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Reactivities of Stable Rotamers. XI. Rotamer Distributions and Some Addition Reactions to the Carbonyl in 9-[2-(Substituted carbonyl)-1-naphthyl]fluorene Rotamers[1)]

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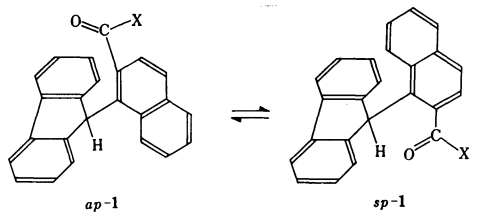
Rotational isomers (*sp* and *ap*) of several 9-[2-(substituted carbonyl)-1-naphthyl]fluorenes where the substituent is methyl, phenyl, hydroxyl, methoxyl, 1-imidazolyl, or others have been obtained as stable entities. Barriers to rotation in these compounds were *ca.* 26.5 kcal for the process *sp*→*ap* but those for the reverse (*ap*→*sp*) were dependent on the substituent, ranging from 23.8 to 25.3 kcal/mol at 55 °C. The difference is reflected in the populations of rotamers: if the substituent is a hydroxyl, the *sp*/*ap* value becomes as large as *ca.* 20. The relative instability of the *ap* form was attributed to twisting of the carbonyl plane from that of naphthalene. Infrared spectra support the twisting. Addition reactions to the carbonyl occur smoothly in the *sp* conformation but they do not occur to a detectable extent in the *ap* conformation, if the substituent on the carbonyl is larger than hydrogen. The results are attributed to the steric effect of the fluorene ring.

In a previous paper,[1)] we have demonstrated that some reactions which take space-demanding transition states are very slow in an *ap* conformation, relative to the *sp*, of 9-(2-formyl-1-naphthyl)fluorene (**1a**). In contrast, an addition reaction of hydroxylamine to the carbonyl of *ap*-**1a** proceeded with a rate comparable with that of the *sp* form. The results imply that the transition state for the addition is not bulky: it may be assumed that, in the transition state for the addition where a tetrahedral carbon is developing from a trigonal, the hydrogen of the formyl group comes closely to the fluorene ring to minimize the transition state energy.

Then a question arises: what will happen when a bulkier substituent than hydrogen has to take a position which is close to the fluorene ring in the transition state of a reaction in the *ap* form? From our previous work, we collect that 9-(2-*t*-butylphenyl)fluorene exists as an *sp* conformation only.[2)] 9-(8-Methyl-1-naphthyl)-fluorene gives an equilibrium constant (*sp*/*ap*) of 25.[3)] These results suggest that, if a bulky group has to take a position which is close to the fluorene ring during a reaction in the *ap* form, the free energy of activation is different by 2 kcal/mol (1 cal=4.18 J) or more between *sp* and *ap* conformations. This should give a very large k_{sp}/k_{ap} value and may result in chemoselective reactions which occur in *sp* conformations only. To achieve this end, we carried out a series of addition reactions to carbonyls in ketones and acid derivatives. This paper reports results of such an investigation together with populations of rotamers and barriers to rotation in these compounds.



ap-1 ⇌ *sp*-1

a: X=H
b: X=CH_3
c: X=C_6H_5
d: X=OH
e: X=OCH_3
f: X=$OC_6H_4NO_2$-*p*
g: X=1-Imidazolyl
h: X=Cl

Barriers to Rotation and Populations of Rotamers. The assignment of the conformation of 9-[2-(substituted carbonyl)-1-naphthyl]fluorene (**1**) relies upon ^{1}H NMR spectral features as reported in previous papers. If the substituent has proton(s) not far from the carbonyl, the proton signal of the *ap* form appears in a high field relative to the *sp* form because of the ring current effect of fluorene. If there is no proton close to the carbonyl in the substituent, we use the method of preparation because barriers to rotation are high enough to retain the conformation when the reaction is carried out at room temperature. As an auxilary support, we may use the chemical shift of the 8-proton in the naphthalene ring: in the *ap* conformation, the proton is close to the plane of fluorene to give a signal at a very low field, whereas, in the *sp* conformation, the 8-proton is over the fluorene ring to exhibit a signal at a high field. It is interesting to note that the 8-H signal appears as an apparent doublet in the *sp* conformation, whereas it is often a multiplet in the *ap*.

