1-3 have been determined and are listed in Table I.[10]

(1) The *high stability* of the chloride cryptates of **1**-H_4^{4+} and **2**-H_4^{4+} is remarkable indeed. The most stable of the reported chloride katapinates, the chloride complex of the diprotonated form of $N[(CH_2)_{10}]_3N$,[2] **5**, is at least three orders of magnitude less stable (Table I). Thus, the present chloride cryptates are by far the most stable anion complexes known to date.

(2) Compounds **1**-H_4^{4+} and **2**-H_4^{4+} also display *high* Cl^-/Br^- *selectivity* (>1000) whereas **3**-H_4^{4+} and **5**-H_2^{2+} are much less selective (Table I).

(3) The results clearly show the operation of a topological *macrotricyclic cryptate effect* on both the stability and the selectivity of the anion complexes. The much higher stability as well as the very high Cl^-/Br^- selectivity of the spheroidal macro*tri*cyclic ligands **1**, **2** as compared to the macro*bi*cyclic ligand **3**, may be ascribed to the presence of a *closed and rigid cavity,* a feature characteristic of a ligand having high dimensionality, high connectivity, and high cyclic order.[1] These large effects arise from a better holding of the ^+N-H binding sites, efficient hindrance to hydration of the ^+N-H sites, and resistance to deformation, rendering the cavity unable to adjust to changes in anion size.

The effect of further structural modifications and the synthesis of other types of molecules will provide strategies for the rational design of organic anion receptors and carriers. Such results should be of interest in biology as well as in chemistry in view of the active current research on anion binding and transport in biological membranes (e.g., in red blood cells).[11]

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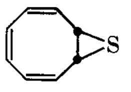
Chemical Exploration of the C_8H_8S Energy Surface under Conditions of Mild Thermal Activation. Bond Relocations and Cycloadditions

Sir:

Prompted by active interest in the factors responsible for the development of heteroaromatic character[1] we recently gained multiple entry into the C_8H_8S system through isomers **1**,[2] **2**,[2,3] and **3**[4] and have since examined the pericyclic response of this well-characterized segment of the system to mild thermal activation (<100 °C) in an effort to (i) better understand the dynamics of isomerization among these systems and (ii) gain knowledge which might aid one in locating and, ultimately, isolating such coveted π members as thionin and **4**, a heteroatomic analogue of the π-stabilized longicyclic carbanion.[5] In a previous publication on the subject we reported that mild heating rapidly and irreversibly effects the conversion of **1** to **2** which (**2**), in turn, resists further change.[2] We now offer a deeper probe into the C_8H_8S energy surface with a description of thermal isomerizations originating from **3**.



