PHOTOCOLOURATION OF 2,4,4,6-TETRAARYL-1,4-DIHYDROPYRIDINES: A SEMIEMPIRICAL QUANTUM CHEMICAL STUDY

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Molecular geometries of 1,4-dihydropyridines *Ia*, *Ib* and their possible photoisomers *IIa* – *Va* and *IIb* – *Vb* were optimized by the PM3 method. The electronic absorption spectra were calculated by the CNDO/S-CI procedure and compared with the experimental spectroscopic data. A probable mechanism of the photocolouration of *Ia*, *Ib*, caused by sunlight or UV illumination, is proposed, and structures *IIIa*, *IIIb* are assigned to violet or green coloured species.

It is well known that colourless 2,4,4,6-tetraphenyl-1,4-dihydropyridine[1 – 5] and its various derivatives[3 – 5] exhibit photocolouration into red, violet, blue or green after UV or sunlight illumination. Although some proposals have been put forward regarding molecular structures of the coloured species responsible for the photochromic behaviour[4], no justified physical and chemical insight into the problem has been formulated yet. In this communication we report a semiempirical MO study of two representatives of the photochromic substances, 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (*Ia*) as well as of its analogue *Ib*, linked at 2-positions of the two 4-phenyl groups. The same approach has been applied to expected possible photoisomers *IIa* – *Va* and *IIb* – *Vb* to find the species responsible for the observed photocolouration effect. The X-ray structure of *Ia* (ref.[6]) and spectroscopic-photochromic properties of *Ia*, *Ib* have been compared with corresponding theoretical characteristics.

EXPERIMENTAL

The melting temperatures were measured on a Boetius apparatus and were not corrected. ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker AM-400 apparatus with TMS as internal standard at 297 K. IR spectra were recorded on a Perkin–Elmer 325 spectrometer. UV-VIS absorption spectra were measured in solution using a Hewlett–Packard 8451A recording spectrophotometer. The spectra of polycrystalline powders were determined on a Perkin–Elmer–Hitachi 340 instrument by the diffuse reflectance under argon in the same way as in preceding paper[5].

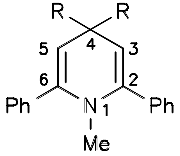
The preparation of 1,4-dihydropyridine *Ia*, m.p. 182 – 184 °C, has been reported previously[7].

4,4-(Biphenyl-2,2′-diyl)-2,6-diphenyl-1-methyl-1,4-dihydropyridine (*Ib*)

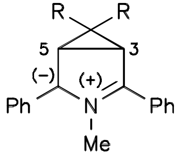
A mixture of 0.3 g 1,3,3,5-tetraphenylpentane-1,5-dione[7] and 500 ml methanol was added to a suspension obtained by successive addition of sodium (14.5 g) and methylammonium chloride (47 g) to 250 ml methanol. The reaction mixture was stirred at 20 °C for 7 days, whereafter it was evaporated under reduced pressure, decomposed with 200 ml water and repeatedly extracted with toluene. Combined extracts were dried with $MgSO_4$ and evaporated to dryness. The crude product was subjected to column chromatography (30 g SiO_2 40 – 100 μm, heptane–toluene 1 : 1) to give 0.28 g (94%) colourless crystals of *Ib*, m.p. 182 – 185 °C, exhibiting a colour change to green under sunlight. For $C_{30}H_{23}N$ (397.5) calculated: 90.68% C, 5.79% H, 3.52% N; found: 90.36% C, 5.95% H, 3.38% N. IR spectrum ($CHCl_3$): 1 658, 1 604 (C=C–N); 1 576 ($C=C_{arom}$). ^1H NMR spectrum ($CDCl_3$): 2.81 s, 3 H (CH_3); 4.79 s, 2 H (H3,5); 7.25 – 7.35 m, 10 H (Ph2,6); 7.47 – 7.53 m, 6 H, 7.70 dd, 2 H (fluorene). ^{13}C NMR spectrum ($CDCl_3$, APT technique): 39.96 (CH_3), 52.60 (C4), 109.76 (C3,5), 119.57, 126.27, 127.57, 127.69, 127.77, 127.92, 128.37, 137.88, 138.84, 145.77 (Ph2,6; fluorene), 154.77 (C2,6).

