Thermal Isomerization of Photochemically Synthesized (*Z*)-9-Styrylacridines. An Unusually High Enthalpy of *Z* ⟶ *E* Conversion for Stilbene-like Compounds

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Eight stable (*Z*)-9-styrylacridines, have been photochemically synthesized and their enthalpies of thermal isomerization ($\Delta H_{Z\rightarrow E}$) determined by means of thermal analysis. The enthalpy values were found to be influenced by both electronic and steric effects. The title compounds were used as models in order to gain insight into the energetic implications involved in the *Z* ⟶ *E* isomerization process and its applicability to photochemical energy conversion by irradiation in the visible wavelength region.

E ⟶ *Z* Photoisomerization of stilbene-like compounds has long been considered as a potential chemical system for the conversion and storage of solar energy.[1]

The isomeric pair (*Z*,*E*) involved in the photoequilibrium must fulful several requirements,[2,3] the most important being a high enthalpy of isomerization energy ($\Delta H_{Z\rightarrow E}$). To date there are no literature reports describing (*Z*)- and (*E*)-1,2-disubstituted ethenes with such specific properties.

The results reported in this paper arose from synthesis of an *E*-alkene derivative, the visible light absorption of which lay in the range $300 < \lambda < 700$ nm, according to the more stringent condition already found by Guilford Jones.[2] Furthermore, the above starting compound could be further modified through appropriate functionalities, in order to monitor the energy difference between the geometric isomers of a series of stilbene derivatives.

Our attention was directed towards the (*E*)-styrylacridines, a class of yellow compounds the synthesis of which was first accomplished by Wilson *et al.*[4] To account for some inconsistent melting point values, it was suggested that the synthetic procedure adopted possibly resulted in a mixture of isomeric products, as a result of adventitious light.

The availability of the above styrylacridines prompted us to prepare and functionalize some of them, so as to obtain systems able to undergo highly efficient photochemical conversion by irradiation in the visible spectral range. Associated thermodynamic parameters, such as enthalpy, enthropy and activation energy, were also determined by thermal analysis, for a fuller approach to the general problem related to the conversion and storage of solar energy.

Experimental

Synthesis of Starting Products.—9-Bromomethylacridine was prepared from diphenylamine by sequential acetylation,[5] cyclization[6] and bromination.[4] Non-commercially available aldehydes were synthesized from the corresponding benzyl halide, by oxidation by the sodium salt of 2-nitropropane.[7] 3,5-Dimethyl-4-nitrobenzaldehyde was obtained by oxidation of 2-nitromesitylene with chromic anhydride.[8]

3,5-*Dimethylbenzyl Bromide.*—Mesitylene (12.0 g, 100 mmol), carbon tetrachloride (385 cm^3), NBS (17.8 g, 100 mmol) and benzoyl peroxide (1.0 g, 4 mmol) were admixed in a 1 dm^3 round-bottomed flask. The reaction was refluxed overnight after which the solvent was evaporated off from the cold, filtered liquid mixture. The very irritant oil obtained was distilled, b.p. 71–72 °C at 1 atm (14.5 g, 73%) (Found: C, 54.3; H, 5.5. $C_9H_{11}Br$ requires C, 54.3; H, 5.6%).

2,3,5,6-*Tetramethylbenzyl Chloride.*—This intermediate was obtained according to the procedure described by Aitken.[9]

2,3,5,6-*Tetramethyl-4-nitrobenzyl Chloride.*—Nitrodurene was obtained by exaustive nitration of durene,[10] followed by selective reduction of the nitro group,[11] and deamination.[12] To the nitrodurene (69.5 g), was added 1,1-dichloromethyl methyl ether (60 cm^3) with stirring. The ice-cooled mixture was cautiously added to chlorosulphuric acid (85.0 g), with vigorous stirring; throughout the addition the temperature was maintained below 10 °C. The reaction was stirred overnight, during which time the temperature was allowed to rise slowly to ambient. The mixture was then poured into water, and repeatedly extracted with chloroform. The organic phase was washed several times with 10% aqueous NaOH and then with water. The solvent was evaporated off, after the traces of water had been removed by azeotropic distillation (by repeated addition of $CHCl_3$ and rotary evaporation). Recrystallization of the product from methanol gave a pale yellow solid, m.p. 110 °C (38.4 g, 47%). $\delta(CDCl_3)$ 2.21 (3 H, s, Me), 2.26 (3 H, s, Me) and 4.62 (2 H, s, CH_2Cl) (Found: C, 58.1; H, 6.2; N, 6.2. $C_{11}H_{14}ClNO_2$ requires C, 58.0; H, 6.2; N, 6.1%).