Barriers to rotation were measured at one temperature. The measurement was carried out for the isomerization of *ap* forms because the *ap*'s are always minorities at equilibrium. The results are summarized in Table 1 together with those of the corresponding aldehyde (**1a**).[1)] Inspection of Table 1 reveals that the barriers to rotation for the process *sp*→*ap* are almost the same whereas those for the *ap*→*sp* processes vary to some extent. Although

Table 1. Barriers to rotation and equilibrium constants in 9-[2-(substituted carbonyl)-1-naphthyl]fluorene (**1**) in benzene-d_6 at 55 °C

Substituent	$k(ap\rightarrow sp)/s^{-1}$	$\Delta G^{\ddagger}$/kcal mol^{-1}		$K(sp/ap)$
		ap→*sp*	*sp*→*ap*	
H[a)]	1.28×10^{-5}	26.7	26.9	1.5
CH_3	2.64×10^{-4}	24.6	26.3	12
C_6H_5	1.86×10^{-4}	24.9	26.6	13
OH[b)]	0.98×10^{-3}	23.8	25.7	~20
OCH_3	9.45×10^{-5}	25.3	26.6	7

a) Hexachlorobutadiene solvent. b) Dimethyl-d_6 sulfoxide solvent.

solvents are different, at least we may compare the barriers including that for the carboxylic acid (**1d**). At any rate, reactivities of rotamers may be investigated without complication due to isomerization, if a reaction is carried out at room temperature, except for the *ap*-carboxylic acid (**1d**). Although not determined, other carbonyl compounds may be assumed to possess similar barriers to rotation.

The barriers of the carbonyl compounds are lower than the corresponding compounds carrying an sp^3-carbon substituent in the 2-position of the naphthalene ring.[4] This must be attributed to the relative size of the carbonyl group, since the van der Waals radius of a methyl group (2.0 Å) is known to be larger than the half-thickness of a π-system (1.8 Å), as discussed before.[1] The lowering of the transition state for rotation by introduction of a π-system, in place of a tetrahedral carbon, to the 2-position of naphthalene is more important than the effect in the ground state.

Similar barriers to rotation for the *sp*→*ap* process for all the compounds examined here mean that the energy difference between the ground state and the transition state for rotation is also similar. If we can assume that the main contribution to the transition state energy is the interaction of the carbonyl oxygen with the fluorene ring, then the ground state conformation will also have the carbonyl oxygen in similar situations. The barrier is highest when the substituent X is hydrogen. Similar barriers to rotation for all the compounds for the *sp*→*ap* process suggest that the lower barriers to rotation in **1b**, **1c**, and **1e** for the *ap*→*sp* process may be attributed to destabilization of the ground state in the *ap* form. Indeed, all the compounds, **1b**—**e**, have larger equilibrium constants (*sp*/*ap*) than **1a** in favor of the *sp* form.

Molecular models of these compounds suggest that, if the carbonyl group takes a planar conformation with the naphthalene ring, either the carbonyl-oxygen or the substituent X gives a severe interaction with the fluorene ring. Thus the carbonyl may not be coplanar with the naphthalene. In contrast, the formyl group can be coplanar with the naphthalene, if the hydrogen directs toward the fluorene ring. In order to get support for the suggestion by the model, infrared C=O stretching spectra were recorded. The results are given in Table 2.

Table 2. Infrared carbonyl stretching frequencies of 9-[2-(substituted carbonyl)-1-naphthyl]-fluorene (**1**)

Substituent	$\nu_{C=O}$/cm^{-1}			
	sp		*ap*	
	Solid	CCl_4 soln[a]	Solid	CCl_4 soln[a]
H	1672 1690 (sh)	1682 (329) 1700 (321)	1672	1692 (627)
CH_3	1688	1692 (378)	1700	1702 (279)
C_6H_5	1665	1688 (354)	1660	1665 (346)
OH	1680	1688 (934)	1700	1700 (374)
OCH_3	1708	1722 (560)	1720	1728 (459)

a) Numericals in parentheses are molecular extinction coefficients.

