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SUBSTITUENT INFLUENCES ON THE COPE EQUILIBRIUM IN SEMIBULLVALENE

SYMMETRICAL HETEROATOMIC 2,8-PENTAMETHYLENE DERIVATIVES[1]

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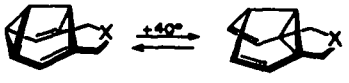
Abstract—Six 2,8-pentamethylene semibullvalenes having a heteroatomic unit (O, NCH_2Ph, S, SO_2, *syn*-SO and *anti*-SO) at the central linkage (to maintain symmetry) have been prepared from a single diazasaoutane precursor. Variable-temp. ^1H NMR studies of the ether gave indication that the ground-state equilibrium is shifted substantially (80–88%) in the direction of tautomer a where the cyclopropane ring is positioned on the periphery of the structure. Progression through the order given above leads to an enhanced partiality for tautomer b (89% in the case of the anti sulfoxide). Entirely comparable equilibrium constants were obtained using ^{13}C NMR methods. Thus, although the hetero atoms are quite adequately insulated from the semibullvalene core, subtle libration effects in the bracket are revealed by large alterations in K_{eq}. Such differences are unlikely to be assessed as quantitatively by other techniques. The possible origin of those factors which contribute to the enhanced concentration of one tricyclic tautomer relative to the other is discussed.

The extraordinary ease of Cope rearrangement in semibullvalene ($\Delta G^{\ddagger} = 5.5$ kcal/mol at $-140°$)[3] causes the two structurally degenerate valence isomers (**1a,b**) to exist in a state of rapid molecular flux at ambient temperatures.

1a **1b**

The 6-electron transition state which controls this fluxional behavior is minimally exothermic due to rigidly constrained nature of the folded molecular framework which cants the internal cyclopropane σ orbital in a fashion particularly suitable for overlap with the two peripheral π bonds.[4] As we have demonstrated previously,[5,6] the electronic influences which prevail in monosubstituted semibullvalenes give rise to pronounced ground-state equilibrium displacements. Additionally revealed by ^1H NMR is the preferential bonding to olefinic > cyclopropyl > aliphatic carbon, independent of the location (two-site restriction) and nature of the R group. The response of the semibullvalene equilibrium to bridging at C_2 and C_8 by aliphatic chains is yet more delicate.[7] The dramatically varied effects produced upon annulation by tri-(2), tetra-(3), and pentamethylene units (4) reveal that the particular characteristics of a given $(CH_2)_x$ bracket can greatly alter ground-state structural features. Intriguingly, the responses of 2 and 4 to changing temperature are diametrically opposite as well. Thus, when CS_2 solutions of 2 are cooled, the concentration

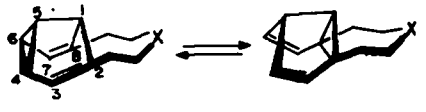


a **b**

2: X = CH_2	43	57
3: X = $(CH_2)_2$	90	10
4: X = $(CH_2)_3$	58	42
5: X = O	0.3	99.7
6: X = S	10.5	89.5
7: X = NCH_2Ph	7.1	92.9

levels of **2a** and **2b** become equalized at $-29°$; below this temperature, **2a** dominates the equilibrium.[7] In the case of **4**, the population crossover occurs at approximately $+17°$ and **4b** is favored at lower temperatures.[7,8] In addition to calling attention to the fact that a diminution in "bracketing strain"[9] does not correlate with an enhanced concentration gradient of the tricyclic valence tautomer having a central cyclopropane ring, these findings show the semibullvalene nucleus to be a "fine tuning device for the probing of ground state perturbational effects".[10]

When the three heteroatomic 2,8-trimethylene derivatives **5–7** were prepared, their equilibria were found to be shifted heavily in the direction of structure b at $+40°$.[10] The effects of diminished eclipsing interactions and enhanced electronegativity were thereby made clear. However, the resultant imbalances were too one-sided to permit meaningful assessment of more subtle effects, particularly since the heavy biases were not significantly altered with temperature (-120 to $+100°$). We reasoned that increased insulation of the semibullvalene nucleus from the hetero-atom while still preserving an element of symmetry as in **8** should lessen electronegativity control

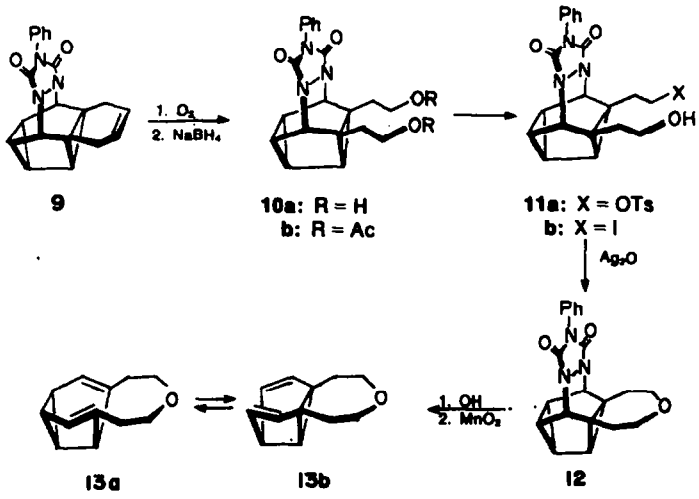


8a **8b**

and make possible the desired evaluation of enthalpic and entropic changes as a function of X. Such effects are frequently not visible when examined by other techniques.

We have now succeeded in preparing six semibullvalene derivatives conforming to general formula **8**. The resultant variations in equilibrium weighting have provided a wealth of information about heteroatom effects in medium rings. These findings gain particular significance when it is recognized that little information on the conformational behavior of saturated medium-ring monoheterocycles is otherwise available.[11]

Synthetic aspects. Scheme 1 depicts the route which has led successfully to oxa derivative **13**. Ozonolysis of



Scheme 1.

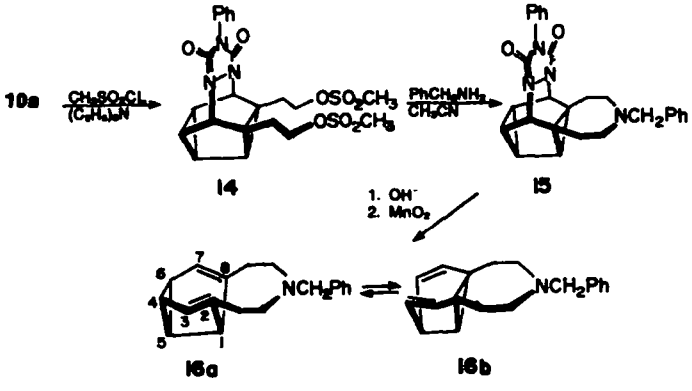
diazasnoutene **9**[7,12] followed by reductive workup with sodium borohydride gave diol **10a** in excellent yields. When various *nucleophilic* cyclizations were attempted on **10a** and selected derivatives, the reactions did not proceed as expected and only trace quantities of the desired oxepane **12** were obtained at best. Included among these methods were treatment of **10a** with one equiv of methanesulfonyl chloride and excess 2,6-lutidine in refluxing tetrahydrofuran (THF),[13] and exposure of monotosylate **11a** to excess triethylamine or sodium hydride in refluxing THF.[14] Utilization of the corresponding mesitylsulfonate in an effort to curb O–S cleavage proved similarly unsuccessful. Admixture of the recently developed N-methyl-N,N'-di-t-butylcarbodiimidium tetrafluoroborate reagent[15] with **10a** and triethylamine afforded **12** in less than 10% yield. It was for these reasons that attention was turned to an intramolecular *electrophilic* cyclization approach.[16] For this purpose, monotosylate **11a** was converted to iodohydrin **11b** by reaction with sodium iodide in hot acetone. When allowed to react with freshly prepared silver oxide in refluxing THF, **11b** was smoothly transformed into **12** (57% isolated yield).

The 100 MHz ^{1}H NMR spectrum of **12** in $CDCl_3$ shows the protons α to the ether oxygen to be widely separated and strongly coupled. One two-proton doublet of quartets (J = 13.0, 5.0 and 3.0 Hz) appears at δ 3.85 while the other is centered at 3.14 (J = 13.0, 8.0 and 2.0 Hz). If, as is often the case, the upfield pattern is due to the axial protons,[17] then the 13.0 Hz splitting may be assigned as the geminal coupling constant ($J_{ax\text{-}eq}$), the 8.0 Hz splitting as the trans coupling ($J_{ax\text{-}ax'}$), and the 2.0 Hz splitting as the gauche coupling ($J_{ax\text{-}eq'}$). The δ 3.85 multiplet is then the result of J_{gem} (13.0 Hz) and J_{gauche} (5.0 and 3.0 Hz) spin interaction with the pair of H_{eq}'s.

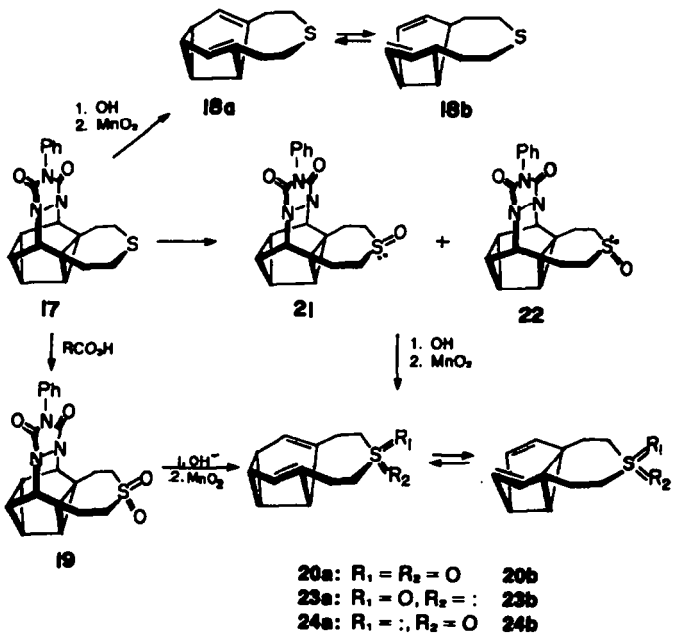
Sequential alkaline hydrolysis and oxidation (MnO_2) of **12** under argon gave **13** in 60.4% yield after two sublimations at 10^{-4} torr. The pale yellow solid was characterized by its accurate mass, IR and UV spectra, and ^{1}H and ^{13}C NMR features (see below).

Access to hexahydroazepine **15** was gained by reaction of **10a** with 2 equiv of sulfene and double nucleophilic displacement of methanesulfonic acid from **14** with excess benzylamine in acetonitrile (Scheme 2). When hydrolyzed and oxidized in an inert atmosphere as before, **15** was transformed via the labile diazasnoutene to the low-melting aza derivative **16**. The UV spectrum of **16**, which consists of three approximately intense shoulders or weak maxima below 250 nm on the fringe of intense end absorption, is typical of the electronic spectra of the other members of the series. The indicated structural assignment to **16** also follows convincingly from its mass, ^{1}H NMR, and ^{13}C NMR spectral parameters as discussed in the following sections.

