

1–3 have been determined and are listed in Table I.<sup>10</sup>

(1) The *high stability* of the chloride cryptates of 1-H<sub>4</sub><sup>4+</sup> and 2-H<sub>4</sub><sup>4+</sup> is remarkable indeed. The most stable of the reported chloride katapinates, the chloride complex of the deprotonated form of N[(CH<sub>2</sub>)<sub>10</sub>]<sub>3</sub>N,<sup>2</sup> **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<sub>4</sub><sup>4+</sup> and 2-H<sub>4</sub><sup>4+</sup> also display *high Cl<sup>-</sup>/Br<sup>-</sup> selectivity* (>1000) whereas 3-H<sub>4</sub><sup>4+</sup> and 5-H<sub>2</sub><sup>2+</sup> 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<sup>-</sup>/Br<sup>-</sup> selectivity of the spheroidal macrotricyclic ligands **1**, **2** as compared to the macrobicyclic 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.<sup>1</sup> These large effects arise from a better holding of the <sup>+</sup>N–H binding sites, efficient hindrance to hydration of the <sup>+</sup>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).<sup>11</sup>

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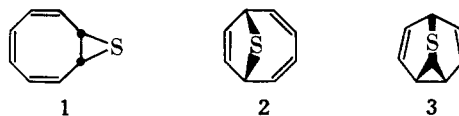
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## Chemical Exploration of the C<sub>8</sub>H<sub>8</sub>S Energy Surface under Conditions of Mild Thermal Activation. Bond Relocations and Cycloadditions

Sir:

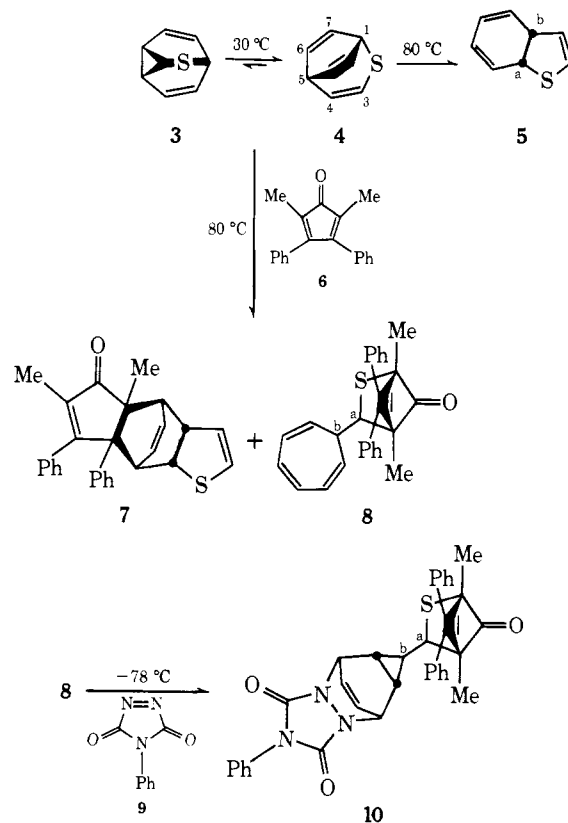
Prompted by active interest in the factors responsible for the development of heteroaromatic character<sup>1</sup> we recently gained multiple entry into the C<sub>8</sub>H<sub>8</sub>S system through isomers **1**,<sup>2</sup> **2**,<sup>2,3</sup> and **3**<sup>4</sup> and have since examined the pericyclic 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  $\pi$  transition and **4**, a heteroatomic analogue of the  $\pi$ -stabilized longicyclic carbanion.<sup>5</sup> 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.<sup>2</sup> We now offer a deeper probe into the C<sub>8</sub>H<sub>8</sub>S energy surface with a description of thermal isomerizations originating from **3**.