3,5-*Dimethylbenzaldehyde.*—To a four-necked round-bottomed flask (condenser with $CaCl_2$ tube, thermometer, mechanical stirrer and dropping funnel) containing absolute ethanol (100 cm^3), was added sodium (2.3 g, 100 mmol). The flask was kept in an ice bath until the sodium had completely reacted after which 2-nitropropane (8.9 g, 100 mmol) was added. The temperature was allowed to rise to ambient and the 2-nitropropane sodium salt was then separated off. 3,5-Dimethylbenzyl bromide (19.9 g, 100 mmol) was then added and the mixture was heated on a water bath (60 °C) for 3 h. The ethanol was distilled off under reduced pressure, and the residue was treated with water (200 cm^3). Usual work-up (ether extraction, NaOH treatment to eliminate oxime, washing with water and solvent evaporation) gave an oil of good purity (TLC and GPC); (11.3 g, 84%). $\delta(CDCl_3)$ 2.35 (6 H, s, Me), 7.30 (1 H, s, ArH), 7.55 (2 H, s, ArH) and 10.02 (1 H, s, CHO) (Found: C, 80.4; H, 7.6. $C_9H_{10}O$ requires C, 80.6; H, 7.5%).

2,3,5,6-*Tetramethylbenzaldehyde.*—2,3,5,6-Tetramethylbenzyl chloride (18.2 g, 100 mmol) was made to react, by a procedure similar to that previously described. An oily product

was obtained, after ether evaporation and subsequent distillation under reduced pressure (135 °C and 15 Torr) (13.2 g, 82%). $\delta(CDCl_3)$ 1.92 (6 H, s, Me_2), 2.04 (6 H, s, Me_2), 6.67 (1 H, s, ArH) and 10.07 (1 H, s, CHO) (Found: C, 81.5; H, 8.6. $C_{11}H_{14}O$ requires C, 81.4; H, 8.7%).

2,3,5,6-*Tetramethyl-4-nitrobenzaldehyde*.—2,3,5,6-Tetramethyl-4-nitrobenzyl chloride (18.2 g, 100 mmol) was made to react, by a procedure similar to that previously described. The crude product was extracted with chloroform, and the organic phase washed with aqueous NaOH and water. After solvent evaporation, a solid product was obtained, m.p. 162–164 °C (from ethanol) (16.3 g, 79%). $\delta(CDCl_3)$ 2.04 (6 H, s, Me_2), 2.27 (6 H, s, Me_2) and 10.01 (1 H, s, CHO) (Found: C, 63.7; H, 6.4; N, 6.8. $C_{11}H_{13}NO_3$ requires C, 63.8; H, 6.3; N, 6.8%).

Diethyl Acridin-9-ylmethylphosphonate.—9-Bromomethylacridine (1.49 g, 5 mmol) and triethyl phosphite (1.24 g, 7.5 mmol) were kept under reflux for 4 h. The red solution obtained was distilled under reduced pressure, to eliminate the excess of triethyl phosphite. The solid residue was recrystallized from ethanol to give a product which decomposed at its m.p. (248–251 °C). $\delta(CDCl_3)$ 1.07 (6 H, t, Me_2), 3.72–4.08 [4 H, m, $(CH_2)_2$], 4.24 (2 H, s, CH_2), 7.49–7.95 (4 H, m, AcrH) and 8.19–8.38 (4 H, m, AcrH).

In the subsequent reaction, the red solution mentioned above was used without further treatment.