Although not observed for the benzoyl compound (**1c**), the carbonyl stretching frequencies for the *ap* forms are generally at higher wave numbers than those due to the *sp* forms. In contrast, the aldehydes (**1a**) show $\nu_{C=O}$ absorptions at about the same frequencies, though the *sp* form gives bifurcated bands probably due to the Fermi resonance. This suggests that the conjugation of the carbonyl with the naphthalene ring is diminished in these compounds and the two groups are not coplanar.[5] Benzophenone derivatives are insensitive to the steric environment because even the simplest example is not coplanar because of the steric effect.[6] Thus the population ratios and the relative barriers to rotation for the *ap*→*sp* process are explained by the destabilization of the *ap* forms.

Even though the above conclusion is reached, the instability of the *ap*-carboxylic acid (**1d**) relative to the *sp* form is unusual. We have tried to increase the population of the *ap* form by various methods, including solvent-change and acidification of a basic solution of **1d** in water, without success. Baeyer-Villiger oxidation of the aldehyde (**1a**) afforded formates instead of the corresponding acid probably due to the steric effect.[7] We suspect that extra stabilization is obtained by the dimeric hydrogen bonds in the *sp* conformation whereas the dimer is unfavorable in the *ap* conformation because of the steric effect.

Conformer distribution in 9-[2-(*p*-nitrophenoxycarbonyl)-1-naphthyl]fluorene (**1f**) is interesting because the *sp*/*ap* value is *ca.* 4 which is small relative to the corresponding methyl ester (**1e**). We wish to attribute the phenomenon to the charge-transfer interaction between the *p*-nitrophenyl group and the fluorene, which stabilizes the *ap* form of **1f**. Such a stabilization of the *ap* form in *p*-nitrobenzoate of 9-(2-hydroxy-1-naphthyl)-fluorene has been reported.[8]

Reactions. The reaction of carbonyl groups proceeds smoothly if the conformation is *sp*. Esterification of *sp*-carboxylic acid (**1d**) proceeded to give *sp* form of the methyl ester (**1e**). The *sp*-**1e** could be equilibrated by heating its solution. The conformational isomers (*ap* and *sp*) were separated. The attempted hydrolysis of the ester was too slow to be suitable for the comparative study of the reactivities of conformational isomers at room temperature. *p*-Nitrophenyl esters (**1f**), though they have been known to be hydrolyzed more easily than alkyl esters,[9] resisted hydrolysis as well. In an effort of searching more easily hydrolyzable acid derivatives, imidazolide (**1g**)[10] was prepared from the *sp*-acid. After equilibration, the rotational isomers (*ap* and *sp*) were isolated. Hydrolysis of the imidazolide in acidic aqueous acetone afforded *sp*-acid (**1d**) from the *sp*-imidazolide but the *ap* form resisted the hydrolysis at room temperature.

Addition of methylmagnesium iodide to *sp*-9-(2-acetyl-1-naphthyl)fluorene (**1b**) proceeds smoothly to afford *sp*-9-[2-(1-hydroxy-1-methylethyl)-1-naphthyl]-fluorene. Attempted isomerization of this compound failed to give any sign of the presence of its *ap* isomer: this type of rotamer distribution is known, if the aryl group in 9-arylfluorene carry a large group on one side.[2,3] In contrast, *ap*-**1b** did not show evidence that

he reaction occurred. Likewise, sodium tetrahydridoborate reduction of the acetyl compound (**1b**) proceeds smoothly if the conformation is *sp*, but does not proceed if the conformation is *ap*.

