2508 © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **55**, *2508—2511 (1982)* [Vol. 55, No. 8

# Restricted Rotation Involving the Tetrahedral Carbon. XLII. Barriers to Rotation and Populations of Rotamers in 9-[2-(Substituted methyl)-1-napthyl]fluorenes[1]

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Rotational barriers in 9-[2-(substituted methyl)-1-naphthyl]fluorenes are found not significantly affected by the substituent on the methyl group, $\Delta G^{\neq}$'s being *ca.* 29 kcal/mol at 373 K. Populations of *sp*- and *ap*-rotamers at equilibriums show that the *sp* form is favored to some extent and the results are attributed to entropy factor. OH···$\pi$ interaction is detected in the *ap* form of 9-(2-hydroxymethyl-1-naphthyl)fluorene.

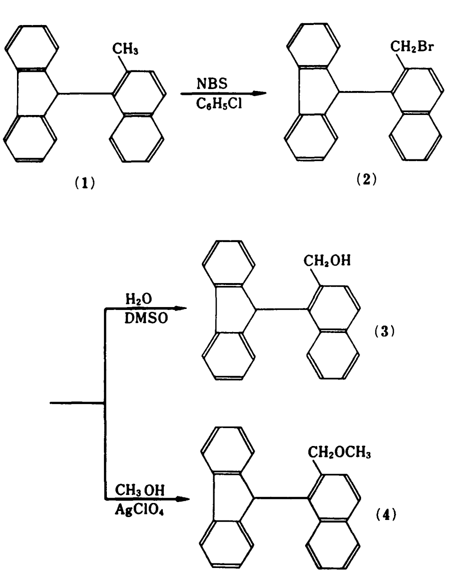
In the classical work of Adams and his collaborators on restricted rotation of biphenyls,[2] it was established that barriers to rotation are determined by the first atom with which substituents in the 2,2′,6,6′-positions are connected to the biphenyl skeleton. The results are understood by assuming that, in the transition state for rotation, atoms which are in a substituent but are not directly connected to the skeleton will avoid further interactions with those in other substituents to minimize the transition state energy.

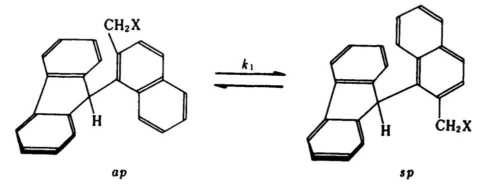
While biphenyls give stable, enantiomeric atropisomers, 9-arylfluorenes give diastereomeric atropisomers.[3] The interactions in the transition state for rotation in diastereomers are expected to be the same with the cases in biphenyls but the populations of diastereomeric atropisomers may be affected by a substituent which is not directly attached to the parent skeleton. Thus this work was undertaken 1) to confirm that the barrier to rotation in 9-arylfluorenes is not affected significantly by a remote substituent and 2) to examine whether the populations of rotamers can be affected by a substituent which is not directly attached to the skeleton.

Syntheses of the compounds examined are straightforward. 9-(2-Methyl-1-naphthyl)fluorene (**1**)[4] was brominated with *N*-bromosuccinimide to give 9-(2-bromomethyl-1-naphthyl)fluorene (**2**) which was hydrolyzed with water in dimethyl sulfoxide to afford 9-(2-hydroxymethyl-1-naphthyl)fluorene (**3**). 9-(2-Methoxymethyl-1-naphthyl)fluorene (**4**) was prepared by substitution reactions of **2** in methanol with the aid of silver perchlorate. *sp*-**4** could be prepared by methanolysis of *sp*-**2** as well.[5]

The rate constants for rotation about the $C_{naph}$–$C_9$ bond obtained at various temperatures are given in Tables 1—3 together with equilibrium constants. Activation parameters calculated from these rate constants are listed in Table 4 together with those of the rotation in **1** for comparison.

