Tetrahedron Letters No. 15, pp 1207 - 1210, 1976. Pergamon Press. Printed in Great Britain.

RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON. XVIII SOLVENT EFFECTS ON EQUILIBRIA BETWEEN ROTAMERS AND ON BARRIERS TO ROTATION IN A 9-ARYLFLUOREN-9-OL DERIVATIVE[1)]

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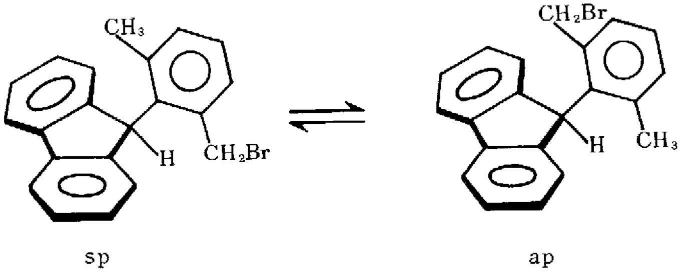
(Received in Japan 31 January 1976; received in UK for publication 2 March 1976)

One of the characteristic features of 9-arylfluorene derivatives is that the barrier to rotation about the C_9-C_{Ar} bond is extraordinarily high [2)] Thus rotational isomers, sp and ap forms, of compound 1 could be isolated as stable entities at room temperature [3)] During the course of extension of our studies on the restricted rotation in the 9-arylfluorene system, we found that the ratio of populations of rotational isomers of 9-(2-methoxy-1-naphthyl)fluoren-9-ol (2), mp 130 0 ∿ 131 0°C, changed drastically depending upon the solvents This paper deals with the striking solvent effect on the equilibria between rotamers together with that on the barrier to rotation in compound 2.



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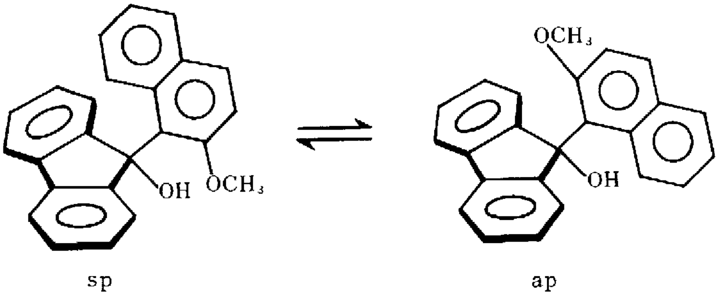


(2)

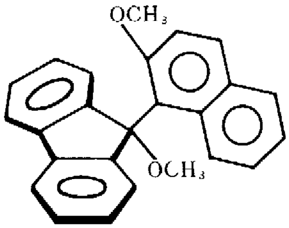
Since the aryl group in compound 2 is structurally analogous to that of compound 1, the barrier to rotation about the bond in question is also high enough to show two signals for the methoxyl group in the ^{1}H NMR spectrum at room temperature. Integration of these two signals revealed that the equilibrium constant (ap/sp) was 0.7 in hexachlorobutadiene (HCB), whereas it amounted to 8.0 when the solvent was changed to dimethyl-d_6 sulfoxide (DMSO). The striking solvent effect on the equilibrium seems to indicate that the integration of the sp and the ap forms in one solvent is quite different from that in another solvent. In order to look into details thermodynamic parameters were obtained and the results are shown in Table 1.

Table 1. Thermodynamic Parameters (sp$\rightleftharpoons$ap) (30°C)

Solvent	HCB	DMSO
ΔH (kcal/mol)	1.3	-1.9
ΔS (eu)	3.6	-2.2
ΔG (kcal/mol)	0.2	-1.2

In a HCB solution, the sp form is 1.3 kcal/mol more stable than the ap form with regard to enthalpy, whereas it is unfavorable by 3.6 eu with regard to entropy. As a result, the sp form is favored by free energy of only 0.2 kcal/mol at 30°C. The positive value of entropy can be taken as a reflection of the presence of the intramolecular hydrogen bond between the hydroxyl and the methoxyl groups in the sp form. This interpretation is supported by a fact that the hydroxyl proton signal of the sp form appeared at quite a low field (δ 6.5), compared with that of the ap form (δ 2.1), in the ^{1}H NMR spectrum.