These reactivities of the substituted carbonyl compounds make a sharp contrast to those of the aldehyde (**1a**). In the aldehyde, the relative reactivities toward Grignard additions and sodium tetrahydridoborate reduction were 1.7 and 7.6, respectively.[1)] Therefore, the addition reaction of the substituted carbonyl compounds (**1b** and **1g**) was definitely slow in the *ap* conformation. The reason for the difference must be of the steric origin. Molecular models suggest that, if it is the aldehyde, the change from the sp^2-carbon to the sp^3-carbon by addition is not too difficult because the hydrogen of the formyl group can direct toward the fluorene ring, the steric hindrance being not large. In contrast, if it is a ketone or an acid derivative, the formation of the tetrahedral carbon by addition is prohibitive, because either oxygen or carbon must become closely located to the fluorene ring. Thus the activation energy must be very high for the *ap* conformation, if the addition to the carbonyl is to occur.

From the stand point discussed above, it is interesting to note that the acid chloride (**1h**) is easily hydrolyzed to yield the corresponding carboxylic acid (**1d**) even in the *ap* conformation. It may be plausible to assume that the addition of water to the carbonyl moiety is also slow in *ap*-**1h**, although this is believed to be the initial step in the hydrolysis of acid chlorides.[11)] It is possible that *ap*-**1h** dissociates to the acyl carbonium ion and the chloride ion, of which the former reacts with water to give the *ap*-carboxylic acid, although definitive support is lacking.

Experimental

*9-(2-Methoxycarbonyl-1-naphthyl)fluorene (**1e**).* A solution of 0.80 g *sp*-9-(2-carboxy-1-naphthyl)fluorene (**1d**)[1)] in 70 mL of methanol was refluxed for 25 h with 2 mL of concentrated sulfuric acid. The mixture was concentrated and poured into water. After extraction with ether followed by washing and drying, the product was separated by silica gel chromatography (benzene eluent) to give 0.69 g of the *sp* ester and 0.09 g of the *ap*.

ap-**1e**, mp 130—131 °C. Found: C, 85.81; H, 5.11%. Calcd for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18%. ^{1}H NMR ($CDCl_3$, δ): 2.83 (3H, s), 6.10 (1H, s), 7.10—8.10 (13H, m), 8.53—8.77 (1H, m).

sp-**1e**, mp 133—134 °C. Found: C, 85.73; H, 4.90%. Calcd for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18%. ^{1}H NMR ($CDCl_3$, δ): 3.95 (3H, s), 6.20 (1H, s), 6.56 (1H, d, J=9.0 Hz), 6.70—7.96 (13H, m).

*9-[2-(1-Imidazolylcarbonyl)-1-naphthyl]fluorene (**1g**).* A mixture of 0.10 g of *sp*-**1d** and 5 mL of thionyl chloride was heated under reflux for 1 h and then excessive thionyl chloride was removed *in vacuo*. The residue was taken up in 20 mL of dichloromethane and was stirred with 0.1 g of imidazole for 30 min. The solvent was evaporated and the residue was purified by preparative TLC on silica gel (dichloromethane solvent) to give *sp*-**1g**, mp 133.5—138.0 °C (decomp), almost quantitatively. High resolution mass spectrum exhibited a molecular ion peak at *m/e* 386.1461, whereas the calculation for $C_{27}H_{18}N_2O$ requires 386.1420. ^{1}H NMR ($CDCl_3$, δ): 5.43 (1H, s), 6.62 (1H, d, J=9.0 Hz), 6.83—8.17 (16H, m).

When the reaction products taken up in dichloromethane was heated for 2 h, a *ca.* 5 : 1 mixture of *sp*- and *ap*-**1g** was obtained. This isomerization was probably catalyzed by imidazole. After evaporation of the solvent, the mixture was separated by preparative TLC as above to give pure *ap*-**1g**, mp 253—257 °C (decomp). High resolution mass spectrum exhibited a molecular ion peak at *m/e* 386.1462, whereas $C_{27}H_{18}N_2O$ requires 386.1420. ^{1}H NMR ($CDCl_3$, δ): 6.17 (1H, s), 6.60—8.20 (16H, m), 8.63—8.88 (1H, m).

