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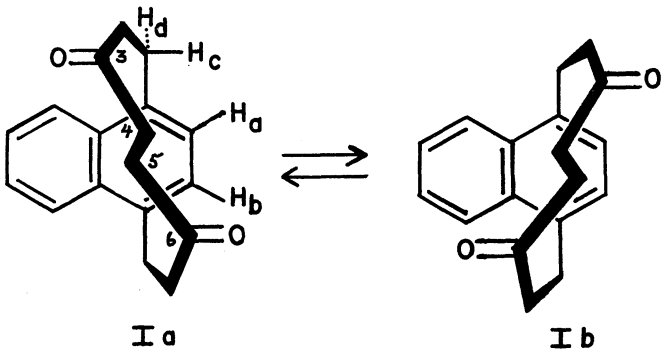
CYCLOPHANES VI. TEMPERATURE DEPENDENT CONFORMATIONS OF 3,6-DIKETO[8]-(1,4)NAPHTHALENEOPHANE AND 3,6-DIKETO[8](2,5)FURANOPHANE [1]

James F. Haley, Jr. and Philip M. Keehn*
Department of Chemistry, Brandeis University, Waltham, MA 02154 U.S.A.

A temperature dependent conformational change in the aliphatic chain of 3,6-diketo[8]naphthalenophane is observed by variable temperature nuclear magnetic resonance spectroscopy; the energy of activation for the process is 9.4 ± 0.2 Kcal/mole. For 3,6-diketo[8](2,5)-furanophane the conformational change of the chain is more facile than that of the ring with a conservative upper limit for ring rotation of about 9.1 Kcal/mole.

Recent conformational studies on cyclophanes has centered on the rotational behavior of the aromatic moieties within the cyclophane macrocycle.[2] Little work has been carried out on the conformational mobility of the aliphatic chain in [n]cyclophanes.[3] We have studied the dynamic behavior of 3,6-diketo[8](1,4)naphthalenophane (I)[1a] by variable temperature nmr spectroscopy and have observed a conformational change in the aliphatic chain which is temperature dependent (see Figure I).

The aromatic portion[4] of the nmr spectrum of naphthalenophane (I) is recorded in Figure II at various temperatures. Of significance for this study is the singlet observed at 7.17 δ in the -40° spectrum (also observed at room temperature). This absorption is due to the a and b naphthalenoid protons and is indicative of their magnetic equivalence above -40°. There are two conformational changes available to this molecule to magnetically equate these two protons: 1) rotation of the naphthalene ring about an axis passing through the naphthalenoid 1,4-carbons and 2) the flipping of carbons 3,4,5 and 6 of the aliphatic chain as indicated in Figure I. Of the above two processes, the former is excluded by the non-equivalence[4] of the H_c and H_d protons, 3.4 δ, (both at high and



Ia Ib

Figure I

low temp.)[5] and by analogy with 3,6-diketo[8]paracyclophane in which the aromatic ring has previously been shown to be immobile.[3] Thus the equivalence of the a and b protons is due to the rapid interconversion of the aliphatic chain. When the temperature is lowered and the process is retarded, coalescing begins to occur, and beyond -80° two absorptions begin to appear for the now non-equivalent a and b protons, ultimately giving rise to an AB quartet at -105°. Assuming a coalescence temperature (T_c) of -85°, this conformational process corresponds to a rate of flipping of 61.2 sec^{-1} and an activation energy $\Delta G^{\pm}$ of 9.4 ± 0.2 Kcal/mole. This energy barrier is quite similar to the 9.3 Kcal/mole barrier observed by Whitesides[3a] for the analogous conformational change of the aliphatic chain in 3,6-diketo[8]paracyclophane, and indicates that the outer fused portion of the naphthalene ring has a minimal effect on the conformational behavior of the aliphatic bridge.

We have begun a similar variable temperature nmr study on 3,6-diketo[8](2,5)-furanophane(II) (see Figure III) in an attempt to observe the conformational changes of both the aliphatic chain and the less-bulky furan ring. Indeed at room temperature both processes are rapidly occurring as indicated in the nmr spectrum of II at 25° (see Figure IV). The singlet for the furanoid protons (H_a and H_b) at 5.85 δ, the singlet for the H_g and H_h protons on the carbon atoms between the two carbonyls at 2.76 δ and the A_2B_2 pattern for the H_c and H_d furfurylic protons and the H_e and H_f α-carbonyl methylenic protons centered at 2.74 δ, all attest to the simultaneous ring and chain inversions. Lowering the temperature to -95° causes a broadening of the aliphatic absorption[6] but maintains the sharp singlet character of the aromatic absorption. This indicates that the barrier for ring rotation is higher than for the chain flipping process. Since total coalescence did not occur down to -95° we can at present only set an upper limit of ca. 9.1 Kcal/mole[7] for the activation energy for the rotation of the furan ring. The energy barrier for the chain flipping process must be even lower since coalescence of the furanoid protons has not even begun at -95°.[8] This upper limit of 9.1 Kcal/mole is however lower than the 9.4 ± 0.2 Kcal/mole observed for the chain flipping process in I and indicates the greater ease of chain flipping in 3,6-diketo-[8]cyclophanes when a naphthalene or benzene[3] ring is replaced by a furan