Synthesis of (E)-*Styrylacridines*

9-*Styrylacridine* (**4**).—Anhydrous tetrahydrofuran (THF, 20 cm^3), sodium hydride (0.12 g, 50 mmol) and 15-crown-5 (50 mg, 0.23 mmol) were placed in a three-necked flask equipped with a thermometer, mechanical stirrer and pressure-equalizing dropping funnel. The contents of the flask were kept at 35–40 °C by means of a water bath during the dropwise addition of a solution of diethyl acridin-9-ylmethylphosphonate (1.96 g, 5.0 mmol) and benzaldehyde (0.53 g, 5.0 mmol) in THF (10 cm^3). Hydrogen was immediately evolved and the reaction mixture became pink. After the addition, the reaction was allowed to stand for 2 h at ambient temperature. A little ethanol was added and the solvent was evaporated off under reduced pressure. The residue was treated with anhydrous ethanol (*ca.* 50 cm^3) and refluxed for 30 min. The filtered solution was then allowed to cool to ambient temperature, and was further cooled to −20 °C. A solid product was obtained, m.p. 195–198 °C (0.67 g, 48%). $\delta(CDCl_3)$ 6.86–7.97 (11 H, m, ArH, AcrH and ethenic H atoms) and 8.16–8.36 (4 H, m, AcrH) (Found: C, 89.7; H, 5.3; N, 5.0. $C_{21}H_{15}N$ requires C, 89.6; H, 5.4; N, 5.0%).

The general procedure described above to obtain compound **4** was followed for all other substituted acridines (see below), with the same molar amounts of reagents.

9-(2,5-*Dimethylstyryl*)*acridine* (**6**). 2,5-Dimethylbenzaldehyde (0.67 g, 5 mmol) yielded a product of m.p. 178–180 °C (from anhydrous ethanol) (0.80 g, 52%). $\delta(CDCl_3)$ 2.37 (3 H, s, Me), 2.45 (3 H, s, Me), 7.12–7.87 (9 H, m, ArH, AcrH and ethenic H atoms) and 8.22–8.40 (4 H, m, AcrH) (Found: C, 89.1; H, 6.2; N, 4.5. $C_{23}H_{19}N$ requires C, 89.3; H, 6.1; N, 4.5%).

9-(3,5-*Dimethylstyryl*)*acridine* (**8**). 3,5-Dimethylbenzaldehyde (0.67 g, 5 mmol) yielded a product of m.p. 180 °C (from absolute ethanol) (0.85 g, 55%). $\delta(CDCl_3)$ 2.36 (6 H, s, Me_2), 7.12–7.87 (9 H, m, ArH, AcrH and ethenic H atoms) and 8.22–8.40 (4 H, m, AcrH) (Found: C, 89.3; H, 6.1; N, 4.5. $C_{23}H_{19}N$ requires C, 89.3; H, 6.2; N, 4.5%).

9-(3,5-*Dimethyl-4-nitrostyryl*)*acridine*. 3,5-Dimethyl-4-nitrobenzaldehyde (0.89 g, 5 mmol) yielded a product (0.97 g, 55%) of m.p. 163–165 °C after recrystallization from absolute ethanol followed by HPLC on a semipreparative column (C 18, 20 cm, ϕ = 3.9 cm, elution solvents acetone–water 4:1). $\delta(CDCl_3)$ 2.33 (6 H, s, Me_2), 7.23–7.82 (8 H, m, ArH, AcrH and ethenic H atoms) and 8.10–8.33 (4 H, m, AcrH) (Found: C, 77.9; H, 5.1; N, 7.9. $C_{23}H_{18}N_2O_2$ requires C, 77.9; H, 5.1; N, 7.9%).

9-(2,3,5,6-*Tetramethylstyryl*)*acridine* (**10**). 2,3,5,6-Tetramethylbenzaldehyde (0.81 g, 5 mmol) yielded a product (0.81 g, 48%) of m.p. 230–232 °C (decomp.) (from absolute ethanol). $\delta(CDCl_3)$ 2.36 (6 H, s, Me_2), 2.48 (6 H, s, Me_2), 7.03–7.86 (7 H, m, ArH, AcrH and ethenic H atoms) and 8.23–8.33 (4 H, m, AcrH) (Found: C, 89.2; H, 6.5; N, 4.1. $C_{25}H_{23}N$ requires: C, 89.0; H, 6.8; N, 4.1%).