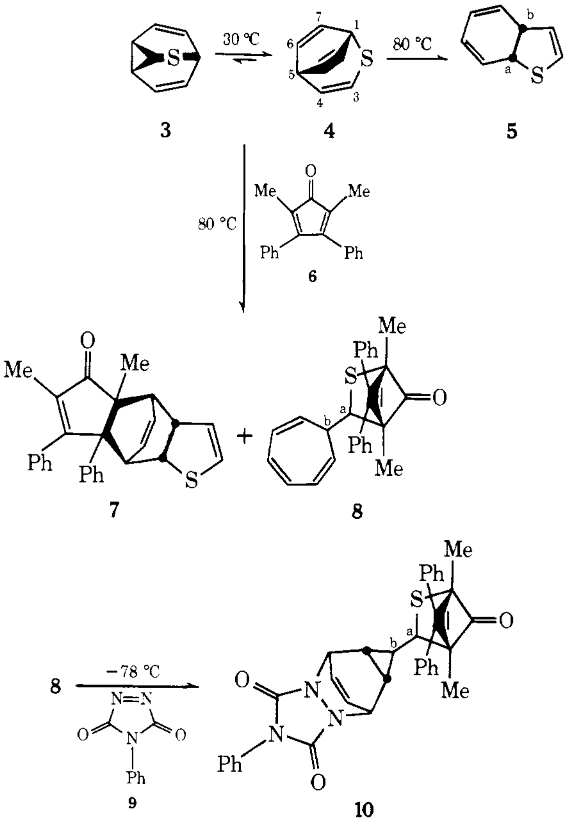
1

2

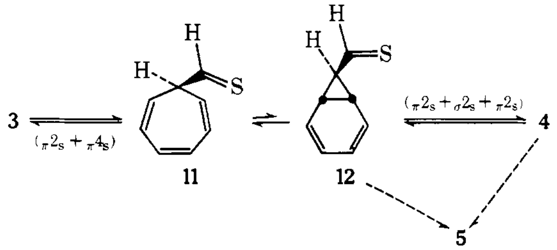
3

As a heteroatomic analogue of the π-destabilized 9-barbaralyl anion,[5] sulfide **3**[3] might be expected to be thermally labile and indeed it is. On warming to ambient temperature, it rapidly equilibrates into a two-component mixture of **4** (85%)[6] (white solid; ^1H NMR (100 MHz; $CDCl_3$) τ 3.60–3.95 (4 H, sym-m, $H_6 + H_7 + H_8 + H_9$), 4.17 (1 H, d d, H_4, $J_{4,3}$ = 11.0 Hz, $J_{4,5}$ = 8.0 Hz), 4.35 (1 H, dt, H_3, J = 11.0 Hz, 2.0 Hz, 1.5 Hz), 6.50 (1 H, m, H_1), 6.85 (1 H, m, H_5); ^{13}C NMR (25 MHz; $CDCl_3$; −31 °C) 31.67 ppm (1 C, C_1 or C_5), 35.39 (1 C, C_1 or C_5), 114.65 (1 C, C_3 or C_4), 118.89 (1 C, C_3 or C_4), 119.77 (2 C), 129.74 (2 C); *m/e* 136 (P^+; 81%), 135 (100%)) and **3** (15%)[6] with $k_3 \rightarrow k_4$ (34.6°) = $(3.22 \pm 0.15) \times 10^{-4}$ s^{-1} ($\Delta G^\ddagger$ = 22.9 kcal/mol)[7] and $k_4 \rightarrow k_3$ (34.6°) = $(9.33 \pm 1.0) \times 10^{-5}$ s^{-1} ($\Delta G^\ddagger$ = 23.7 kcal/mol).[7] The structural assignment depicted in **4** draws primarily from the ^{13}C NMR spectrum which shows four of the molecule's six olefinic carbons, i.e., those associated with the isolated ethylenes, to occur in magnetically equivalent pairs. In turn, the mixture of **3** and **4** readily undergoes irreversible isomerization in boiling benzene to produce **5** (^1H NMR (100 MHz; $CDCl_3$) τ 3.60 (1 H, d d, J = 6.5 Hz, 2.0 Hz), 3.9–4.3 (3 H, m), 4.4–4.6 (2 H, m), 5.24 (1 H, d d, H_a, J = 12.0 Hz, 4.0 Hz), 6.15 (1 H, *b*d, H_b, $J_{a,b}$ = 12.0 Hz), λ_{max} (CH_3CN) 237 nm (ϵ 5000), 260 (2200); *m/e* 136 (P^+; 83%), 135 (100%)), in ca. 75% yield. Besides resting on fully consistent spectroscopic data, the structural assignment depicted in **5** receives added support from the ready conversion of this substance to benzothiophene (ir, NMR) on exposure to *o*-chloranil.

Scheme I



Scheme II



In an effort to gain some mechanistic insight into the thermal transformations described in Scheme I, we searched for possible fleeting intermediates with the use of dienone **6,** a powerful "Diels-Alder" trap.[8] In brief, we find that exposure of the **3**/**4** equilibrium mixture to an equivalent amount of **6** in boiling benzene leads to two 1:1 cycloadducts,[9] **7**[10] (24% yield) (white needles, mp. 233.5-234 °C; ν_{CO} (KBr) 1690 cm^{-1}, ^1H NMR (100 MHz; $CDCl_3$) τ 2.5-2.9 (8 H, m, phenyl), 3.4-3.6 (2 H, m, phenyl), 3.7-4.0 (2 H, m), 4.10 (1 H, d d, J = 6.5 Hz, 2.5 Hz), 4.75 (1 H, d d, J = 6.5 Hz, 3.0 Hz), 5.40 (1 H, d d, J = 10.0 Hz, 2.0 Hz), 6.25 (1 H, dq, J = 10.0 Hz, 3.0 Hz), 6.75 (1 H, m), 7.12 (1 H, m), 8.30 (3 H, s), 8.94 (3 H, s); λ_{max} (95% EtOH) 250 nm (ϵ 1070), 266 (1050); *m/e* 396 (P^+; 32%) 116 (100%)) and **8** (37% yield) (white crystals, mp 164-164.5 °C; ν_{CO} (KBr) 1760 cm^{-1}. ^1H NMR (100 MHz; $CDCl_3$) τ 2.7-3.1 (10 H, m, phenyl), 3.3-3.5 (2 H, m), 3.72 (1 H, d d, J = 9.5 Hz, 5.5 Hz), 3.98 (1 H, d d, J = 9.5 Hz, 5.5 Hz), 4.70 (1 H, d d, J = 9.5 Hz, 7.0 Hz), 4.94 (1 H, d d, J = 9.5 Hz, 7.0 Hz), 6.10 (1 H, d, H_a, $J_{a,b}$ = 11.0 Hz), 7.78 (1 H, d t, H_b, J = 11.0 Hz, 7.0 Hz), 8.40 (3 H, s), 8.55 (3H, s); λ_{max} (95% EtOH) 242 nm (ϵ 7700), 216 (14,500); *m/e* 396 (P^+; 3%), 91 (tropylium; 100%) as well as unreacted **5** (15% recovery). Chemically, the structure assigned to **7** was confirmed by independent preparation of an identical sample (ir, NMR, mixture melting point) upon exposure of authentic **5** to **6** in benzene at 80 °C. Structure **8**[11] derives its support chiefly from the ^1H NMR spectrum whose "aliphatic" region consists of two mutually coupled resonances, a doublet (H_a) and a doublet of triplets (H_b) with the latter being further coupled, equally, to two *nonadjacent*[12] "olefinic" protons. Moreover, the key presence of a tropilidine appendage in **8** was securely established by further cycloaddition. In brief, we find that **8** readily reacts with triazoline dione **9** to produce the 1:1 cycloadduct **10** (white solid, mp 196 °C dec; ν_{CO} (KBr) 1710, 1760 cm^{-1}, ^1H NMR (100 MHz; $CDCl_3$) τ 2.5-3.0 (15 H, m, phenyl), 3.90 (1 H, td, J = 6.0 Hz, 2.0 Hz), 4.17 (1 H, td, J = 6.0 Hz, 2.0 Hz), 4.80 (1 H, m), 5.08 (1 H, m), 6.75 (1 H, d, H_a, $J_{a,b}$ = 10.0 Hz), 8.2-8.4 (2 H, m), 8.40 (3 H, s), 8.50 (3 H, s), 9.22 (1 H, dt, H_b, J = 10.0 Hz, 4.0 Hz); *m/e* 91 (tropylium; 100%)). Significantly, one notes that while the key NMR signals due to H_a and H_b retain their structure on passing from **8** to **10** the H_b signal moves substantially to higher field (~1.4 ppm) due to the newly developed cyclopropane environment in **10.**