Elaboration of sulfide **17** was similarly achieved by reaction of **14** with sodium sulfide in N,N-dimethylacetamide-ethanol solution. Thiasemibullvalene **18**, its sulfone counterpart **20**, and the pair of sulfoxide epimers



Scheme 2.



20a: $R_1 = R_2 = O$ 20b
23a: $R_1 = O, R_2 = :$ 23b
24a: $R_1 = :, R_2 = O$ 24b

Scheme 3.

23 and 24 were then prepared by predescribed methods (Scheme 3). The sulfoxides present an opportunity to examine bridging and substituent effects at a level of refinement not previously possible. The two isomers presumably possess similar bond lengths and angles, identical electronic demands from the heteroatom, etc, but differ in those features induced by the reversed relative positioning of the oxygen atom and the lone pair of electrons on sulfur. Nevertheless, as will be made evident, the extent of the perturbation on the semibullvalene equilibrium is substantial.

In view of the well-established tendency for *m*-chloroperbenzoic acid to oxidize sulfides with preferential formation of the kinetic product,[18] it came as no surprise that treatment of 17 with this reagent gave an 80:20 mixture of two sulfoxides. Addition of Eu(fod)$_3$ to $CDCl_3$ solutions of this mixture caused efficient differential shielding of the ^{1}H NMR absorptions, most clearly evident for the $\rangle CHN\langle$ protons. When sodium metaperiodate, generally considered to afford preferentially the thermodynamically favored sulfoxide,[18] converted 17 to the identical mixture, we concluded that the kinetic product is likely also the thermodynamically favored isomer.

The individual components were isolated in a pure state by preparative tlc. The minor sulfoxide was noted to undergo exceptionally facile epimerization to the major constituent. After 2 hr at 70° in $CDCl_3$, the apparent thermodynamic equilibrium (*ca* 80:20) was essentially established. The upfield portion of the ^{1}H NMR spectrum in $CDCl_3$ [δ 3.60–2.20 (m, 6), 2.05 (m, 4) and 2.00–1.20 (m, 2)] is distinctively different from that of the dominant epimer [δ 3.40–2.80 (m, 4), 2.60–2.30 (m, 4) and 2.08 (m, 4)]. The rather dramatic deshielding which affects two methylene protons is undoubtedly due to the anisotropy of the sulfoxide group.

To demonstrate unequivocally the epimeric nature of these substances and to allow preparation of adequate amounts of the minor isomer to continue the synthetic sequence, the major sulfoxide was subjected to the Johnson–McCants procedure.[19] O-methylation with Meerwein's reagent followed by treatment with aqueous sodium hydroxide led to net stereochemical inversion in high yield.

The configurations of these sulfoxides have been assigned on the basis of the following evidence. For example, the well recognized fact that β protons in cyclic 6-membered sulfoxides are always strongly deshielded when positioned in a 1,3-diaxial relationship to an S=O group, but not otherwise,[20–23] could allude to the possible axial nature of the O atom in minor isomer 22. The other stereochemical effects sometimes observed in sulfoxides are the greater nonequivalence of the methylene protons α to the S=O function when the oxygen is equatorial,[20,24] and the somewhat more negative (larger in absolute magnitude) geminal coupling constant for α protons in the axial isomers.[24] The magnetic anisotropy phenomenon is not always encountered because of a geometric dependence,[25] and therefore its use as a proof of configuration should not be emphasized. As seen in Fig. 1, the chemical shift criterion for H_a is also not of great use in the present study. Likewise, the effect of the oxygen in 22 is to enhance $J_{CH_{2a}}$ somewhat, but the cause of this phenomenon is unclear. Obviously, the total spectral profile does not converge to a fully convincing, internally consistent proof of configuration. Therefore, a solution to the question was sought by less equivocal chemical methods.

Recent work has shown that singlet ($^1\Delta_g$) oxygen is deactivated upon interaction with a urazole ring and that such quenching can be utilized effectively in controlling the stereospecificity of allylic hydroperoxidation.[26a] In like fashion, exposure of 17 to $^1O_2$ leads to formation of a single sulfoxide identified as 22.[26b] Since effective approach of this reagent to 17 in a manner which will eventuate in sulfoxidation is restricted to that surface *syn* to the cyclopropane rings, the configurational assignment to 22 is no longer arbitrary.

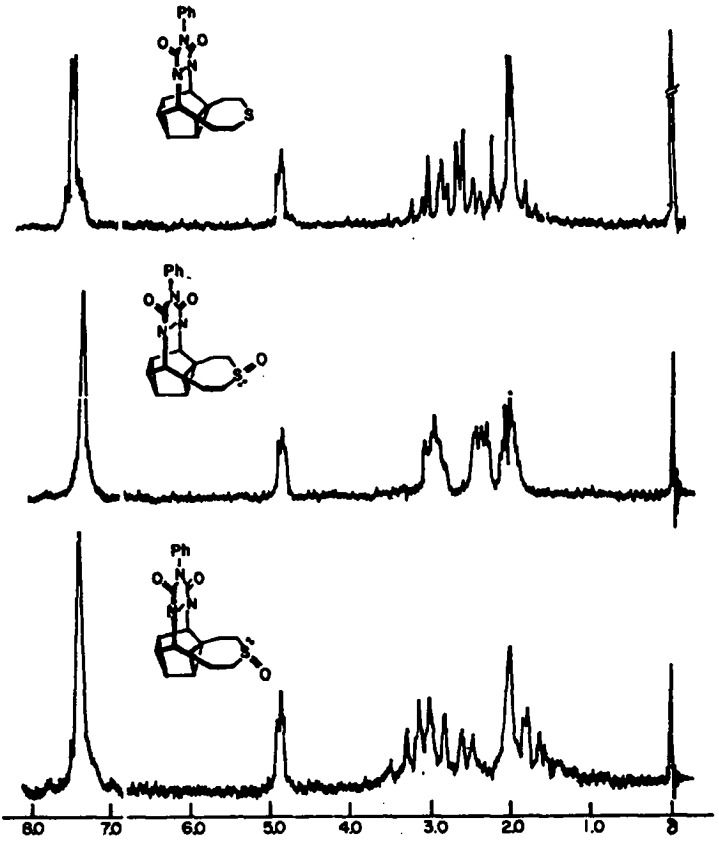


Fig. 1. ^{1}H NMR spectra (60 MHz) in $CDCl_3$ solution of 17 (top), 21 (middle) and 22 (bottom).

Of interest is the additional observation that the dominance of sulfoxide 21 from peracid and periodate oxidations of 17 parallels the stereochemical preference (anti to cyclopropane) exhibited as well by the lower homologous trimethylene sulfide.[26c] The latter epimeric sulfoxides exhibit clean first-order spectra, thereby greatly facilitating configurational assignment to these compounds.

The ^{1}H NMR spectra of annulated semibullvalene sulfoxides 23 and 24 exhibit entirely similar features (Fig. 4). ^{13}C NMR studies on these molecules show C_α in 23 (19.26 ppm) to resonate at somewhat higher field than that in 24 (20.39 ppm, see Table 12). Recently, three groups have independently examined the ^{13}C NMR spectra of thiane S-oxides and demonstrated that the carbon α to an axial S=O group resonates at somewhat higher field than the α carbon of the equatorial isomer.[27-29]

However, the differences are quite small (less than 8 ppm in the most rigid system). It is not immediately clear whether the larger ring size contained in 23 and 24 so alters the geometrical relationship of the neighboring carbons and protons that the prevailing electric field effects generate somewhat different shielding contributions to $\Delta\alpha$, or the oxygen atom in 23 is indeed axial. The data in Table 14 are seen to be most consistent with the latter conclusion.

NMR results

^{1}H *magnetic resonance data.* The 100 MHz ^{1}H NMR spectrum of pentamethylene hydrocarbon 4 in $CDCl_3$ at +40° which is illustrated in Fig. 2 is characterized by an equilibrium-diagnostic multiplet at 3.75 due to H_4 and H_6 which reveals the distribution of valence isomers a (58%) and b (42%) to be closely balanced. It will be recalled that it is this substance which in its non-fluxional state at −120° provides the reference chemical shift values which are utilized to determine its specific equilibrium partitioning at more elevated temperatures and K_{eq} for all other annulated semibullvalenes.[7,8,10]

By comparison, the ether analog strikingly favors tautomer 13a under comparable conditions. Its very distinctive spectrum (Fig. 2) shows the time-averaged H_4, H_6 doublet of doublets to be centered at δ 2.87, thereby indicating that 13a is present to the extent of 80% (Table 1). The axial and equatorial β protons are strongly coupled much as in the precursor oxepane (12). In this case, the axial protons which appear as a doublet of triplets at δ 3.19 reflect a geminal coupling of 11.6 Hz and an additional spin interaction of 6.5 Hz. The equatorial protons also give rise to a doublet of triplets pattern centered at δ 4.03 with J = 11.6 and 5.0 Hz. Variable temperature studies carried out in CS_2 (Table 2) and CD_2Cl_2–CF_2Cl_2 solutions (Table 3) revealed the concentration gradient of 13a to increase as the temperature was lowered. In CS_2, the isomer distribution ranged from 12% of 13b at 32.3° to 3.7% of this tautomer at −99.9°. Graphic analysis of these data determined the thermodynamic parameters associated with the 13b→13a conversion to be $\Delta H° = -1.06 \pm 0.10$ kcal/mol and $\Delta S° = 0.43 \pm 0.40$ eu. In CD_2Cl_2–CF_2Cl_2, the concentration of 13b at +32.3° was 18%, while at −99.9° there was 8% less of this tautomer. By plotting $\ln K_{eq}$ vs $1/T$, the thermodynamic parameters $\Delta H° = -593 \pm 61$ cal/mol and $\Delta S° = 1.05 \pm 0.28$ eu were obtained.

