Tetrahedron Letters,Vol.30,No.11,pp 1429-1432,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

A DNMR STUDY OF *SYN/ANTI*-ISOMERIZATION IN Z,Z-9,10-BIS(STYRYL)ANTHRACENE.

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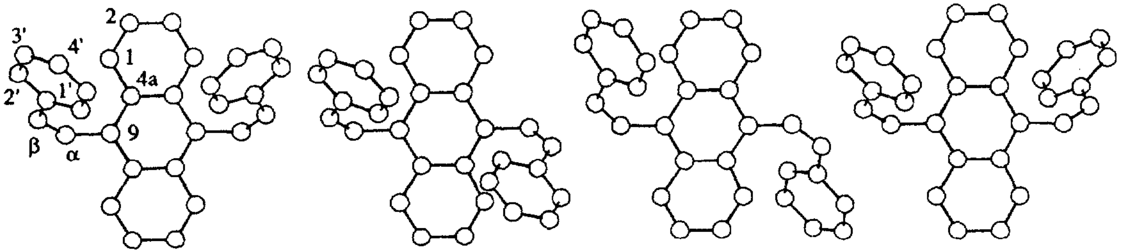
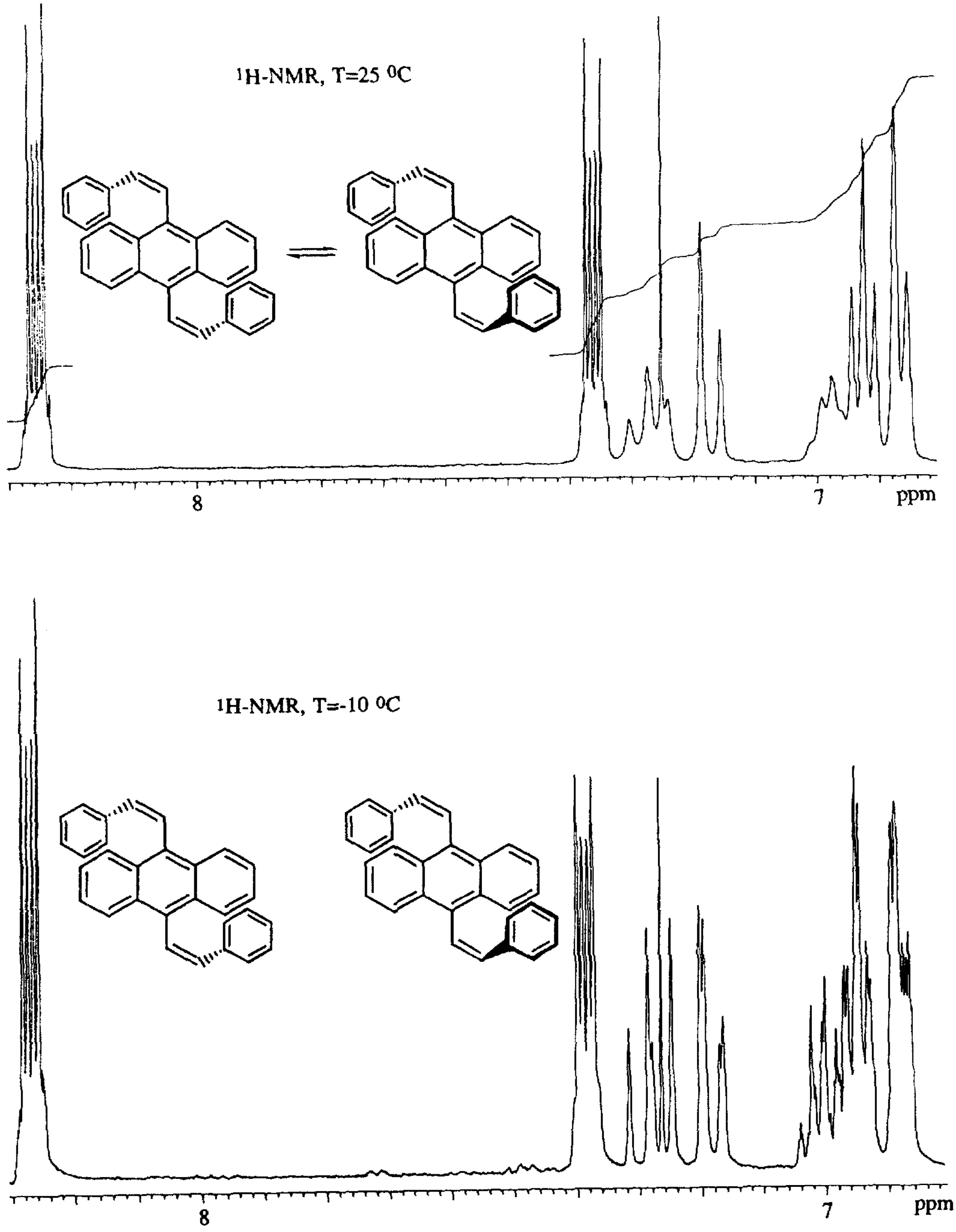
Abstract. Two isomers of Z,Z-9,10-bis(styryl)anthracene have been observed by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C chemical shifts were assigned by the ^{13}C-^{1}H *HETCOR* technique. The barrier to interconversion of these two isomers is measured to 18 kcal/mol. The *syn* isomer forms a charge transfer complex with trinitrobenzene (TNB) as determined by ^{1}H NMR methods while the other, the *anti* isomer, does not. The isomers have almost the same energy in solution whereas molecular mechanics calculations (MMP2) place the *syn* isomer ~1 kcal/mol lower than the *anti* isomer.

