

**PHOTOCOLOURATION OF 2,4,4,6-TETRAARYL-4H-THIOPYRANS:
A SEMIEMPIRICAL QUANTUM CHEMICAL STUDY**Stanislav BOHM^a, Pavel SEBEK^b, Stanislav NESPUREK^c and Josef KUTHAN^a^a Department of Organic Chemistry,

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Molecular geometries of 4H-thiopyrans *Ia*, *Ib* and their possible photoisomers *IVa* – *VIIa* and *IVb* – *VIIb* were optimized by the AM1 and PM3 method and used for the calculation of electronic absorption spectra by the CNDO/S-CI procedure. Comparison of the theoretical data with experimental UV-VIS absorption spectra made it possible to postulate two probable mechanisms of the photocolouration of *Ia*, *Ib* caused by sunlight or UV-illumination.

Even when the photocolouration of 4H-pyrans and 1,4-dihydropyridines of types *II* and *III* has been known for a longer time^{1–7}, the light induced optical changes of π -isoelectronic 4H-thiopyrans of type *I* was discovered comparatively later^{8–11}. Recently, we have reported on the most probable structures of the coloured photoisomers of 1,4-dihydropyridines *IIIa*, *IIIb* (R = Me) resulting from our study of their UV-VIS absorption by appropriate MO models¹². The same approach, i.e. the AM1 and PM3 geometry optimization and subsequent CNDO/S-CI calculation has been used in this paper for photoisomers *IVa* – *VIIb* to interpret the observed changes in optical absorption caused by UV-illumination of 4H-thiopyrans *Ia*, *Ib*. In addition, internal coordinates of molecule *Ia* obtained by the X-ray diffraction¹¹ and AM1 optimization have been compared.

EXPERIMENTAL

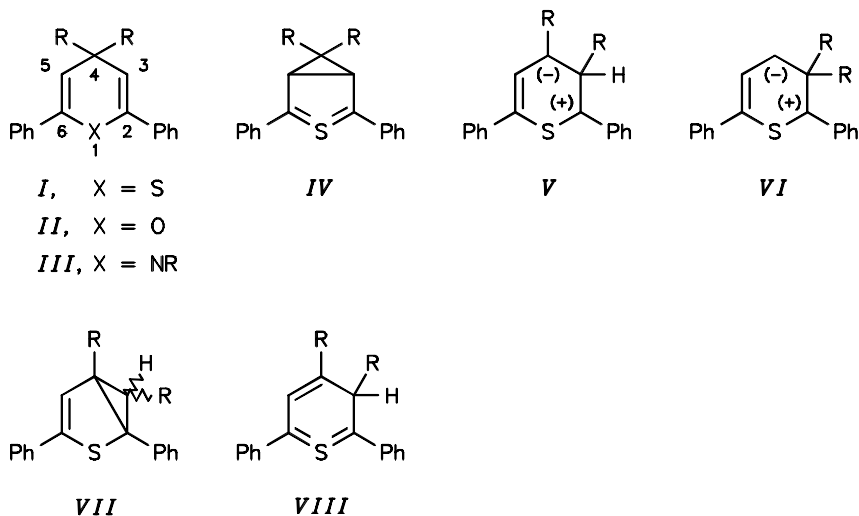
2,4,4,6-Tetraphenyl-4H-thiopyran (*Ia*), m.p. 160 – 161 °C, and 4,4-(biphenyl-2,2'-diyl)-2,6-diphenyl-4H-thiopyran (*Ib*), m.p. 185 – 186 °C, were prepared by employing a procedure described previously¹⁰. UV-VIS absorption spectra were measured in solution using a Hewlett-Packard 8451A recording spectrophotometer. The spectra of polycrystalline powders were determined on a Perkin-Elmer-Hitachi 340 instrument by the diffuse reflectance technique under argon by the way described in a previous paper⁷.