Unlike 13, aza derivative 16 was found to experience a

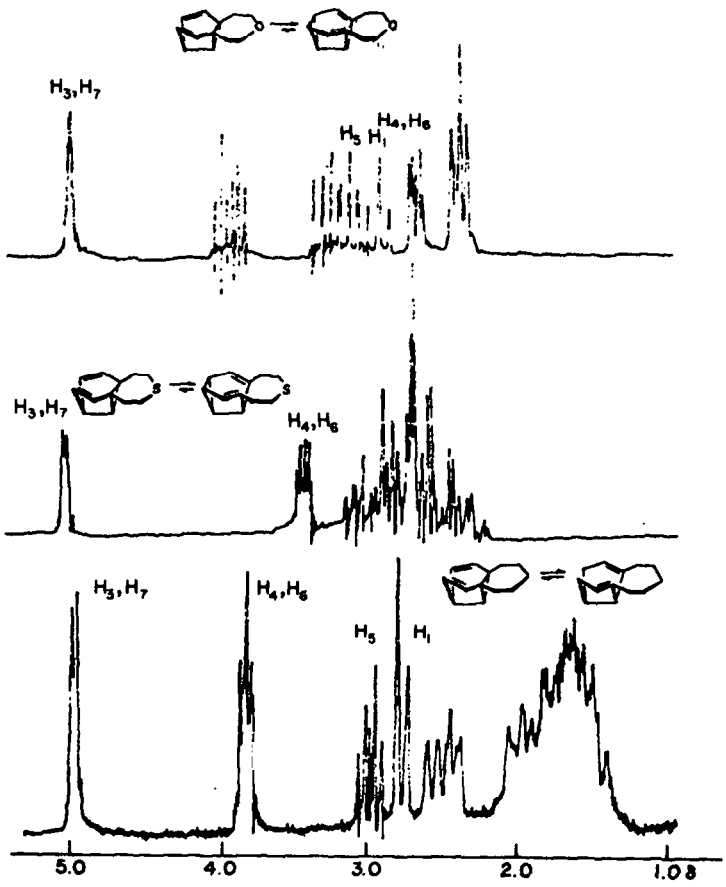


Fig. 2. ^{1}H NMR spectra (100 MHz) of **13** (top), **18** (middle) and **4** (bottom) recorded in $CDCl_3$ solution at +40°.

Table 1. ^{1}H NMR data (100 MHz, $CDCl_3$), computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the heteroatomic 2,8-pentamethylene semibullvalenes (40°)

Bracket Substituent	Chemical Shift,[a] δ	Mol Fraction[b] isomer b	K_{eq} a/b	ΔG° cal/mole
O (13)	3.00	0.20	4.00	-863
S (18)	3.57	0.38	1.63	-305
NCH_2Ph (16)	3.75	0.43	1.33	-176
CH_2 (4)	3.75	0.43	1.33	-176
syn-SO (24)[c]	4.57	0.68	0.47	470
SO_2 (20)	4.76	0.75	0.33	684
anti-SO (23)	5.22	0.89	0.12	1300

[a] Protons H_4 and H_8 relative to internal TMS. [b] The method employed is not considered to provide accuracy levels of better than 1% at best. [c] In CD_2Cl_2 solution.

more equitable distribution of its two forms in $CDCl_3$ at +40° (57% of **16a**, Table 1). As seen in Fig. 3 where a revealing comparison is made with its trimethylene counterpart, the H_4, H_6 protons of **16** appear at δ 3.75, the same position observed for the fluxional protons in **4**! The permanently olefinic protons (H_3, H_7) resonate at 5.00; spin decoupling measurements confirmed these assignments. This spectrum was temperature-dependent as the studies in CS_2 (Table 4) and CD_2Cl_2–CF_2Cl_2 (Table 5) exhibit. In actuality, the equilibrium distribution in CS_2 ranges from 37% of **16b** at +34.2° to 52% of **16b** at −85.6°. At −75.4°, an equal proportion of the two tautomers was seen. These data gave enthalpy (ΔH° = 582 ± 20 cal/mol) and entropy (ΔS° = 2.91 ± 0.09 eu) values for **16b** → **16a**, entirely comparable with those determined in CD_2Cl_2–CF_2Cl_2 solution (427 ± 17 cal/mol; 1.37 ± 0.18 eu).

Somewhat surprisingly, sulfide **18** favored tautomer a to a greater extent than did **16**. This is in contrast to the ordering observed in the trimethylene series.[10] Given that the key H_4, H_6 absorption appears at δ 3.57 (Fig. 2), application of the standard equations shows **18a** to

Table 2. Variable temperature ^{1}H NMR data,[a] computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the fluxional system 13b ⇌ 13a

Temp, °C	Chemical Shift[b] H_4,H_8	Mol Fraction 13b	K_{eq}, (13a/13b)	ΔG° (13b → 13a), kcal/mol
+32.3	2.73	0.120	7.3	1.21
+3.7	2.68	0.105	8.6	1.18
-29.6	2.64	0.092	9.8	1.13
-44.4	2.57	0.071	13.1	1.17
-56.3	2.56	0.068	13.8	1.13
-72.8	2.52	0.055	17.1	1.13
-88.4	2.47	0.040	24.0	1.17
-99.9	2.46	0.037	26.1	1.13

[a]100 MHz in CS_2-TMS. [b]Referenced to internal TMS and corrected so that H_8 and H_7 resonance remained constant at 5.04 δ.

Table 3. Variable temperature ^{1}H NMR data,[a] computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the fluxional system 13b ⇌ 13a

Temp, °C	Chemical Shift[b] H_4,H_8	Mol Fraction 13b	K_{eq}, (13a/13b)	ΔG° (13b → 13a), cal/mol
+32.3	2.92	0.178	4.60	928
+3.7	2.90	0.172	4.80	865
-24.6	2.84	0.154	5.50	843
-44.4	2.77	0.132	6.56	856
-56.3	2.76	0.129	6.74	823
-72.8	2.72	0.117	7.55	806
-88.4	2.67	0.102	8.85	802
-99.9	2.66	0.098	9.16	764

[a]100 MHz in 1:1:1 CD_2Cl_2-CF_2Cl_2-TMS. [b]Referenced to internal TMS and corrected so that the $CHDCl_2$ resonance remained constant at 5.32 δ.

Table 4. Variable temperature ^{1}H NMR data,[a] computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the fluxional system 16b ⇌ 16a

Temp, °C	Chemical Shift[b] H_4,H_8	Mol Fraction 16b	K_{eq}, (16a/16b)	ΔG° (16b → 16a), cal/mol
+34.2	3.54	0.37	1.71	327
-3.4	3.66	0.41	1.46	204
-9.7	3.70	0.42	1.39	172
-34.3	3.79	0.45	1.24	103
-51.2	3.83	0.46	1.18	71
-51.7	3.87	0.47	1.12	53
-56.7	3.88	0.47	1.12	45
-66.0	3.94	0.49	1.04	15
-75.4	3.96	0.50	1.00	0
-85.6	4.04	0.52	0.91	-34

[a]100 MHz in CS_2-TMS. [b]Relative to internal TMS and corrected so that the aryl-CH_3- resonance remained constant at 3.51 δ.

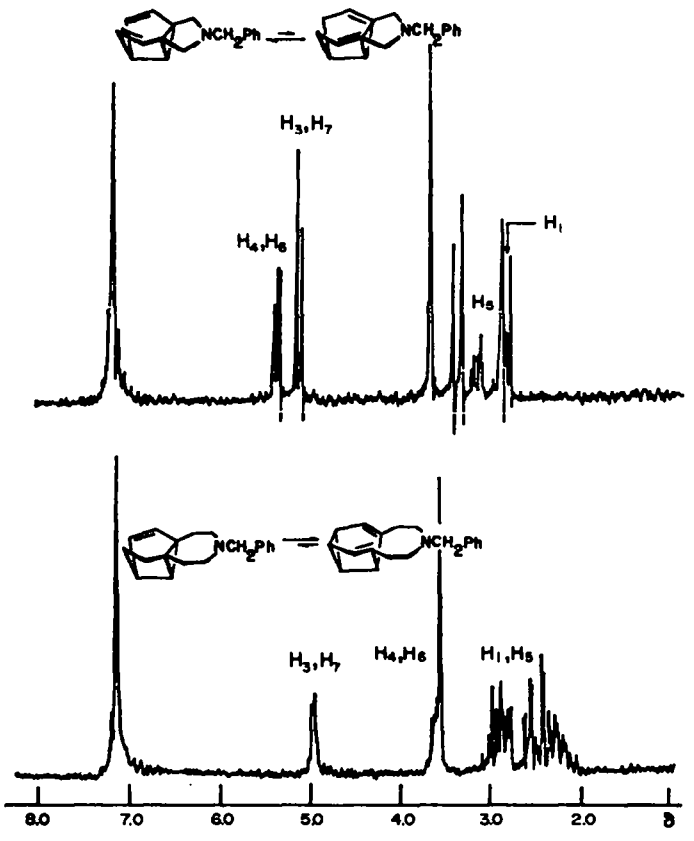


Fig. 3. ^{1}H NMR spectra (100 MHz, $CDCl_3$ solution, +40°) of **16** (bottom) and its trimethylene counterpart.

Table 5. Variable temperature ^{1}H NMR data,[a] computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the fluxional system **16b** ⇄ **16a**

Temp, °C	Chemical Shift[b] H_4,H_6	Mol Fraction 16b	K_{eq}, (16a/16b)	ΔG° (16b → 16a), cal/mol
-34.3	4.19	0.57	0.76	130
-51.7	4.27	0.59	0.68	170
-56.7	4.29	0.60	0.67	173
-66.0	4.32	0.61	0.64	184
-75.4	4.35	0.62	0.62	188
-85.6	4.39	0.63	0.58	203

[a] 100 MHz in 1:1:1 CD_2Cl_2–CF_2Cl_2–TMS. [b] Relative to internal TMS and corrected so that the $CHDCl_2$ resonance remained constant at 5.32 δ.

comprise 62% of the mixture in $CDCl_3$ at +40°. Variable temperature studies in CS_2 (Table 6) demonstrated further that the equilibrium distribution of this tautomer varies from 64% at +33.5° to 50% at −92.5°. Treatment of these data gives $\Delta H^\circ = 555 \pm 13$ cal/mol and $\Delta S^\circ = 3.09 \pm 0.06$ eu. In CD_2Cl_2–CF_2Cl_2 solution, the distribution of valence isomers was somewhat less temperature-dependent ($\Delta H^\circ = 187 \pm 29$ cal/mol; $\Delta S^\circ = 1.04 \pm 0.14$ eu; Table 7).

Tautomer **b** was found to be the favored form of the sulfoxides and sulfone. Of these, the syn sulfoxide **24** was found to possess the most equitable distribution of tautomers with **24b** favored to the extent of 68% (Table 1). In CD_2Cl_2 solution at +40° (Fig. 4), H_4 and H_6 appeared as a triplet at δ 4.57; as the temperature was decreased, the population of **24b** increased to 89% (−73°, Table 8), corresponding to a ΔH° of 1.43 ± 0.12 kcal/mol and a ΔS° of 3.15 ± 0.51 eu.

