Cl_2^-, is endothermic by 2.4 eV and an ion-neutral clustering energy of 0.4 eV is reasonable. Further studies of this and other symmetric displacement reactions are currently in progress to explore more fully the nature of the potential energy surfaces for these important processes.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation under Grant CHE-8508629. We are indebted to Professor Charles DePuy for his support and insight throughout this project. We thank Mark Jones for his assistance in the analysis of the methyl chloride, Thuy Dang for her help in data acquisition, and Professor Michael Bowers for valuable discussions.

Electron-Transfer Reactions in the Marcus Inverted Region: Differences in Solvation and Electronic Coupling between Excited Charge-Transfer Complexes and Geminate Radical Ion Pairs

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We have recently shown that the rate constants for return electron transfer within photochemically generated, solvent-penetrated, geminate radical ion pairs ($A^{\bullet -}/D^{\bullet +}$) decrease with increasing exothermicity (the Marcus "inverted region"),[1] which results in widely varying quantum yields for separated ion formation as a function of the energy stored in the radical ion pairs. Radical ions can also be formed by direct excitation in the charge-transfer bands of ground-state donor/acceptor complexes in polar solvents, and there are several reports of reactions via this route,[2] although, in other cases, virtually no free-radical ions are formed.[3,4a] Evidently the yield of free-radical ions from excited CT complexes also varies over a wide range.

Excited CT complexes can be characterized as radical ions at contact distances ($A^{\bullet -}D^{\bullet +}$),[5] which, in polar solvents, yield the solvent-penetrated radical ion pairs ($A^{\bullet -}/D^{\bullet +}$). These intermediates are equivalent to the classical contact and solvent-separated ion pairs. According to Scheme I, energy-wasting return electron transfer reactions within both the excited complex, $(k_{-et})_{ct}$, and the geminate pair, $(k_{-et})_{rip}$, compete with solvent penetration (k_{solv}) and the separation to free-radical ions (k_{sep}). In this communication we report the results of a systematic comparison of the rates of these two electron-transfer reactions, for the same donor/acceptor pairs.

The reaction constants $(k_{-et})_{rip}$ were previously determined for several alkylbenzenes as donors reacting with excited 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA) as electron acceptors.[1] Weak CT complexes are formed between TCA and alkylbenzenes with low oxidation potentials.[8]

Scheme I

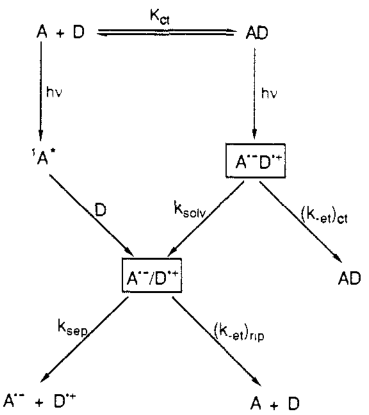
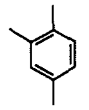
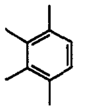
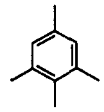
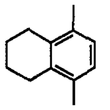
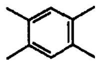
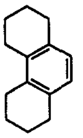
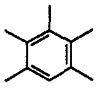
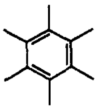


Table I. Quantum Yields of Free Ion Formation and Rate Constants for Return Electron Transfer for Excited CT Complexes (Contact Ion Pairs) and Solvent-Penetrated Ion Pairs of TCA/Benzene Derivatives in Acetonitrile

donor	$(E^{ox})_D - (E^{red})_A$	$(\Phi_{ions})_{ct}$[a]	$(k_{-et})_{ct}$ ($\times 10^{-9}$ s^{-1})	$(\Phi_{ions})_{rip}$[b]	$(k_{-et})_{rip}$[c] ($\times 10^{-9}$ s^{-1})
	2.36	0.0301	0.86	0.056	8.4
	2.28	0.0114	2.68	0.042	11.4
	2.27	0.0103	2.98	0.041	11.7
	2.25	0.0091	3.40	0.040	12.0
	2.22	0.0093	3.41	0.041	11.7
	2.21	0.0074	4.00	0.037	13.0
	2.15	0.0036	8.72	0.035	13.8
	2.03	0.0016	18.12	0.0306	15.8

