enhanced kinetic stability of the trimers **10** and **13** as compared to **18**.

Conclusions

The electronic and structural properties of 1,3,7,9,13,15-hexadehydro[18]annulene (**18**) and 1,3,7,9,13,15,19,21-octadehydro[24]annulene (**19**), and the corresponding cyclobutene-annelated derivatives **10–15** were compared in an experimental and computational study. On the basis of analysis of their electronic absorption and ^{1}H NMR spectra, the trimers **10** and **13** are assigned a planar diatropic [18]annulene perimeter and the tetramers **11** and **14** a planar paratropic [24]annulene perimeter. The chromophores in the pentamers **12** and **15** are conformationally more flexible, and the diatropic character of these [30]annulenes is strongly reduced. Cyclobutene annelation kinetically stabilizes all macrocycles as compared to the parent dehydroannulene perimeters **18** and **19**. In particular, the fusion of cyclobutene rings stabilizes dramatically the planar [24]-annulene perimeter in the tetramers **11** and **14** and is responsible for their preferred formation in the oxidative coupling reactions. The crystalline tetramers **11** and **14** are stable for months at room temperature and ambient Los Angeles atmosphere. AM1 and MM2 computational studies reproduce well the experimentally observed conformational preferences of all annulene perimeters considered in this study. The calculations show that the peculiar stereochemistry of the 1,2-diethynyl-1-cyclobutene unit defines the unique properties of the cyclobutenoannulenes. With its larger C=C—C angle α of 136°, the 1,2-diethynyl-1-cyclobutene unit is accommodated in a nearly strainfree way into the planar tetramers **11** and **14**, whereas its incorporation into the planar trimers **10** and **13** generates considerable angle strain. The enhanced kinetic stability of the cyclobutene-fused dehydroannulene perimeters is explained by energetically more difficult bending and out-of-plane distortions, normally required to reach reaction transition states. The computational studies suggest that diethynylcyclopropenone (**21**) derivatives with their very large C=C—C angle α of ~150° should be ideally suited to generate even larger dehydroannulene perimeters in oxidative coupling reactions. With protected derivatives of **21**, currently under preparation, planar [30]-, [36]-, and [42]annulene perimeters should be accessible as potential precursors to the cyclo[*n*]carbons C_{30}, C_{36}, and C_{42}.

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Supplementary Material Available: Listing of Cartesian coordinates of optimized geometries calculated by AM1 (6 pages). Ordering information is given on any current masthead page.

Communications to the Editor

Low-Temperature Conformational Transition within the [Zn-Cytochrome *c* Peroxidase, Cytochrome *c*] Electron-Transfer Complex

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Whereas protein systems that incorporate redox partners held at fixed distance and orientation are of extreme interest for studying the fundamentals of long-range electron transfer (ET),[1-3] interprotein ET typically involves protein complexes that associate through electrostatic and hydrophobic interactions, for example, [cytochrome *c* peroxidase, cytochrome *c*],[4] [cytochrome *c*, cytochrome b_5],[5] [plastocyanin, cytochrome *c*],[6] [flavodoxin, cytochrome *c*],[7] and [hemoglobin, cytochrome b_5].[8] Although such complexes are thought to exhibit a preferred binding mode, they are not necessarily restricted to a unique, static docking geometry[9,5b] as might be inferred from the earlier molecular graphics modeling studies. We now show that studies of interprotein triplet-state quenching may be used to probe the dynamics of docking rearrangements within ET complexes: we report that the [ZnCcP, Fe^{3+}Cc] complex[10] undergoes a remarkable conformational transition at low temperature.

The intrinsic triplet decay traces for ZnP incorporated into CcP, as measured with the [ZnCcP, Fe^{2+}Cc] complex[11,12] in ethylene glycol (EGOH)/KP$_i$ buffer, are rigorously single-exponential for ≥5 half-lives, and the decay rate constant (k_D) decreases smoothly[13] from $k_D = (126 \pm 4)\ s^{-1}$ at 293 K to $k_D = (66 \pm 2)$

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(10) The following abbreviations will be used in this report: [ZnCcP, FeCc], the 1:1 complex between Zn-substituted yeast cytochrome *c* peroxidase and yeast cytochrome *c* having Cys 102 replaced with Thr; EGOH, ethylene glycol; ET, electron transfer; ZnP, zinc protoporphyrin IX.