9-(1-*Naphthyl*)*acridine* (**12**). Naphthalene-1-carbaldehyde (0.78 g, 5 mmol) yielded a product (0.74 g, 45%) of m.p. 230–231 °C (from absolute ethanol). $\delta(CDCl_3)$ 7.45–8.12 (13 H, m, ArH, AcrH and ethenic H atoms) and 8.26–8.50 (4 H, m, AcrH) (Found: C, 90.6; H, 5.1; N, 4.2. $C_{25}H_{17}N$ requires C, 90.6; H, 5.2; N, 4.2%).

9-(2,3,5,6-*Tetramethyl-4-nitrostyryl*)*acridine*. 2,3,5,6-Tetramethyl-4-nitrobenzaldehyde (1.02 g, 5 mmol) yielded a product (0.97 g, 51%), of m.p. 243–245 °C (from absolute ethanol) $\delta(C_5D_5N)$ 2.25 (6 H, s, Me_2), 2.50 (6 H, s, Me_2), 7.19–7.80 (6 H, m, AcrH and ethenic H atoms) and 8.23–8.43 (4 H, m, AcrH) (Found: C, 78.5; H, 5.7; N, 7.3. $C_{25}H_{22}N_2O_2$ requires C, 78.5; H, 5.8; N, 7.3%).

9-(4-*Nitrostyryl*)*acridine*. 4-Nitrobenzaldehyde (0.75 g, 5 mmol) yielded a product (0.93 g, 57%), of m.p. 293–294 °C, after recrystallization from pyridine, in agreement with Sharp.[4] $\delta(CDCl_3)$ 7.21–7.83 (10 H, m, ArH, AcrH and ethenic H atoms) and 8.21–8.40 (4 H, m, AcrH).

9-(4-*Aminostyryl*)*acridine* (**14**). The product, m.p. 296 °C, was obtained by reduction of the nitro group in the previously described acridine, following the Porai–Koschitz method, as reported by Sharp.[4]

9-(4-*Amino*-3,5-*dimethylstyryl*)*acridine*. Following the method previously reported, 9-(3,5-dimethyl-4-nitrostyryl)acridine (1.06 g, 3 mmol) was reduced with a solution of $SnCl_2$. The mixture was kept under reflux for 3 days, and the solid obtained (0.90 g, 93%) had m.p. 234–235 °C (from absolute ethanol). $\delta(CDCl_3)$ 2.42 (6 H, s, Me_2), 4·85 (2 H, s, NH_2), 7.13–7.85 (9 H, m, ArH, AcrH and ethenic H atoms) and 8.23–8.45 (4 H, m, AcrH) (Found: C, 85.0; H, 6.1; N, 8.6. $C_{23}H_{20}N_2$ requires: C, 85.2; H, 6.2; N, 8.6%).

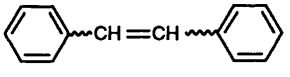
9-(4-*Amino*-2,3,5,6-*Tetramethylstyryl*)*acridine* (**16**). 9-(2,3,5,6-Tetramethyl-4-nitrostyryl)acridine (1.15 g, 3 mmol) was reduced with a solution of $SnCl_2$. The resulting reaction mixture was then refluxed for 4 days. The solid product obtained (0.94 g, 89%) had m.p. 226 °C (from absolute ethanol). $\delta(C_5D_5N)$ 2.30 (6 H, s, Me_2), 2.47 (6 H, s, Me_2), 4.87 (2 H, s, NH_2), 7.21–7.90 (6 H, m, AcrH and etheric H atoms) and 8.45–8.70 (4 H, m, AcrH) (Found: C, 85.2; H, 6.8; N, 7.9%. $C_{25}H_{24}N_2$ requires C, 85.2; H, 6.9; N, 7.9%).