CALCULATIONS

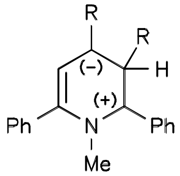
The molecular geometries of structures *Ia* – *Va* and *Ib* – *Vb* were obtained by the PM3 optimization[8]. Calculations of the electronic spectra were performed by the CNDO/ S-CI using the parameter κ = 0.585 for the resonance integrals of π-bonds[9]. The integrals were calculated according to Mataga and Nishimoto[10]. For *Ia*, *Ib* the size of CI was 100 singly excited *i*–*j* configurations, for *IIa*, *IIb* – *Va*, *Vb* the size of CI was limited to 225 singly excited *i*–*j* configurations corresponding to electron excitations from the *i*-th bonding MO to the *j*-th antibonding MO (Table VI).



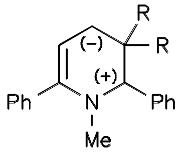
I



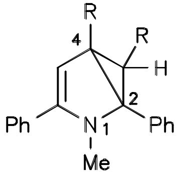
II



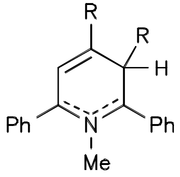
III



IV



V

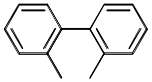


VI

In formulae *I*–*VI* :

a, R = Ph;

b, R =



RESULTS AND DISCUSSION

First, the applicability of the PM3 and CNDO/S-CI methods to 1,4-dihydropyridines *Ia*, *Ib* was tested and then the calculations were extended to expected photoisomers *IIa* – *Vb* in their ground states.

Molecular Energies and Structures

All molecular structures *Ia* – *Vb* were optimized by the PM3 procedure. The assumed species *IIa* – *Va* and *IIb* – *Vb* were found to be physically justified. Calculated molecu-

TABLE I
PM3 energies of molecules *I* – *V* at their optimized geometries

Compound	ΔH_f[a]	E_{rel}[b]	Compound	ΔH_f[a]	E_{rel}[b]
Ia	607.4	0.0	*Ib*	615.6	0.0
IIa	702.4	95.0	*IIb*	731.9	116.3
IIIa	630.6	23.2	*IIIb*	627.3	11.7
IVa	690.1	82.7	*IVb*	665.2	49.6
Va	692.2	84.8	*Vb*	640.3	24.7

[a] Heats of formation in kJ mol^{-1}; [b] relative molecular energies in kJ mol^{-1}.

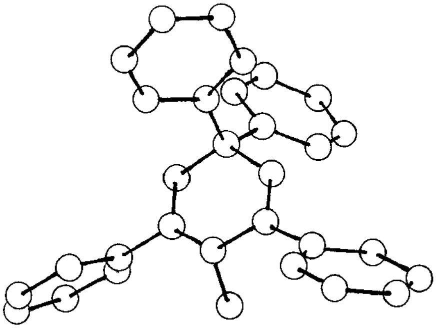


FIG. 1
Molecular skeleton of 1,4-dihydropyridine *Ia* resulting from the PM3 optimization. Pyramidal configuration at N1 is characteristic and in agreement with the X-ray analysis[6]

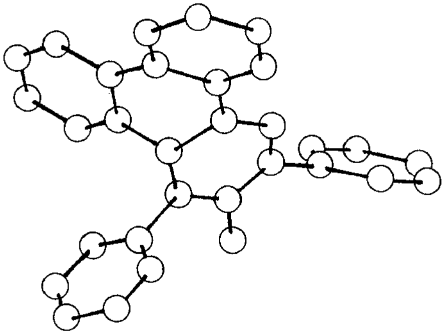


FIG. 2
Molecular skeleton of 1,3-dihydropyridine *IIIb* resulting from the PM3 optimization. Almost planar configuration at N1 is characteristic

lar energies (Table I) enable some reasonable conclusions to be made: (i) The most stable molecules seem to be the starting 1,4-dihydropyridines *Ia*, *Ib*. (ii) Compared to *IIa*, *IIb*, *IVa*, *IVb* and *Vb*, molecules *IIIa*, *IIIb* are rather stable intermediates and they may be considered as possible candidates for photocolouring species or photodegradation products.