(11) (a) Preparation of ZnCcP, to be described later, is a modification of that described in the following: Yonetani, T. *J. Biol. Chem.* **1967**, *242*, 5008-5013. (b) Preparation of cytochrome c (T102) is based on the following: Cutler, R. L.; Pielak, G. J.; Mauk, A. G.; Smith, M.; *Protein Eng.* **1987**, *1*, 95-99. It included final FPLC purification.

(12) Emission experiments were performed by using a xenon flash (baseline pulse width = 80 μs) excitation source (excitation at 430 ± 10 nm); emission was detected by using a red-extended PMT (Hamamatsu R446).

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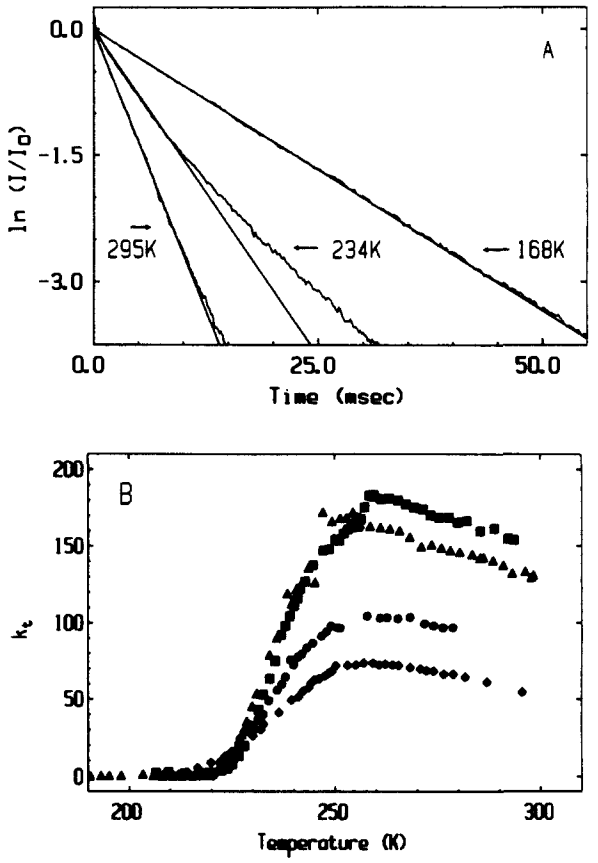

Figure 1. Triplet-state decay as a function of temperature for [ZnCcP, Fe^{3+}Cc]. (A) Triplet decay traces above (295 K), below (168 K), and near T_{mid} = 234 K. The solid lines are fits to a single-exponential decay. Conditions: 30% EGOH/10 mM KP_i buffer; pH = 6 at 4 °C. (B) Temperature dependence of the intracomplex quenching rate constant, k_t, obtained from eq 2: 15% (■), 30% (▲), 45% (●), and 60% (◆) EGOH/10 mM KP_i buffer at pH 6.

s^{-1} at T = 190 K. Quenching of ^{3}ZnP by the Cc ferriheme within the [ZnCcP, Fe^{3+}Cc] complex (rate constant, k_t) increases the triplet-decay rate constant at 293 K to $k_p = k_D + k_t = (279 \pm 16)$ s^{-1} in 30% EGOH (Figure 1A).[4a] Down to 250 K, $k_t \sim 150$ s^{-1}, roughly independent of temperature, but upon further lowering of the temperature by only 30 K, the quenching vanishes ($k_t \rightarrow 0$) (Figure 1B). The triplet decay traces for the [ZnCcP, Fe^{3+}Cc] complex also exhibit single-exponential kinetics for ≥5 half-lives outside the transition range of $220 \leq T \leq 250$ K (Figure 1A). However, within the transition range, heterogeneous kinetics are observed (Figure 1A) and the decay traces are well-described with either a two-exponential kinetic equation,

$$A = A_0[(1 - f)\exp(-k_D t) + f\exp(-k_p t)] \quad (1)$$

or a stretched exponential equation in which the quenching rate constant (k_t) is distributed,[14]

$$A = A_0\exp[-(k_D t) - (k_t t)^n] \quad (2)$$

Equation 1 describes a partition between two forms of the complex: one, with fraction f, that exhibits quenching and one that does not. Equation 2 corresponds to a distribution of forms with a range of quenching rates whose breadth varies inversely with n; such a distribution is well-established for proteins at low temperatures.[15] In either case, the nonexponential kinetics necessitate that conformational interconversion in the transition range is slow compared to the lifetime of the triplet state.

