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THE FLUCTIONAL BEHAVIOR OF 9-HETEROBARBARALANES

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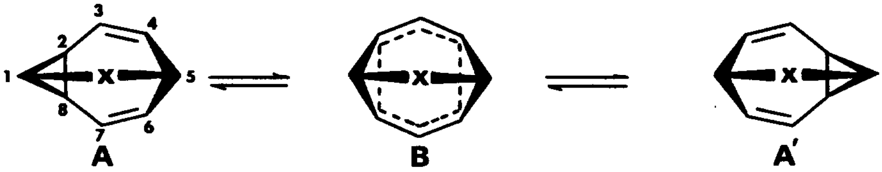
The six-electron transition state controlling the fluxional behavior of bridged homotropilidines (1), renders these substances suitable for the study of a novel type of nonclassical "aromaticity", i.e., one materializing as a result of rapid molecular flux. And while this intriguing possibility has yet to materialize in the laboratory, recent theoretical examination of the problem by EH[2] or MINDO/$_2$[3] calculation has revealed that the desired inequality, E(B)<E(A) or E(A'), might well be realizable with a properly perturbed semibullvalene (1e), specifically one whose electron density is reduced at the potentially "aromatic" C_6 segment and enhanced at the bridgeheads, i.e., C(1) and C(5).



1a; X=NH
b; X=NCN
c; X=S
d; X=SO_2
e; X= —
f; X=CH_2
g; X=C=O
h; X=$\overset{+}{C}$–OH
i; X=CH=CH
j; X=CH_2-CH_2

The recent synthesis of the 9-thia[4]- and 9-azabarbaralane[5] frames in these laboratories coupled with our active interest in the concept of heteroaromaticity[6] prompted us to examine the possible influence that heteroatomic bridging might have on the rate of homotropilidine interconversion, i.e., $A \rightleftharpoons A'$. To this end, we studied azabarbaralanes 1a[7] and 1b[5] and thiabarbaralanes 1c[4] and 1d[8] by variable-temperature (vt) pmr spectroscopy and are now in position to describe and rationalize our findings along these lines.

Pertinent activation constants for the "Cope" interconversion (A $\rightleftarrows$ A') of 9-heterobarbaralanes 1a-1d are given in the Table.[9] It is noted that the thia analogs 1c and 1d are associated with $\Delta G^{\dagger}(T_c)$ terms which are invariably 2-2.5 kcal./mol. higher than those of their aza counterparts and, further, that the rate of flux remains essentially invariant within each bridge group despite of major variations in lone-pair availability, (effective electronegativity) on passing from NH to NCN and from S to SO_2. The rate of the A to A' interconversion is thus seen not to respond to the electronic demands imposed by the bridging heteroatom but rather to its size. In other words, the heteroatom in each 1a-1d appears to operate in the capacity of a relatively inert bridging unit whose size is reflected primarily in the separation between C(1) and C(5), estimated ("Dreiding" molecular models) at 2.50 Å in 1a and 1b and 2.75-2.80 Å in 1c and 1d.

Table.[9] Activation Constants for Homotropilidine Interconversion in Heterobarbaralanes 1a, 1b, 1c, and 1d.

Bridge(X)	T_c [a]	$\Delta G^{\dagger}(T_c)$ [b]	log A	E_a [b]	$\Delta H^{\dagger}$ [b]	$\Delta S^{\dagger b}$
NH	-110 ± 5°	7.2 ± 0.2				
NCN	-110 ± 5°	7.2 ± 0.2	13.9 ± 0.6	8.6 ± 1.3	8.2 ± 1.3	+6
S	- 60 ± 5°	9.7 ± 0.3	13.1 ± 0.4	9.7 ± 0.6	10.3 ± 0.7	+3
SO_2	- 55 ± 5°	9.5 ± 0.3	12.5 ± 0.4	8.9 ± 0.6	9.4 ± 0.6	~0

(a) °C, (b) kcal./mol., (c) eu

Interestingly, the situation encountered here with the heterobarbaralanes, *i.e.,* the inverse relationship between rate of A to A' interconversion and C(1)-C(5) separation, parallels that noted previously[10,11] for the hydrocarbon analogs where the rate of molecular flux increases in the order 1i<1f<1e. In fact, it is significant to note that by combining the information collected on certain representative members of both types of bridged homotropilidine one finds good linear correlation between $\Delta H^{\dagger}$[12] and r[C(1)-C(5)]. This is depicted in Figure 1[13] and serves, we believe, as a strong indication that the crucial energy difference between ground state (A or A') and activated complex (B) in a 1,5-bridged (unsubstituted) homotropilidine is chiefly a function of the C(1) to C(5) internuclear separation, showing little if any dependence on the electronic demands of the bridging unit. Moreover, judging from the fact that barbaralone[14] (1g; $\Delta H^{\dagger}$ = 9.6 kcal./mol.)[14a] shows the greatest deviation (*ca.* 8%) from the plot of Figure 1, and to the extent that the activation barrier of its protonated form has been correctly estimated to be in excess of 13.8 kcal./mol.,[14a] we must conclude that the bridging unit will exert maximal influence on the rate of the "Cope" process when endowed with strong π-acceptor character. Possibly, the validity of the observed linear correlation is most convincingly demonstrated by its correct reproduction (within ca. 5%!) of the experimental $\Delta H^{\dagger}$(4.8 kcal./mol.)[16] for the "Cope" process in semibullvalene (1e), in spite of the major concentration of data points in an entirely different region of r[C(1)-C(5)], i.e., 2.5-3.0 Å. Note also, that at $\Delta H^{\dagger} = 0$, i.e., the energy turning point between classical [E(A)<E(B)] and "aromatic" [E(B)<E(A)] character, the line intercepts the abscissa at the unrealistically short distance of 0.32 Å, a fact which serves to further stress the physical impossibility of attaining "σ→π-aromaticity" with an unperturbed bridged homotropilidine.

