

A HIGH ENTHALPY VALUE IN THERMAL ISOMERIZATION OF PHOTOSYNTHEZIZED CIS-9-STYRYLACRIDINES

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Summary Four stable stilbene-like cis-isomers - i.e. 9-styrylacridines - were photosynthesized and their $\Delta H_{cis \rightarrow trans}$ thermal isomerization determined

In the trans $\frac{\lambda}{\Delta}$ cis interconversion of stilbenes and their analogues, an important role is played by the dihedral angle θ , formed by the planes containing the benzene rings and the double bond. The highest resonance energy occurs when $\theta=0^\circ$, and the lowest when $\theta=90^\circ$.¹ In the trans derivatives the size of the dihedral angle is affected by the steric hindrance between ethylenic and aromatic hydrogens, in the cis-derivatives, the four hydrogens ortho and peri to the two σ bonds are involved. In order to obtain cis-isomers with the minimum expected value of resonance energy and high energetic content, we synthesized four cis-9-styrylacridines with the dihedral angle of ca. 70° estimated from molecular models. For these molecules, the planes containing benzene and acridine systems are almost aligned, however resonance energy is not affected by through-space conjugation, arising from partial overlap between non-parallel π -orbitals of two aromatic systems.²

The coloured trans-acridines were synthesized according to the Wadsworth-Ammons³ method for crown-ether assisted olefin formation. The corresponding cis-isomers were obtained from the trans-acridines in 100% yield (HPLC) by visible light irradiation ($\lambda \geq 400$ nm). All products were identified by IR and NMR spectroscopy. Thermal analyses were performed with a differential scanning calorimeter Perkin-Elmer Mod. DSC-2, in sealed ultrapure aluminium sample pans, dynamic ($5^\circ\text{C}/\text{min}$) and isothermal models were applied for transition phase and isomerization process measurements, respectively.

We report the thermal and thermodynamic data of isomeric acridines, together with the corresponding values for stilbene, as a reference. A close similarity exists between ΔH_{1som} values for cis-stilbene and cis-acridines 3, 5 and 7 (Table). The results indicate that the three cis-structures considered are not as rigid as supposed on the basis of their molecular models.

On the other hand, compound 9 exhibits a far higher ΔH_{1som} value (-13.2 Kcal/mole). The peculiarity of its structure is represented by two ortho methyl groups. The striking difference in ΔH_{1som} can therefore be attributed to a steric hindrance due to both methyl groups, which is different in cis and trans compounds. In this case, two methyl groups force the cis-isomer into

a constrained configuration, whilst their effect on the trans-isomer should be smaller. Therefore, the rather high value of enthalpy refers to a remarkable steric relief when 9 → 10 conversion takes place.

TABLE

SAMPLE	No	M.p.	$\Delta H_{m p}^a$ (Kcal/mole)	230°		$E_{a(cis-trans)}^{11q}$ (Kcal/mole)	$A(s^{-1})$
				$\Delta H_{(cis-trans)}^{11q}$ (Kcal/mole)	$\Delta H_{(300^\circ C)}^c$ (Kcal/mole)		
STILBENE	cis	1 5	0.1				
	trans	2 125		6.7 ^b	-1.2 ± 0.1 ^c (300°C)	37.2 ± 3.7 ^d	1.2 × 10 ¹⁵
ACRIDINES							
9-(styryl)-	cis	3 120	4.3				
	trans	4 178		5.0	-1.2 ± 0.1	17.9 ± 1.8	5.0 × 10 ⁸
9-(2,5-dimethylstyryl)-	cis	5 138	5.9				
	trans	6 176		6.1	-1.0 ± 0.1	3.4 ± 0.3	0.2 × 10 ³
9-(3,5-dimethylstyryl)-	cis	7 115	5.0				
	trans	8 164		3.5	-2.1 ± 0.1	7.6 ± 0.7	9.0 × 10 ³
9-(2,3,5,6-tetramethylstyryl)-	cis	9 142	4.6				
	trans	10 224		7.0	-13.2 ± 0.1	7.5 ± 0.7	2.5 × 10 ³

a) Enthalpy value of solid → liquid transition b) 7.2 Kcal/mole, Ref. 4 c) This value is in agreement with the one reported by Wolf and Cammenga which is calculated by taking into account the $\Delta S_{(cis-trans)}$, Ref. 1. d) 42.8 ± 2.0 Kcal/mole, 42.6 ± 2.0 Kcal/mole, Ref. 5,6

A $\Delta H_{isom.} > 25$ Kcal/mole is considered desirable in order to utilize this type of isomerization in photochemical conversion and storage of solar energy.⁷

According to the low activation energy and the reduced frequency factors obtained (Table), the isomerization seems to involve a triplet transition state mechanism, at least when methyl substituted styrylacridines 5,7, and 9 are taken into account.

Acknowledgments We thank the Italian C.N.R. for financial support. We also wish to thank Prof. U. Mazzucato for encouragement and discussion.

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(Received in UK 7 July 1983)