In a DMSO solution, energy levels of both the sp and the ap forms will be lowered than those in HCB since the former solvent is an extremely strong proton acceptor. The degree of stabilization, caused by the change of the solvent, is considered to be larger in the ap form than in the sp form because, in the latter, the intermolecular hydrogen bond is possible only at the expense of the intramolecular hydrogen bond. Actually the ap form is 1.9 kcal/mol more favorable than the sp form with respect to enthalpy. The consideration leads to an assumption that if the intramolecular hydrogen bond were absent in the sp form, the ap form would be more stable than the sp form. This is supported by a fact that only the ap form exists in compound 3, mp 157.5∼158.0°C, in which the hydroxyl group in position 9 is methylated to erase the possibility of hydrogen-bond formation.



(3)

The activation parameters for rotation were then obtained to get the information on the solute-solvent interaction in the transition state. The total line shape analysis yielded the data listed in Table 2.

Table 2. Activation Parameters for Rotation (30°C).

Solvent	HCB		DMSO	
Process	sp → ap	ap → sp	sp → ap	ap → sp
$\Delta H^{\ddagger}$ (kcal/mol)	16.5	15.2	12.2	14.1
$\Delta S^{\ddagger}$ (eu)	-3.2	-6.6	-10.8	-8.6
$\Delta G^{\dagger}$ (kcal/mol)	17.5	17.2	15.4	16.7

As for the enthalpy of activation, the values in DMSO are less than those in HCB by ca. 4 and 1 kcal/mol for the processes, sp → ap and ap → sp, respectively. Since the energy levels of both the sp and the ap forms are supposed to be lower in DMSO than those in HCB because of the formation of the strong intermolecular hydrogen bond, an interpretation for lowering the enthalpy of activation is possible only when the solute-solvent interaction in the transition state for rotation is assumed to be stronger than that in the ground state. This is in accord with the value of the entropy of activation: the large negative values obtained with the DMSO solution clearly indicate the occurence of the stronger reorientation of the solvent in the transition state for rotation.

Inspection of the molecular model also reveals that the hydroxyl group is less hindered in the transition state, as shown in Fig. 1. This conformation will facilitate the formation of the solute-solvent interaction.

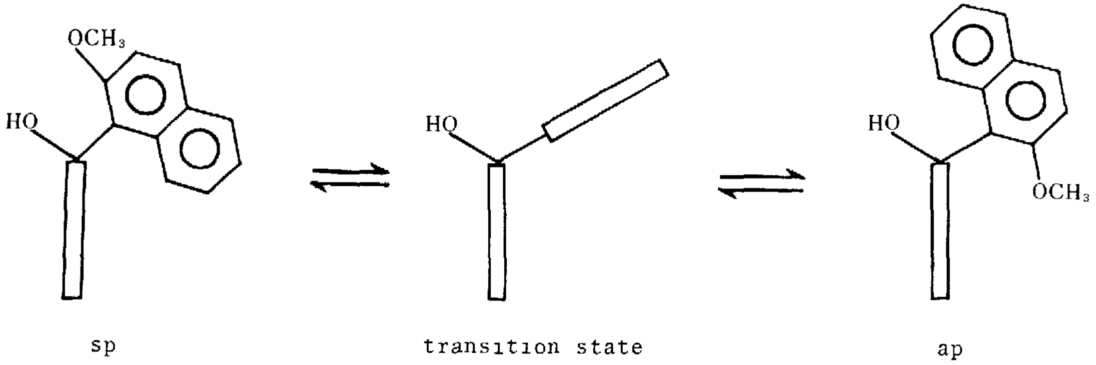


Fig. 1 Schematic Views of Molecular Models of Compound 2

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