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C-N Bond Atropisomerism of 1-(2,4-Dimethyl-3-pentyl)cyclohepta[*b*]pyrrol-2(1*H*)-one

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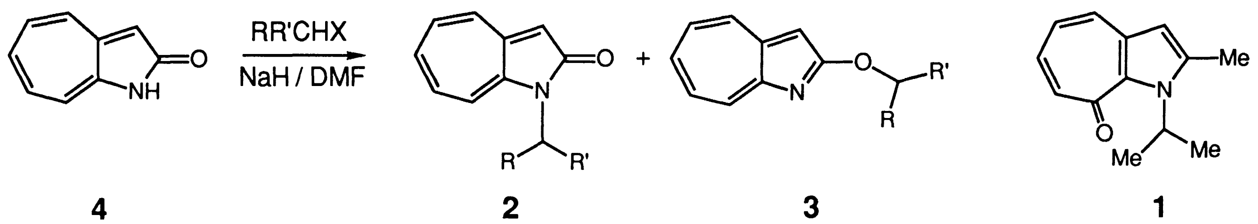
Two rotamers of 1-(2,4-dimethyl-3-pentyl)cyclohepta[*b*]pyrrol-2(1*H*)-one could be isolated by means of the HPLC at 0 °C. Its rotational barrier, measured by the line shape analysis of the low-temperature ^{1}H NMR spectra, was 86.8 kJ/mol at 25 °C in $CDCl_3$.

The isolation of stable rotational isomers, atropisomerism,[1] has been of considerable interest. The recent success with a triptycene derivative by Yamamoto represented the sp^3 C-C bond atropisomerism.[2] Previously, we found a temperature-dependence of the ^{1}H NMR spectrum of 1-isopropyl-2-methylcyclohepta[*b*]pyrrol-8(1*H*)-one (**1**),[3] which prompted us to study conformations of 1-alkylcyclohepta[*b*]pyrrol-2(1*H*)-ones (**2**).[4] A derivative (**2a**) having a bulky 1-(2,4-dimethyl-3-pentyl) group was shown to be atropisomeric around the C-N bond as described.[5]

Compounds (**2**) were prepared together with O-alkylation products (**3**) by the alkylation of cyclohepta[*b*]pyrrol-2(1*H*)-one (**4**).[6] The ^{1}H NMR spectrum of **2a** in $CDCl_3$ at 270 MHz displayed a pair of two doublets for the methyl group, a pair of septets for the methine group, a pair of triplets for the methine group, and a pair of singlets of H-3 in 53:47 at 27 °C. At 150 °C in DMF-d_7, the signals of H-3 became homotropic. These NMR behaviors verified an existence of two conformers **2aA** and **2aB** [δ4.51(t) and δ3.66(t) in $CDCl_3$]. The structures of conformers were deduced from the chemical shifts of these triplet methine signals and proven by the differential NOE experiment. The ^{1}H NMR of **2a** showed a distinct NOE between the peri-hydrogen (H-8) at δ6.96 and the triplet at δ3.66 (of **2aB**), but no such an effect between the signal of H-8 at δ6.97 and the triplet at δ4.51 (of **2aA**). Therefore, the H-8 is facing to the triplet methine proton in conformer **2aB**.



a : R = R' = ^{i}Pr, **b** : R = Ph, R' = ^{i}Pr, **C** : R = R' = Me, **d** : R = R' = Ph

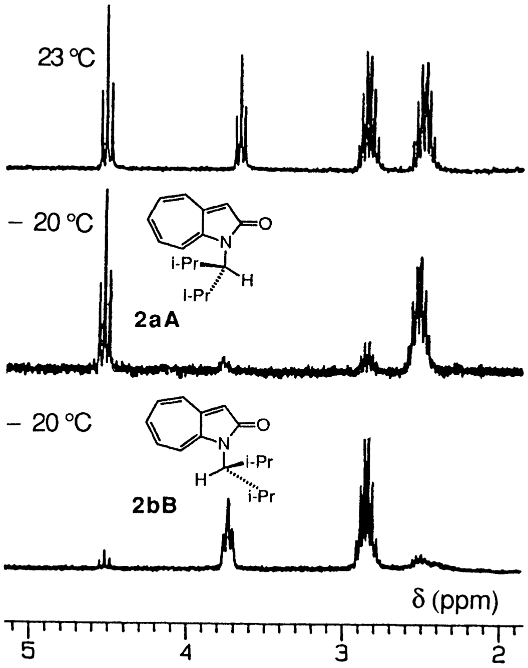
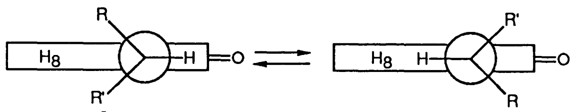


Fig.1. ^{1}H NMR spectrum of **2a** ($CDCl_3$).

Table 1. Rotational barrier

Compounds	$\Delta G^\ddagger$ (at 298 K, kJ/mol)	
2a	86.8	a)
b	51.1	b)
c	44.0	c)
d	——	

a) $\Delta H^\ddagger$ = 74.3 (kJ/mol), $\Delta S^\ddagger$ = -41.9 (J/mol).
b) $\Delta H^\ddagger$ = 45.8 (kJ/mol), $\Delta S^\ddagger$ = -17.7 (J/mol).
c) At coalescence temperature.



Conformers **2aA** and **2aB** could be isolated by means of HPLC at 0 °C and characterized by the ^{1}H NMR spectra (Fig. 1). At room temperature, the ^{1}H NMR spectrum of each conformer changed to that of the original equilibrium mixture **2a**. The line shape analyses of the singlet signal of H-3 estimated the rotational barrier to be 86.8 kJ/mol at 25 °C.

Changing the substituent of **2a** to smaller ones, the rotamers were still detectable but could not be isolated. Thus, the ^{1}H NMR spectrum of 1-(2-methyl-1-phenyl-1-propyl)-cyclohepta[*b*]pyrrol-2(1*H*)-one (**2b**) indicated the presence of two conformers (**2bA** and **2bB**) in 79:21 at −55.4 °C. The line shape analyses of the benzyl methine proton signal estimated the rotational barrier as 51.1 kJ/mol at 25 °C. The rotational barrier of 1-isopropylcyclohepta[*b*]pyrrol-2(1*H*)-one (**2c**) was estimated as 44.0 kJ/mol from the coalescence temperature.[7] Due to the low rotational barrier, the methine proton signal of 1-diphenylmethyl derivative (**2d**) still remained unchanged at −80.5 °C.

Related studies on the C-N atropisomerism of cyclohepta[*b*]pyrrolones are in progress.

References

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2) G. Yamamoto, *Chem. Lett.*, **1990**, 1373.
3) H. Takeshita, A. Chisaka, and H. Mametsuka, *Bull. Chem. Soc. Jpn.*, **53**, 3373 (1980).
4) I. Nilsson, U. Berg, and J. Sandstrom, (*Acta Chem. Scand.*, *Ser. B*, **40**, 625 (1986); *Ser. B*, **38**, 491 (1984)) also observed temperature-dependent ^{1}H NMR spectra of 1-isopropyl- and 1-(1-phenylmethyl)indoles.
5) An example was reported. See V. Dave, J. B. Stothers, and E. W. Warnhoff, *Tetrahedron Lett.*, **1973**, 4229.
6) T. Nozoe, S. Seto, S. Matsumura, and T. Terasawa, *Chem. Ind.*, **1954**, 1356.
7) T_c=-44.9 °C, δ_A-δ_B=184.27 Hz, τ=1.2215x10^{-3}s.

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