It is obvious from the spectrum of sulfone **20** (Fig. 4) that a still greater bias toward tautomer **b** exists at +40°. In this example, the rather wide separation of the upfield proton chemical shifts facilitated the double resonance experiments. The effect of the added O atom on sulfur was to increase the relative concentration of **20b** to a level of 77% (δ H_4, H_6 = 4.76). Variable temperature studies in CD_2Cl_2–CF_2Cl_2 (Table 9) demonstrated the

Table 6. Variable temperature ^1H NMR data,[a] computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the fluxional system 18b ⇌ 18a

Temp, °C	Chemical Shift[b] H_4, H_8	Mol Fraction 18b	K_{eq}, (18a/18b)	ΔG° (18b → 18a), cal/mol
+33.5	3.44	0.34	1.95	-412
+33.4	3.46	0.35	1.90	-393
+30.0	3.50	0.36	1.80	-356
-2.6	3.53	0.37	1.73	-297
-12.4	3.58	0.38	1.62	-251
-16.6	3.59	0.39	1.58	-241
-26.8	3.61	0.39	1.58	-219
-33.0	3.65	0.40	1.48	-189
-34.4	3.66	0.41	1.45	-180
-41.8	3.68	0.41	1.45	-164
-44.3	3.70	0.42	1.39	-150
-54.6	3.74	0.43	1.31	-121
-55.0	3.75	0.43	1.31	-116
-63.1	3.79	0.45	1.22	-90
-67.8	3.81	0.45	1.22	-78
-79.5	3.86	0.47	1.14	-50
-92.5	3.96	0.50	1.00	0

[a] 100 MHz in CH_2-TMS. [b] Relative to internal TMS.

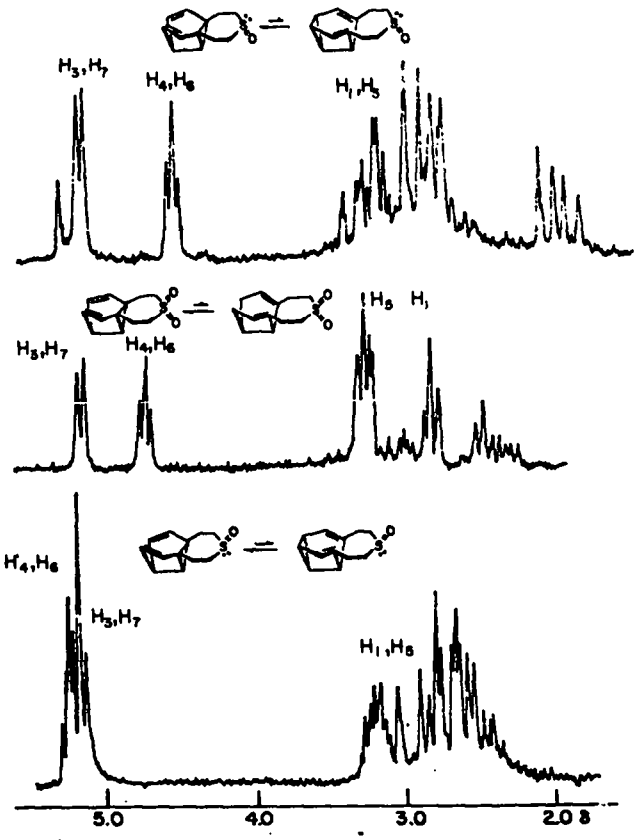


Fig. 4. ^1H NMR spectra of 24 (top), 20 (middle) and 23 (bottom) recorded at +40° in $CDCl_3$ solution at 100 MHz except for 24 where solubility dictated the use of CD_2Cl_2 and Fourier Transform techniques (90 MHz).

Table 7. Variable temperature ^{1}H NMR data,[a] computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the fluxional system 18b ⇌ 18a

Temp, °C	Chemical Shift[b] H_4,H_8	Mol Fraction 18b	K_{eq}, (18a/18b)	ΔG° (18b → 18a), cal/mol
-33.0	3.85	0.46	1.15	-68
-41.8	3.88	0.47	1.11	-48
-55.0	3.90	0.48	1.08	-35
-67.8	3.92	0.49	1.05	-23
-79.5	3.93	0.49	1.05	-17

[a]100 MHz in 1:1:1 CD_2Cl_2-CF_2Cl_2-TMS. [b]Referenced to internal TMS and corrected so that the $CHDCl_2$ resonance remained constant at 5.32 δ.

Table 8. Variable temperature ^{1}H NMR data,[a] computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the fluxional system 24b ⇌ 24a

Temp, °C	Chemical Shift[b] H_4,H_8	Mol Fraction 24b	K_{eq}, (24a/24b)	ΔG° (24b → 24a) cal/mol
+30.9	4.54	0.68	0.48	444
+20.0	4.68	0.72	0.39	549
0.0	4.76	0.75	0.34	586
-15.0	4.84	0.77	0.30	618
-30.0	4.90	0.79	0.27	633
-44.0	5.02	0.83	0.21	711
-57.0	5.10	0.85	0.18	737
-73.0	5.22	0.89	0.13	812

[a]90 MHz in CD_2Cl_2-TMS. [b]Relative to internal TMS corrected so that the $CHDCl_2$ resonance remained constant at 5.32 δ.

Table 9. Variable temperature ^{1}H NMR data,[a] computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the fluxional system 20b ⇌ 20a

Temp, °C	Chemical Shift[b] H_4,H_8	Mol Fraction 20b	K_{eq}, (20b/20a)	ΔG° (20b → 20a), cal/mol
+32.6	4.86	0.78	.29	778
+26.0	4.90	0.79	.27	779
+14.8	4.96	0.81	.24	818
+6.6	4.98	0.81	.24	817
+3.3	5.02	0.83	.21	859
+1.5	5.02	0.83	.21	853
-1.5	5.04	0.83	.21	844
-9.1	5.08	0.84	.19	882
-11.2	5.08	0.84	.19	875
-15.2	5.13	0.86	.17	923
-18.3	5.13	0.85	.17	912
-20.8	5.16	0.87	.15	943
-27.9	5.20	0.88	.14	962
-45.5	5.27	0.90	.11	1000
-61.9	5.34	0.92	.08	1045

[a]100 MHz in 1:1:1 CD_2Cl_2-CF_2Cl_2-TMS. [b]Referenced to internal TMS and corrected so that the $CHDCl_2$ resonance remained constant at 5.32 δ.

same increasing partiality to **23b** as the temperature was lowered (92% at −61.9°). In this case, $\Delta H^\circ = 1.72 \pm 0.07$ kcal/mol and $\Delta S^\circ = 3.16 \pm 0.25$ eu.

Anti sulfoxide **23** exhibits a room temperature spectrum (in $CDCl_3$) where the chemical shift of the time-averaged protons H_4, H_6 (δ 5.22) indicates the valence isomer with the central cyclopropane ring (**23b**) to be present at the highest concentration level (89%) of all the 2,8-pentamethylene semibullvalenes (Fig. 4). Due to the insolubility of **23** in CD_2Cl_2 at low temperatures, the temperature-dependent study was limited to −29.3° and above (Table 10). However, since the distribution of isomers was already biased to the 98% level at this temperature, the practical limit for computational analysis was already realized. The enthalpy ($\Delta H^\circ = 3.35 \pm 0.22$ kcal/mol) and entropy ($\Delta S^\circ = 6.17 \pm 0.82$ eu) for this semibullvalene were derived from the data in Table 10. For ease of comparison, the thermodynamic data for the entire range of semibullvalenes are presented in summary form in Table 11.

^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of non-fluxional semibullvalene recorded at −167° is comprised of five signals at 131.8 (C_4, C_6), 121.7 (C_3, C_7), 53.1 (C_5), 48.0 (C_1) and 42.2 ppm ($C_{2,8}$).[3] While the displacements of the equilibrium position noted herein do not necessarily affect the rate of Cope rearrangement (and consequently the rapid time averaging of the C atoms), alterations in the chemical shifts do result. Previously, we have shown these shifts to parallel quantitatively the equilibrium distributions of the two tautomeric forms.[7,10] An excellent correlation has again been found in the present investigation (Table 12) as reflected in the remarkably close correspondence with the ^1H NMR derived data (Table 13).[30] The trends in the pentamethylene series deserve further mention. The first and most obvious regular variation is the downfield shifting of the C_4, C_6 resonance as the degree of olefinic character increases at these sites. As one again progresses downward in Table 12, the gradual change in C_3 from primarily cyclopropyl in **13** to predominantly bis-allylic in **23** is similarly clearly outlined. An opposite trend is seen for C_1, although here steric and/or electronic forces arising from differences in the bracketing ring becloud the incremental alteration in hybridization. Variations in the shifts of those carbons α to the heteroatoms are, as usual, primarily a reflection of the electronegativity of X. In actuality, these data are inexcellent agreement with those reported by Lambert and coworkers for six-membered saturated heterocycles.[29]

Although the β carbons and C_2, C_8 are progressively more removed from the heteroatomic center, each is still slightly affected by the electronegativity differences in X. By merely subtracting the ^{13}C shift of the cyclohexane carbons (27.7 ppm) from those of the more remote carbons in the appropriate heterocycle, a rather precise measurement of the "full effect" of X can be realized.[29] These values can then be utilized to correct the original shifts so that the influence of the heteroatom is removed. Contributions from other sources to the chemical shift are thereby made evident. When this factoring is applied

Table 10. Variable temperature ^1H NMR data,[a] computed equilibrium constants (K_{eq}) and Gibbs free energy values (ΔG°) for the fluxional system **23b** ⇌ **23a**

Temp, °C	Chemical Shift[b] H_4,H_6	Mol Fraction **23b**	K_{eq}, (**23b**/**23a**)	ΔG° (**23b** → **23a**), kcal/mol
+32.5	5.33	0.92	0.087	1.49
+16.9	5.38	0.94	0.069	1.54
+3.0	5.43	0.95	0.052	1.63
-17.1	5.49	0.97	0.032	1.75
-29.3	5.52	0.98	0.022	1.85

[a] 100 MHz in CD_2Cl_2-TMS. [b] Referenced to internal TMS and corrected so that the $CHDCl_2$ resonance remained constant at 5.32 δ.

Table 11. Summary of thermodynamic data for the heteroatomic 2,8-pentamethylene semibullvalenes

Bracket Substituent	ΔH°,[a] kcal/mol	ΔS°,[a] eu	ΔH°,[b] kcal/mol	ΔS°,[b] eu
O (**13**)	-0.59	1.1	-1.06	0.4
S (**18**)	0.19	1.0	0.56	3.1
NCH_2Ph (**16**)	0.43	1.4	0.58	2.9
CH_2 (**4**)	1.13	3.9	0.70	2.9
syn-SO (**24**)	1.43	3.2		
SO_2 (**20**)	1.72	3.2		
anti-SO (**23**)	3.35	6.2		

[a] In CD_2Cl_2-CF_2Cl_2-TMS (1:1:1) or CD_2Cl_2-TMS. [b] In CS_2-TMS.