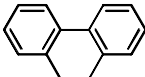
CALCULATIONS

The molecular geometries of structures *Ia*, *IIIa* – *VIIa* and of structures *Ib*, *IIIb* – *VIIb* were obtained by the AM1 (ref.¹³) and PM3 (ref.¹⁴) optimizations, respectively, using the parametrization for sulfur¹⁵. Calculations of the electronic spectra were performed by the CNDO/S-CI method¹⁶ using the parameters $\chi = 0.858$ for the integrals of π -bonds according to Mataga and Nishimoto¹⁷ and $\chi = 1.267$ for γ -sigma types of integrals. Otherwise the parameters for the sulfur spd basis set were also taken from ref.¹⁵. For all the studied MO models the size of CI was limited to 226 singly excited *i-j* configurations corresponding to electron transitions from the *i*-th occupied to the *j*-th unoccupied MO.

RESULTS AND DISCUSSION

The applicability of the AM1 and CNDO/S-CI procedures to our purposes was tested by the comparison of the calculated and X-ray molecular geometries of 4*H*-thiopyrans *Ia* as well as on the basis of relationships of UV-absorption curves with theoretical electron transitions for both 4*H*-thiopyrans *Ia*, *Ib*. After that the calculations were applied to expected photoisomers *IVa* – *VIIa* and *IVb* – *VIIb* in their ground states.



In formulae *I* – *VIII* : *a*, R = Ph; *b*, R, R = 

Molecular Energies and Structures

All optimized molecular structures *Ia* – *VIIb* may be considered as physically justified. Their calculated molecular energies (see Table I) suggest the same relative thermodynamic stabilities in the two isomeric series, e.g. *I* > *VII* > *V* > *VI* > *IV*. As expected all molecules of the assumed photoisomers *IV* – *VII* are rich in energy compared to *Ia*, *Ib*. The energy–structure relationships can be partly understandable considering the shapes of the optimized molecules. A tendency to coplanarity of the two 2,2'-linked aromatic rings seems to be a typical feature of molecules *IVb*, *Vb* and *VIIb* (Figs 1 – 3). Thus, it is difficult to judge relative contributions of delocalization and relaxation effects to the final structures. Successful attempts to isolate the relatively stable 2,4-bridged photointermediate *VIIa* (ref.¹⁰) may be mentioned in this connection. The energy considerations

TABLE I
PM3 energies of molecules *I* and *IV* – *VII* at their optimized geometries

Compound	ΔH_f^a	E_{rel}^b	Compound	ΔH_f^a	E_{rel}^b
<i>Ia</i>	625.38	0.0	<i>Ib</i>	637.70	0.0
<i>IVa</i>	781.57	155.9	<i>IVb</i>	820.33	182.6
<i>Va</i>	725.56	99.9	<i>Vb</i>	734.81	97.1
<i>VIa</i>	781.19	155.6	<i>VIb</i>	782.66	145.0
<i>VIIa</i>	686.38	60.7	<i>VIIb</i>	676.12	38.4

^a Heats of formation in kJ mol⁻¹; ^b relative molecular energies in kJ mol⁻¹.

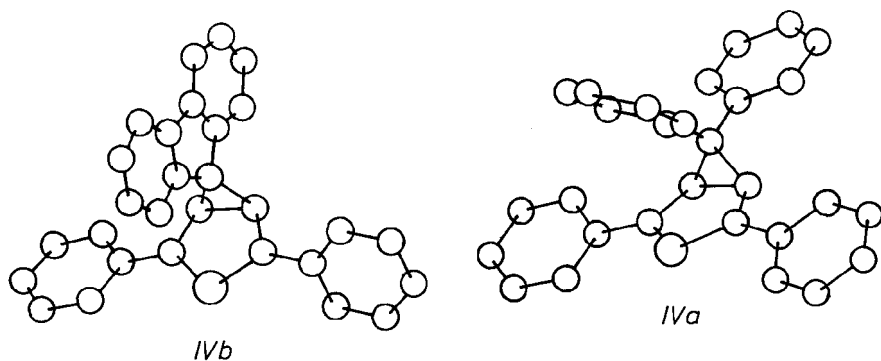


FIG. 1

Comparison of molecular skeletons *IVa* and *IVb* resulting from the PM3 optimizations

suggest *IVa* – *VIIb* could be acceptable candidates for photocoloring or photodegradation species.

