complexes with elastase, i.e., productive ones able to transform into irreversibly inhibited enzyme and nonproductive ones unable to undergo further reaction. This explains unambiguously why the TFA-peptide-CMK possess higher affinities and lower rate constants than the corresponding acetyl-peptide-CMK (Table I).

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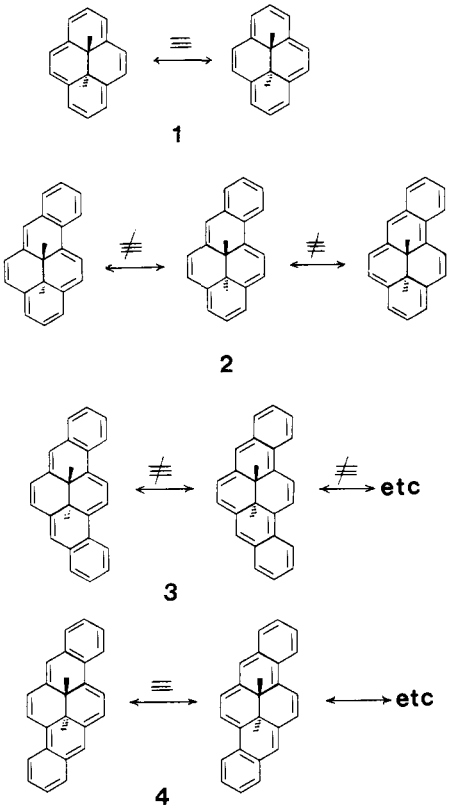
A Clear Demonstration of Importance of Symmetrical Kekulé Structures to Diatropicity (Aromaticity). Synthesis of a Stable, Highly Diatropic, Dibenzannulene[1]

Sir:

Although the concept of aromaticity is often introduced by consideration of the two identical Kekulé structures of benzene, when the aromaticity of larger annulenes is discussed (usually by comparison of diatropicities), such structures are normally neglected. We present here a clear experimental demonstration that, all other things being equal, the equivalence of Kekulé structures can have a profound effect on the diatropicity of an annulene. Nakagawa[2] has obtained results in the [18]annulene series which in our opinion also support the hypothesis, even though he suggests that his more recent[3] results throw doubt on his initial conclusions. This may be, however, because he is not comparing geometrically equivalent systems, or because of the inclusion of cumulated bonds. We believe that Boekelheide's[4] *trans*-15,16-dimethyldihydropyrene[5] (**1**) with its planar,[6] rigid [4n + 2] π-electron periphery, and easily discernable, highly shielded (δ −4.25) internal methyl protons is an excellent system to study to detect any such effect.

We thus now report the synthesis and properties of the mono- and bisbenzannelated derivatives of **1**, namely **2**, **3**, and **4**.



Reaction of 1,3-bis(bromomethyl)-2-methylnaphthalene,[7a,8] respectively, with 2,6-bis(mercaptomethyl)toluene[7b] and 1,3-bis(mercaptomethyl)-2-methylnaphthalene[8] (mp 88–89 °C prepared by the thiourea method[7b]) under high dilution conditions yielded the thiacyclophanes **5** (mp 188–190 °C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 8.3–7.0 (m, 8 H, ArH), 4.16, 4.13, 3.75, 3.70, 3.40, 3.35 (all s, 1 H, 1 H, 2 H, 2 H, 1 H, 1 H, $-CH_2-$), 1.42 (s, 3 H, -Np-CH_3), and 0.92 (s, 3 H, -PhC**H**$_3$))

Table I

Compd	Color of crystals	Mp, °C	NMR spectra: External H, δ	External C, ppm	Internal bridge C, ppm	Internal methyl H, δ	Internal methyl C, ppm
1[a]	Green		8.7–8.1	137–123	30.0	−4.25[b]	14.0
2	Orange-purple	115–116	8.7–7.1	139–117	35.5, 36.0	−1.60[b]	17.0, 17.7
3	Green	218–220	8.2–6.9	139–117	39.5	0.02[b]	19.2
4	Blue	195–196.5	9.8–7.8	137–124	32.8	−3.58[c]	15.9[d]

[a] R. DuVernet and V. Boekelheide, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 2961 (1974). [b] $CDCl_3$. [c] THF-d_8. [d] Tentative; this peak is very weak, possibly owing to relaxation time difficulties. The ^{1}H NMR spectra were recorded on a Perkin-Elmer R32 90-MHz spectrometer and ^{13}C NMR spectra in $CDCl_3$ on a Nicolet TT-14 60-MHz Fourier transform spectrometer, the chemical shifts being given in parts per million downfield from Me_4Si.