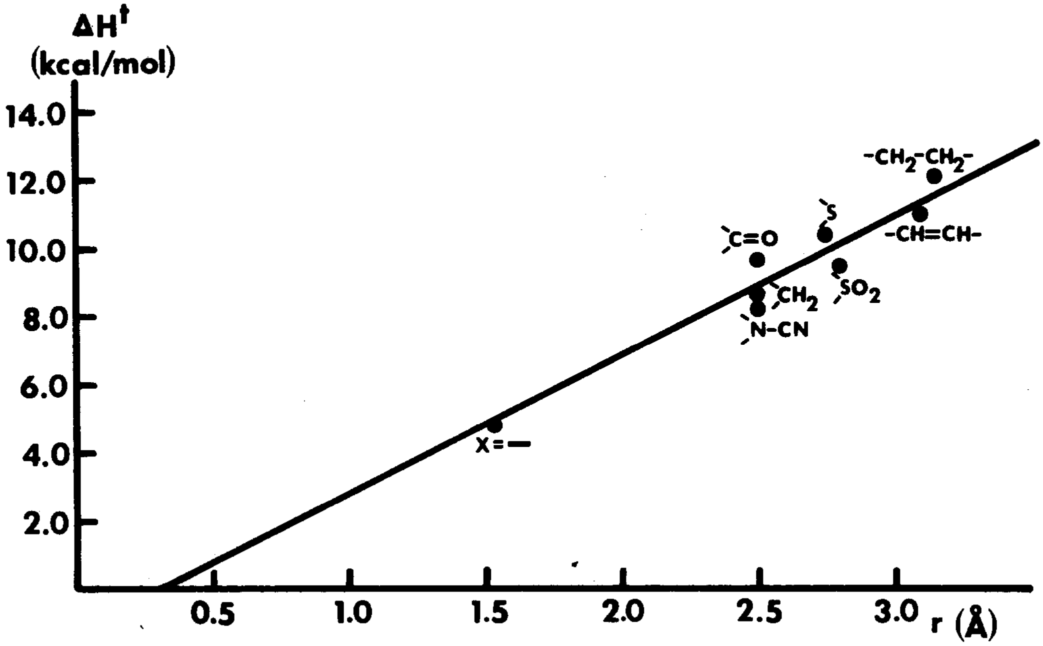


Figure 1[13] Plot of experimentally determined $\Delta H^{\dagger}$ values (•) for the degenerate rearrangement of bridged homotropilidines (1), vs. C(1)-C(5) internuclear separation.

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(7) The preparation and properties of this substance will be described in a later report.

(8) We are grateful to Professor L. A. Paquette for supplying us with the detailed procedure employed in the preparation of 9-thiabarbaralane dioxide 1d; L. A. Paquette, U. Jacobson and M. Oku, Chem. Commun., in press.

(9) All nmr determinations were made at 100 MHz and temperatures ranging from -140°C to ambient. In each case a ca. 4% solution of substrate in 1:1 (v/v) $CD_2C\ell_2$/THF-d_8 was employed. $\Delta F^{\ddagger}(T_c)$ was calculated from knowledge of the coalescence temperature and the temperature-invariant maximum separation between $H_2(H_8)$ and $H_4(H_6)$ at the lowest attainable temperature (ca. -140°). The remaining activation constants were obtained from a line-shape analysis above T_c; complications arising from overlapping resonances precluded the analysis of 9-azabarbaralane (1a) by this method.

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(12) Our choice of $\Delta H^{\ddagger}$ instead of $\Delta F^{\ddagger}$ or the rate, as the activation constant in this correlation was dictated by the need to correct for any random variations introduced by $\Delta S^{\ddagger}$ terms which while far from insignificant (values of +11.0 eu for 1i, and +11.5 eu for 1f have been recorded)[10], are for the most part not directly pertinent to the condition of flux (entropy changes should be close to zero in degenerate "Cope" rearrangements; see footnote 7 in reference 11) but are rather reflective of the changed mobility imparted to the non-participating bridge on passing from A (or A') to B.

(13) C(1)-C(5) internuclear distances were measured from "Dreiding" molecular models while the corresponding $\Delta H^{\ddagger}$ values were obtained, either directly or by calculation, from the following sources: 1i and 1j (ref. 10), 1f (ref. 15), 1g (ref. 14a), 1b, 1c, 1d (this work) and 1e (ref. 16).

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