Comparison of the PM3 calculated and X-ray determined[6] internal coordinates of 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (*Ia*) is given in Tables II and III. A satisfactory agreement was found for the bond lengths and angles. A worse correspondence between the calculated and found dihedral angles may be caused by crystal matrix fields. Nevertheless, the PM3 method seems to give a true picture of the molecular shape of *Ia*. Figures 1 to 5 show the molecular conformations of *Ia*, *IIIb*, *IIa*, *IIIa* and

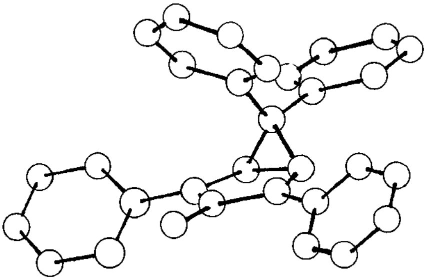


FIG. 3
Molecular skeleton of the 3,5-bridged photoisomer *IIa* resulting from the PM3 optimization. Planar configuration at N1 is characteristic

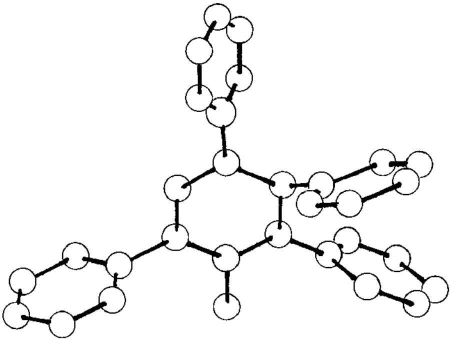


FIG. 4
Molecular skeleton of 1,3-dihydropyridine *IIIa* resulting from the PM3 optimization. Almost planar heterocycle is characteristic

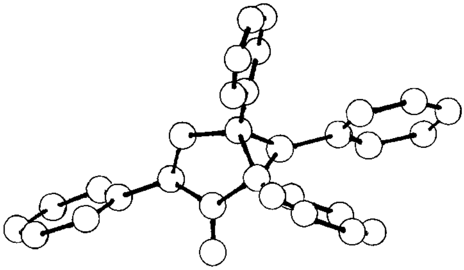


FIG. 5
Molecular skeleton of the 2,4-bridged photoisomer *Va* resulting from the PM3 optimization

Va obtained by the the PM3 optimization procedures. The heterocyclic bridged systems were found to exhibit typical shapes (Figs 3 and 5). The heterocyclic rings in the formally mesoionic molecules *IIIa*, *IIIb* (Figs 2 and 4) exhibit similar planar shapes with bond lengths approximately expressed by the formulae *VIa*, *VIb* (Table IV).

Table II
Comparison of calculated and observed bond lengths (pm) and bond angles (deg) for 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (*Ia*)

Bond	X-Ray[a]	PM3	Bond angle	X-Ray[a]	PM3
N1–C2	140.4	144.0	C6–N1–C2	116.8	116.5
C2–C3	132.4	134.6	N1–C2–C3	122.9	122.3
C3–C4	151.9	150.4	C2–C3–C4	125.2	123.6
C4–C5	150.6	150.3	C3–C4–C5	107.2	111.5
C5–C6	133.3	134.7	C4–C5–C6	125.8	123.2
C6–N1	147.4	148.0	Me–N1–C2	116.5	115.3
C2–Ph2	149.5	148.1	Ph2–C2–N1	116.2	117.7
C4–Ph4	155.0	152.8	Ph4–C4–Ph4′	110.0	110.5
C4–Ph4′	154.1	152.8	Ph4–C4–C5	112.3	111.6
C6–Ph6	147.7	147.8	Ph4′–C4–C3	112.2	111.5
			Ph6–C6–N1	116.4	117.3

[a] Taken from ref.[6].

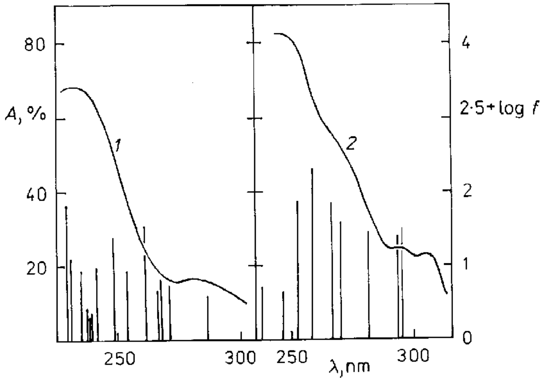


Fig. 6
Comparison of the absorption curves of 1,4-dihydropyridines in 1,2-dichloroethane with the CNDO/S-CI calculated spectra. *1* Compound *Ia*; *2* compound *Ib*

