinic acid) containing the cyclopropane ring in a chiral environment provide further

<sup>†</sup> This paper is dedicated to Professor Harry M. Walborsky on the occasion of his 65th birthday.

(1) Meyers, A. I.; Lefker, B. A. *Tetrahedron* **1987**, *43*, 5663 and earlier references cited therein.

(2) (a) Salaun, J.; Karkour, B. *Tetrahedron Lett.* **1987**, *28*, 4669 and references cited therein. (b) Kleschick, W. A.; Reed, M. W.; Bordner, J. *J. Org. Chem.* **1987**, *52*, 3168. (c) Arai, I.; Mori, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 8254. (d) Mash, E. A.; Fryling, J. A. *J. Org. Chem.* **1987**, *52*, 3000. (e) Barbachyn, M. R.; Johnson, C. R. *Asymmetric Synthesis*; Morrison, J. D., Scott, J. W., Eds.; Academic Press: New York, 1984; p 247. (f) Nogradi, M. *Stereoselective Synthesis*; VCH: New York, 1987; pp 277-280.

(3) (a) *Handbook of Terpenoids*; Dev, S., Ed.; CRC: Boca Raton, FL, 1982; Vol. 2. (b) Wender, P. A.; Keenan, R. M.; Lee, H.-Y. *J. Am. Chem. Soc.* **1971**, *109*, 4390. (c) Arlt, D.; Jaulelat, M.; Lantzsch, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 703.

(11) Complete experimental details can be found in the M.S. Thesis of M. J. Cooney, University of Nevada-Reno, 1987.

(12) Uncertainties are given as twice the standard deviation of the mean, according to the usual thermochemical convention.

(13) This standard deviation includes a 0.7 kcal/mol estimate of errors due to weighing and handling small samples.

(14) The Macintosh version of the MMX program distributed by Serena Software, Bloomington, IN (March 1988 edition) was used for these calculations and is very reliable for acyclic saturated hydrocarbons. This program has no means for finding the global minimum energy conformation, so 2 kcal/mol must be considered an upper limit for the strain energy.