Comparison of the calculated and experimental X-ray internal coordinates of *Ia* (Tables II and III) shows that the AM1 method gives a realistic picture of the molecular shape. As expected, a somewhat worse correspondence between theoretical and experimental data was found for dihedral angles than for bond lengths and angles (these are less affected by crystal matrix fields). As for the optimized conformations of *Ia*, *Ib*, *IVa*, *IVb* and *Va*, *Vb* (Figs 1 – 3), the highest attainable C_{2V} molecular symmetry is entirely conserved only in the cases of *Ib* and *IVa* while in the other molecules the symmetry is slightly perturbed due to steric interactions of phenyl groups.

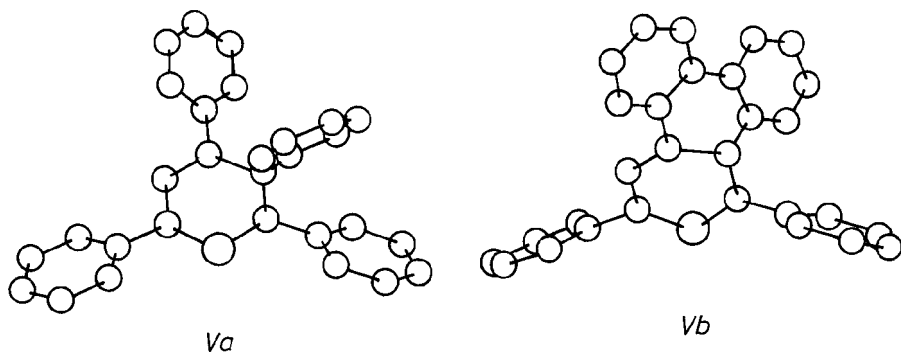


FIG. 2

Comparison of molecular skeletons *Va* and *Vb* resulting from the PM3 optimizations

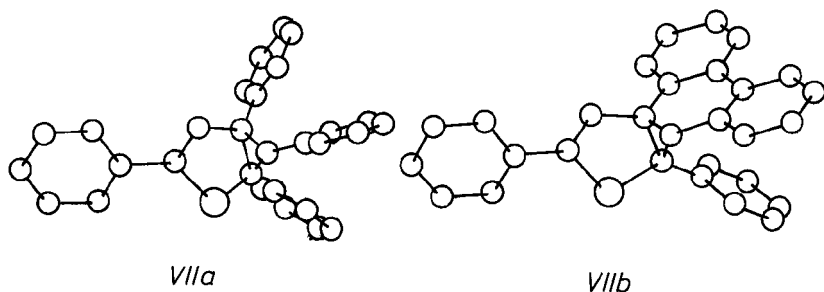


FIG. 3

Comparison of molecular skeletons *VIIa* and *VIIb* resulting from the PM3 optimizations

TABLE II
Comparison of calculated and observed bond lengths (pm) and bond angles (deg) for 2,4,4,6-tetra-phenyl-4*H*-thiopyran (*Ia*)

Bond	X-Ray ^a		AM1	Bond angle	X-Ray ^a		AM1
	A	B			A	B	
S1–C2	1.76	1.75	1.69	C6–S1–C2	101.1	101.6	104.0
C2–C3	1.34	1.33	1.35	S1–C2–C3	124.9	124.9	124.8
C3–C4	1.51	1.53	1.50	C2–C3–C4	127.8	128.0	126.0
C4–C5	1.52	1.51	1.50	C3–C4–C5	112.5	111.1	114.3
C5–C6	1.32	1.34	1.35	C4–C5–C6	127.7	128.4	125.7
C6–S1	1.76	1.73	1.69	Ph2–C2–S1	112.5	111.5	113.0
C2–Ph2	1.48	1.49	1.47	Ph4–C4–Ph4	111.2	112.0	110.0
C4–Ph4	1.56	1.55	1.52	Ph4–C4–C5	106.9	106.9	110.2
C4–Ph4	1.55	1.55	1.52	Ph4–C4–C3	106.8	106.6	110.1
C6–Ph6	1.50	1.48	1.47	Ph6–C6–S1	113.5	112.8	113.3

^a Taken from ref.¹¹; A and B denote two different molecular conformations of *Ia* in the unit cell.

