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# A New Type of Torsional Stereoisomerism

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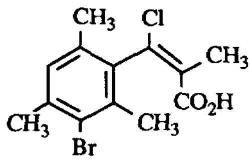
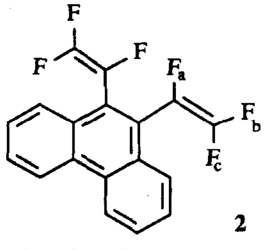
*Abstract:* Through the use of $^{19}F$ nmr spectroscopy, it has been shown that 9,10-bis(trifluorovinyl)phenanthrene exists as a pair of torsional diastereoisomers.

Stereoisomerism of the type where isomers can be isolated due to restricted rotation about single bonds has been known since the 1920's,[1] when the first chiral biphenyls were discovered. Since that time numerous examples of "atropisomers", or what have simply become known as "torsional" enantiomers and diastereoisomers have been reported.[2]

We wish to report at this time the discovery of a new type of torsional diastereoisomerism. Our observation is not unrelated to the enantiomerism exhibited by the multisubtituted styrene species, **1**, which can be resolved and is optically stable in boiling butanol.[3] During the synthesis of 9,10-bis(trifluorovinyl)phenanthrene, **2**, for a study of its thermal isomerization,[4] two sets of signals (ratio = 0.515) were observed in its $^{19}F$ nmr for each of its three magnetically non-equivalent fluorine substituents. It was hypothesized that these observed dual sets of peaks were due to torsional diastereoisomerism of **2**. The validity of this hypothesis was readily demonstrated by the observed temperature dependendence of the spectrum, the signals for $F_b$ at -17, 47 and 84 °C being shown in Figure 1.



**1**



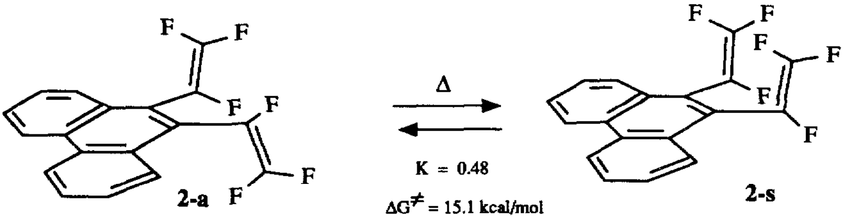
**2**

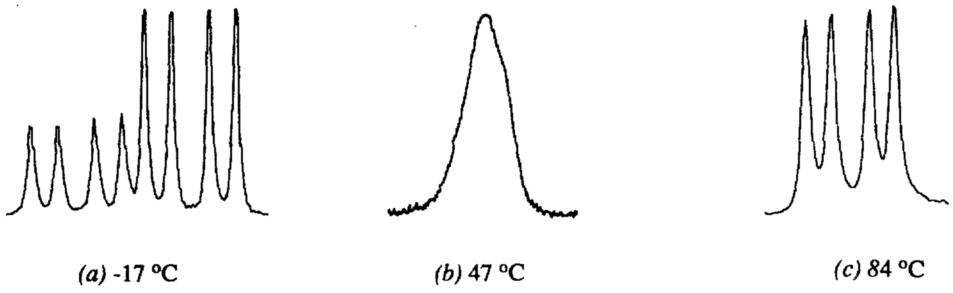
Classical theory with respect to equilibrium and nmr spectra[5,6] allows calculation of the free energy of activation for interconversion of the two torsional stereoisomers from knowledge of the shift difference and the coalescence temperature for each of the pairs of signals. Table 1 provides such data as well as our calculated values of $\Delta G^{\neq}$ for each of the fluorine signals.

Table 1. Temperature Dependence Data for $^{19}F$ NMR of **2**

| Fluorine | $T_{Coalesce}$ °C | $\Delta\upsilon$ (Hz) | $\Delta G^{\neq}$ (kcal/mol) |
|---|---|---|---|
| $F_a$ | 60° | 355.0 | 15.2 |
| $F_b$ | 45 | 122.5 | 15.1 |
| $F_c$ | 43 | 203.2 | 14.7 |

It is proposed that the torsional diastereoisomers which give rise to the observed pairs of signals are of a novel syn and anti type, **2-s** and **2-a**, wherein the two trifluorovinyl groups may assume either a syn or an anti conformational orientation with respect to the plane of the phenanthrene ring system.




(a) -17 °C

(b) 47 °C

(c) 84 °C

*Figure 1. Temperature Dependence of* $^{19}F$ *NMR Signal of* $F_b$ *of* ***2***

The observed 15 kcal/mole free energy of activation for the interconversion of the syn and anti diastereoisomers is due to a combination of steric factors which derive from the nature of the phenanthrene ring system. Outward rotation of either of the trifluorovinyl groups through the plane of the phenanthrene ring is inhibited by steric interaction between the respective $F_C$'s and the phenanthrene hydrogen substituents at the 1 and 8 positions. Likewise, rotation inward leads to similarly repulsive interactions of this same $F_C$ substituent with the other trifluorovinyl group.

The observed significant barrier to interconversion should enable us to examine the potentially distinctive photochemical behavior of the two isomers at low temperature.[4] Moreover, substitution of atoms other than H at the phenanthrene 1 and 8 positions may serve to increase the barrier to interconversion of such torsionally isomeric species so as to allow room temperature isolation. Such studies are currently underway.

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## References

1. Christie, G. H.; Kenner, J. *J. Chem. Soc.* **1920**, *121*, 614.
2. Eliel, E. L. *Stereochemistry of Carbon Compounds*, McGraw-Hill, New York, **1962**, 156-179.
3. Adams, R.; Anderson, A. W.; Miller, M. W. *J. Am. Chem. Soc.* **1941**, *63*, 1589.
4. Dolbier, W. R., Jr.; Palmer, K.; Koroniak, H.; Zhang, H.W.; Geodkin, V. L. *J. Am. Chem. Soc.* **1991**, *113*, 1059.
5. Abraham, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy,* John Wiley and Sons, New York, **1988**, 195.
6. Sundstrom, *Dynamic NMR Spectroscopy*, Academic Press, New York, **1982**, 79.

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