

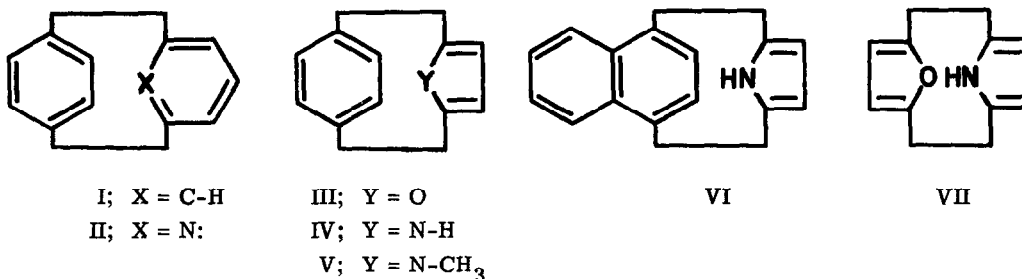
CYCLOPHANES II. CONFORMATIONAL MOBILITY IN [2. 2] (2, 5)PYRROLOPHANES

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(Received in USA 3 August 1973; received in UK for publication 3 September 1973)

Variable Temperature Nuclear Magnetic Resonance (VTNMR) has proven useful in the determination of energy barriers for meta-bridged ring inversion in [2. 2] cyclophanes containing both meta- and para-bridged nuclei. For example, [2. 2] metaparacyclophane (I) exhibits a coalescence temperature (T_c) of 157°C, $E_{act} = 20$ Kcal/mol,^{1, 2, 3} for the coalescence of the AA'XX' pattern of the protons on the para-bridged ring, while [2. 2] (2, 5) furanoparacyclophane (III) undergoes much more facile ring inversion yielding coalescence of the AA'XX' pattern of the analogous set of protons at ca. -40°C, $E_{act} = 11.1$ Kcal/mol.⁵ The lower activation energy is presumably due to the smaller steric bulk of the atom (oxygen in the case of III) which passes through the cavity. The newest member in this series is



[2. 2] (2, 6)pyridinoparacyclophane (II), which exhibits a $T_c = -50^\circ\text{C}$ ⁶ corresponding to an E_{act} of ca. 11 Kcal/mol.⁷ Although steric size most certainly plays a major role in determining the barrier to rotation, the lack of relevant data makes it difficult to evaluate the importance that other factors⁸ have on this barrier. We now wish to describe the VTNMR behavior of a series of [2. 2] (2, 5)pyrrolophanes reported in the preceding communication⁹ (namely [2. 2] (2, 5)pyrroloparacyclophane (IV), N-methyl[2. 2] (2, 5)pyrroloparacyclophane (V), [2. 2] (2, 5) pyrrolo(1, 4)naphthalenophane (VI) and [2. 2] (2, 5) pyrrolofuranophane (VII) using standard VTNMR methods.¹⁰

The chemical shifts (ambient temperature) for the protons in compounds IV-VII are given in Table I. At room temperature, the protons on the benzene nuclei in both compounds IV and V appear as a well separated AA'XX' multiplet, similar to that observed for III at low temperatures, providing strong evidence for a frozen conformation for both IV and V. Upon raising the sample temperature, IV exhibits a broadening and coalescence ($T_c = 105^\circ\text{C}$) of the multiplets associated with protons a and b (see Table I) until at 190°C a sharp singlet at a point halfway between the original two multiplets is observed. This behavior is completely

	Compound	a	b	c	d	e	f	g	bridge
IV		3.29	2.85	4.55	5.0	-	-	-	7.40*
V		3.88	3.05	4.40	-	-	-	-	7.15* 7.5 (N-CH ₃)
VI		3.50	-	4.50	6.2	1.95	2.36	-	6.25* and 7.50*
VII		-	-	4.05	3.6	-	-	3.95	7.35*

TABLE I. Chemical Shifts (τ) for Protons in IV-VII. * Multiplet center.

in accord with an averaging of the environment of these benzenoid protons by rapid flipping of the heterocyclic nucleus. The above T_c corresponds to E_{act} of ca. 17 Kcal/mol.¹¹ This energy barrier is thus greater than that associated with either II or III but, as might be expected from the size of the N atom and the length of the N-H bond, less than that for I. The protons on the ethylene bridges, which give rise to an ABCD multiplet at ambient temperatures, show a corresponding spectral change and appear as a symmetrical A_2B_2 multiplet at 190°C.

