yielding 30 mg: mp 148–149° (evacuated sealed capillary tube, uncorrected); λ_{max} ($CHCl_3$), mμ ($\epsilon \times 10^{-3}$), 432 sh (73.9), 454 (103), 482 (89.5); λ_{max} (petroleum ether), mμ, 420, 448, 472; ν (KBr pellet) 3450, 1040, 1025, 1005 cm^{-1}; nmr τ 9.15 (s, 3), 9.00 (s, 3), 8.92 (s, 6), 8.39 (s, 3), 8.26 (s, 3), 8.10 (s, 3) 8.04 (s, 6), 5.46 (s, 2), 4.58 (m, 2), 3.68 (m, 13).

Oxidation of Pyrenoxanthin.—Pyrenoxanthin (2 mg) in 5 ml benzene was treated with NiO_2 (30 mg, available oxygen 4.1 × 10^{-3} g-atom/g of NiO_2 determined by titration) for 60 min.[5] The oxidized product purified by column chromatography on Micro-Cel C exhibited a bathochromic shift in its visible absorption maxima: λ_{max} (petroleum ether), mμ, 450 broad. It was reduced with $LiAlH_4$ in dry ether to a product which was identical by tlc with pyrenoxanthin.

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9-Arylfluorenes. The Energy Barrier for the Inversion of 9-Chloro-9-durylfluorene

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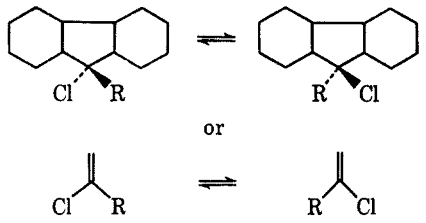
In a recent investigation of the properties of 9-chloro-9-arylfluorenes,[2] it was noted that the presence of substituents in the two *ortho* positions of the aryl group made the nmr spectrum of such a compound temperature dependent, and that this effect was not due to rotation of the aryl group, but rather to a reversible inversion at C-9 in the fluorene nucleus, *e.g.*, to a migration of the chlorine from one side of the fluorene plane to the other (Chart I).[3] Of the various substances investigated, 9-chloro-9-durylfluorene (I) stands out, since its nmr spectrum was the only one which contained more than one temperature-dependent methyl signal. This would permit the calculation of the activation enthalpy and entropy for the inversion of I by a very simple procedure which is based on coalescense parameters only and which was proposed recently by one of us.[5] Herein are reported the results of this study.

Chart I



I, R = *o*,*o'*,*m*,*m'*-$(CH_3)_4$-phenyl
II, R = phenyl

The coalescence parameters of the two collapsing nmr signals of I in $CDCl_3$,[6] which are both due to an exchange of protons between two uncoupled sites, are shown together with the calculated free energy, enthalpy, and entropy of activation ($\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$) in Table I. The determination of entropies of activation from nmr data is notorious for the errors involved,[7] and this is compounded in the present case by the fact that the rate is known at only two different temperatures. In order to ensure that our conclusions are meaningful, we have therefore calculated $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, using the worst combinations of errors. For this we estimate the maximum errors in the experimental data as: $T_c = \pm 1°$; $\delta\nu = \pm 2$ cps.

Table I

Nmr and Kinetic Parameters for the Inversion of 9-Chloro-9-durylfluorene[a]

	Position of CH_3 group	
	o,*o'*	*m*,*m'*
Signal parameters		
T_c, °K	335 ± 1	319 ± 1
δ_ν, cps	113.5 ± 2	18.5 ± 2
k_c, sec^{-1} [b]	244–253 (488–506)	33.6–42.5 (85.0–67.2)
$\Delta F^{\ddagger}$, kcal/mol[c]	15.52–15.64 (15.06–15.18)	15.87–16.13 (15.44–15.69)
$\Delta H^{\ddagger}$, kcal/mol[d]	20–30 (20–30)	
$\Delta S^{\ddagger}$, eu[e]	11–45 (13–46)	