Photoisomerization of Styrylacridines.—The *Z* isomers were obtained by irradiation (Philips 120 WEC cool-spot visible lamp, 12 °C) of a solution in acetone of the corresponding *E*-isomer, followed by spontaneous solvent evaporation once the photoequilibrium had been established. Acetone, as the solvent of choice, is sufficiently volatile at ambient temperature not to require heating; the undesirable retroisomerization is thus avoided. The photoequilibrium of all products previously described is completely shifted towards the *Z*-isomer, as ascertained by HPLC monitoring of the acetone solution of the acridines during the irradiation (Bandpack C18 column, 20 cm, ϕ = 1.5 cm, acetone–water 4:1 as eluent solvents; a differential refractometer or photometric detectors were used). At 365 nm, the radiation adsorbed was essentially the same for both isomers, while the retention time of each *E*-acridine were *ca.* 1 min longer than those of the corresponding *Z*-isomer.

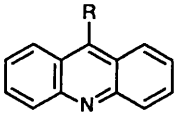
Table 1 Thermal analysis data

Compound	Isomer	M.p./°C	$\Delta H_{m.p.}$/kcal mol^{-1}	$\Delta S_{m.p.}$/cal mol^{-1} K^{-1} [a]	$\Delta H^{230}_{Z\rightarrow E}$(liq.)/kcal mol^{-1}	$E_{a,Z\text{-}E}$(liq.)/kcal mol^{-1}
1	*Z*	5	0.1	0.3	−1.2 ± 0.1 (300 °C)	37.2 ± 3.7
2	*E*	125	6.7 [b]	16.8		
3	*Z*	120	4.3	10.9	−1.2 ± 0.1	17.9 ± 1.8
4	*E*	178	5.0	11.2		
5	*Z*	138	5.9	14.4	−1.0 ± 0.1	3.4 ± 0.3
6	*E*	176	6.1	13.6		
7	*Z*	115	5.0	12.8	−2.1 ± 0.1	7.6 ± 0.7
8	*E*	164	3.5	8.0		
9	*Z*	142	4.6	11.2	−13.2 ± 0.1	7.5 ± 0.7
10	*E*	224	7.0	14.1		
11	*Z*	168	5.0	11.4	−4.9 ± 0.1	40.3 ± 4.0
12	*E*	224	8.0	16.1		
13	*Z*	248	7.8	15.0	−4.3 ± 0.1 [c]	15.1 ± 1.5
14	*E*	246	8.3	16.0		
15	*Z*	227	6.8	13.6	−24.9 ± 3.5	12.2 ± 0.2
16	*E*	226	6.9	13.8		

[a] Calculated. [b] Lit.,[6] 7.2 kcal mol^{-1} (1 cal = 4.184 J). [c] At 260 °C.



1 *Z*
2 *E*



3 Ph-CH=CH$_2$- (*Z*)
4 Ph-CH=CH$_2$- (*E*)
5 2,5-Me$_2$C$_6$H$_3$-CH=CH$_2$- (*Z*)
6 2,5-Me$_2$C$_6$H$_3$-CH=CH$_2$- (*E*)
7 3,5-Me$_2$C$_6$H$_3$-CH=CH$_2$- (*Z*)
8 3,5-Me$_2$C$_6$H$_3$-CH=CH$_2$- (*E*)
9 2,3,5,6-Me$_4$C$_6$H-CH=CH$_2$- (*Z*)
10 2,3,5,6-Me$_4$C$_6$H-CH=CH$_2$- (*E*)
11 1-Naphthyl (*Z*)
12 1-Naphthyl (*E*)
13 4-NH$_2$C$_6$H$_4$-CH=CH$_2$- (*Z*)
14 4-NH$_2$C$_6$H$_4$-CH=CH$_2$- (*E*)
15 2,3,5,6-Me$_4$-4-NH$_2$-C$_6$-CH=CH$_2$- (*Z*)
16 2,3,5,6-Me$_4$-4-NH$_2$-C$_6$-CH=CH$_2$- (*E*)

In the case of acridines containing an amino group, HPLC monitoring was not feasible, owing to retroisomerization. An alternative procedure was followed, in which infrared spectra were recorded, with the absorption at 960 cm^{-1} (CH stretching vibration of the *E*-isomer) being used as a probe.