Charge Distribution

Some values of total charge distribution for 1,4-dihydropyridines *Ia*, *Ib* and their assumed photoisomers *IIIa*, *IIIb* are given in Table V. Charge alternation typical of relatively stable π-electron systems results only from the calculations of the starting compounds *Ia*, *Ib*. In addition, high electron densities on C3 and C5 centres (–0.206) agree well with the known[11] electrophilic substitutions in the positions 3 and 5 of 1,4-dihydropyridine *Ia*. On the other hand, charge distributions within the heterocyclic

TABLE III

Comparison of calculated and observed dihedral angles (deg) for 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (*Ia*)

Dihedral angle	X-Ray[a]	PM3	Dihedral angle	X-Ray[a]	PM3
N1–C2–C3–C4	2.7	–1.6	N1–C2–Ph2[b]	57.0	70.1
C2–C3–C4–C5	–3.7	1.7	N1–C6–Ph6[b]	–51.0	–62.6
C3–C4–C5–C6	–3.0	–3.7	C3–C2–N1–Me	37.3	36.0
C4–C5–C6–N1	–1.3	5.6	C3–C4–Ph4[b]	75.1	76.7
C5–C6–N1–C2	–0.3	–4.9	C3–C4–Ph4′[b]	0.5	15.4
C6–N1–C2–C3	–0.4	2.9			

[a] Taken from ref.[6]; [b] orientation of the phenyl group as in ref.[6].

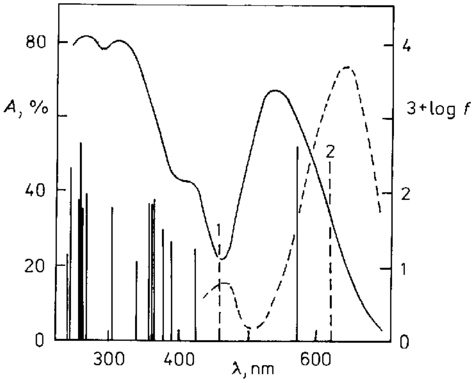


FIG. 7

Comparison of the absorption curves of UV illuminated 1,4-dihydropyridines *Ia*, *Ib* (powders/MgO) with the CNDO/S-CI calculated spectra for 1,3-dihydropyridines *IIIa*, *IIIb*. Full lines: compound *IIIa*; dashed lines: compounds *IIb* (1) and *IIIb* (2) parts of molecules *IIIa*, *IIIb* seem to be unusual, especially as far as the N1 centre is concerned (+0.115). An additional information on the π-electron delocalization follows from the values of π-bond orders (Table IV). It also shows that the electron structures of possible photoproducts *IIIa*, *IIIb* are better expressed by the formulae *VIa*, *VIb*. The latter appear to be derivatives of parent 1,3-dihydropyridine which has not yet been mentioned in special reviews on dihydropyridine chemistry[12,13].

TABLE IV
Calculated bond characteristics for 1,3-dihydropyridines *IIIa*, *IIIb*

Bond	Bond length[a], pm		π-Bond order			
	IIIa	*IIIb*	*IIIa*[a]	*IIIa*[b]	*IIIb*[a]	*IIIb*[b]
N1–C2	135	135	0.502	0.526	0.512	0.487
C2–C3	151	150	0.037	0.033	0.035	0.037
C3–C4	150	150	0.034	0.032	0.031	0.033
C4–C5	135	135	0.755	0.805	0.779	0.744
C5–C6	143	143	0.204	0.167	0.172	0.206
C6–N1	137	137	0.325	0.387	0.394	0.349

[a] Optimized and calculated by the PM3 method; [b] calculated by the AM1 method.