[a] Quantum yield for formation of free-radical ion formation for photolysis of the CT complexes at 460 nm. [b] Quantum yield for formation of free-radical ions for photolysis of the acceptor at 410 nm, extrapolated to zero concentration of the donor.[1a,9] [c] Calculated assuming $k_{sep} = 5 \times 10^8$ s^{-1}.[1]

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(1) (a) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 1991. (b) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

(2) (a) Farid, S.; Hartman, S. E.; Evans, T. R. In *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; p 327. (b) Arnold, D. R.; Wong, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 1894. (c) Wong, P. C.; Arnold, D. R. *Can. J. Chem.* **1980**, *58*, 918. (d) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152. (e) Lewis, F. D.; Simpson, J. T. *J. Phys. Chem.* **1979**, *83*, 2015. (f) Jones, G., II; Haney, W. A.; Phan, X. T. *J. Am. Chem. Soc.* **1988**, *110*, 1922. (g) Jones, G., II; Becker, W. G. *J. Am. Chem. Soc.* **1983**, *105*, 1276. (h) Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 2780.

(3) Ledwith, A. In *The Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic Press: New York, 1975; p 209.

(4) (a) Mataga, N.; Shioyama, H.; Kanda, Y. *J. Phys. Chem.* **1987**, *91*, 314. (b) Mataga, N.; Okada, T.; Kanda, Y.; Shioyama, H. *Tetrahedron* **1986**, *42*, 6143.

(5) (a) This theoretical prediction (ref 5b) has been verified experimentally (ref 4, 6, and 7). (b) Mulliken, R. S.; Pearson, W. B. *Molecular Complexes: A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969.

(6) (a) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 1441. (b) Goodman, J. L.; Peters, K. S. *J. Phys. Chem.* **1986**, *90*, 5506. (c) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6459. (d) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 1700.

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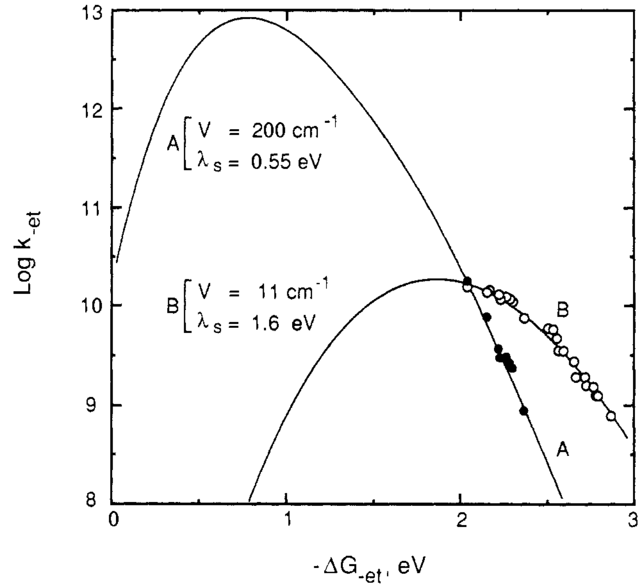

Figure 1. (A) Log $(k_{-et})_{ct}$ for excited CT complexes of TCA and alkyl benzenes and (B) log $(k_{-et})_{rip}$ for solvent-penetrated ion pairs of DCA and TCA radical anions and alkyl benzene radical cations, as a function of $-\Delta G$, in acetonitrile at 25 °C. The curves are calculated as described in the text by using the parameters shown in the figure and 0.3 eV and 1500 cm^{-1} for the internal reorganization energy and the averaged vibrational frequency, respectively (see text). A range of values for V and λ_s can be found to give acceptable fits to the excited complex data,[16] and typical values for these parameters are shown here (see text).

By using the transient absorption technique described previously,[1] the quantum yields of free-radical ion formation, $(\Phi_{ions})_{ct}$, were determined for laser excitation in the CT bands at 460 nm (Table I).[9] According to Scheme I, $(\Phi_{ions})_{ct}$ is given by eq 1.[10] The

$$(\Phi_{ions})_{ct} = \frac{k_{solv}}{(k_{-et})_{ct} + k_{solv}}(\Phi_{ions})_{rip} \qquad (1a)$$

$$(\Phi_{ions})_{rip} = \frac{k_{sep}}{(k_{-et})_{rip} + k_{sep}} \qquad (1b)$$

efficiency of free ion formation from the solvent-penetrated radical ion pair, $(\Phi_{ions})_{rip}$, is obtained by selectively exciting the free cyanoanthracene acceptors at 410 nm (Table I).[9] From $(\Phi_{ions})_{ct}$ and $(\Phi_{ions})_{rip}$, the rate $(k_{-et})_{ct}/k_{solv}$ is thus obtained for the different excited complexes.

