

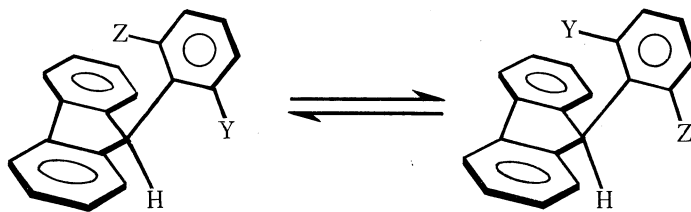
RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON. XIX. EFFECTS ON
CHARGE-TRANSFER INTERACTION ON THE POPULATION OF ROTAMERS AND ON
BARRIERS TO ROTATION IN 1-(9-FLUORENYL)-2-NAPHTHYL AROATES¹⁾

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Equilibrium constants between ap and sp forms of 1-(9-fluorenyl)-2-naphthyl aroates suggest the presence of charge-transfer interaction between the fluorenyl group and an aroyl group with a nitro substituent. The barriers to rotation of the nitro compound were also consistent with the presence of the charge-transfer interaction.

The barriers to rotation about C_9-C_{Ar} bonds in 9-arylfluorene derivatives (1) are extraordinarily high, as studied by both DNMR²⁾ and classical³⁾ methods. The equilibria between rotamers in these compounds are known to be primarily determined by the bulkiness of substituents Y and Z. That is, the predominant conformation is the one in which a bulkier substituent approximates the hydrogen in position 9.



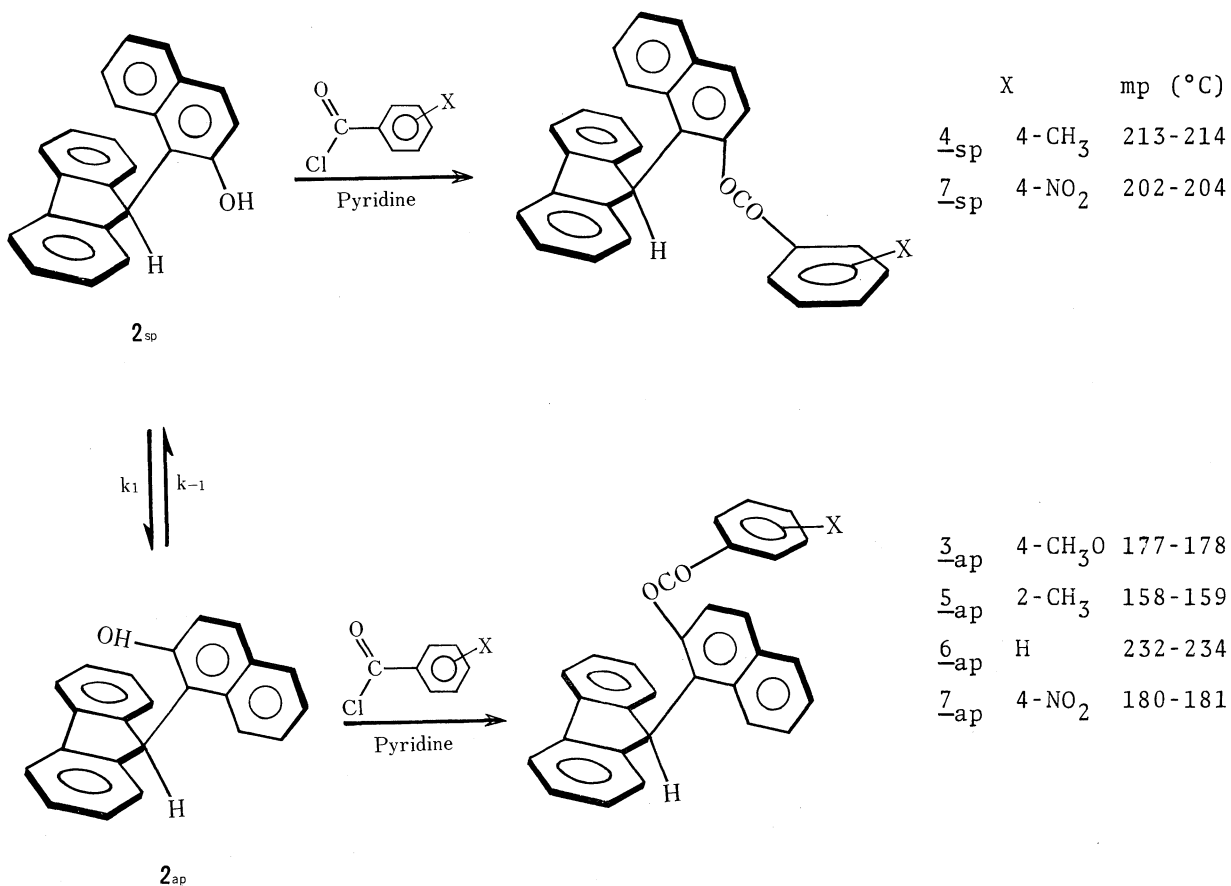
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Since the substituent Y or Z in each rotamer is quite close to the fluorene ring, electronic interaction may ensue, if the substituent has a proper character, to affect the equilibria. Such a possibility is most likely to occur if the substituent has electron-accepting ability: the charge-transfer interaction will take place between the fluorene ring (an electron-donor) and the substituent (an

electron-acceptor).