TABLE V
Total charge densities calculated for PM3 geometries of isomeric dihydropyridines *Ia* and *IIIa*

Position	Compound *Ia*			Compound *IIIa*		
	AMI	PM3	CNDO/S	AMI	PM3	CNDO/S
C(H$_3$)	–0.093	–0.116	+0.025	–0.132	–0.244	+0.029
N1	–0.195	+0.131	–0.203	+0.115	+0.785	–0.029
C2	+0.039	–0.066	+0.071	–0.167	–0.474	–0.003
C3	–0.206	–0.193	–0.065	+0.065	+0.149	+0.030
C4	+0.111	+0.154	+0.042	–0.152	–0.173	–0.022
C5	–0.206	–0.193	–0.060	–0.052	0.000	–0.052
C6	+0.039	–0.066	+0.068	–0.239	–0.500	–0.079

Electronic Absorption Spectra

Figures 6 and 7 show good agreement between the experimental absorption curves and corresponding calculated CNDO/S-CI spectral characteristics of 1,4-dihydropyridines *Ia* and *Ib*. These findings support adequacy of our semiempirical approach.

All spectral characteristics calculated for the compounds *Ia*, *Ib* and for the considered photoisomers *IIa* – *Va* and *IIb* – *Vb* are given in Table VI. In the case of compound *Ia*, the entries of Table VI suggest that only mesoionic molecules *IIIa* and *IVa* can be taken into the consideration as possible candidates responsible for the photocolouration. Taking into account both measured absorption bands in the regions 380 – 410 (shoulder) and 480 – 600 nm (Fig. 7) no decision can be made between the isomers *IIIa* and *IVa*. However, it can be made considering the photocolouration of spirocyclic 1,4-dihydropyridine *Ib* exhibiting a new bathochromically shifted absorption band near 650 nm. This fact can be explained only by the formation of molecules *IIIb* in which the π-electron system is extended over the both benzenoid fragments at the positions 3 and 4. On the other hand, any occurrence of the isomeric structure *IVb* may hardly cause significant changes in the absorption with respect to that of isomers *IIIa* or *IVa*. This conclusion was further supported by the CNDO/S-CI calculations resulting in the prediction of the observed bathochromic shift for expected compound *IIIb* but not for its isomer *IVb* (Table VI).

In Fig. 7 the experimental reflectance absorption curves obtained after UV illumination of solid state 1,4-dihydropyridines *Ia*, *Ib* are compared with the corresponding CNDO/S-CI transition energies and oscillator strengths. From a general point of view, the character of the experimental visible absorption seems to follow the calculated data. The agreement between theory and experiment has been particularly improved if the size of LCI is extended from original 100 up to 225 singly excited configurations. It may be, however, noted that the less intense absorption band at about 470 nm (Fig. 7) may perhaps be assigned to the 3,5-linked isomer *IIb* (Table VI) arising as a possible intermediate in a competitive photoprocess.

Photocolouration and Bleaching Mechanisms

As follows from the above noted arguments, photocolouration of 1,4-dihydropyridines *Ia*, *Ib* can be ascribed to the formation of coloured 1,3-dihydro derivatives *IIIa*, *IIIb* arising by the photochemical di-π-methane rearrangements[14]. Formation of the 3,5-bridged molecules *IIa*, *IIb* seems to be photochemically less probable. This process may be viewed as a photochemical cyclization of enamines[15] isoelectronic with the pentadienyl anion. According to the Woodward–Hoffmann rules[16] it should be a conrotatory process. In our case, however, the *I* → *II* cyclization corresponds to a forbidden disrotatory process, and *II* may be expected to be formed only in a small amount as a byproduct.

TABLE VI
Calculated electronic spectra of the studied compounds (wavelengths, oscillator strengths, assignments to electronic transitions and weights)