The rate constant k_{solv}, the rate for solvation of an excited complex to form a solvent-penetrated geminate pair, has previously been determined to be ca. 1.5–2.0 × 10^9 s^{-1} by picosecond absorption spectroscopy.[4b,6] Rate constants for the analogous reaction of exciplex solvation to form geminate ion pairs have been determined to be ca. 0.5–1.0 × 10^9 s^{-1}.[11] It is thus assumed that k_{solv} is 10^9 s^{-1} and that this rate is constant for the closely related excited complexes of this study. On the basis of this assumption, the rate constants $(k_{-et})_{ct}$ for the different excited complexes are determined (Table I). Comparing $(k_{-et})_{ct}$ and $(k_{-et})_{rip}$ reveals that whereas both decrease with increasing reaction exothermicity ($-\Delta G$),[12] $(k_{-et})_{ct}$ is much more dependent than $(k_{-et})_{rip}$, in the $-\Delta G$ range studied (Figure 1).[13]

Electron-transfer theories describe the reaction rate as the product of an electronic coupling matrix element squared (V^2) and a Franck–Condon weighted density of states.[14] The dependence of V upon the distance between the ions is given by eq 2,[15] in which β is a constant of ca. 1.5 Å^{-1}, R is the center-to-center distance between the ions, and R_0 is the corresponding distance when in contact (ca. 3.5 Å). In excited CT complexes, the ions are in contact, whereas in the more solvated geminate pair, R is ca. 7 Å.[11a] Thus, V for the excited complex should be approximately an order of magnitude or more higher than that for the solvent-penetrated geminate pair, which was previously determined to be ca. 11 cm^{-1}.[1a]

$$V = V_0 e[-\beta(R - R_0)/2] \qquad (2)$$

As described previously,[1] the data were fitted to a theoretical relationship between the electron-transfer rate constant and $-\Delta G$,[14] in which the fitting parameters are V, the solvent and internal reorganization energies (λ_s and λ_v), and a vibrational frequency ν. For λ_v and ν, constant values of 0.3 eV and 1500 cm^{-1} were used for both sets of ion pairs.[1] Despite the small range of $-\Delta G$ for the excited CT data, it is clear that the larger negative slope of the plot of $(k_{-et})_{ct}$ versus $-\Delta G$ compared to that for $(k_{-et})_{rip}$ requires a larger value of V to fit this data. Indeed, as predicted, good fits are obtained for $V = 200 \pm 50$ cm^{-1}. The corresponding value for λ_s is 0.55 ∓ 0.05 eV,[16] which has an additional, estimated error margin of ca. 0.1 eV due to uncertainties in the values of $-\Delta G$.[12] This λ_s is considerably smaller than the ca. 1.6 eV required to fit the data for $(k_{-et})_{rip}$.[1a] The difference of ca. 1 eV in solvent reorganization energy, $\Delta\lambda_s$, is, however, consistent with the predictions of the Marcus dielectric continuum model for λ_s.[17] According to Marcus' equation, $\Delta\lambda_s$ (in eV) for an ion pair in acetonitrile with separation distances R and R_0 (in Å) is given by eq 3. Thus for $\Delta\lambda_s$ of 0.9–1.2 eV and using R of 7 Å for the solvent-penetrated pair, one obtains 3.6 ± 0.3 Å for R_0, which is a reasonable value for the interplanar separation in an excited π complex.

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(7) (a) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167. (b) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071. (c) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 1126.

(8) (a) Equilibrium constants for formation of the CT complexes, determined spectrophotometrically (ref 8b), range from ca. 1 to 7 M^{-1}. (b) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

(9) Irradiation at 460 nm results in excitation of the CT complexes only and the determination of $(\Phi_{ions})_{ct}$ directly. Irradiation at 410 nm results in excitation, at an isosbestic point, of both the free cyanoanthracene acceptor and the CT complex. The quantum yields were thus extrapolated to zero donor concentration in order to obtain $(\Phi_{ions})_{rip}$ (ref 1b).