During our studies on the reactivities of stable rotamers,⁴⁾ we found that the ratio of populations and the rates of isomerization between rotamers are remarkably affected by the substituent on the benzoyl-benzene ring in a series of compounds 3-7. This paper reports the results and discusses the origin of such phenomena.

9-(2-Hydroxy-1-naphthyl)fluorene (2) was synthesized and two rotamers, sp and ap forms, were separated by the chromatography on silica gel. The melting point of the sp form was 88.0-89.0°C, whereas that of the ap form was 170.0-170.5°C. The stereochemistry of the rotamers were assigned by comparison of the ¹H NMR spectral data with those of 9-(2-methoxy-1-naphthyl)fluorene.⁴⁾ The rates of interconversion between the rotamers were measured to be $k_1 = 7.3 \times 10^{-5} \text{ sec}^{-1}$, and $k_{-1} = 4.4 \times 10^{-5} \text{ sec}^{-1}$ at 56°C. Compounds 3-7 were obtained by treating either the sp form or the ap form of 2 with corresponding aroyl chlorides in pyridine at room temperature. Under these conditions the configuration of the starting material was retained.



CDCl_3 solutions of these compounds were heated at 69°C and ^1H NMR spectra were measured. New peaks attributable to ap forms gradually increased in those intensities when the sp forms were heated and vice versa. The equilibria were reached within ca. 12 hours. The characteristic features in ^1H NMR spectra of sp and ap forms are that the chemical shifts of the 9-H signal of the former are 0.1-0.2 ppm higher than those of the latter due to the anisotropy effect of the aroyl group.

By monitoring the increase or the decrease in intensities of the 9-H signals and/or methyl(or methoxyl) signals, the rates of isomerization between rotamers were obtained by assuming the unimolecular reversible processes. The rates afforded the free energies of activation for isomerization at 69°C which are listed in Table 1 together with the equilibrium constants.

Table 1. Equilibrium Constants and Kinetic Data for the sp-ap Systems of 1-(9-Fluorenyl)-2-naphthyl Aroates at 69°C .

	$K(\text{ap/sp})$	$k_{\text{sp} \rightarrow \text{ap}}$ ($\times 10^5 \text{ s}^{-1}$)	$k_{\text{ap} \rightarrow \text{sp}}$	$\Delta G_{\text{sp} \rightarrow \text{ap}}^\ddagger$ (kcal/mol)	$\Delta G_{\text{ap} \rightarrow \text{sp}}^\ddagger$
<u>3</u>	0.82 ± 0.03	2.7 ± 0.1	3.3 ± 0.1	27.3 ± 0.1	27.2 ± 0.1
<u>4</u>	0.83 ± 0.03	2.8 ± 0.1	3.4 ± 0.1	27.3 ± 0.1	27.2 ± 0.1
<u>5</u>	0.67 ± 0.03	1.8 ± 0.1	2.6 ± 0.1	27.6 ± 0.1	27.4 ± 0.1
<u>6</u>	0.90 ± 0.03	2.7 ± 0.1	2.9 ± 0.1	27.3 ± 0.1	27.3 ± 0.1
<u>7</u>	2.9 ± 0.2	2.7 ± 0.1	0.92 ± 0.1	27.3 ± 0.1	28.1 ± 0.1

The equilibrium constants indicate that the sp forms are slightly more stable than the ap forms in compounds 3-6 whereas the ap form is ca. 0.7 kcal/mol more stable than the sp form in compound 7. This striking contrast means that the introduction of a nitro group in place of an electron-releasing group either destabilizes the sp form or stabilizes the ap form.

Although it is not possible to distinguish the two possibilities from the equilibrium data, the rates for isomerization lend help to differentiate the cause. The rate constant from the ap form to the sp in compound 7 is about a fourth of that of compound 3, whereas the rate for the reverse remains almost equal for the two compounds. These results strongly suggest that the ap form of 7 is stabilized relative to those of 3-6. The most probable reason for the stabilization is the charge-transfer interaction,⁵⁾ the fluorene ring acting as an electron-donor and the nitrobenzoyl group acting as an electron-acceptor. The molecular models show that

a conformation is possible in which benzoyl and fluorene planes are almost parallel at a distance of 3-4 Å, as shown in Fig. 1: the conformation will make the charge-transfer interaction possible.

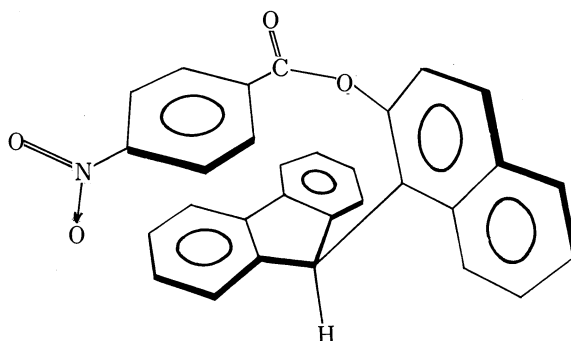


Fig. 1: A conformation of the ap form of 1-(9-fluorenyl)-2-naphthyl p-nitrobenzoate

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