The results indicate that the barriers to rotation in compounds **1**—**4** are about the same, thus confirming that a substituent on the methyl group has little effect on the height of the barrier to rotation: the $CH_2$ group determines the barrier to the first approximation in these compounds. Although the hydroxy compound (**3**)





(Designation of stereochemistry is reversed if X=H.)

Table 1. Rate constants of rotation about the $C_9$–$C_{naph}$ bond and equilibrium constants in 9-(2-bromomethyl-1-naphthyl)fluorene (**2**) in hexachlorobutadiene

| Temp/°C | $k_1$/s$^{-1}$ | $K(sp/ap)$ |
|---|---|---|
| 95.1 | $1.53\times10^{-5}$ | 2.78 |
| 106.0 | $4.24\times10^{-5}$ | 2.98 |
| 114.0 | $1.11\times10^{-4}$ | 2.83 |
| 124.0 | $2.62\times10^{-4}$ | 2.76 |

Table 2. Rate constants for rotation about the $C_9$–$C_{naph}$ bond and equilibrium constants in 9-(2-hydroxymethyl-1-naphthyl)fluorene (**3**) in hexachlorobutadiene

| Temp/°C | $k_1$/s$^{-1}$ | $K(sp/ap)$ |
|---|---|---|
| 77.0 | $6.40\times10^{-6}$ | 1.80 |
| 95.0 | $4.37\times10^{-5}$ | 1.73 |
| 104.0 | $1.18\times10^{-4}$ | 1.70 |
| 114.0 | $2.97\times10^{-4}$ | 1.80 |

Table 3. Rate constants for rotation about the $C_9$–$C_{naph}$ bond and equilibrium constants in 9-(2-methoxymethyl)-1-naphthyl)fluorene (**4**) in hexachlorobutadiene

| Temp/°C | $k_1$/s$^{-1}$ | $K(sp/ap)$ |
|---|---|---|
| 77.0 | $4.09\times10^{-6}$ | 2.40 |
| 95.0 | $3.12\times10^{-5}$ | 2.35 |
| 104.0 | $8.47\times10^{-5}$ | 2.33 |
| 114.0 | $2.32\times10^{-4}$ | 2.25 |

Table 4. Activation parameters for rotation about the $C_9$–$C_{naph}$ bond in 9-[2-(substituted methyl)-1-naphthyl]fluorenes

| Compound | Subst. | $\Delta H^{\ddagger}$ / kcal mol$^{-1}$ | $\Delta S^{\ddagger}$ / e.u. | $\Delta G^{\ddagger}_{373}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| **1**[5)] | H | 25.6 | −9.7 | 29.0 |
| **2** | Br | 28.3±0.8 | −4.3±2.0 | 29.9 |
| **3** | OH | 27.4±0.6 | −4.5±1.7 | 29.0 |
| **4** | $OCH_3$ | 28.7±0.1 | −1.5±0.3 | 29.3 |

Table 5. Rate constants for rotation about the $C_9$–$C_{naph}$ bond and equilibrium constants in 9-(2-bromomethyl-1-naphthyl)-fluorene (**2**) in toluene-$d_8$

| Temp/°C | $k_1$/s$^{-1}$ | $K(sp/ap)$ |
|---|---|---|
| 87.3 | $6.74\times10^{-6}$ | 3.13 |
| 96.0 | $1.73\times10^{-5}$ | 3.06 |
| 105 | $4.43\times10^{-5}$ | 3.05 |
| 114 | $1.03\times10^{-4}$ | 2.92 |

Table 6. Infrared O–H stretching spectra of rotameric 9-(2-hydroxymethyl-1-naphthyl)fluorene (**3**)[a)]

| State | | $\nu_{OH}$ Frequencies/cm$^{-1}$ | |
|---|---|---|---|
| | | *sp* | *ap* |
| Solid | | 3320(s) broad | 3570(m) sharp |
| | | | 3450(s) broad |
| Solution | 9.8 mM | 3620(62.4) | 3580(44.4) |
| | | | 3630(33.5) |
| | 0.20 M | 3610(26.8) | 3630(14.4) |
| | | 3320(24.8) | 3580(29.8) |
| | | | 3480(13.3) |

a) Numericals in parentheses are molecular extinction coefficients. Those in parentheses for the solid state are as follows. s: Strong, m: medium.

gives a little low barrier, if we compare the rate constant at a given temperature with that of **4**, the reason for this lowering is not well understood at the moment.