[a] In this table, the customarily calculated energy parameters of inversion are given, together with a set of values (in parentheses) which was calculated with twice the values of k_c as rate. The comparison with energy barriers of solvolytic reactions should be done with these latter values, since in inversions only half of the activated molecules proceed to inverted molecules (and k_c is the measured rate of inversion), whereas in solvolytic reactions all the activated molecules yield solvolysis products. It is interesting to note that energy parameters are remarkably insensitive to the use of k_c and $2 \times k_c$ in the calculation, whereas the main importance is apparently on the value of T_c. [b] $k_c = \frac{\pi}{\sqrt{2}} \times \delta\nu \times \left[1 \times \frac{3\sqrt{2}}{8}\left(\frac{b_E}{\delta\nu}\right) + \frac{21}{64}\left(\frac{b_E}{\delta\nu}\right)^2\right]^{-1}$. See H. H. Schmid, H. Friebolin, S. Kabuss, and R. Mecke, *Spectrochim. Acta*, **22**, 623 (1966); b_E = 2.5 cps[7] was used for these calculations. [c] $\Delta F^{\ddagger} = 1.987 \times T_c \times 2.303 \times (10.035 + \log T_c/k_c)$. [d] $\Delta H^{\ddagger} = -1.987 \times 2.303 \times (\Delta \log k_c/T_c)/(\Delta 1/T_c)$. [e] $\Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta F^{\ddagger})/T_c$.

In spite of the uncertainty in $\Delta S^{\ddagger}$, the large positive value obtained is clearly meaningful and an indication that the inversion of I in $CDCl_3$ is an unimolecular reaction. We therefore can compare the values in Table I with the known parameters of the energy barrier in the ethanolysis of 9-chloro-9-phenylfluorene (II) in 9:1 ethanol–acetone[8] ($\Delta F^{\ddagger}$ = 21.2 kcal/mol; $\Delta H^{\ddagger}$ = 18.1 kcal/mol; $\Delta S^{\ddagger}$ = −11.4 eu), which is known to have S_N1 character.[9]

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(6) (a) The $\delta\nu$ values were reported erroneously as 87 and 24 cps in the text of ref 2; (b) determined at 60 Mcps.

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(9) The semiquantitative observation that the solvolysis of II is much slower than that of 9-chloro-9-mesitylfluorene[2] already indicates that $\Delta F^{\ddagger}$ is lowered by the introduction of two *ortho* methyl groups in the phenyl radical.

It is not surprising that $\Delta H^{\ddagger}$ for the ethanolysis of II in ethanol–acetone is lower than that for the inversion of I in chloroform, since the highly polar medium used in the former case should solvate the ions much more strongly. This difference in the solvation of the ions should also lead to a more negative $\Delta S^{\ddagger}$ for the solvolysis of II than for the inversion of I, if both reactions proceed *via* the same type of intermediate. A further reduction of the absolute value of $\Delta S^{\ddagger}$ can be expected for the inversion of I if this reaction proceeds through a tight ion pair instead of well developed ions, since the solvent should not interact appreciably with such an ion pair.[10] This ion-pair mechanism would actually allow the introduction of a positive term into $\Delta S^{\ddagger}$, since one can expect the existence of a variety of isoenergetic geometries for this intermediate.

Another factor affecting the entropies of activation of the two situations in the opposite direction involves the rotational freedom of the 9-aryl substituent. In II, the phenyl group is relatively free to rotate in the ground state,[4] whereas this rotation is restricted in the intermediate carbonium ion. The result is therefore a negative term for the activation entropy related to II. Contrary to this, the steric effect of the *ortho* methyl groups in I precludes rotation in either the covalent or the ionic species, and ionization would therefore not affect this aspect of the internal entropy.

In summary, the inversion of the configuration at C-9 in 9-chloro-9-durylfluorene (as an example of *o,o'*-dimethylphenylfluorene derivatives) apparently proceeds *via* a tight ion pair which, owing to the relative mobility of the component ions and the low degree of solvation, has appreciably more freedom than the ground-state molecules.

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[10] The lack of interaction of the solvent and the intermediate in such an ion-pair mechanism is also in agreement with the observation[3] that the temperature dependence of the nmr spectrum of the related 9-chloro-9-mesitylfluorene is apparently independent of the nature of the solvent.