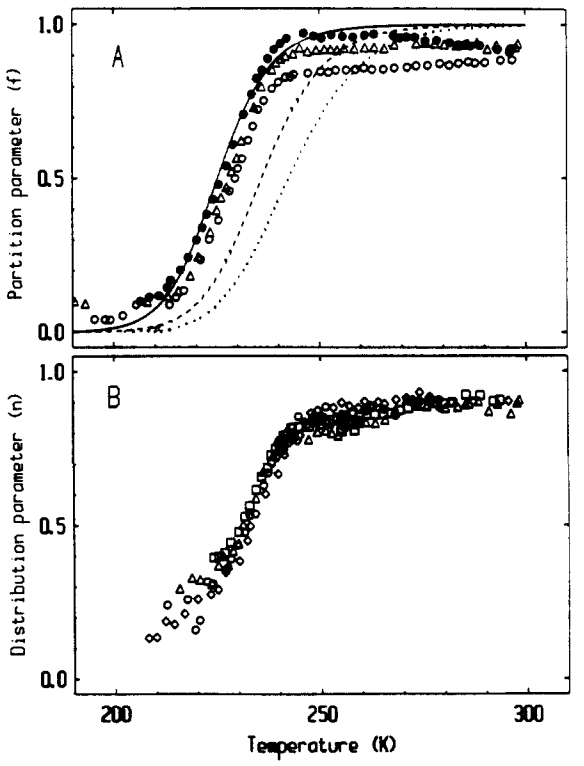

Figure 2. Temperature dependence for the parameters that characterize the partitioning of the [ZnCcP, Fe^{3+}Cc] complex into different forms. (A) Partition parameter, f, determined by fitting triplet-state progress curves to eq 1, for R = [Cc]/[CcP] = 2.01 (○), 4.16 (△), and 18.4 (●). Included are a nonlinear least-squares fit for R = 18.4 to a temperature-dependent dissociation equilibrium (ref 16) (—) and predictions from this fit for R = 4.16 (– – –) and R = 2.01 (···). (B) Distribution parameter, n, from eq 2: 15% (□), 30% (△), 45% (○), and 60% (◇) EGOH/10 mM KP_i buffer.

The partition parameter, f, from the two-state fit (eq 1, Figure 2A) and those from the distributed fit, eq 2 (k_t, Figure 1B; n, Figure 2B), change abruptly with temperature. The parameter f drops in a sigmoidal fashion as the temperature is lowered through the transition range; for the distributed fit, both the "$1/e$" rate, k_t, and the distribution parameter, n drop correspondingly through this transition. The decrease in n corresponds to broadening of the distribution in k_t.

The two-state model was used to test whether characteristics of the low-temperature cryosolvent cause the equilibrium constant for complex formation, $K(T)$, to fall precipitously as the temperature is lowered through T_{mid}. In this case, the slow phase that appears below ~250 K would correspond to uncomplexed ZnCcP. This interpretation fails because within the transition range the fraction, $f(T)$, is unaffected by a 10-fold reduction in the ratio, R = [Cc]/[Ccp], whereas calculation of $K(T)$ from the $f(T)$ measured with R = 18.4 would predict a much smaller $f(T)$ for R = 2.01 and R = 4.16 (Figure 2A).[16] Alternatively, the two-state model would apply if a low-temperature form of the complex were created by a change in ligation of either ZnP or FeP. This is ruled out by optical and MCD spectra,[17] which sharpen smoothly

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(16) (a) The R = 18.4 data (—) was fit to $f(T) = [1 + K(T)]^{-1}$, giving $f(T) = \{1 + \exp[(7790/T) - 34.6]\}^{-1}$. $K(T)$ was then used to predict $f(T)$ for R = 4.16 (– – –) and R = 2.01 (···). R was determined by using $\epsilon_{410}(Fe^{3+}Cc)$ = 106.1 mM^{-1} cm^{-1} (ref 16b) and ϵ_{432}(ZnCpP) = 180 mM^{-1} cm^{-1}. (b) Margoliash, E.; Frohwirt, N.; Wiener, E. *Biochem. J.* **1959**, *71*, 559–572.

throughout the transition range, but do not show any shifts or anomalies that would accompany changes in the coordination state of either protein. Instead, we tentatively interpret the abrupt disappearance of quenching as signaling a transition in the interfacial docking geometry *within* the protein complex,[18] the alternate possibility being freezing of one or both proteins into a set of non-redox-active conformational substates.[15] This interpretation is congruent with data suggesting that intracomplex ET near ambient temperatures involves a conformational conversion from inactive to active forms (conformational "gating").[19]