We have recently observed that Z,Z-4,4'-bis(3,5-di*tert*-butylstyryl)benzene on irradiation undergoes a two-fold adiabatic *Z*/*E*-isomerization to the *E*,*E*-isomer on the singlet energy surface[1]. In an earlier study Sandros and Becker have shown that Z-9-styrylanthracene also undergoes an adiabatic *Z*/*E*-photoisomerization[2]. We thus became interested in the title compound, *Z*,*Z*-9,10-bis(styryl)anthracene (Scheme 1) for a photochemical study. The compound was prepared by the standard method, hydrogenation of 9,10-bis(phenylethynyl)-anthracene over the Lindlar catalyst[3]. The NMR spectra of the product were more complicated than expected for a single isomer (Scheme 2) and in this paper we report a DNMR study of the *syn*/*anti*-isomerization of the compound. Restricted rotation and flip around the C-α, C-9 single bond in *Z* and *E*-isomers of 1,2-di-9-anthrylethene have been considered previously.[4] However, the symmetry properties of these isomers exclude the experimental verification of the restricted rotation by ^{1}H NMR metods.



1a *syn* **1b** **2a** *anti* **2b**

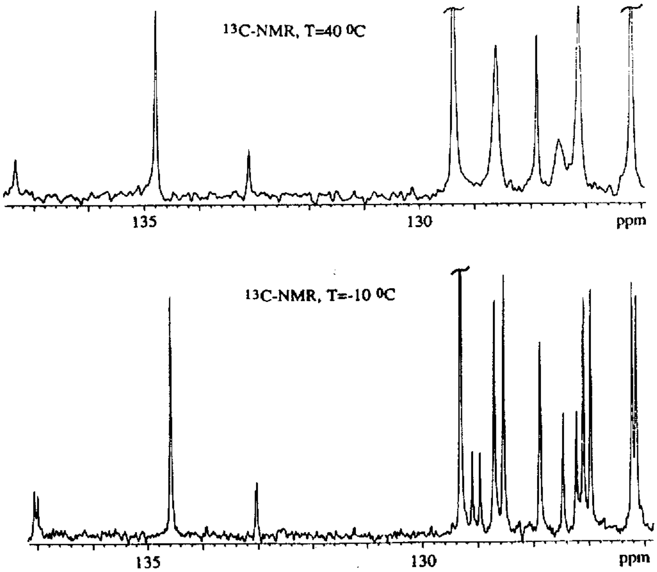
Scheme 1. The four different (MMP2 calculated) low energy conformations of the title compound. Hydrogens omitted for clarity. Carbon radii set to 0.3 Å.



Scheme 2. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of the title compound at two different temperatures

Both ^{1}H and ^{13}C NMR spectra (400 and 100 MHz, respectively, $CDCl_3$), of the title compound were run at different temperatures. At room temperature some of the signals are broadened, while at lower temperature two partly overlapping spectra for the two isomers are observed and at higher temperatures only one set of signals is obtained. The barrier to isomerization is most easily obtained from the coalescence of the ^{13}C signals from the meta carbons, C-3', in the benzene rings, $\Delta G^{\neq}=18$ kcal/mol (Scheme 3). One of the isomers is present in a slight excess (ratio 1.06 at -10 ^{0}C). Inspection of molecular models of *Z,Z*-9,10-bis(styryl)anthracene reveals that the barrier for *syn*/*anti*-isomerization could fit the observed one. We have thus assigned the two isomers as the *syn* and *anti* conformers (Scheme 1). The origin of the observed barrier is partly due to steric interactions between the hydrogens on C-α and C-1 and the interaction between the π-cloud in the passing benzene ring in the activated complex.[5]