Table 12. Summary of ^{13}C NMR data (22.6 Hz, $CDCl_3$, 40°) for the heteroatomic 2,8-pentamethylene semibullvalenes

Compound	Chemical Shifts, ppm from TMS						
	C_1	C_2,C_8	C_3,C_7	C_4,C_6	C_5	β	α
13	59.49[a]	129.06	120.22	54.68	48.85[a]	34.13	74.06
18	59.62[a]	118.54	121.83	70.46	54.22[a]	31.62[b]	33.88[b]
16[c]	58.81[a]	118.64	121.45	80.21	52.77[a]	29.51	54.74
4	59.6[a]	109.1	121.4	82.2	52.4[a]	d	d
24	53.36[a]	90.86	122.47	97.93	57.24[a]	20.39	51.74
20	54.12[a]	89.67	123.01	99.92	57.30[a]	24.49	56.11
23	54.60[a]	72.40	124.09	118.59	61.24[a]	19.26	49.10

[a] These values may be interchanged. [b] These values may be interchanged. [c] Additional resonances include: 61.35, benzyl; 127.06, 128.25, 129.11, and 140.0, aryl. [d] α, β, and γ carbons appear at 28.0, 29.0, and 30.0.

Table 13. Comparison of equilibrium distributions calculated by ^1H and ^{13}C NMR ($CDCl_3$, 40°)

Annulated Semibullvalenes	Mol Fraction Isomer b (^{13}C NMR)	Mol Fraction Isomer b (^1H NMR)
13 (X = -O-)	0.1[illegible]	0.[illegible]
18 (X = -S-)	0.32	0.38
16 (X = >NCH$_2$Ph)	0.42	0.43
4 (X = -CH$_2$-)	0.45	0.43
24 (X = syn >SO)	0.62	0.66
20 (X = >SO$_2$)	0.64	0.74
23 (X = anti >SO)	0.85	0.89

Table 14. Adjusted ^{13}C NMR shifts of carbons β, 2 and 8

X	$\Delta\beta$[a]	β_{corr}	$\Delta\gamma$[b]	$C_2,C_8{}_{corr}$
O	-0.5	34.6	-3.3	132.4
S	+0.5	31.1	-2.4	120.9
NR	-1.3[c]	30.8[d]	-3.3[c]	121.9[d]
CH$_2$	0.0	e	0.0	109.1
SO$_{eq}$[f]	-12.2	32.6	-3.0	93.9
SO$_2$	-2.6	27.2	-3.4	93.1
SO$_{ax}$[f]	-4.4	23.7	-3.0	69.4

[a] β carbon in $(CH_2)_5X$ - 27.7 ppm (cyclohexane resonance). [b] γ carbon in $(CH_2)_5X$ - 27.7 ppm. [c] R = CH_3. [d] R = CH_2Ph. [e] 28.0, 29.0, and 30.0 ppm. [f] Reversal of the axial and equatorial assignments would give β_{corr} values of 24.8 and 31.5, respectively.

to the heteroatomic 2,8-pentamethylene semibullvalenes, the ordering of the adjusted shifts continues to follow the trend previously outlined (Table 14).

Lastly, we note that the shifts of C_3, C_7 remain essentially constant (120.2–124.1 ppm) throughout both the pentamethylene and trimethylene series,[10] in agreement with our original premise that the semibullvalene framework is relatively unperturbed during such alterations in the bracket.

DISCUSSION

For our purposes, it is necessary that the additional methylene groups contained in the pentamethylene bridged series provide sufficient insulation from the effects of heteroatom electronegativity to permit the valence isomeric equilibria to be largely dependent upon the subtle steric influences of X. The slight shielding effects in the γ C atoms of simple heterocycles (2.4–3.4 ppm upfield)[20] and the relatively constant shifts of C_3

and C_7 suggest that such a situation does indeed prevail. This facilitates the analysis of the dynamic behavior of **13, 16, 18, 20, 23** and **24**.

A first criterion derives from the established experimental fact that attachment of an alkyl group to an sp^2-hybridized semibullvalene carbon is thermodynamically favored in the absence of steric effects.[5] In this regard, ether **13** gives evidence of near ideality. At +40°, **13a** dominates the equilibrium to the extent of 80–88% and is favored by an enthalpy difference of 0.59–1.06 kcal/mol depending upon the particular solvent. This $\Delta H°$ value begins to approach the 1–2 kcal/mol expected for sp^2 bonding of two alkyl substituents with no steric complications.[5] As the C–X bond length increases (O < N < C < SO_2, see Table 5), the size of the bracket must become progressively larger with the result that nonbonded interactions typical of medium-sized rings should gain increasing importance. Certainly the various bridges are reasonably mobile conformationally and enjoy the latitude for intramethylene rotations and the like to minimize ground state energy. However, increasing bond lengths will certainly permute the characteristics of the bracket in a way to generate greater internal strain. On this basis, we would expect the bonding preference seen in **13** to be incrementally altered in favor of tautomer **b** with increasing C–X bond length because of enthalpy considerations. The present results support this analysis.

Of course, tautomer **a** should uniformly be favored by entropy factors since the larger bracketing ring in this isomer should have the greater degree of freedom. Indeed, progression through the series of seven available 2,8-pentamethylene semibullvalenes reveals that the entropy term does increase in magnitude with projected increased flexibility of the ring (Table 11).

While the above explanation adequately orders O < NR < CH_2 < SO_2, it does not serve to suitably rank sulfide **18** and the sulfoxides **23** and **24**. Previously, we considered only bond lengths and did not comment on the fact that the internal C–X–C bond angles for O, N, C and SO_2 are likewise grouped together in a very narrow range (108–110°, Table 15). The average angle in sulfides is some 3° less than that observed for typical saturated amines, ether, hydrocarbons, or sulfones. This smaller bond angle has the effect of offsetting the comparatively longer C–S bond distance. This intriguing interplay presumably serves to place the sulfide at a position intermediate between **13** and **16** (Table 13).

Sulfoxides are significantly different from the other members of a heterocyclic series in many ways. They possess extremely long C–X bonds, parallelling sulfides and sulfones in this respect (Table 15). However, the C–X–C bond angle in sulfoxides (98°) is greatly reduced when compared to the situation generally prevailing in sulfones (107°) and even sulfides (105°). In these terms, the effective ring size in **23** and **24** should be less than that in sulfide **18**. Yet tautomer **b** is dominant in the sulfoxides. The response of the semibullvalene frame to the sulfoxide linkage could well be complicated by a third factor, the highly polarized nature of the S=O double bond where sulfur may possess as much as one-third of a full charge.[31] In no other example is there charge polarization of this magnitude. The sulfoxide oxygen atom could also cause substantial perturbation of the 7- and 8-membered ring conformations. Molecular models suggest, for example, that the differing equilibrium constants in **23** and **24** may arise in large part from entirely different sets of nonbonded steric interactions which may be partially offset by minor conformational readjustments. We emphasize that enthalpy and entropy increments are sufficiently independent that they sometimes exhibit the same sign and sometimes opposite signs. When several effects are operating concurrently as they are in the sulfoxide examples, it clearly becomes difficult to disentangle the combination of effects which contribute to $\Delta H°$ and $T\Delta S°$, respectively. Given the somewhat checkered history of conformational analysis in the thiane S-oxides,[32] we shall not elaborate further on the equilibrium characteristics of **23** and **24**.

In summary, the varied ground-state equilibrium imbalances of the heteroatomic 2,8-pentamethylene semibullvalenes are seen to provide in quantitative terms unusually clear glimpses of conformational effects caused by different X substituents which are unlikely to be assessed in comparable terms by other techniques. Because a twofold degenerate host molecule such as semibullvalene is involved, subtle libration effects make their appearance since an energy term associated with a predetermined enthalpic weighting toward one of the valence isomers is absent. The application of bond angle and bond length criteria to the O, NR, CH_2, S and SO_2 derivatives was capable of rationalizing the relative

Table 15. Selected molecular parameters

X	van der Waals radius (Å)[a]	Covalent single bond radius (Å)[a]	Average C–X bond length (Å)	Electronegativity[a]	Bond angle (°)
$-CH_2-$	2.00	0.77	1.54[b]	2.5	109[b]
-O-	1.40	0.74	1.43[b]	3.5	110[b]
-NR-	1.5	0.73	1.47[b]	3.0	108[b]
-S-	1.85	1.02	1.82[b]	2.5	105[b]
-SO-			1.80[c,d]		98[c,d]
$-SO_2-$			1.76[e]		107[e]

[a] L. Pauling, "Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y. (1960). [b] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Chem. Soc. Spec. Publ., No. 11 (1958). [c] R. Thomas, C. B. Shoemaker, and K. Eriks, Acta. Cryst., 21, 12 (1966). [d] M. A. Viswamitra and K. K. Kannen, Nature, 290, 1016 (1966). [e] R. K. Bullough and P. J. Wheatley, Acta. Cryst., 10, 233 (1957).

ordering of their equilibrium constants. Both sulfoxide isomers exhibit interesting features, but the combination of factors which control their K_{eq}'s remains to be unraveled.

EXPERIMENTAL

M.ps are corrected. PMR spectra were obtained on Varian T-60, A-60A and HA-100 spectrometers; apparent splittings are given in all cases. ^{13}C NMR spectra were recorded with a Bruker 90 spectrometer. IR spectra were obtained with Perkin–Elmer Model 137 and 467 spectrometers, whereas mass spectra were measured with an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Hexahydro - 1,6 - bis(2 - hydroxyethyl) - N - phenyl - 1,2,3 - metheno - 1H - 4,5 - diazacycloprop[cd]indene - 4,5 - dicarboximide (**10a**). A soln of 9[7,12] (2.00 g, 6.05 mmol) in 250 ml chloroform was allowed to react with excess O_3 at 0°. The mixture, diluted with 40 ml of abs EtOH, was reduced with 2.29 g (60.5 mmol) $NaBH_4$ as previously described.[10] A similar work-up afforded 2.17 g (97.8%) of frothy solid diol **10a**; ν_{max}^{KBr} 3430, 2925, 1750, 1690, 1500, 1410, 1265 and 1020 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 7.43 (m, 5, aryl), 5.08 (t, J = 2.5 Hz, 2, >CHN<), 3.72 (t, J = 6.5 Hz, 4, $-CH_2OH$), 3.00 (concentration dependent) (s, 2, $-OH$) and 1.50–2.20 (m, 8, cyclopropyl and cyclopropylcarbinyl).

The crude diol (113 mg, 0.31 mmol) was dissolved in 12 ml dry pyridine and treated with excess Ac_2O (628 mg, 6.16 mmol). The soln was stirred overnight at 25° under anhydrous conditions, then evaporated to dryness *in vacuo*. Thick layer silica gel chromatography (ether elution) followed by recrystallization from THF–ether gave 39 mg (30%) of colorless crystalline diacetate **10b**, m.p. 112.4–113.3°; ν_{max}^{KBr} 1740, 1695, 1495, 1405 and 1235 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 7.45 (m, 5, aryl), 5.05 (m, 2, >CHN<), 4.0–4.50 (m, 4, $-CH_2O_2CCH_3$), 2.03 (s, 6, CH_3CO_2-) and 1.65–2.15 (m, 8, cyclopropyl and cyclopropylcarbinyl); calc. *m/e* 451.1743, found 451.1750. (Found: C, 63.74; H, 5.64; N, 9.28. Calc. for $C_{24}H_{25}N_3O_6$: C, 63.85; H, 5.58; N, 9.31%).

