Tetrahedron Letters No. 17, pp 1645 - 1646, 1972. Pergamon Press. Printed in Great Britain.

[7](3,5)PYRAZOLOPHANES. RESTRICTED FLIPPING OF THE HEPTAMETHYLENE CHAINS

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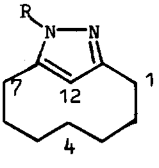
(Received in Japan 29 February 1972; received in UK for publication 14 March 1972)

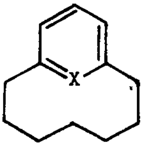
The heptamethylene chain of [7](2,6)pyridinophane (III)[1] or of [7]metacyclophane (IV)[2] is flipping up and down at room temperature. The present communication will describe the rigid conformation of [7](3,5)pyrazolophane (I) and its N-phenyl derivative (II) which are the lowest homologues of [n](3,5)pyrazolophane series ever synthesized.[3,4]

The bromination of cyclodecanone ethylene acetal (V) with Br_2 gave α-bromo derivative (VI, 75%, bp 80°/0.04 mm).[5] The dehydrobromination of VI with t-BuOK in DMSO afforded 2-cyclodecenone ethylene acetal (VII, 58%, bp 100°/5 mm, IR 1629, 1105, 1051 cm^{-1}, M^+ m/e 196),[5] which was hydrolyzed to 2-cyclodecenone (VIII, 80%, IR 3020, 1688, 1629 cm^{-1}, NMR δ 5.4-6.5 (=C-H), M^+ m/e 152)[5] with dil H_2SO_4. Treatment of VIII with $NH_2NH_2 \cdot H_2O$ gave the corresponding pyrazoline (IX, 55%, bp 80°/0.12 mm, IR 3290, 1622 cm^{-1}, M^+ m/e 166).[5] Freshly distilled IX was admixed with powdered S_8 and dehydrogenated at 210° to afford pyrazolophane I (75%, mp 71.5-72.0°, IR (KBr) 3155, 1575, 1450 cm^{-1}, M^+ m/e 164).[5] The heating[6] of VIII with phenylhydrazine afforded X (18%, bp 100-110°/0.18 mm, IR 3290, 1600 cm^{-1}, M^+ m/e 242),[5] which was dehydrogenated with S_8 to give N-phenyl-[7](3,5)pyrazolophane (II, 86%, bp 125-130°/0.08 mm, IR 1598, 1550, 1500, 763, 696 cm^{-1}, M^+ m/e 240).[5]

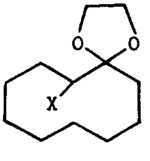
The NMR spectra of I and II shown in Fig 1 raise several points to be noted: (1) Approximately 4 out of 14 protons of the heptamethylene chain are so shielded magnetically as to exhibit the signals at δ 0.5-1.0. This fact is ascribed to a long-range shielding effect by the anisotropy of the pyrazole ring. (2) Particularly, the signal (one proton) of C(4)-H appeared at δ -1.96 for I and δ -1.66 for II. Thus, at room temperature, the heptamethylene bridge appears to be fixed to such an extreme conformer as XI, which is assumed to be most plausible energetically by inspection of the molecular models. In XI, one proton (H_x) on C(4) is forced into the shielding cone of the pyrazole ring. (3) The signals (I: δ -1.96, II: δ -1.66 in hexachlorobutadiene) of the C(4) protons did not coalesced even at 205° (at 60 MHz). The energy barriers ($\Delta G^{\ddagger}_c$) of the



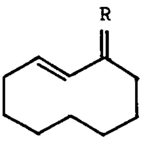
I R = H
II R = Ph

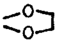


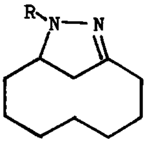
III X = N
IV X = CH



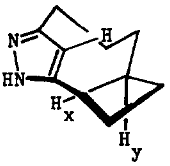
V X = H
VI X = Br



VII R =

VIII R = O



IX R = H
X R = Ph



XI

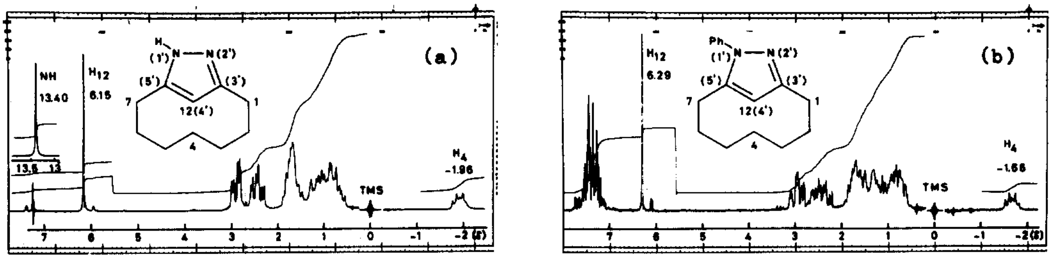


Fig 1. The NMR Spectra of I (a) and II (b) (at 31.5°, 100MHz, in CCl_4, Internal TMS Standard)

flipping were estimated to be $>$ 23 kcal/mole for both I and II. In contrast, the bridges of III and IV have been reported to be flipping even at room temperature.[1,2] The difference among them can be explained by the fact that the bond angle between C(3')-H and C(5')-H of pyrazole is 153°,[7] while the corresponding one of benzene is 120°. (4) The chemical shift of C(12)-H of I is δ 6.15, while [9](3,5)pyrazolophane exhibited the corresponding aromatic signal at δ 5.93.[3] Thus, the deshielding effect due to the steric compression[2] may compensate for the up-field shift to be induced by distortion of the pyrazole ring. (5) The distortion of the pyrazole ring of I was clarified by its UV spectrum (λ_{max}^{EtOH} 222 nm (log ϵ 3.57)). The bathochromic shift and the decrease in absorbance were observed as compared with the higher homologues of [n](3,5)pyrazolophane (n = 9: λ_{max}^{EtOH} 217 nm (log ϵ 3.69),[8] n = 10: 216 nm (3.69)[9]).

REFERENCES AND FOOTNOTES

The NMR spectra were determined in CCl_4 on a Varian HA 100 spectrometer unless otherwise stated.

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