Molecular mechanics calculations (MMP2)[6] reveal two local minima for each isomer: (**1a**) and (**1b**) for the *syn* isomer, (**2a**) and (**2b**) for the *anti* isomer with the relative energies 0.7, 0, 1.2 and 1.0 kcal/mol, respectively. Thus, the calculation favors the *syn* isomer. The calculated structures show a dihedral angle between the anthracene and the double bond planes of 60^0. This is consistent with the upfield shift of, the ^{13}C signals from the 9-carbon and the α-carbon. The ^{13}C NMR shifts were assigned to the respective carbon atoms by running ^{13}C-^{1}H *HETCOR* NMR[7] (Table 1).



Scheme 3. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) at two different temperatures.

		^{1}H shifts	
assignment	^{13}C shifts	directly bonded	long-range
C-2	126.2	7.36	8.25, 7.36
C-1	127.1	8.25	8.25
C-α	127.5	7.27	7.27
C-4'	127.9	6.98	6.98, 6.86
C-3'	128.6	6.93	6.93
C-2', C-4a	129.4	6.86	8.25, 7.17 6.98, 6.86
C-9	133.1		8.25, 7.17
C-β	134.8	7.17	7.27, 7.17 6.86
C-1'	137.4		7.27, 6.93

Table 1. Correlation between ^{1}H and ^{13}C shifts. Shifts in ppm δ-scale.

The chemical shift difference between the two isomers is too small to be sufficient for an unambiguous assignment. In order to solve this problem we have studied the charge transfer complex with TNB assuming that only the *syn* isomer can form a face to face complex with TNB in analogy with the well studied complex between TNB and anthracene[8]. On addition of a large excess of TNB to the title compound in $CDCl_3$ and subsequent cooling, we observed that only one of the two sets of signals in the ^1H spectrum was significantly affected. The change increased on further cooling and that particular isomer increased in relative amount (up to 1.34 at -30 ^0C). The shift change for the protons in the anthracene unit was similar to that in the complex between TNB and anthracene. All data are thus consistent with the assumption that only the *syn* isomer can form a TNB complex easily. From a study of the shift change we conclude that the *syn* isomer is slightly favored even without addition of TNB. The MMP2 calculations also favor the syn isomer, but the calculated energy difference, between the *syn* and *anti* isomer, is exaggerated. This is due to positive van der Waals interactions between the benzene rings in the *syn* isomer. In solution, such intramolecular van der Waals interactions are of much less relevance.

Conclusions. We have observed two isomers of 9,10-bis(styryl)anthracene assigned as the *syn* and *anti* isomers, which interconvert slowly on the NMR time scale. The energies of the two isomers are almost the same in solution but only one isomer, the *syn* isomer, is able to form a complex with TNB. Further studies will reveal whether both isomers show similar photochemical behaviour upon irradiation or if they have different pathways from their respective excited states.

Acknowledgement. We thank Dr D. Tanner for improving the manuscript. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

References

1. To be published. Partially presented as posters at the Euchem Conference on Photoisomerism and Rotamerism in Organic Molecules, Assisi Italy 1988 and at the XII IUPAC Symposium on Photochemistry, Bologna Italy 1988.
2. Sandros, K., Becker, H.-D. *J. Photochem. 1987,* **39**, 301.
3. Ried, W., Donner, W., Schlegelmilch, W. *Chem. Ber. 1961,* **94**, 1051.
4. Geiger, J. H., Mislow, K. *J.Org. Chem. 1986,* **51**, 5471.
5. See *eg* Nachbar, R. B., Jr., Hounshell, W. D., Naman, V. A., Wennerstöm, O., Guenzi, A., Mislow, K. *J. Org. Chem. 1983,* **48**, 1227.
6. Burkert, U., Allinger, N.L. "Molecular Mechanics", ACS Monograph *1982*, 177.
7. Bax, A. "Topics in ^{13}C NMR Spectroscopy", Wiley, New York *1984*, **4**, 197.
8. Foster, R. "Organic Charge-Transfer Complexes", Academic Press, London *1969* and references therein.

(Received in UK 5 January 1989)