Hexahydro - 1 - (2 - hydroxyethyl) - 6 - (2 - p - toluenesulfonyloxyethyl) - N - phenyl - 1,2,3 - metheno - 1H - 4,5 - diazacycloprop[cd]indene - 4,5 - dicarboximide (**11a**). To a soln of 420 g (1.14 mmol) of unpurified diol **10a** in 25 ml anhyd THF was added 216 mg (1.14 mmol) of recrystallized *p*-toluenesulfonyl chloride and 1.4 ml (9.36 mmol) purified Et_3N. The resulting soln was stirred at room temp. under N_2 for 5 hr and heated at reflux for 14 hr prior to cooling, concentration *in vacuo*, and dilution with 75 ml chloroform. The organic layer was rinsed with 10% HCl, water, and brine before drying, filtration, and evaporation. There was obtained 523 mg (88%) of **11a** as a light tan oil; ν_{max}^{neat} 1770, 1700, 1495, 1410, 1360, 1190, 1175 and 750 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 7.15–7.83 (m, 9, aryl), 5.10 (t, J = 2.5 Hz, 1, >CHN<), 4.88 (t, J = 2.5 Hz, 1, >CHN<), 4.18 (t, J = 6.0 Hz, 2, $-CH_2OTs$), 3.73 (t, J = 6.5 Hz, 2, $-CH_2OH$), 2.58 (s, 1, $-OH$), 2.38 (s, $-CH_3$) and 1.75–2.20 (m, 8, cyclopropyl and cyclopropylcarbinyl).

Hexahydro - 1 - (2 - hydroxyethyl) - 6 - (2 - iodoethyl) - N - phenyl - 1,2,3 - metheno - 1H - 4,5 - diazacycloprop[cd]indene - 4,5 - dicarboximide (**11b**). Unpurified **11a** (523 mg, 1.00 mmol) was dissolved in 50 ml purified acetone and stirred with NaI (280 mg, 1.87 mmol) under N_2 for 1 hr at ambient temp. and for 18 hr at reflux. The flocculent, white ppt was filtered from the warm soln and the filtrate was evaporated to dryness. A chloroform soln of the filtrate residue was rinsed with water, 10% $Na_2S_2O_3$ aq, water, and brine before drying. Filtration and evaporation of solvent left 348 mg (73%) of crude **11b**. Chromatography on silica gel with ether elution gave 310 mg of pure **11b** as a frothy white solid; ν_{max}^{KBr} 3430, 1755, 1695, 1500, 1410 and 1260 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 7.48 (m, 5, aryl), 5.15 (t, J = 2.5 Hz, 1, >CHN<), 5.02 (t, J = 2.5 Hz, 1, >CHN<), 3.78 (t, J = 6.0 Hz, 2, $-CH_2OH$), 3.29 (t, J = 8.0 Hz, 2, $-CH_2I$), 2.95 (br s, 1, $-OH$) and 1.60–2.20 (m, 8, cyclopropyl and cyclopropylcarbinyl).

Decahydro - N - phenylcyclopropa[3',4']pentaleno[1',6':1,3,2]cycloprop[1,2-d]oxepin - 1,7 - biimine - 8,9 - dicarboximide (**12**). Purified **11b** (310 mg, 0.65 mmol) was dissolved in 50 ml anhyd THF and stirred under N_2 with freshly prepared Ag_2O[33] (309 mg, 1.33 mmol) overnight at room temp. and for 24 hr at reflux. The brown suspension was cooled and the solid was removed by filtration. The yellow filtrate was evaporated to dryness and the residue was taken up in chloroform. The organic soln was rinsed with water (2x) and brine, dried, filtered, and evaporated to dryness. Preparative tlc with chloroform elution provided 130 mg (57%) of **12**, m.p. 184.3–184.7° (from chloroform–cyclohexane); ν_{max}^{KBr} 2890, 1770, 1700, 1505, 1495, 1410, 1295, 1275, 1135, 1115, 1110, 1070, 1005, 765 and 710 cm^{-1}; ^1H NMR (δ, $CDCl_3$), 100 MHz) 7.25–7.65 (m, 5, aryl), 4.85 (t, J = 2.5 Hz, 2, >CHN<), 3.85 (dq, J = 13.0, 5.0 and 3.0 Hz, 2, >CHO–), 3.14 (dq, J = 13.0, 8.0 and 2.0 Hz, 2, >CHO–) and 1.87–2.50 (m, 8, cyclopropyl and cyclopropylcarbinyl); calc. *m/e* 349.1426, found 349.1433. (Found: C, 68.41; H, 5.42; N, 12.01. Calc. for $C_{20}H_{19}N_3O_3$: C, 68.75; H, 5.48; N, 12.03%).

1,2,4,5,6a,6b,7b,7c - Octahydrocyclopropa[3,4]pentaleno [1,6-de]oxocin (**13a**) ≠ *2a,5,6,8,9,9b - hexahydropentaleno [1',6':1,3,2]cycloprop[1,2-d]oxepin* (**13b**). A mixture of 460.8 mg (1.32 mmol) of **12**, 741 mg (13.2 mmol) powdered KOH and 30 ml 2-propanol was mechanically stirred and heated at reflux under argon for 1 hr in a 250 ml 3-necked round bottom flask fitted with a septum-covered gas inlet with stopcock and a condenser topped with a gas inlet. The milky, yellow soln was cooled to 0°, acidified (pH 6) with 50% aqueous AcOH, stirred for 10 min, basified (pH 9) with 50% NH_4OH aq, and diluted with 50 ml pentane. To the clear yellow soln was added in one portion 1.16 g (13.2 mmol) of Attenburrow MnO_2[34] which triggered immediate gas evolution. Stirring was continued under argon at ambient temp. for 9 hr,[35] whereupon the mixture was filtered through Celite to give a clear yellow soln which was extracted with pentane (3 × 25 ml). The combined pentane extracts were rinsed with water (5 × 25 ml) and dried over Na_2SO_4. The soln was filtered and concentrated by careful distillation with argon bubbling. The viscous concentrate was transferred to a sublimator and the remaining solvent was evaporated. Double sublimation (40–80°/1.5 × 10^{-4} torr) of the residue gave 138.9 mg (60.4%) of semibullvalene **13**, m.p. 42–53°; ν_{max}^{neat} 3035, 2920, 2860 and 1110 cm^{-1}; $\lambda_{max}^{isooctane}$ 212.5 (ε 9.0 × 10^3), 230.0 (4.7 × 10^3) and 250.0 nm (2.8 × 10^3); ^1H NMR (δ, $CDCl_3$, 100 MHZ) 5.20 (D, $J_{3,4} = J_{6,7}$ = 1.5 Hz, 2, H_3 and H_7), 4.03 (dt, J = 11.6 and 5.0 Hz, 2, >CHO–), 3.35 (d, $J_{1,5}$ = 7.0 Hz, 1, H_1), 3.19 (dt, J = 6.5 and 11.6 Hz, 2, >CHO–), 2.94 (t, $J_{1,5}$ = 7.0 Hz, $J_{4,5} = J_{5,6}$ = 5.5 Hz, 1, H_5), 2.87 (dd with additional splitting, $J_{3,4} = J_{6,7}$ = 1.5 Hz, $J_{4,5} = J_{5,6}$ = 7.0 Hz, 2, H_4 and H_6), 2.50 (m, 4, $-CH_2CHO-$). Spin decoupling: saturation of the signal at δ 5.20 collapsed the signal centered at 2.87 to a doublet $J_{4,5} = J_{5,6}$ = 7.0 Hz. Conversely, double irradiation of the 2.87 signal simplified the 5.20 signal to a singlet. ^{13}C NMR (ppm, $CDCl_3$) 129.06 (s, C_2 and C_8), 120.22 (d, C_3 and C_7), 74.06 (t, $-CH_2O-$), 59.49 (d, C_1 or C_5), 54.68 (d, C_4 and C_6), 48.83 (d, C_5 or C_1) and 34.13 (t, $-CH_2CH_2O-$); calc. *m/e* 174.1044, found 174.1049.

Hexahydro - 1,6 - bis(2 - hydroxyethyl) - N - phenyl - 1,2,3 - metheno - 1H - 4,5 - diazacycloprop[cd]indene - 4,5 - dicarboximide bismethanesulfonate (**14**). Methanesulfonylchloride (1.04 g, 4.10 mmol) was added dropwise to a stirred soln of **10a** (1.50 g, 4.10 mmol) and purified Et_3N (1.24 g, 12.3 mmol) in 100 ml dichloromethane at −10° under N_2. After 15 min, the organic phase was washed with ice water, cold 5% HCl, cold sat $NaHCO_3$ aq, and brine. The soln was dried, filtered and evaporated to give a quantitative yield of **14** as a tan semi-solid; ν_{max}^{neat} 1755, 1596, 1500, 1410, 1350, 1170, 955, 800, 765, 745 and 710

cm^{-1}; ^1H NMR (δ, $CDCl_3$) 7.45 (m, 5, aryl), 5.01 (t, $J = 2.5$ Hz, 2, $>CHN<$), 4.37 (t, $J = 6.5$ Hz, 4, $-CH_2O_3SCH_3$), 2.97 (s, 6, $-O_3SCH_3$) and 1.75–2.10 (m, 8, cyclopropyl and cyclopropylcarbinyl).

4 - *Benzyldecahydro* - N - *phenyl* - 1,7 - *biimino* - 2H - *cyclopropa*[3',4']*pentaleno*[1',6':1,3,2]*cycloprop*[1,2-d]*azepine* - 8,9 - *di* - *carboximide* (**15**). A soln of 523 mg (1.00 mmol) of **14** and 348 mg (3.25 mmol) freshly distilled benzylamine in 75 ml acetonitrile was stirred at ambient temp. under N_2 for 44 hr. The soln was filtered and evaporated to dryness to leave a tan oil which, after chromatography on silica gel (elution with 50% ether–petroleum ether), afforded 266 mg (61%) of **15** as a white solid, m.p. 184.5–185.4° (from chloroform–ether); ν_{max}^{KBr} 1770, 1705, 1505, 1495, 1405, 1128 and 768 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 7.47 (m, 5, aryl), 7.25 (s, 5, aryl), 4.78 (t, $J = 2.0$ Hz, 2, $>CHN<$), 3.52 (s, 2, benzyl) and 1.70–2.90 (m, 12, methylene and cyclopropyl); calc. *m/e* 438.2055, found 438.2060. (Found: C, 73.51; H, 5.95; N, 12.78. Calc. for $C_{27}H_{26}N_4O_2$: C, 73.95; H, 5.98; N, 12.78%).