*Acid Hydrolysis of Imidazolide (**1g**).* To a solution of 20 mg of *sp*-**1g** in 15 mL of acetone, 5 mL of water and 1 mL of concentrated hydrochloric acid were added and the mixture was allowed to stand overnight. The mixture was poured into water and extracted with ether. The ether extract gave *sp*-acid (**1d**) almost quantitatively.

A similar treatment of *ap*-**1g** gave no carboxylic acid but the imidazolide was recovered in good yield.

*9-[2-(p-Nitrophenoxycarbonyl)-1-naphthyl]fluorene (**1f**).* The acid chloride (**1h**) was prepared from 100 mg of the *sp*-acid (**1d**) and 5 mL of thionyl chloride as above. The chloride was dissolved in 20 mL of dichloromethane and stirred with 0.5 mL of pyridine and 100 mg (2.4 equiv.) of *p*-nitrophenol for 30 min at room temperature. After evaporation of the solvent, the residue was taken up in ether and washed with water. The ethereal layer was dried and evaporated. The residue was submitted to TLC on silica gel (2 : 1 benzene–hexane solvent) to give *ca.* 70 mg of *sp*-**1f**, mp 166—167 °C. Found: C, 78.65; H, 4.03; N, 3.06%. Calcd for $C_{30}H_{19}NO_4$: C, 78.76; H, 4.19; N, 3.06%. ^{1}H NMR ($CDCl_3$, δ): 6.38 (1H, s), 6.66 (1H, d, J=8.7 Hz), 6.7—8.3 (17H, m). IR (KBr disk): 1740, 1523, 1347 cm^{-1}.

The *sp* form of **1f** in benzene was refluxed overnight to give a 4 : 1 *sp* and *ap*-**1f**. The solvent was evaporated and the residue was submitted to TLC as above to give pure *ap*-**1f**, mp 162—163 °C. Found: C, 78.42; H, 3.96; N, 3.00%. Calcd for $C_{30}H_{19}NO_4$: C, 78.46; H, 4.19; N, 3.06%. ^{1}H NMR ($CDCl_3$, δ): 6.17 (1H, s), 6.33 (2H, d, J=9.0 Hz), 7.1—8.4 (15H, m), 8.57—8.85 (1H, m). IR (KBr disk): 1748, 1520, 1350 cm^{-1}.

Attempted Hydrolysis of p-*Nitrophenyl Ester (**1f**).* A solution of 30 mg of *sp*-**1f** in 5 mL of acetic acid was left to stand for a week at room temperature with 5 mL of water and 1 mL of concentrated sulfuric acid. No carboxylic acid (**1d**) was detected after this period and the ester was recovered almost quantitatively. Similarly *ap*-**1f** was recovered after attempted hydrolysis.

ap-*9-(2-Carboxy-1-naphthyl)fluorene* (ap-***1d***). The corresponding acid chloride (**1h**), prepared from 0.1 g of the *sp*-acid and 5 mL of thionyl chloride as described above, was dissolved in 20 mL of acetone and was treated with 5 mL of water at *ca.* 0 °C. After 1 h, the product was taken up in ether and evaporated. Preparative TLC on silica gel (ethyl acetate–dichloromethane 1 : 2) afforded *ca.* 5 mg of the *ap*-acid, mp 226—228 °C, and *ca.* 60 mg of *sp*-acid. High resolution MS showed a molecular ion peak at 336.1159, whereas the molecular formula $C_{24}H_{16}O_2$ requires 336.1151. ^{1}H NMR ($CDCl_3$, δ): 6.08 (1H, s), 7.07—8.07 (13H, m), 8.53—8.83 (1H, m).