In the case of (*Z*)-9-(4-amino-2,3,5,6-tetramethylstyryl)-acridine (**15**), the purity was determined by ^{1}H NMR spectroscopy; the spectrum showed two singlets due to the methyl groups at δ = 1.90 and 2.08, while the same signals for the *E*-isomer (**16**) appeared at δ = 2.30 and 2.47, respectively.

Thermal Z ⟶ E *Isomerization, via DSC.*—Thermal analysis data were obtained with a Perkin-Elmer Model DSC-2c apparatus, equipped with a Perkin-Elmer Model 3600 Data Station. Indium was used as a standard for temperature and enthalpic output. The instrument was preset at 308 K. The weighed sample (1–3 mg) was sealed in an aluminium pan and then either heated at 5 °C min^{-1} (dynamic tests) or rapidly brought to a predetermined temperature (isothermal tests). Dynamic and isothermal models were applied for transition-phase and isomerization process measurements, respectively.

The enthalpy values and the energies of activation were calculated from isothermal measurements, carried out in the range 473–538 K, according to Barton.[13]

Table 1 lists the data obtained by thermal analysis.

Chemical and Photochemical Properties of the Isomers (**15**) *and* (**16**).—(*Z*)-9-(2,3,5,6-Tetramethylstyryl)acridine (**15**) isomerizes back to the *E*-isomer **16** at pH < 5, probably because of the contribution of the ionic resonance structure (Fig. 1) which is a quinonoid structure without an alkenic double bond. Experimental evidence supporting such an interpretation was obtained by determining the rate of *Z* ⟶ *E* isomerization, at different pH values (8.68, 8.04 and 6.44) and in the temperature range 23–54 °C, through the absorbance increase at 410 nm. The activation energy of the reaction was also calculated: E_a/kcal mol^{-1} 9.83 (pH = 8.68), 9.28 (pH = 8.04) and 9.21 (pH = 6.44). These preliminary data give enough evidence to support the hypothesis of an acid-catalysed mechanism.

The *Z*-isomer **15** was not stable in polar protic solvents, but its stability increased in non-protic solvents, especially those having basic properties. When pyridine–acetic acid (9:1) was used, a rapid (15 min) *E* ⟶ *Z* photoisomerization took place, as observed spectrophotometrically at 910 nm. When the same solution was kept in the dark for 90 min, complete isomerization to the *E* form occurred. No side-reactions were observed during these measurements. Furthermore, there were no significant variations in the UV spectrum of the solution during 180 *E* ⟶ *Z* ⟶ *E* isomerization cycles.

The quantum yield for the *E* ⟶ *Z* isomerization of compound **15** was determined, and the value obtained (ϕ_t = 0.03) is extremely low.

Results and Discussion

Solar energy conversion by means of a chemical transformation is exemplified by reversible organic chemical processes, such as the *Z* ⟶ *E* photoisomerization of a highly hindered, appropriately 1,2-disubstituted carbon–carbon double bond.