3 - *Benzyl* - 2,3,4,5,6a,6b,7b,7c - *octahydro* - 1H - *cyclopropa*[3,4]*pentaleno*[1,6-de]*azocine* (**16a**) ⇄ 7 - *benzyl* - 2a,6,7,8,9,9b - *hexahydro* - 5H - *pentaleno*[1',6':1,3,2]*cycloprop*[1,2-d]*azepine* (**16b**). The hydrolysis and oxidation of 455 mg (1.04 mmol) of **15** was carried out in the predescribed manner using 346 mg (8.66 mmol) powdered NaOH, 30 ml of 2-propanol, 900 mg (8.66 mmol) activated MnO_2 and 30 ml pentane to give after sublimation (40–60°/1.2×10^{-3} torr) 145 mg (53%) of **16** as a low melting (*ca.* 10–15°) light yellow solid; ν_{max}^{neat} 3040, 2930, 2815, 2790, 1730, 1605, 1530, 1500, 1455, 1445, 1375, 1350, 1315, 1220, 1180, 1150, 1115, 1028, 772, 750, 730 and 698 cm^{-1}; $\lambda_{max}^{isooctane}$ 230 (ϵ 7.5×10^3), 240 (5.1×10^3) and 255 m (2.5×10^3); ^1H NMR (δ, $CDCl_3$, 100 MHz) 7.17 (s, 5, aryl), 5.00 (d, $J_{3,4} = J_{6,7} = 5.0$ Hz, 2, H_3 and H_7), 3.75 (m, 2, H_4 and H_6), 3.53 (s, 2, benzylic) and 2.10–3.20 (m, 10, methylenes, H_1 and H_5). Spin decoupling: double irradiation at δ 5.00 collapsed the multiplet at 3.75 to a doublet, $J_{4,5} = J_{5,6} = 5.0$ Hz, while irradiation at 3.75 simplified the doublet at 5.00 to a singlet. H_5 could not be specifically located. ^{13}C NMR (ppm, $CDCl_3$) 129.11, 128.25 and 127.06 (d, aryl), 123.23 (s, aryl quaternary), 121.45 (d, C_3 and C_7), 118.64 (s, C_2 and C_8), 80.12 (d, C_4 and C_6), 61.35 (t, benzylic), 58.81 (d, C_1 or C_5), 54.74 (t, $-CH_2CH_2N-$), 52.77 (d, C_5 or C_1) and 29.51 (t, $-CH_2N-$); calc. *m/e* 263.1674, found 263.1677.

Decahydro - N - *phenylcyclopropa*[3',4']*pentaleno*[1',6':1,3,2]*cyclopropa*[1,2-d]*thiepin* - 1,7 - *bilmine* - 8,9 - *dicarboximide* (**17**). To 250 ml of refluxing EtOH was added simultaneously a soln of 1.97 g (3.75 mmol) of **14** in 60 ml N,N-dimethylacetamide and a soln of 0.90 g (3.75 mmol) of $N_2S \cdot 9H_2O$ in ethanol-N,N-dimethylacetamide (1:1). The addition, carried out under N_2, was complete after 8 hr and the resulting suspension was stirred and heated overnight at the reflux temp. After the solvent had been removed via bulb-to-bulb distillation at high vacuum (*ca.* 1 mm) with minimum heat, the mixture was chromatographed on 75 g of silica gel [chloroform–ether (1:1) elution] to give 0.88 g (64%) of **17**, m.p. 209.3–210.5° (from chloroform–ether); ν_{max}^{KBr} 2920, 1750, 1690, 1495, 1455, 1410, 1293, 1125, 770, 755 and 697 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 7.47 (m, 5, aryl), 4.89 (m, 2, $>CHN<$), 2.10–3.30 (m, 5, methylene and cyclopropyl syn to thiepane ring) and 2.00 (m, 3, cyclopropyl); calc. *m/e* 365.1198, found 365.1203. (Found: C, 65.50; H, 5.26; N, 11.50. Calc. for $C_{20}H_{19}N_3O_2S$: C, 65.73; H, 5.24; N, 11.50%).

1,2,4,5,6a,6b,7b,7c - *Octahydrocyclopropa*[3,4]*pentaleno* [1,6-de]*thiocin* (**18a**) ⇄ 2a,5,6,8,9,9b - *hexahydropentaleno*[1',6':1,3,2]*cyclopropa*[1,2-d]*thiepin* (**18b**). In a fashion which strictly parallels the preparation of **13**, 599.2 mg (1.62 mmol) of **17** was hydrolyzed with 650 mg (16.0 mmol) of powdered NaOH in 30 ml 2-propanol and oxidized with 1.41 g (16.2 mmol) of Attenburrow MnO_2. Sublimation (75–100°/1.6×10^{-3} mm) afforded 185 mg (60%) of semibullvalene **18** as a low melting, light yellow solid, m.p. 23–25°; ν_{max}^{KBr} 3045, 2940, 2920, 2880, 2855, 2825, 1735, 1605, 1530, 1500, 1455, 1445, 1430, 1335, 1315, 1300, 1280, 1255, 690, 635, 625 and 600 cm^{-1}; $\lambda_{max}^{isooctane}$ 225 (ϵ 1.7×10^3), 235 (1.5×10^3) and 240 nm (1.2×10^3); ^1H NMR (δ, $CDCl_3$, 100 MHz), 5.13 (d, $J_{3,4} = J_{6,7} = 3.0$ Hz, 2, H_3 and H_7), 3.57 (dd, $J_{3,4} = J_{6,7} = 3.0$ Hz, $J_{4,5} = J_{5,6} = 5.9$ Hz, 2, H_4 and H_6) and 2.10–3.35 (m, 10, methylenes, H_1 and H_5). Spin decoupling: double irradiation at δ 5.13 caused the peak at 3.57 to collapse to a doublet, $J_{4,5} = J_{5,6} = 5.9$ Hz. Saturation at 3.57 simplified the signal at 5.13 to a singlet, but H_5 could not be located exactly. ^{13}C NMR (ppm, $CDCl_3$) 121.83 (d, C_3 and C_7), 118.54 (s, C_2 and C_8), 70.46 (d, C_4 and C_6), 59.62 (d, C_1 or C_5), 54.22 (d, C_5 or C_1) and 33.88 and 31.62 (t, $-CH_2S-$ and $-CH_2CH_2S-$); calc. *m/e* 190.0816, found 190.0818.

Decahydro - N - *phenylcyclopropa*[3',4']*pentaleno*[1',6':1,3,2]*cyclopropa*[1,2-d]*thiepin* - 1,7 - *biimine* - 8,9 - *dicarboximide* 4,4 - *dioxide* (**19**). To a stirred, cold (0°) soln of 365 mg (1.00 mmol) of **17** in 25 ml chloroform was added dropwise a soln of 346 mg (2.00 mmol) *m*-chloroperbenzoic acid in 5 ml chloroform. The soln was stirred with protection from moisture for 5 hr after warming to ambient temp. The mixture was diluted to 75 ml with chloroform, rinsed with sat $NaHCO_3$ aq, dried, filtered, and evaporated to dryness to give, after recrystallization from chloroform–ether, 330.7 mg (83%) of **19** as a white solid, m.p. 338.5–339.5° (dec, sealed tube); ν_{max}^{KBr} 1755, 1700, 1495, 1455, 1415, 1328, 1282, 1132, 1106, 762 and 698 cm^{-1}; ^1H NMR (δ, $CDCl_3$, 90 MHz) 7.51 (m, 5, aryl), 4.93 (t, $J = 3.1$ Hz, 2, $>CHN<$), 3.70 (t, $J = 13.0$ Hz, 2, $>CHSO_2-$), 2.82–3.13 (m, 2, $>CHSO_2-$), 2.60 (d, $J = 6.0$ Hz, cyclopropyl syn to thiepane ring) and 1.87–2.17 (m, 7, cyclopropyl and cyclopropylcarbinyl). (Found: C, 60.02; H, 4.88; N, 10.41. Calc. for $C_{20}H_{19}N_3O_4S$: C, 60.44; H, 4.82; N, 10.57%).

1,2,4,5,6a,6b,7b,7c - *Octahydrocyclopropa*[3,4]*pentaleno* [1,6-de]*thiocin* 3,3 - *dioxide* (**20a**) ⇄ 2a,5,6,8,9,9b - *hexahydro* - *pentaleno*[1',6':1,3,2]*cyclopropa*[1,2-d]*thiepin* 7,7 - *dioxide* (**20b**). In a way exactly analogous to the preparation of **13**, the hydrolysis and oxidation of **19** (493 mg, 1.24 mmol) was carried out using 496 mg (12.4 mmol) of powdered NaOH, 50 ml 2-propanol, 1.08 g (12.4 mmol) activated MnO_2 and 50 ml pentane. Because the product was only slightly soluble in pentane, the aqueous soln was shaken with ether (5 × 25 ml) after filtration of the mixture. The combined extracts were washed with water (5 × 25 ml) and dried. Filtration and evaporation (no heat) left a suspension of the product in 2-propanol. Trituration with pentane gave 116 mg (42%) of **20** as a light yellow air sensitive solid, dec >120° (sealed tube); ν_{max}^{KBr} 2950, 2925, 1408, 1398, 1352, 1315, 1275, 1130, 1112, 845, 808, 759, 734, 480 and 445 cm^{-1}; $\lambda_{max}^{isooctane}$ 225 (ϵ 1.9×10^3), 235 (1.5×10^3) and 245 nm (1.3×10^3); ^1H NMR (δ, $CDCl_3$, 100 MHz) 5.19 (d, $J_{3,4} = J_{6,7} = 3.8$ Hz, 2, H_3 and H_7), 4.76 (t, $J_{3,4} = J_{6,7} = 3.8$ Hz, $J_{5,6} = J_{4,5} = 3.5$ Hz, 2, H_4 and H_6), 3.30 (m, 1, H_5), 3.20–3.25 (m, 4, $-CH_2SO_2-$), 3.00 (m, 1, H_1) and 2.75–2.90 and 2.20–2.50 (m, 4, $-CH_2CH_2SO_2-$). Spin decoupling: saturation at δ 5.19 simplified the triplet at 4.76 to a doublet, $J_{4,5} = J_{5,6} = 3.5$ Hz. Double irradiation at 4.76 caused the signal at 5.19 to collapse to a singlet and the multiplet at 3.30 to simplify to a doublet, $J_{1,5} = 3.5$ Hz. The location of H_5 was confirmed by saturation at 3.30 which collapsed the signal at 4.76 to a doublet, $J_{3,4} = J_{6,7} = 3.8$ Hz. H_1 must therefore resonate at 3.00. ^{13}C NMR (ppm, $CDCl_3$) 123.01 (d, C_3 and C_7), 99.92 (d, C_4 and C_6), 89.67 (s, C_2 and C_8), 57.30 (d, C_1 or C_5), 56.11 (t, $-CH_2SO_2-$), 54.12 (d, C_5 or C_1) and 24.49 (t, $-CHCH_2SO_2-$); calc. *m/e* 222.0714, found 222.0718.