(10) The back formation of $A^{\bullet-}D^{\bullet+}$ from $A^{\bullet-}/D^{\bullet+}$ (k_{-solv}) is omitted to simplify Scheme I, since it has a negligible effect on the data. k_{-solv} is either equal to or less than k_{solv} depending on whether the energy of $A^{\bullet-}D^{\bullet+}$ is equal to or higher than that of $A^{\bullet-}/D^{\bullet+}$. Including k_{-solv} of 10^9 s^{-1} in Scheme I leads to a minor decrease in the computed $(k_{-et})_{ct}$ values which results, for example, in a decrease in λ_s of only 0.01 eV.

(11) (a) Weller, A. *Z. Phys. Chem. Neue Folge* **1982**, *130*, 129. (b) For the exciplex of DCA/durene in acetonitrile, which can be described as a contact ion pair and is thus a reasonable model for the excited CT complexes, we obtain ca. 10^9 s^{-1} for k_{solv} (unpublished results).

(12) (a) $-\Delta G$ for both ion pair reactions is obtained from $(E^{ox})_D - (E^{red})_A$, which represents the energy stored in the solvated radical ions. The compensating effects of stabilization due to coulombic attraction and destabilization due to the lower solvation of the geminate pair compared to the free ions amount to an overall stabilization of only ca. 60 mV for the geminate pairs (ref 12b) and is thus ignored. Contact ion pair energies were estimated from equilibrium constants for reversible formation of related CT exciplexes, which were taken as models for the excited complexes. Exciplexes of TCA with *m*- and *p*-xylenes in cyclohexane were found to be ca. 0.2 eV higher in energy than $(E^{ox})_D - (E^{red})_A$ of the components in polar solvents. The energy of such exciplexes is expected to be ca. 0.2 eV lower in acetonitrile (ref 12b) and thus isoenergetic with the solvated ions. We assume, therefore, that $-\Delta G$ for the contact ion pairs is given by $(E^{ox})_D - (E^{red})_A$, recognizing an error margin of ca. 0.1 eV in this estimate. (b) Weller, A. *Z. Phys. Chem. Neue Folge* **1982**, *133*, 93.

(13) Mataga has observed a similar decrease in $(k_{-et})_{ct}$ with increasing $-\Delta G$ for excited CT complexes (ref 4b) although in that study different types of ion pairs in different solvents were compared.

(14) (a) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. (b) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (c) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741, 748. (d) Closs, G. L.; Miller, J. R. *Science (Washington, D. C.)* **1988**, *240*, 440.

(15) (a) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437. (b) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746. (c) Strauch, S.; McLendon, G.; McGuire, M.; Guarr, T. *J. Phys. Chem.* **1983**, *87*, 3579. (d) Guarr, T.; McGuire, M.; Strauch, S.; McLendon, G. *J. Am. Chem. Soc.* **1983**, *105*, 616.

(16) For example, using values for V of 150, 200, and 250 cm^{-1}, the corresponding values of λ_s required to fit the data are 0.60, 0.55, and 0.51 eV, which yield maximum values for $(k_{-et})_{ct}$ of 4.6, 8.2, and 13.0 × 10^{12} s^{-1}, respectively. The fitting procedure assumes the electron-transfer reactions are nonadiabatic, although, for electronic couplings larger than ca. 200 cm^{-1}, the reactions may acquire significant adiabatic character and thus become less dependent on V (ref 14).

(17) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

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

Alternatively, based on the values for $\Delta\lambda_s$, V and V_0 of 1.05 eV, 11 cm^{-1}, and 200 cm^{-1}, and assuming a value of 1.5 ± 0.2 Å^{-1} for β, 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 ∓ 0.2 and 7.6 ∓ 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 $(k_{-\mathrm{et}})_{\mathrm{ct}}$ 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 $(k_{-\mathrm{et}})_{\mathrm{ct}}$ exceeds 10^{11} s^{-1}, or approach unity, when $(k_{-\mathrm{et}})_{\mathrm{ct}}$ drops below 10^8 s^{-1}. In addition, the different dependencies of $(\Phi_{\mathrm{ions}})_{\mathrm{ct}}$ and $(\Phi_{\mathrm{ions}})_{\mathrm{rip}}$ 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[1]