In contrast, we see that the equilibrium constants are appreciably larger than 1.0 which is the value reported for compound **1** in tetrachloroethene.[4)] In hexachlorobutadiene the *sp*/*ap* ratio of **1** becomes 1.14,[6)] which is still close to unity. Therefore the increase in the equilibrium constants on substitution of a substituent for hydrogen of the methyl group is significant. One of the possibilities which favor the *sp* form is the dipolar interaction between the C-substituent bond and the C–Cl in the solvent molecule. We therefore determined the barrier to rotation and the equilibrium constants in compound **2** in toluene-$d_8$. The results shown in Table 5 yield $\Delta H^{\ddagger}$ 27.6±0.2 kcal/mol (1 cal=4.18 J) and $\Delta S^{\ddagger}$ −5.9±0.5 e.u. (1 e.u.=4.18 J mol$^{-1}$ K$^{-1}$) for the *ap*→*sp* process. Thus $\Delta G^{\ddagger}$ at 373 K is 29.8 kcal/mol. Interestingly the equilibrium constants are 3.0 which are not different from those in hexachlorobutadiene. Independence of the population ratios from the solvent nature may mean that the solvation is not an important factor in determining the *sp*/*ap* ratio.

We wish to attribute the large equilibrium constants for compounds **2**—**4**, from the above results, to the entropy effect. If one considers conformations which change by rotation about the $XCH_2$-naphthyl bond, there is a restriction in some of the conformations in the *ap* form. Since X is larger than hydrogen, a conformation in which X is close to the fluorene ring is strongly disfavored due to the steric effect. That kind of steric effect is less severe in the *sp* form. This factor should contribute to decrease in entropy in the *ap* form relative to the *sp* form.

Close examination of the *sp*/*ap* ratios reveals that the *ap* form of the hydroxy compound (**3**) is slightly favored relative to other *ap* forms. One of the possibilities that favor the *ap* conformation in **3** is the presence of OH···π interactions. If the aryl group in 9-arylfluorenes is either 2-hydroxy-1-naphthyl or 2-hydroxy-4,6-dimethylphenyl, strong stabilization of the *ap* form is reported.[7)] Thus infrared $\nu_{OH}$ spectra of these compounds were recorded. The results are shown in Table 6.

Since the frequencies are not calibrated, the absorption at *ca.* 3620 cm$^{-1}$ may be considered to correspond to the benzylic OH···π type band.[8)] We may call this band "free," since its shift is small from the really free band and there is another bonded band in *ap*-**3**. Then the *sp* form shows only a free band in 9.8 mM solution and, in more concentrated solution and in the solid state, it shows a polymeric band. In contrast, the *ap* form shows two $\nu_{OH}$ bands in 9.8 mM solution: the band due to a free form at 3630 cm$^{-1}$ and that due to an OH···π bonded form at 3580 cm$^{-1}$. In 0.2 M solution, the *ap* form is present as free, OH···π bonded, and polymeric forms, whereas in the solid state it is still possible to see a band due to monomeric species. In the sterically hindered alcohols, the monomeric form is often observed even in the condensed phase,[9)] and *ap*-**3** is another example of such a case.

