CHEMISTRY LETTERS, pp. 271-274, 1982.

LOWERING OF THE ROTATIONAL BARRIER ON INTRODUCTION OF A FLUORO GROUP INTO 1-POSITION OF 9-(1-NAPHTHYL)FLUORENE SYSTEMS[1)]

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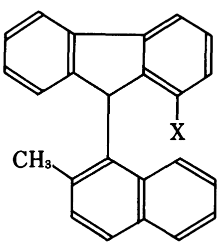
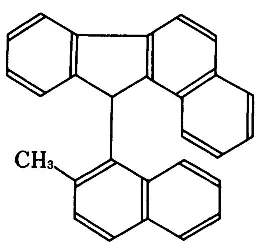
Rotational barriers in 1-fluoro-9-(1-naphthyl)fluorene and 1-fluoro-(2-methyl-1-naphthyl)fluorene were found to be lower by ca. 0.5 kcal/mol than those of their parent hydrocarbons. The results are attributed to raising of the ground state energy due to introduction of the fluoro group.

9-Arylfluorene systems have drawn attention of a number of chemists, because they give rise to a pair of stable rotational isomers if the aryl group is substituted properly.[2)] The rotational barriers are dependent on the substitution pattern on the aryl ring. If an aryl group is given, the rotational barrier is believed to increase on introduction of a substituent into the 1-position of the fluorene ring, because the substituent raises the energy of the transition state for rotation due to its steric effects. Thus Ford et al. showed that the barrier to rotation in 1-methyl-9-(2-methyl-1-naphthyl)fluorene (1a) was 33.3 kcal/mol at 166°C[3)] which was higher than the barrier in 9-(2-methyl-1-naphthyl)fluorene (1b)[4)] by ca. 4 kcal/mol. Kajigaeshi and his coworkers[5)] were able to show that the barrier to rotation in a benzo-annelated derivative (2) of 1b was nearly the same with 1a and were able to isolate even one rotational isomer of the 9-OH derivative of 2 although substitution of a hydroxyl group for a hydrogen in the 9-position of 9-arylfluorene systems had been known to lower the barrier to rotation of the 9-aryl group relative to the 9-H compound.[6)]



1a : X=CH_3
1b : X=H
1c : X=F



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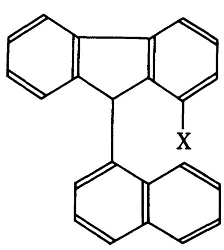


3a : X=H
3b : X=F

During the course of our study on the restricted rotation in 9-arylfluorene systems, we have encountered a curious phenomenon on the ground which is described above. When we compared the rotational barriers, as obtained by the coalescence method of NMR spectroscopy (Table 1), of 9-(1-naphthyl)fluroene (3a) and its 1-fluoro derivative (3b), the barrier was higher in the former, although it lacks the 1-substituent in fluorene, than that in the latter. Since we are dealing with a subtle difference and the reading of the coalescence temperature may involve some errors in the case of unequal populations of the rotamers, we felt that a more reliable technique should be used to clarify whether the fluoro group in the 1-position of the fluorene really lowers the barrier to rotation relative to the compound which lacks the fluoro group.

Table 1 ^{1}H NMR Data and Kinetic Data for Rotation in 9-(1-Naphthyl)fluorenes at Coalescence Temperatures[a)]

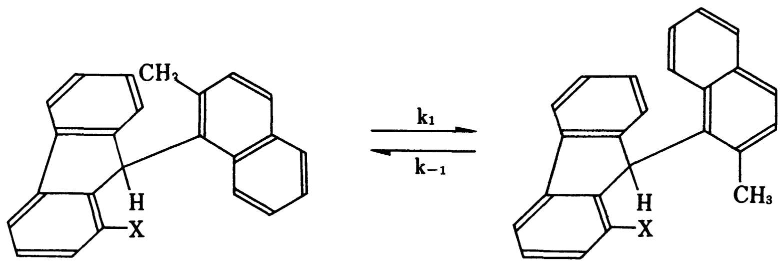
Substituent in 1-Position	$\Delta\delta$ (Hz)[b)]	T_c (°C)	k_c (s^{-1})[c,d)]	$\Delta G_c^{\ddagger}$ (kcal/mol)[d)]	K[e)]
H[f)]	43	96	40	19.0	0.50
F	41	84	34	18.5	0.45

a) Hexachlorobutadiene solvent
b) Chemical shift differences of 9-H's for the respective rotamers at 60 MHz
c) Obtained by the graphical method of Jaeschke et al.[7)]
d) For the process from the more populated to the less populated
e) Equilibrium constants: ap/sp for 3a and ±sc/±ac for 3b at coalescence temperature
f) The barrier to rotation in this compound was determined by two groups of workers.[4,8)] The data reported here are generally in good agreement with those reported.