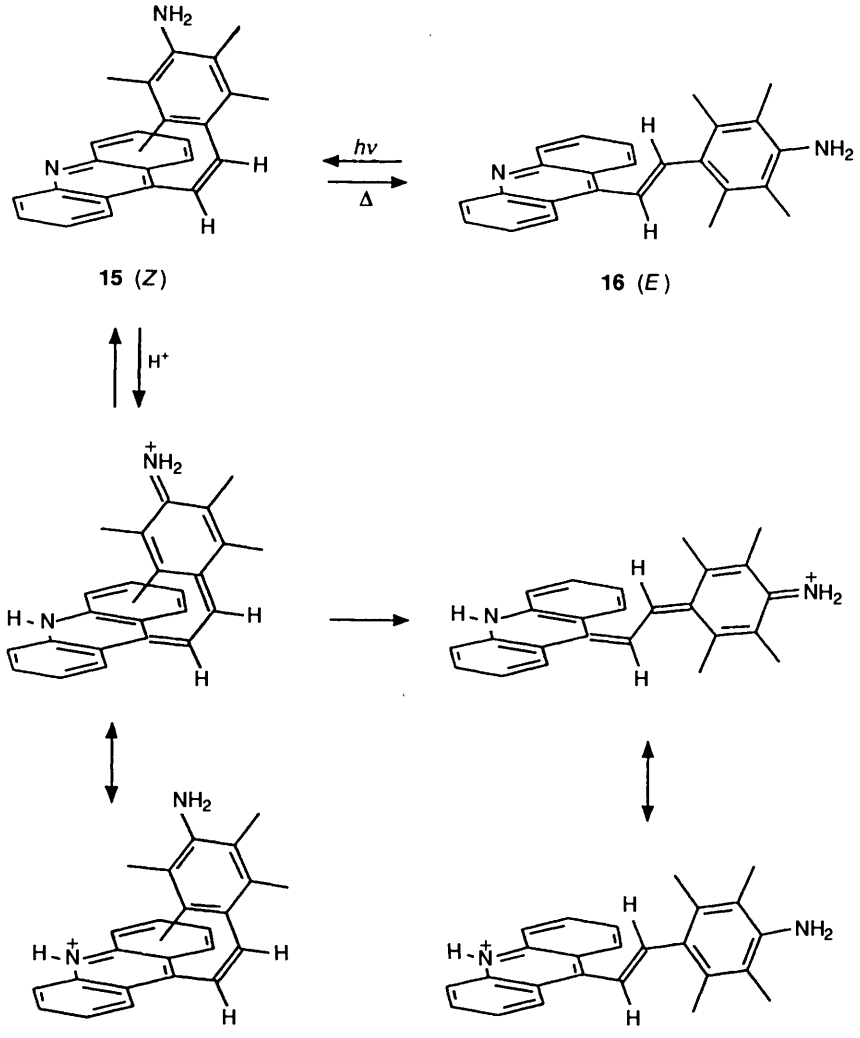


Fig. 1 $Z \rightleftharpoons E$ Isomerisation of the styrylacridines **15** and **16**

From a range of potentially useful compounds, we selected the 9-styrylacridines, which, structurally, were able to withstand many repeated cycles of isomerization, because of their thermodynamic properties.

In a preliminary communication[14] we reported some thermal parameters of (*Z*)- and (*E*)-9-styrylacridine (Table 1; **3** and **4**) and some of its derivatives, and commented especially on their enthalpy of isomerization, $\Delta H_{Z\rightarrow E}$. As a more systematic approach to solar energy conversion, we undertook an extended program of research involving synthetic procedures and thermodynamic measurements; Table 1 summarizes all data obtained on several substituted styrylacridines, including the stilbenes (**1** and **2**) as model compounds for comparison.

The numerical values of the enthalpy of isomerization in the 9-styrylacridine pairs (**3**, **4**) and (**9**, **10**) are rather different, *i.e.* -12 ± 0.1 and -13.2 ± 0.1 kcal mol^{-1}, respectively. This can be explained in terms of structural destabilization, due to the somewhat higher energy of the *E*-isomer. In the case of **9**, the two *ortho*-methyl substituents force both aromatic moieties involved, namely the acridine and durene ring systems, into a rather rigid conformation, whereby only a minimum of flexibility is possible. Moreover, an inspection of the molecular models shows that the maximum value of the dihedral angle which can be formed between the planes containing the two aromatic systems is *ca.* 15°.