The above results clearly indicate that there is an OH···π interaction in the *ap* form at the concentration (0.2 M) of the NMR measurement. We may attribute the favoredness of *ap*-**3** relative to other *ap*-forms to the OH···π interaction. It is interesting to note that the OH···π interaction is detected even though the OH group and the π-system are separated by 4 carbon atoms. Among 4-phenyl-1-butanol derivatives, even *p*-aminophenylbutanol, which should facilitate the interaction because of the high electron density of the phenyl group, failed to show an OH···π bond.[10)] *o*-(2-Phenylethyl)phenol shows a weak intramolecular OH···π interaction, whereas such an interaction is not detected in *o*-(3-butenyl)phenol:[11] the results are partly attributed to the entropy effect because the π-system in the former distributes widely relative to the latter. The skeleton of *ap*-**3** is fixed except the $HOCH_2$ part. Therefore the presence of the fairly strong intramolecular OH···π interaction in *ap*-**3** can be attributed to the favorable entropy factor. If the conformation of a molecule is fixed favorably, the intramolecular interaction may be found even though the two groups are separated by more than 4 carbons.

We may now compare the effect of a 1-naphthyl group with that of *o*-tolyl on the barrier to rotation, because a pair of compounds both of which carry a bromomethyl group next to the carbon connected to fluorene is available. Activation parameters for rotation in 9-(2-bromomethyl-6-methylphenyl)fluorene in hexachlorobutadiene are as follows for the *ap*→*sp* process: $\Delta H^{\neq}$ 26.3 kcal/mol, $\Delta S^{\neq}$ −9.3 e.u., and $\Delta G^{\neq}_{373}$ 29.8 kcal/mol.[6] Comparing these data with those for **2**, we see that the enthalpy of activation is definitely larger for **2** than for 9-(2-bromomethyl-6-methylphenyl)fluorene, although the free energy for activation at 373 K is the same. This enthalpy difference must be the reflection of the rigidity of the 1-naphthyl group relative to the *o*-tolyl, as suggested before.[6]

## Experimental

*9-(2-Bromomethyl-1-naphthyl)fluorene (2).* A solution of 13.0 g (43 mmol) of a mixture of rotamers of 9-(2-methyl-1-naphthyl)fluorene (**1**)[4] and 18 g (100 mmol) of *N*-bromosuccinimide in 400 mL of chlorobenzene was refluxed for 1 h with stirring. After cooling, succinimide was removed by filtration and chlorobenzene was distilled off *in vacuo*. The residue was chromatographed on silica gel with hexane. *sp*-**1**, *ap*-**1**, *ap*-**2**, and *sp*-**2** were eluted successively. A typical run gave 0.8 g of *ap*-**2** and 3.6 g of *sp*-**2** with 2.7 g of a mixture containing *sp*-**2**, *ap*-**2**, and starting materials.

*ap*-**2**, mp 132—133.5 °C. Found: C, 74.99; H, 4.32; Br, 21.13%. Calcd for $C_{24}H_{17}Br$: C, 74.81; H, 4.45; Br, 20.74%. $^1H$ NMR ($CDCl_3$, δ): 3.56 (2H, s), 6.12 (1H, s), 7.0—8.0 (13H, m), 8.37—8.57 (1H, m).

*sp*-**2**, mp 123—124 °C. Found: C, 75.07; H, 4.29; Br, 21.05%. Calcd for $C_{24}H_{17}Br$: C, 74.81; H, 4.45; Br, 20.74%. $^1H$ NMR ($CDCl_3$, δ): 4.96 (2H, s), 5.81 (1H, s), 6.47 (1H, d, *J*=8.7 Hz), 6.7—8.0 (13H, m).

*9-(2-Hydroxymethyl-1-naphthyl)fluorene (3).* To a solution of 4.0 g of the bromo compound (**2**) in 50 mL of dimethyl sulfoxide, was added 20 mL of water with heating and stirring. The heating and the stirring were continued for 2 h. The mixture was poured into water and the organic material was extracted with ether. The ethereal layer was thoroughly washed with water and dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel with benzene. *ap*-**3** and *sp*-**3**, eluted in this order, were obtained in 0.4 g and 2.0 g yield with 2.0 g of a mixture of rotamers of **3**.