The structure of cycloadduct **8** clearly implicates thioaldehyde **11** as an active intermediate in the thermal interconversion between **3** and **4.** The overall process is then best viewed to materialize by the three symmetry-allowed reversible steps depicted in Scheme II. Ultimate conversion to **5** is of course disallowed by orbital symmetry (${}_{\sigma}2_s + {}_{\pi}2_s$ from either **4** or **12**) but the process is no doubt aided by lone pair participation and/or the weak nature of the C–S link.

While the extent of rearrangement is not as extreme as with the iso-π-electronic carbanions where the barbararyl skeleton is known[5] to *irreversibly* rearrange to the [3.2.2] frame there is little doubt that the C_8H_8S system does gain in overall stability on passing from **3** to **4.** Moreover, judging from the known skeletal stability of the various known barbaralanes[5,13] one finds it tempting to ascribe the observed population imbalance in favor of **4** chiefly to the presence of the heteroatomic lone pair.

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(11) The presence of a sulfide function in **8** was confirmed by oxidative conversion to the corresponding sulfoxide (mp 148–149 °C) whose ^1H NMR spectrum closely resembles that of **8.**
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Optical Spectroscopic Study of (Chl a$\cdot H_2O)_2$ According to the Proposed C_2 Symmetrical Molecular Structure for the P700 Photoactive Aggregate in Photosynthesis

Sir:

It is widely believed that the aggregation of Chl a and H_2O lies at the heart of the photosynthesis problem. As early as 1931 the possible role of Chl a-H_2O complexes in photosynthesis was postulated.[1] In the succeeding decades, the aggregation properties[2-5] and photoactivity[6,7] of Chl a-H_2O aggregates have been extensively investigated by a large number of researchers.[8,9] Latest developments indicate that Chl a exists in two states of hydration.[9-12] Under excess water conditions Chl a crystallizes to yield the dihydrate crystal.[4,9-11] The monohydrate of Chl a can be prepared[9-12] by heating under vacuum up to 80 °C for a prolonged period. At temperatures $\gtrsim$120 °C Chl a$\cdot H_2O$ becomes dehydrated leading to at least partial degradation of the chlorophyll.[12]

The balance of the available experimental observations on in vitro and in vivo systems has led to the proposal that the photoactive aggregate P700[13-15] in photosystem I is (Chl a$\cdot H_2O)_2$, a C_2 symmetrical dimeric adduct of Chl a monohydrate.[9,16] At low temperatures ($\lesssim$150 K) in homogeneous hydrocarbon solutions, it is possible to prepare[10] in high yield (~85%) the 700 nm-absorbing (A700) dimer (Chl a$\cdot H_2O)_2$ whose optical and redox properties resemble closely those of the in vivo P700 aggregate.[9,17] The observation of significant photocurrents in the 700-nm region of the action spectrum of the recently developed reversible Chl a photogalvanic cell suggests that (Chl a$\cdot H_2O)_2$ can also be stabilized at room temperatures in a two-dimensional space where the negative configuration entropy change of the Chl a$\cdot H_2O$ dimerization process is apparently suppressed to a sufficient extent.[18]