The VTNMR behavior of V was also studied. Its spectrum, however, remained unchanged from ambient temperature to 190°C, indicating a greater energy barrier to inversion. No broadening of the multiplets due to the benzenoid protons was observed up to 190°C suggesting an activation energy in excess of 27 Kcal/mol;^{1, 2, 12} an expectedly high barrier in view of the steric bulk of the methyl group.

A priori, it might be reasoned that VI should exhibit VTNMR behavior similar to that shown by I, II, III, or IV. However, while the barriers to inversion in I-IV are for the most part due to the bulky size of the atoms or group of atoms passing through the cavity during the inversion process, there is an added interaction in VI which can contribute to the energy barrier of inversion in converting the anti- to the syn-conformation (see Fig. 1). Inspection

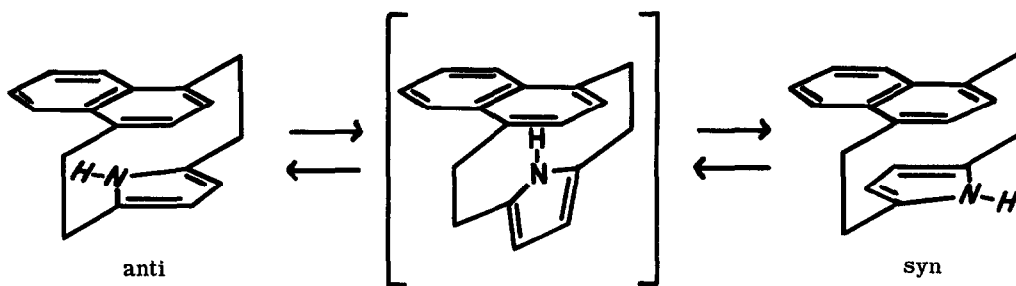


Figure I

of models shows that the syn-conformer is indeed more energetic due to an added trans-annular π - π interaction. The barrier to rotation would, therefore, be somewhat perturbed as compared with that of IV, depending upon the magnitude of this π - π interaction.

It was found that the aromatic region of the NMR spectrum of VI remained unchanged from room temperature to 190°C. Apparently despite the capability of the N-H to pass through an aromatic π cloud (as demonstrated from the VTNMR data on compound IV), the syn-conformer of VI, being relatively energy rich, is not populated to an appreciable extent. Thus, an averaged spectrum, nearly identical with that of the anti-conformation, is obtained. While the above NMR data does not allow for the acquisition of rotational data, it does indicate that other influences,⁸ aside from steric bulk, effect the rotation in these cyclophanes.

We have also carried out studies on the VTNMR behavior of VII from -35°C to 190°C. The number of lines and intensities of the multiplets arising from the bridge protons do change but these changes are not easily interpreted since the multiplet is narrow, making it difficult to observe line broadening. We are presently preparing deuterated analogues of VII in order to simplify the spectra of VII and obtain further information on rotational processes in VII.

In further studies we will be focusing on what other factors influence rotational barriers in [2.2] cyclophanes and on how to approach the problem of obtaining rotational data on conformations which are not energetically equivalent.

Acknowledgement - We wish to acknowledge the partial support of this work from the following institutions: NSF, Grant GU-3852; NIH, Biomedical Sciences Support Grant RR-7044-07; ACS, PRF-2786-G1.

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