As a natural choice, 1-fluoro-9-(2-methyl-1-naphthyl)fluorene (1c) was chosen as a compound to determine the barrier because 1b was known to give a pair of stable rotational isomers[4)] and the fluoro derivative (1c) of 1b was predicted to give rise also to a pair of stable rotamers: after isolating the rotamers, re-equilibration should be possible at convenient temperatures and should give more reliable data.

Synthesis of compound 1c was accomplished by the Grignard reaction of 1-fluoro-9-fluorenone, which was prepared by the Schiemann reaction of 1-aminofluorenone,[9)] with 2-methyl-1-napthylmagnesium bromide followed by reduction with hydriodic acid in acetic acid. The rotational isomers [±ac, mp. 159-160°C, and ±sc, mp. 140-141°C][10)] were separated by silica gel chromatography.

The rates of interconversion of ±ac to ±sc of 1c are summarized in Table 2 together with those (sp → ap) of 1b for comparison. The rates of rotation in 1b in tetrachloroethene have been reported.[4)] Our results are in good agreement with those reported, although the equilibrium constants are different to some extent. The difference may be caused by the use of a different solvent. Putting these data into the Eyring's equation, we obtain the following activation parameters. 1b: $\Delta H^{\ddagger}$ 25.6 kcal/mol, $\Delta S^{\ddagger}$ -9.7 e. u., $\Delta G^{\ddagger}_{353}$ 29.0 kcal/mol. 1c: $\Delta H^{\ddagger}$ 24.7 kcal/mol, $\Delta S^{\ddagger}$ -10.8 e. u., $\Delta G^{\ddagger}_{353}$ 28.5 kcal/mol.



1b : X=H sp ap

1c : X=F ±ac ±sc

Table 2 Rate Constants for Rotation (sp → ap or ±ac → ±sc) in 9-(2-Methyl-1-naphthyl)fluorenes in o-Dichlorobenzene

Temperature (°C)	1b[a)] k_1 (× 10^5 s^{-1})	1c[b)] k_1 (× 10^5 s^{-1})
69.5	0.278	0.478
81.1	1.01	1.79
102	7.88	12.8
112	19.1	30.1

a) The equilibrium constant (ap/sp) was constant at 1.14 ± 0.02 throughout the temperature range.
b) The equilibrium constant (±sc/±ac) was constant at 1.52 ± 0.04 throughout the temperature range.

Since the rate constants are more sensitive in detecting the difference than the free energies of activation, the results clearly show that the difference is significant: the rates of rotation in 1c are larger than those in 1b by a factor of 1.5-1.7 in the temperature range. The results are reflected in the activation parameters. Examining the differences in activation parameters one notices that the difference is mainly caused by the enthalpy of activation. Although the difference in entropy of activation can be caused by various reasons including solvation effects, the main difference in enthalpy of activation is certainly caused by the stabilities of both the ground state and the transition state for rotation because both the solute and the solvent are relatively nonpolar. Therefore, we may discuss the difference by considering the molecular structures in the ground and the transition states for rotation.

As to the transition state for rotation, the maximum interaction takes place between C_1-H or C_8-H of the fluorene ring and the 2-methyl-1-naphthyl moiety. Since the van der Waals radius of fluorine is larger than that of hydrogen, the repulsive interaction should be enhanced by introduction of a fluoro group into the 1-position of the fluorene in the transition state for rotation. Since the barrier to rotation is the difference between the ground and the transition states, the observed low barrier in 1c relative to 1b, then, must be attributed to raising of the ground state energy in 1c.

In the ground state of 1c, repulsion between the 1-fluoro group and the naphthyl moiety may be considered. A Dreiding model of 1c shows that the distance between the 1-H of the fluorene and the 1-C of the naphthyl group is ca. 3.0 Å, which is close to the sum of the van der Waals radius of fluorine (1.35 Å) and the half-thickness of a benzene ring (1.70 Å). Therefore, there is a possibility that the repulsive interaction between these two groups causes the raise in the ground state energy. As auxiliary evidence, we have X-ray crystallographic data of 1-methyl-9-(8-methyl-1-naphthyl)fluorene in hand, which show significant deformation of the angles concerned with the 1-methyl and the 8-methyl-1-naphthyl groups.

Thus we conclude that the introduction of the fluoro group into the 1-position of the fluorene ring of 1b contributes more to raise the ground state energy than to raise the transition state for rotation. The lowering of the rotational barrier by going from a small substituent to a large one is not without a precedent: 9-mesitylfluorene is known to exhibit a low barrier to rotation when the size of a 9-substituent becomes large.[4] An example in triptycene systems which shows low barrier to rotation in a more crowded compound relative to a less crowded compound has also been reported.[11] Being larger and longer, a methyl group in the 1-position of 1b seems to raise the transition state for rotation more than the ground state.

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(Received December 18, 1981)