Decahydro - N - *phenylcyclopropa*[3',4']*pentaleno*[1',6':1,3,2]*cyclopropa*[1,2-d]*thiepin* - 1,7 - *biimine* - 8,9 - *dicarboximide* 4α - *oxide* (**21**) *and decahydro* - N - *phenylcyclopropa*[3',4']*pentaleno*[1',6':1,3,2]*cyclopropa*[1,2-d]*thiepin* - 1,7 - *biimine* - 8,9 - *dicarboximide* 4β - *oxide* (**22**)

(a) *Oxidation with m-chloroperbenzoic acid.* To a stirred, cold (0°) soln of 365 mg (1.00 mmol) of **17** in 25 ml chloroform was added drop-wise with protection from moisture a soln of 173 mg (1.00 mmol) *m*-chloroperbenzoic acid in 5 ml chloroform. The soln was slowly warmed to room temp. and stirred for an additional 5 hr. Following dilution with 75 ml of chloroform, the

1245, 1220, 1175, 1110, 930, 915, 875, 845, 830, 800, 755, 740, 730, mixture was rinsed with sat $NaHCO_3$ aq, dried, filtered, and evaporated to leave 297 mg (78%) of product. Proton NMR ($CDCl_3$) with the addition of europium shift reagent revealed the presence of two isomers whose bridgehead signals (>CHN<) integrated to an 80:20 ratio. The isomers were separated by preparative thin layer chromatography which required five elutions with 10% acetone–chloroform.

The major isomer (**21**) was recrystallized from chloroform–petroleum ether (65–110°) to give a white solid, m.p. 292.5–293.5° (dec); ν_{max}^{KBr} 1755, 1700, 1495, 1415, 1278, 1258, 1130, 1068, 1027, 1015, 785, 770, 765, 717 and 710 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 7.50 (s, 5, aryl), 4.95 (t, $J = 2.5$ Hz, 2, >CHN<), 3.00 (m, 4, $-CH_2SO_2-$), 2.43 (m, 4, cyclopropylcarbinyl) and 2.08 (m, 4, cyclopropyl). (Found: C, 62.52; H, 5.02; N, 10.91. Calc. for $C_{20}H_{19}N_3O_2S$: C, 62.97; H, 5.02; N, 11.02%).

The minor isomer (**22**) was found to interconvert to **21** upon heating during recrystallization and was therefore not purified further; ν_{max}^{KBr} 1755, 1700, 1500, 1495, 1410, 1125, 1020 and 765 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 7.50 (s, 5, aryl), 4.95 (t, $J = 2.5$ Hz, 2, >CHN<), 2.20–3.60 (m, 6, $-CH_2SO-$ and $-CHCH_2SO-$), 2.05 (m, 4, cyclopropyl) and 1.20–2.00 (m, 2, >CHCH$_2$SO–).

(b) *Oxidation with sodium metaperiodate.* To a soln of 365 mg (1.00 mmol) of **17** in 50 ml of ice-cold MeOH was added dropwise a soln of 213.9 g (1.00 mmol) of sodium metaperiodate in 10 ml water. After the soln had been stirred overnight at ambient temp., solid was filtered off, and the solvent was removed *in vacuo* to yield 330 mg (87%) of product. Utilization of proton NMR with lanthanide shift reagent revealed the presence of two isomers, as before, in an 80:20 ratio.

Thermal interconversion of sulfoxides **21** *and* **22.** A soln of carefully recrystallized (dichloromethane–acetone–petroleum ether and low heat) sulfoxide **22** in $CDCl_3$–tms contained in a sealed NMR tube was heated in a constant temp. bath at 70.0° and was periodically monitored. Interconversion was immediately apparent. After 2 hr, the thermodynamic equilibrium ratio was nearly established. There was no apparent change in the appearance of the spectra after 6 hr and at this time the spectrum had an appearance nearly identical to those of the crude reaction mixtures from oxidation of sulfide **17**.

Recrystallization of isomerically pure **22** from chloroform, acetone, or ethyl acetate also affected the interconversion.

Chemical epimerization of sulfoxide **21.** To a solution of **21** (190 mg, 0.5 mmol) in 10 ml dichloromethane under argon was added 64.4 mg (0.5 mmol) trimethyloxonium fluoroborate. The Meerwein's reagent gradually dissolved and after 30 min a white, flocculent ppt appeared. Filtration gave 200.5 mg of white solid; ν_{max}^{KBr} 1755, 1700, 1490, 1420, 1410, 1275, 1120, 1075, 1020 and 780 cm^{-1}. The solid was suspended in 30 ml water and 5.5 ml of 0.1 N NaOH was added to cause complete soln. This soln became cloudy with the appearance of a white ppt. After stirring for 30 min, the mixture was extracted with dichloromethane (4 × 10 ml) and the combined organic extracts were rinsed with water (10 ml) and brine (10 ml), dried, filtered, and evaporated to afford 176.2 mg (92.7%) of **22** identical to the minor product from the oxidation of **17**.

1,2,4,5,6a,6b,7b,7c - *Octahydrocyclopropa*[3,4]*pentaleno* [1,6-de]*thiocin* 3*α* - *oxide* (**23a**) ⇄ 2a,5,6,8,9,9b - *hexahydro* - *pentaleno*[1′,6′:1,3,2]*cyclopropa*[1,2-d]*thiepin* 7*α* - *oxide* (**23b**). A mechanically stirred mixture of 494 mg (1.30 mmol) of **21**, 730 mg (13.0 mmol) powdered KOH, and 30 ml 2-propanol was heated at reflux for 45 min under argon in a 250 ml 3-necked round bottom flask fitted with a septum covered gas inlet with stopcock and a condenser topped with a gas inlet.[35] The dark soln was cooled to 0°, acidified (pH 6) with 50% aqueous AcOH, stirred for 10 min, basified (pH 9) with 50% NH_4OH aq, and diluted with 50 ml of ether. Activated MnO_2 (1.13 g, 13.0 mmol) was added in one portion and the chocolate colored suspension was stirred under argon for 9 hr. The mixture was filtered through Celite and the aqueous phase was extracted with ether (3 × 25 ml). The combined ethereal solns were rinsed with water (5 × 25 ml), dried over Na_2SO_4, filtered, and evaporated to dryness. Recrystallization from ether–petroleum ether (65–110°) gave 43 mg (16%) of **23a** as a tan solid, m.p. > 120° (dec, sealed tube); ν_{max}^{KBr} 2950, 1695, 1450, 1395, 1340, 1315, 1280, 1260, 1110, 1040, 1015, 795, 750 and 740 cm^{-1}; ^1H NMR (δ, $CDCl_3$, 100 MHz) 5.22 (dd, $J_{4,5} = J_{5,6} = 7.5$ Hz, $J_{3,4} = J_{6,7} = 4.5$ Hz, 2, H_4 and H_6), 5.18 (d, $J_{3,4} = J_{6,7} = 4.5$ Hz, 2, H_3 and H_7), 2.75–3.40 (m, 6, $-CH_2SO-$, H_1 and H_5) and 2.45–2.75 (m, 4, $-CH_2CH_2SO-$). Spin decoupling: saturation at δ 5.22 simplified the multiplet at 2.75–3.40, thus confirming the location of H_5. ^{13}C NMR (ppm, $CDCl_3$) 124.09 (d, C_3 and C_7), 118.59 (d, C_4 and C_6), 72.40 (s, C_2 and C_8), 61.24 (d, C_5 or C_1), 54.60 (d, C_1 or C_5), 49.10 (t, $-CH_2SO-$) and 19.20 (t, $-CH_2CH_2SO-$); calc. *m/e* 206.0765, found 206.0768.

1,2,4,5,6a,6b,7b,7c - *Octahydrocyclopropa*[3,4]*pentaleno* [1,6-de]*thiocin* 3*β* - *oxide* (**24a**) ⇄ 2a,5,6,8,9,9b - *hexahydro* - *pentaleno*[1′,6′:1,3,2]*cyclopropa*[1,2-d]*thiepin* 7*β* - *oxide* (**24b**). A suspension of 657 mg (1.72 mmol) of a mixture of **21** and **22** (*ca* 1:1) and 1.93 mg (34.4 mmol) of powdered KOH in 50 ml 2-propanol was mechanically stirred and heated at reflux under argon for 40 min in a 250 ml 3-necked round bottom flask fitted with a septum covered gas inlet with stopcock and a condenser topped with a gas inlet.[35] The dark mixture was cooled to 0°, acidified (pH 6) with 50% aqueous AcOH, stirred 10 min, basified (pH 9) with 50% NH_4OH, diluted with 100 ml ether. To the clear, brown soln was added, in one portion, 1.49 g (17.2 mmol) of Attenburrow MnO_2. The coffee colored mixture was stirred under argon at ambient temp. for 12 hr, then filtered through Celite to give a clear, yellow soln. Water was added (200 ml) and the layers were separated. The aqueous phase was washed with ether (5 × 30 ml) and the combined ether extracts were washed with water (5 × 30 ml). The soln was dried over Na_2SO_4, filtered, and evaporated to give a brown oil which contained some product. Extraction of the aqueous solns with dichloromethane (5 × 30 ml) and similar processing of the extracts provided additional product as a tan solid. The crude **24** was dissolved in a minimum volume of dichloromethane and triturated with ether to give 30 mg of brown impurities. Recrystallization of the mother liquor from dichloromethane–petroleum ether (65–110°) provided 127 mg (36%) of **24** as a tan solid, m.p. > 170° (dec, sealed tube); ν_{max}^{KBr} 3030, 2920, 1430, 1335, 1020, 925, 820 and 730 cm^{-1}; ^1H NMR (δ, $CDCl_3$, 100 MHz) 5.20 (d, $J_{3,4} = J_{6,7} = 3.5$ Hz, 2, H_3 and H_7), 4.85 (t, $J_{3,4} = J_{6,7} = 3.5$ Hz, 2, H_4 and H_6), 2.4–4.0 (m, 8, H_1, H_5, $-CH_2SO-$ and $-CHCH_2SO-$) and 1.50–2.20 (m, 2, $-CHCH_2SO-$); ^{13}C NMR (ppm, $CDCl_3$) 122.47 (d, C_3 and C_7), 97.93 (d, C_4 and C_6), 90.86 (s, C_2 and C_8), 57.24 (d, C_5 or C_1), 53.36 (d, C_1 or C_5), 51.47 (t, $-CH_2SO-$) and 20.39 (t, $-CH_2CH_2SO-$); calc. *m/e* 206.0765, found 206.0768.

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