*Addition of Methylmagnesium Iodide to 9-(2-Acetyl-1-naphthyl)-fluorene (**1b**).* A 2 mL portion of a Grignard reagent, which was prepared from 0.77 mL of methyl iodide, 0.25 g of magnesium, and 10 mL of ether, was added to 30 mg of *sp*-**1b**[1)] and the mixture was allowed to stand for 1.5 h. The mixture was decomposed with 5% aqueous ammonium chloride and the product was treated in a usual manner. *sp*-9-[2-(1-Hydroxy-1-methylethyl)-1-naphthyl]fluorene, mp 133—134

°C was obtained almost quantitatively. Found: C, 89.20; H, 6.18%. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33%. ^{1}H NMR ($CDCl_3$, δ): 1.97 (6H, s), 6.81 (1H, s), 6.43 (1H, d, J=9.0 Hz), 6.63—8.00 (13H, m). The OH proton was not detected.

Similar treatment of *ap*-**1b** gave no sign of the reaction. The starting material was recovered almost quantitatively.

*Reduction of 9-(2-Acetyl-1-naphthyl)fluorene (**1b**) with Sodium Tetrahydridoborate.* A solution of 30 mg of *sp*-**1b** in 20 mL of methanol was mixed with 8 equivalents of sodium tetrahydridoborate. After 10 min, the mixture was poured into water and extracted with ether. The ethereal layer was washed and dried over magnesium sulfate. After evaporation of the solvent, the residue was found to be an almost pure *sp*-9-[2-(1-hydroxyethyl)-1-naphthyl]fluorene by its ^{1}H NMR spectrum.[1)]

The similar treatment of the *ap* form did not show any sign of the reduction. Although the same portions of sodium tetrahydridoborate were added three times to the mixture and the mixture was stirred for 80 more min at 0 °C and then for 1 h at room temperature, the *ap* form was recoved unreacted.

*Baeyer-Villiger Oxidation of 9-(2-Formyl-1-naphthyl)fluorene (**1a**).* To a solution of 20 mg of *ap*-**1a** in 20 mL of acetic acid was added 1 mL of a mixture prepared from 2 mL of 90% formic acid and 2 mL of 38% hydrogen peroxide. The whole was allowed to stand for 2 d and treated in a usual way. Purification of the product by chromatography on silica gel (benzene eluent) gave *ap*-9-(2-formyloxy-1-naphthyl)fluorene, mp 142—143 °C, almost quantitatively. Found: C, 85.73; H, 4.81%. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%. ^{1}H-NMR ($CDCl_3$, δ): 5.90 (1H, s), 6.98 (1H, s), 6.90—8.07 (13H, m), 8.52 (1H, d, J=9.0 Hz). IR (KBr disk): 1740 cm^{-1}.

Similar treatment of *sp*-**1a** gave *sp*-(2-formyloxy-1-naphthyl)fluorene, oil, in *ca.* 50% yield. The *sp*-formate is relatively easily hydrolyzed and formation of *sp*-(2-hydroxy-1-naphthyl)fluorene was detected during silica gel TLC (benzene eluent). High resolution MS showed a molecular ion peak at *m/e* 336.1189, whereas calculation for $C_{24}H_{16}O_2$ requires 336.1151. ^{1}H NMR ($CDCl_3$, δ): 5.70 (1H, s), 6.45 (1H, d, J=9.0 Hz), 6.73—8.07 (13H, m), 8.47 (1H, s).

Barriers to Rotation. Pure *ap* isomer (30 mg) of the carbonyl compounds was dissolved in 0.4 mL of benzene-d_6 or dimethyl-d_6 sulfoxide and the solution was placed in an NMR sample tube. The tube was immersed in a boiling-acetone bath and the rate of isomerization was followed by ^{1}H NMR spectroscopy. The data were treated by assuming a reversible first order reaction to give a rate constant. The rate constant was put into the Eyring equation and the free energy of activation was obtained.

Spectral Measurement. Infrared spectra were obtained with a Hitachi EPI-G spectrophotometer. With solid samples, KBr discs were used. For the measurement of the spectra of solutions, the sample was dissolved in carbon tetrachloride to make up *ca.* 0.05 mol/L solution for the carbonyl region and a KBr cell of 0.25 mm length was used.

^{1}H NMR spectra were obtained with a Varian EM 390 spectrometer. The integration of peak areas was repeated several times and the average was used for the kinetic measurement.

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