The next step towards an understanding of the energetic implications of the $Z \longrightarrow E$ isomerization and their applicability to the photoconversion process was to synthesize and study other model compounds of the same isomeric pair series, namely the (*E*)-9-(1-naphthyl)- (**12**), (*E*)-9-(4-aminostyryl)- (**14**) and (*E*)-9-(4-amino-2,3,5,6-tetramethylstyryl)-acridine (**16**), and the corresponding *Z*-isomers **11**, **13** and **15**, which were obtained by preparative photochemical conversion. Their thermal and thermodynamic properties were accurately determined (Table 1). In the case of **4**, remarkable steric hindrance occurs between the hydrogen atoms on carbons 1 and 8 of the acridine moiety and on the ethenic double bond. The dihedral angle between the plane of the acridine ring and ethenic double bond plane is *ca.* 65.5°;[15] such a value corresponds to that obtained for 9-styrylanthracene.

In view of the above findings, we attempted to improve the stability of the *E* isomer in terms of electronic delocalization energy. This could be achieved either by introduction of an electron-donating primary amino group in a conjugated position or by substitution of the styryl ring with a naphthyl ring, which increased the electronic delocalization over the whole molecular system. Accordingly, for the isomeric pairs **11**, **12** and **13**, **14**, $\Delta H_{Z\rightarrow E}$ values are approximately four times greater than that of the corresponding derivatives **3** and **4**, as shown in Table 1. We consider that such high values, 4.9 and 4.3 kcal mol^{-1}, respectively, result from the electronic stabilization of the *E*-isomers, which makes them lower in energy and gives rise to a greater difference between the energy levels of the same *Z*–*E* isomeric pair. Such an effect is termed 'vertical' electronic delocalization. This does not greatly affect the *Z*-isomers, because of their strained angular geometry; in these

compounds, the dihedral angle between the two planes involved is 78.4°.[15]

The $Z \longrightarrow E$ isomerization enthalpy measured for the pair **15**, **16** reached a value of 24.9 ± 3.5 kcal mol^{-1}, and was the result of two concomitant but opposing effects: (*i*) *E*-isomer stabilization by 'vertical' electronic delocalization and (*ii*) *Z*-isomer destabilization by steric hindrance. The high average deviation (±3.5 kcal mol^{-1}) is a consequence of the experimental difficulties involved in taking measurements at such high temperatures, 535–540 K. The above data were, however, obtained from ten independent runs, taken under accurate isothermal conditions, followed by linear regression numerical treatment.

At first, this surprisingly high $\Delta H_{Z\rightarrow E}$ value appeared quite unusual. The aromatic rings of *E*-isomer **16** do not adopt a coplanar ring structure because of the concomitant steric interactions between the two hydrogen atoms on C-1 and C-8 of the acridine moiety and the *ortho*-methyl hydrogen atoms on the styryl ring, with respect to the hydrogen atoms on the ethenic double bond. However, a molecular model makes it possible to depict a conformation in which 'vertical' electronic delocalization takes place. The major increase in the difference between the energetic levels of the two isomers could be ascribed to the *Z*-isomer destabilization. In the *Z* compound, the planes of the acridine and benzene rings should be at 90° to the plane of the ethenic double bond, an arrangement of rather hindered geometry and restricted motion.

Taking into account the results of Fisher *et al.*[16] for stilbene derivatives, we note that in the corresponding styrylacridine series the same *ortho*-substituents give rise to exactly the opposite effect on $\Delta H_{Z\rightarrow E}$, as far as delocalization energy is concerned. The *ortho*-functionalities on the stilbene ring system are unable to destabilize the *Z*-isomer, in that no sterically cumbersome ring is present (as is the case with the acridine moiety), which accounts for the enthalpic decrease with respect to the unsubstituted parent stilbene.

In conclusion, a systematic investigation has enabled us to determine, with appropriate models and by means of a direct thermodynamic approach, how $\Delta H_{Z\rightarrow E}$ of a selected pair of geometric isomers is influenced by a combination of electronic and steric effects. In view of these results, together with the activation energy values obtained, we suggest that it is possible to prepare new compounds, in which there are no steric interactions between ethenic and 1- and 8-hydrogen atoms in a condensed aromatic ring, a situation that could give rise to even higher ΔH isomerization values. A $\Delta H_{Z\rightarrow E}$ value of >25 kcal mol^{-1} is considered appropriate for this reaction to be an efficient means of photochemical conversion and storage of solar energy.[3]

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