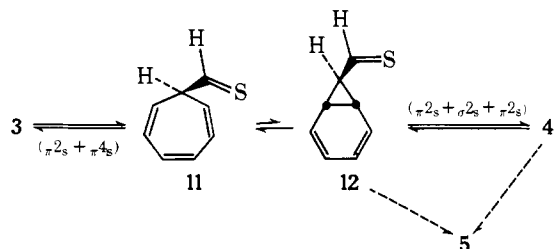


As a heteroatomic analogue of the  $\pi$ -destabilized 9-barbaralyl anion,<sup>5</sup> sulfide **3** might be expected to be thermally labile and indeed it is. On warming to ambient temperature, it rapidly equilibrates into a two-component mixture of **4** (85%)<sup>6</sup> (white solid; <sup>1</sup>H NMR (100 MHz; CDCl<sub>3</sub>)  $\tau$  3.60–3.95 (4 H, sym-m, H<sub>6</sub> + H<sub>7</sub> + H<sub>8</sub> + H<sub>9</sub>), 4.17 (1 H, d, H<sub>4</sub>, J<sub>4,3</sub> = 11.0 Hz, J<sub>4,5</sub> = 8.0 Hz), 4.35 (1 H, dt, H<sub>3</sub>, J = 11.0 Hz, 2.0 Hz, 1.5 Hz), 6.50 (1 H, m, H<sub>1</sub>), 6.85 (1 H, m, H<sub>5</sub>); <sup>13</sup>C NMR (25 MHz; CDCl<sub>3</sub>; –31 °C) 31.67 ppm (1 C, C<sub>1</sub> or C<sub>5</sub>), 35.39 (1 C, C<sub>1</sub> or C<sub>5</sub>), 114.65 (1 C, C<sub>3</sub> or C<sub>4</sub>), 118.89 (1 C, C<sub>3</sub> or C<sub>4</sub>), 119.77 (2 C), 129.74 (2 C); m/e 136 (P<sup>+</sup>; 81%), 135 (100%)) and **3** (15%)<sup>6</sup> with k<sub>3</sub> → k<sub>4</sub> (34.6°) = (3.22 ± 0.15) × 10<sup>-4</sup> s<sup>-1</sup> ( $\Delta G^\ddagger$  = 22.9 kcal/mol)<sup>7</sup> and k<sub>4</sub> → k<sub>3</sub> (34.6°) = (9.33 ± 1.0) × 10<sup>-5</sup> s<sup>-1</sup> ( $\Delta G^\ddagger$  = 23.7 kcal/mol).<sup>7</sup> The structural assignment depicted in **4** draws primarily from the <sup>13</sup>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** (<sup>1</sup>H NMR (100 MHz; CDCl<sub>3</sub>)  $\tau$  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<sub>a</sub>, J = 12.0 Hz, 4.0 Hz), 6.15 (1 H, b, d, H<sub>b</sub>, J<sub>a,b</sub> = 12.0 Hz),  $\lambda_{\text{max}}$  (CH<sub>3</sub>CN) 237 nm ( $\epsilon$  5000), 260 (2200); m/e 136 (P<sup>+</sup>; 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 benzothioephene (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.<sup>8</sup> 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.<sup>9</sup> **7**<sup>10</sup> (24% yield) (white needles, mp. 233.5–234 °C;  $\nu_{\text{CO}}$  (KBr) 1690  $\text{cm}^{-1}$ ,  $^1\text{H NMR}$  (100 MHz;  $\text{CDCl}_3$ )  $\tau$  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);  $\lambda_{\text{max}}$  (95% EtOH) 250 nm ( $\epsilon$  1070), 266 (1050);  $m/e$  396 ( $\text{P}^+$ ; 32%) 116 (100%) and **8** (37% yield) (white crystals, mp 164–164.5 °C;  $\nu_{\text{CO}}$  (KBr) 1760  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (100 MHz;  $\text{CDCl}_3$ )  $\tau$  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 (3 H, s);  $\lambda_{\text{max}}$  (95% EtOH) 242 nm ( $\epsilon$  7700), 216 (14,500);  $m/e$  396 ( $\text{P}^+$ ; 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**<sup>11</sup> derives its support chiefly from the  $^1\text{H NMR}$  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*<sup>12</sup> "olefinic" protons. Moreover, the key presence of a tropilidene 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;  $\nu_{\text{CO}}$  (KBr) 1710, 1760  $\text{cm}^{-1}$ ,  $^1\text{H NMR}$  (100 MHz;  $\text{CDCl}_3$ )  $\tau$  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 ( $\sim 1.4$  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- $\pi$ -electronic carbanions where the barbararyl skeleton is known<sup>5</sup> to *irreversibly* rearrange to the [3.2.2] frame there is little doubt that the  $\text{C}_8\text{H}_8\text{S}$  system does gain in overall stability on passing from **3** to **4**. Moreover, judging from the known skeletal stability of the various known barbaralanes<sup>5,13</sup>

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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- (10) The stereochemistry and relative disposition of the five-membered segments shown in **7** were deduced on the basis of  $^1\text{H LIS}$  studies.
- (11) The presence of a sulfide function in **8** was confirmed by oxidative conversion to the corresponding sulfoxide (mp 148–149 °C) whose  $^1\text{H NMR}$  spectrum closely resembles that of **8**.
- (12) The nonadjacent nature of these olefinic protons was established by spin decoupling.
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## Optical Spectroscopic Study of $(\text{Chl a} \cdot \text{H}_2\text{O})_2$ According to the Proposed $\text{C}_2$ Symmetrical Molecular Structure for the P700 Photoactive Aggregate in Photosynthesis

Sir:

It is widely believed that the aggregation of Chl a and  $\text{H}_2\text{O}$  lies at the heart of the photosynthesis problem. As early as 1931 the possible role of Chl a– $\text{H}_2\text{O}$  complexes in photosynthesis was postulated.<sup>1</sup> In the succeeding decades, the aggregation properties<sup>2–5</sup> and photoactivity<sup>6,7</sup> of Chl a– $\text{H}_2\text{O}$  aggregates have been extensively investigated by a large number of researchers.<sup>8,9</sup> Latest developments indicate that Chl a exists in two states of hydration.<sup>9–12</sup> Under excess water conditions Chl a crystallizes to yield the dihydrate crystal.<sup>4,9–11</sup> The monohydrate of Chl a can be prepared<sup>9–12</sup> by heating under vacuum up to 80 °C for a prolonged period. At temperatures  $\geq 120$  °C Chl a– $\text{H}_2\text{O}$  becomes dehydrated leading to at least partial degradation of the chlorophyll.<sup>12</sup>

The balance of the available experimental observations on in vitro and in vivo systems has led to the proposal that the photoactive aggregate P700<sup>13–15</sup> in photosystem I is  $(\text{Chl a} \cdot \text{H}_2\text{O})_2$ , a  $\text{C}_2$  symmetrical dimeric adduct of Chl a monohydrate.<sup>9,16</sup> At low temperatures ( $\leq 150$  K) in homogeneous hydrocarbon solutions, it is possible to prepare<sup>10</sup> in high yield ( $\sim 85\%$ ) the 700 nm-absorbing (A700) dimer  $(\text{Chl a} \cdot \text{H}_2\text{O})_2$  whose optical and redox properties resemble closely those of the in vivo P700 aggregate.<sup>9,17</sup> 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  $(\text{Chl a} \cdot \text{H}_2\text{O})_2$  can also be stabilized at room temperatures in a two-dimensional space where the negative configuration entropy change of the Chl a– $\text{H}_2\text{O}$  dimerization process is apparently suppressed to a sufficient extent.<sup>18</sup>