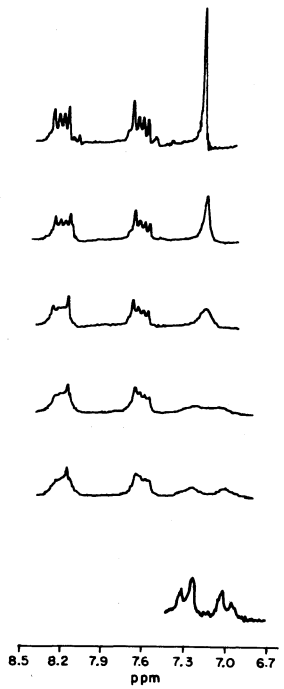
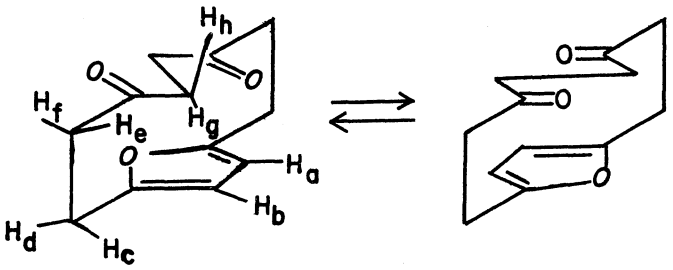


FIGURE II

Figure III



IIa IIb

ring.

A more detailed analysis of the variable temperature nmr spectra of the deuterated analogues of II as well as the pyrrolo- and thiopheno-3,6-diketo-[8]phanes is in progress.

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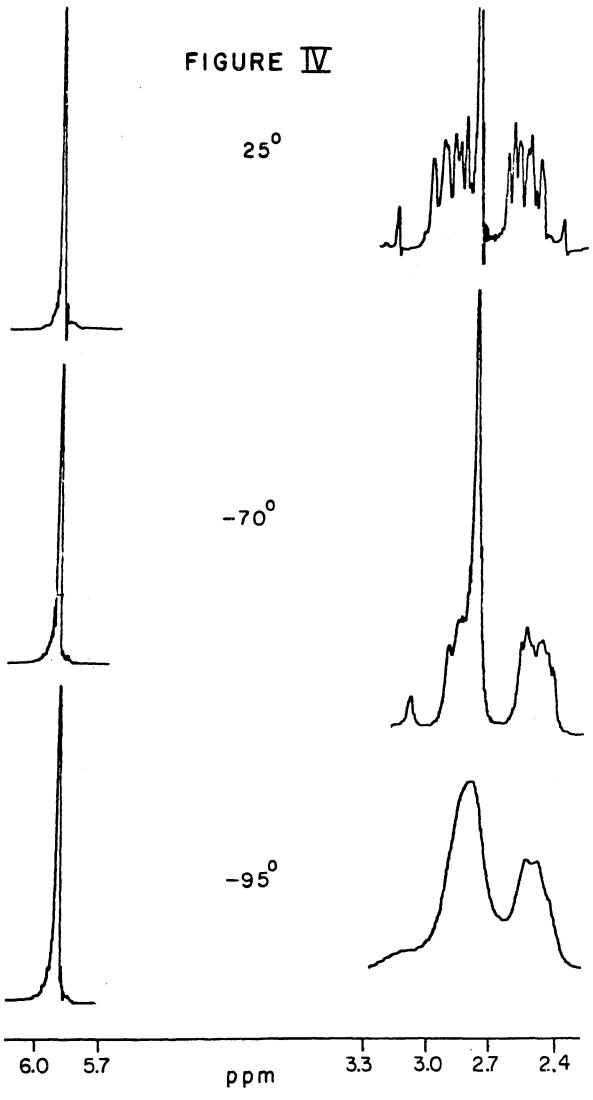
FIGURE IV



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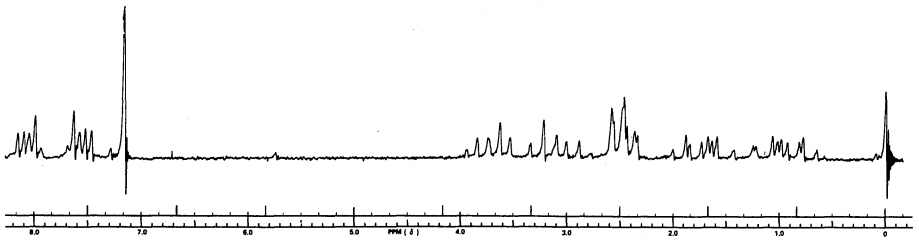
4. The nmr spectrum of I (see reference 1a) ($CDCl_3$) is reproduced below:



5. An analogous non-equivalency for the α-naphthalenoid protons has been observed in [2.2](1,4)naphthalenoparacyclophane. The nmr spectrum is invariant in the temperature range of 25°-200° indicative of the non-mobility of the naphthalene ring; albeit in a more strained system. See H. H. Wasserman and P. M. Keehn, J. Amer. Chem. Soc., 94, 298 (1972).
6. Octadeuterio II (in which positions e,f,g and h are deuterated) exhibits a deuterium broadened singlet (width at half-height, 3 Hz) at 2.9 δ for the H_c and H_d protons in its ambient temperature nmr spectrum. Low temperature nmr spectra of this deuterated compound shows this singlet to be broadened at -95° (width at half-height, 11 Hz). This broadening indicates the beginning of the non-equivalence of the c and d protons by the retardation of the ring flipping process.
7. This value was obtained with equations described in reference 2b using -95° as a T_c and an approximate $\Delta\nu$ of 11 Hz, derived from the width at half-height of the broadened singlet in the -95° nmr spectrum of octadeuterated II. Without calibration of the temperature, we have cooled the nmr probe to -105° and still observed no total coalescence of the aliphatic region in either the deuterated or non-deuterated II. If -105° is used as a T_c ($\Delta\nu$ = 42 Hz) then the upper limit is calculated to be ca. 8.1 Kcal/mole.
8. At -105° (see reference 7) the furanoid protons still exhibit a sharp single absorption.

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