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Donald W. Rogers,*[2b] and Kosol Dejroongruang[2b]

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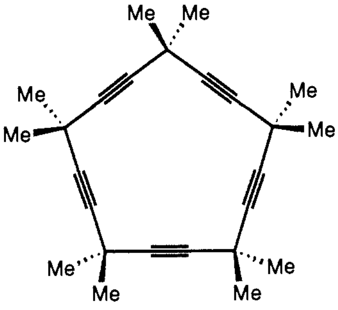
Received May 19, 1988

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.[3,4] In particular, the photoelectron spectrum of **1** shows a splitting of the degeneracy of filled π 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.[4] 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,[5,6] but the evidence for homoaromaticity in neutral organic molecules is sparse,[6,7] and much controversy surrounds the question of homoaromaticity in anions.[6,8]



decamethyl[5]pericyclyne

1

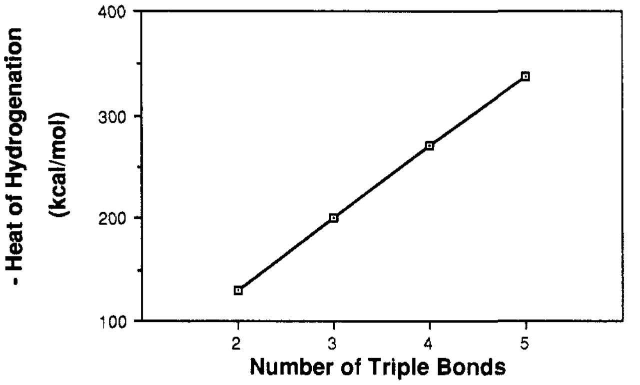
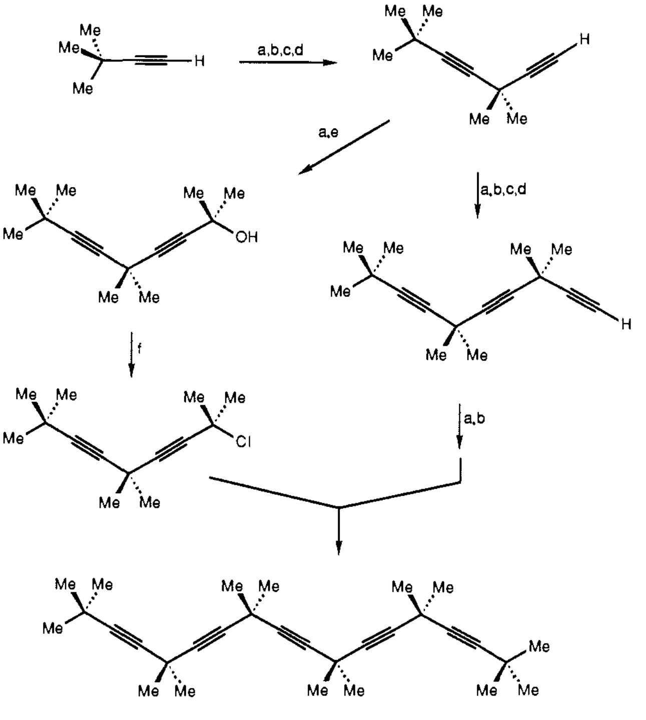


Figure 1. Heats of hydrogenation of polyacetylenes **2**, **3**, **4**, and **5**.

Scheme I[a]



5

[a] (a) EtMgBr; (b) CuCl catalyst; (c) Me$_2$C(Cl)—C≡C—TMS; (d) KOH, MeOH; (e) CH$_3$COCH$_3$; (f) HCl, CaCl$_2$, Cu powder.

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 π bonds.[9] One dramatic consequence of cyclic electron delocalization is the exceptionally large thermodynamic stabilization of benzene relative to acyclic conjugated π systems. From heats of hydrogenation measurements, an experimental value of the 36 kcal/mol has been determined for the resonance stabilization of benzene.[10] By using this same classical technique, we have now determined the extent to which the closed cycle of *homo*conjugation 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

---

[1] Part 6 in the series "Cyclynes". 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.

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[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.

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