Remarkably, the transition temperature is independent of the solvent composition (Figures 1B and 2B), occurring in the same temperature range for solutions that glass below T_{mid} (60% EGOH) as for those solutions that crystallize at a temperature comparable to (45% EGOH) or greater than (15% and 30% EGOH) T_{mid}.[20] Clearly, the abrupt change in kinetics is an intrinsic molecular phenomenon that, unlike the CO rebinding to myoglobin,[18] is not "slaved" to the solvent.[21] However, the intracomplex quenching rate constant does vary with the solvent composition in the high-temperature region (Figure 1B), which may reflect a more subtle change in the mode of docking for the [ZnCcP, Fe^{3+}Cc] complex. To elucidate the structural basis for this fluctional process, we are extending these studies to include nonhomologous complexes as well as complexes in which the intracomplex interface is modified by site-directed mutagenesis.[22]

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(22) Interestingly, we have seen that the midpoint of the transition in a given solvent changes with the cytochrome.

New Germanium-Containing Polymers via Alternating Copolymerization of a Germylene with *p*-Benzoquinone Derivatives

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Much attention has been paid to polymers having silicon in the main chain due to their scientific and application importance.[1] Few studies on polymers containing atoms of other IVB elements, however, have been reported in spite of their unique properties.[2-5]

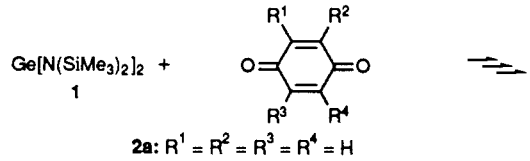
Table I. Copolymerization of Germylene **1** with *p*-Benzoquinone Derivatives **2**[a]

entry	oxidant monomer **2**	copolymer **3** yield,[b] %	M_w[c]	M_w/M_n[c]
1[d]	**2a**	quant	1.4×10^5	2.32
2	**2a**	85	1.3×10^5	2.36
3[e]	**2a**	94	1.4×10^5[f]	2.63
4	**2b**	94	5.8×10^4	2.51
5	**2c**	quant	2.9×10^4	1.98
6	**2d**	89	8.6×10^4	2.72
7	**2e**	96	3.6×10^5	2.15
8[e]	**2e**	93	2.0×10^5[g]	2.69

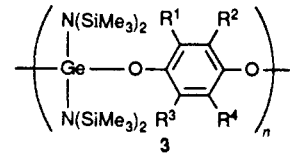
[a] Copolymerization was carried out by using 2.0 mmol each of **1** and **2** in 10 mL of toluene at -78 °C for 1 h under argon. [b] Isolated yield. [c] Determined by gel permeation chromatography (GPC): eluent, $CHCl_3$; flow rate, 1.0 mL/min; column, TSK-GEL G5000H, polystyrene standard. [d] Copolymerization was carried out at 0 °C for 1 h. [e] THF was used as solvent. [f] $M_n = 4.0 \times 10^4$ (determined by vapor pressure osmometry (VPO) in benzene at 40 °C). [g] $M_n = 7.9 \times 10^4$ (determined by VPO in benzene at 40 °C).

Organogermane polymers were photoactive and showed bleaching behavior,[2] strong thermochromic properties,[3] and semiconductivity.[4] Tin-containing polymers of alkoxy or ester type showed biological activity such as fungicidal properties.[5] Synthesis of these polymers utilizes the sodium coupling of a IVB metal dihalide[2,3] or polycondensation between a IVB metal dihydroxide or dihalide and a bifunctional organic compound such as a diol or dicarboxylic acid.[4,5]

The present communication describes a novel synthesis of germanium-containing polymers **3** by copolymerization of a divalent germanium compound (germylene), bis[bis(trimethylsilyl)amido]germanium (**1**),[6] with various *p*-benzoquinone derivatives **2**. The resulting copolymer **3** has alternating germanium(IV) and *p*-hydroquinone units in the main chain. All copolymers **3** are of relatively high molecular weight and soluble in organic solvents. During the copolymerization, germylene **1** (reductant monomer) is oxidized and *p*-benzoquinone derivative **2** (oxidant monomer) is reduced.[7] Thus, we propose the term "oxidation-reduction copolymerization" for the reaction.



2a: $R^1 = R^2 = R^3 = R^4 = H$
b: $R^1 = R^4 = {}^tBu$, $R^2 = R^3 = H$
c: $R^1 = R^4 = Cl$, $R^2 = R^3 = H$
d: $R^1 = R^4 = Ph$, $R^2 = R^3 = H$
e: $R^1 = R^2 = H$, $R^3 + R^4 = CH{=}CHCH{=}CH$



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