*ap*-**3**, mp 134—135.5 °C. Found: C, 89.18; H, 5.44%. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.63%. $^1H$ NMR ($CDCl_3$, δ): 0.87 (1H, t, *J*=6.0 Hz), 3.55 (2H, d, *J*=6.0 Hz), 6.10 (1H, s), 7.0—8.0 (13H, m), 8.40—8.60 (1H, m).

*sp*-**3**, mp 103—105 °C. Found: C, 89.29; H, 5.52%. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.63%. $^1H$ NMR ($CDCl_3$, δ): 2.07 (1H, t, *J*=6.0 Hz), 5.05 (2H, d, *J*=6.0 Hz), 5.76 (1H, s), 6.45 (1H, d, *J*=9.0 Hz), 6.6—8.0 (13H, m).

*9-(2-Methoxymethyl-1-naphthyl)fluorene (4).* To a solution of 0.30 g (0.78 mmol) of *ap*-**2** in 30 mL of methanol was slowly added 0.16 g (0.77 mmol) of silver perchlorate in 5 mL of methanol. A small amount of chloroform may be used to facilitate dissolution of *ap*-**2** in methanol. After excess of silver perchlorate was decomposed by adding aqueous lithium chloride, the precipitate was removed by filtration and the filtrate was poured into water. The organic material was extracted with ether. The ethereal extract was washed with water and dried over magnesium sulfate. Evaporation of the solvent afforded almost pure *ap*-**4**, oil, in 96% yield. High resolution mass spectrum showed a molecular ion peak at *m*/*e* 336.1544, whereas the calculated mass of the molecule for $C_{25}H_{20}O$ is 336.1514. $^1H$ NMR ($CDCl_3$, δ): 2.53 (3H, s), 3.33 (2H, s), 6.12 (1H, s), 7.1—8.0 (13H, m), 8.43—8.60 (1H, m).

*sp*- **4**, mp 114—115 °C, was prepared similarly in 94% yield. Found: C, 89.22; H, 5.89%. Calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99%. $^1H$ NMR ($CDCl_3$, δ): 3.45 (3H, s), 4.93 (2H, s), 5.82 (1H, s), 6.47 (1H, d, *J*=9.0 Hz), 6.7—8.0 (13H, m).

*sp*-**4** was also prepared by methanolysis of *sp*-**2**. A solution of 0.30 g of *sp*-**2** in 30 mL of methanol was refluxed for 15 h. After evaporation of the solvent, the residue was recrystallizaed from 1 : 5 benzene–hexane to give 0.21 g of *sp*-**4**. A small amount of *ap*-**4** was detected in the reaction mixture before recrystallization. Methanolysis of *ap*-**3** was too slow to be practical.

*Determination of Barriers to Rotation.* A solution was prepared by dissolving 30 mg of the *ap* form of arylfluorenes in 0.4 mL of hexachlobutadiene or toluene-$d_8$ and was placed in an NMR sample tube. The tube was immersed in an appropriate boiling-solvent bath, the temperature of which was directly measured by a thermometer. The rate of isomerization was followed by $^1H$ NMR spectroscopy and was treated assuming a reversible first-order reaction. The rate constants thus obtained were put into the Eyring equation to obtain activation parameters. The following solvents were used for the bath (solvent and approximate boiling points given): benzene (77 °C), 1 : 1 benzene–toluene (87 °C), dioxane (95 °C), toluene (104 °C), 1 : 1 chlorobenzene–toluene (114 °C), chlorobenzene (124 °C).

*Determination of Infrared Spectra.* The spectra were recorded on a Hitachi EPI-G spectrometer. The wave numbers reported are not calibrated. The spectra of solid were obtained as KBr discs. The spectra of solution were obtained with a KBr cell of variable length. With solutions of *ca.* 0.2 M in carbon tetrachloride, the cell length was 0.25 mm and, with those of 9.8 mM, the cell length was 5.0 mm.

$^1H$ NMR spectra were obtained with either a Hitachi R-20B or a Varian EM 390 spectrometer.

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