Compound	λ_{max}, nm	*f*	*i–j*	*w*, %	λ_{max}, nm	*f*	*i–j*	*w*, %
Ia	287.1	0.0122	1-1′	83.2	266.3	0.0154	5-3′	28.0
	270.6	0.0206	3-5′	18.7	261.5	0.2067	1-2′	70.0
	268.4	0.0009	3-7′	16.0	253.8	0.0269	1-6′	69.1
	267.5	0.0205	4-4′	27.4				
Ib	293.8	0.1297	1-1′	32.1	269.7	0.1211	1-1′	35.7
	293.1	0.0857	1-2′	19.7			1-7′	33.7
			4-1′	19.7	265.4	0.1473	2-1′	68.1
	281.1	0.0879	2-2′	56.2	257.7	0.5688	1-3′	35.2
	274.6	0.0010	2-5′	29.0			2-3′	32.2
	270.6	0.0065	5-4′	28.7	251.9	0.2222	1-2′	25.1
IIa	475.4	0.7912	1-1′	94.7	354.4	0.0160	1-7′	46.9
	364.4	0.0021	1-2′	88.0	337.3	0.0132	1-4′	41.9
	357.2	0.0340	1-3′	65.5	313.6	0.0075	1-9′	48.0
	355.5	0.0321	1-6′	78.0	309.4	0.0006	1-5′	62.3
IIb	457.2	0.8684	1-1′	94.4	347.4	0.0238	1-7′	90.0
	386.7	0.1043	1-2′	69.8	338.1	0.0303	1-5′	84.5
	366.5	0.0722	1-4′	73.7	312.3	0.0596	1-6′	74.1
	353.0	0.0025	1-3′	95.6	300.1	0.0002	1-8′	74.0
IIIa	570.1	0.3002	1-1′	94.8	362.6	0.0631	1-5′	87.3
	425.0	0.0159	1-3′	91.5	361.2	0.0555	1-4′	38.0
	390.0	0.0188	1-2′	88.0			1-6′	21.2
	388.1	0.0968	1-8′	36.4	355.0	0.0677	1-9′	50.4
	379.7	0.0272	1-4′	39.0	340.5	0.0113	1-7′	52.6
			1-6′	36.7	305.0	0.0533	1-10′	74.5
IIIb	621.5	0.2222	1-1′	94.6	383.6	0.0560	1-7′	53.1
	424.2	0.1157	1-4′	53.7	373.2	0.0118	1-5′	56.8
			1-2′	35.7	358.3	0.0044	1-6′	75.1
	418.9	0.1032	1-2′	50.2	349.4	0.1007	1-8′	70.2
			1-4′	40.5	320.4	0.0448	2-1′	68.6
	386.5	0.0063	1-3′	81.1	305.5	0.0776	1-9′	62.0
IVa	570.6	0.2389	1-1′	94.9	360.6	0.0058	1-6′	91.4
	418.7	0.0258	1-3′	67.7	356.4	0.0332	1-8′	31.9
	396.5	0.1337	1-5′	45.3			1-9′	27.7
			1-2′	31.2	345.8	0.0143	1-7′	45.2
	385.1	0.0294	1-2′	51.0			1-8′	32.6
	370.9	0.0048	1-7′	48.3	302.8	0.0472	1-8′	70.0
	369.9	0.0225	1-4′	59.0				

TABLE VI
(*Continued*)

Compound	λ_{max}, nm	*f*	*i–j*	*w*, %	λ_{max}, nm	*f*	*i–j*	*w*, %
IVb	570.0	0.2523	1-1′	95.6			1-7′	36.6
	453.5	0.0003	1-2′	83.2	364.5	0.0646	1-7′	37.4
	418.2	0.0058	1-4′	84.9			1-8′	29.7
	389.9	0.0360	1-8′	59.1	359.6	0.0056	1-4′	94.5
	385.7	0.0027	1-3′	86.5	313.0	0.0497	1-10′	47.9
	373.1	0.0127	1-6′	42.6			2-1′	22.1
Va	272.3	0.0491	1-1′	23.0	266.3	0.0186	8-1′	24.7
	271.5	0.1946	1-1′	58.4			1-3′	19.7
	268.1	0.0004	3-4′	13.2	265.6	0.0042	4-2′	11.8
			3-8′	10.2				
Vb	298.3	0.1679	1-1′	53.9	369.3	0.0059	4-4′	16.1
	296.3	0.0311	2-1′	24.6			4-2′	13.5
	279.0	0.1922	1-1′	33.3	258.1	0.3344	2-3′	35.3
	269.5	0.0082	8-3′	17.4				

Consider next the bleaching reaction. Since this reaction is not fully reversible and a weak residue absorption above 400 nm was observed, a bicyclic degradation product as *Va*, *Vb* may be assumed to be formed irreversibly by a thermal process. This cyclization should be disrotatory and therefore allowed according to the Woodward–Hoffmann rules. Consequently, the following general mechanism of the colour changes can be postulated:

$$\mathit{Ia} \xrightarrow{h\nu} \mathit{IIIa} \xrightarrow{kT} \mathit{Va} \quad \text{and analogously} \quad \mathit{Ib} \xrightarrow{h\nu} \mathit{IIIb} \xrightarrow{kT} \mathit{Vb}\,.$$

Similar mechanisms are applicable for the photoinduced colour changes of oxa and thia analogues of *Ia*, *Ib* (refs[5,17]). The research is being in progress.

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