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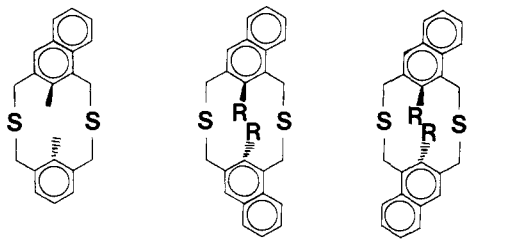

5 6a R=CH_3 b R=H 7a R=CH_3 b R=H

and a mixture of **6a** (mp 290–292 °C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 8.4–7.3 (m, 10 H, ArH), 4.5–3.4 (m, 8 H, $-CH_2-$), and 1.0 (s, 6 H, $-CH_3$)) and **7a** (mp 296–298 °C; ^{1}H NMR δ 8.4–7.3 (m, 10 H, ArH), 4.25 and 3.6 (AB q, 4 H each, $-CH_2-$)and 1.1 (s, 6 H, $-CH_3$)), respectively. These assignments could be unambiguously made by comparison with spectra obtained for the analogous compounds with internal hydrogens **6b** and **7b** which at the end of the sequence described below gave known dibenzopyrenes. In each case the cyclization also yielded some *syn*-methyl isomers (readily distinguishable by their ^{1}H NMR spectra since the internal methyl protons appear at δ 2.6). Separation was achieved by fractional crystallization and chromatography on silica gel.

When the *anti*-cyclophanes were subjected to a Wittig rearrangement–Hofmann elimination sequence,[9] the highly colored dihydropyrenes **2–4** were obtained directly, in 50–80% yields; no trace of the photoisomers were present. The physical properties and ^{1}H and ^{13}C NMR spectra are listed in Table I. All three compounds appear to be stable in the solid state; however, chlorocarbon solutions decompose fairly rapidly (**3** > **4** > **2**) even at −20 °C in the dark.

The magnetic resonance data are astoundingly clear and support the hypothesis that equivalent Kekulé structures lead to stronger diatropism. Simple ring-current theory[10] would predict similar shieldings for the internal methyl protons of **1–4** based on the peripheral current. In practice, however,[11] benzannelation of conjugated macrocyclic systems (with the exception[2] noted above) has always led to a marked reduction in diatropicity of the large ring. Clearly, for compounds **2** and **3**, which do not possess equivalent Kekulé structures, this is true here, where both the internal methyl protons and internal carbons become progressively less shielded in the series **1** → **2** → **3**. Compound **4**, however, which has two sets of equivalent Kekulé structures, shows almost the full ring current expected, with both the internal methyls and bridge carbons almost as shielded as in **1**, and is probably better considered a macrocyclic annulene than a bisbenzannelated dihydropyrene. This in our view clearly shows the importance of Kekulé structures to macrocyclic systems. Recently several theoretical papers have appeared[12] on the use of Kekulé structures. It will be interesting to see if the theoreticians can concur with our results.[13]

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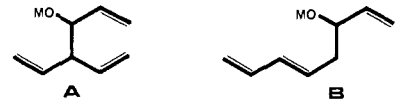
Deep-Seated Rearrangement in the Anionic Oxy-Cope System. Extremely Facile Epimerically Unfavorable Anionic Oxy-Cope Rearrangement of Anti-Bisallylic 1,5,7-Triene Alkoxides[1]

Sir:

In recent years, much attention has been focused on sigmatropic rearrangements[2,4] of anionic oxy-Cope systems which represent substantial improvements in rate and yield relative to the neutral counterparts.[2,4,5] Nevertheless, there still remain some ambiguities concerning the mechanism and the versatility. We wish to report here [1,3]-, [1,5]- and [3,3]-sigmatropic rearrangements of 1,5,5′-[6] and *anti*-bisallylic 1,5,7-triene alkoxides (A and B) incorporated within tricyclic homotropilidenes **2** and **3**, respectively. These observations



A B

would provide not only the wider versatility of an anionic oxy-Cope process but also some insight into the mechanism of formally induced [1,3]-sigmatropic rearrangements in the oxy-Cope related systems.[7] One of intriguing features is the first example of the epimerically unfavorable anionic oxy-Cope rearrangement[8] of **3** which represents sharp contrast to thermal behavior of anti-bisallylic 1,5-diene alkoxides of 2-*exo*-vinyl-2-*endo*-hydroxybicyclo[2.2.2]oct-5-ene (**1**)[2] which is reported not to undergo any sigmatropic rearrangement even after heating at 66 °C for 24 h.

When the vinylcarbinol **2** (M = H, mp 44 °C)[9] was heated with NaH in refluxing tetrahydrofuran (THF), **2** disappeared completely within 3 h with a half-life of 2280 s at 66 °C and, upon quenching with water, 4-hydroxytricyclo[5.3.2.$0^{4,8}$]-dodeca-2,9,11-triene (**7**, mp 77 °C) was obtained quantitatively as the sole product (Scheme I). The structure of **7** was established by the spectral characteristics[11] and chemical evidence that symmetrical hydrocarbons (**9** and **10**)[12,14] were derived from **8**. The potassium alkoxide **2b** (M = K), on the

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