TABLE III
Comparison of calculated and observed dihedral angles (deg) for 2,4,4,6-tetra-phenyl-4*H*-thiopyran (*Ia*)

Dihedral angle	X-Ray ^a		AM1	Dihedral angle	X-Ray ^a		AM1
	A	B			A	B	
S1–C2–C3–C4	-1.1	1.2	0.0	C6–S1–C2–C3	6.8	-6.2	0.0
C2–C3–C4–C5	-7.7	6.9	1.5	S1–C2–Ph2 ^b	-42.3	40.5	45.8
C3–C4–C5–C6	10.4	-9.9	-2.2	S1–C6–Ph6 ^b	-37.8	36.9	46.0
C4–C5–C6–S1	-4.0	4.4	1.9	C3–C4–Ph4 ^b	0.1	1.2	17.8
C5–C6–S1–C2	-4.4	3.6	0.0	C3–C4–Ph4 ^{rb}	69.4	67.5	76.0

^a Taken from ref.¹¹; ^b orientation of the phenyl group from the same reference.

Charge Distribution

Some characteristics of the total charge distribution for 4*H*-thiopyran *Ia* as well as for the assumed photoisomers *IVa* – *Va* are given in Table IV. The MO models of the starting 4*H*-thiopyrans *Ia*, *Ib* do not exhibit alternant charge distribution as found¹² in π -isoelectronic 1,4-dihydropyridines *III* (R = Me). In the couples *IVa*, *IVb* and *Va*, *Vb*, the 2,2'-linked derivatives *IVb* and *Vb* seem to have a somewhat less developed π -bonds between the sulfur S1 and the neighbouring C2, C6 centres, as suggested by the entries of Table V. This observation may be associated with the above mentioned tendency to hold a coplanarity of the benzenoid rings (see Figs 1 – 3).

TABLE IV

Net atomic charges calculated for AM1 geometries of 2,4,4,6-tetraphenyl-4*H*-thiopyran (*Ia*) and its photoisomers *IVa* and *Va*

Position	Compound <i>Ia</i>		Compound <i>IVa</i>		Compound <i>Va</i>	
	AM1	CNDO/S	AM1	CNDO/S	AM1	CNDO/S
S1	0.407	0.009	1.096	0.098	1.230	0.107
C2	-0.257	-0.089	-0.603	-0.112	-0.682	-0.132
C3	-0.148	-0.029	-0.087	-0.043	0.071	0.023
C4	0.094	0.057	-0.041	0.026	-0.135	0.172
C5	-0.148	-0.029	-0.089	-0.045	-0.048	-0.062
C6	-0.258	-0.089	-0.612	-0.111	-0.683	-0.108

TABLE V

Calculated bond characteristics for photoisomers *IVa*, *Va*, *IVb* and *Vb*

Bond	Bond length, pm				π -Bond order			
	<i>IVa</i>	<i>IVb</i>	<i>Va</i>	<i>Vb</i>	<i>IVa</i>	<i>IVb</i>	<i>Va</i>	<i>Vb</i>
S1–C2	1.59	1.66	1.54	1.62	0.429	0.370	0.520	0.440
C2–C3	1.46	1.47	1.50	1.50	0.093	0.109	0.001	0.036
C3–C4	1.52	1.52	1.50	1.50	0.034	0.032	0.033	0.031
C4–C5	1.52	1.52	1.35	1.35	0.034	0.033	0.820	0.766
C5–C6	1.47	1.47	1.43	1.43	0.092	0.106	0.148	0.196
C6–S1	1.59	1.66	1.56	1.64	0.421	0.370	0.399	0.383

A general character of the electron distribution in the possible intermediates *Va*, *Vb* may be better expressed by the formulae *VIIIa*, *VIIIb*, similarly as in the analogous photoisomers¹² of 1,4-dihydropyridines *III*.

Electronic Absorption Spectra

From Fig. 4 it follows that the interpretation of the electronic absorption spectra of 4H-thiopyrans *Ia*, *Ib* by the CNDO/S-CI method is satisfactory. The UV photocoloration has been recognized¹⁰ to be sufficiently influenced by substitution at the position 4. While the photochromic absorption maximum of *Ia* lies at 564 nm, the 2,2'-linking in the molecule of *Ib* causes a bathchromic shift to 666 nm. This "bridged effect" ($\Delta\lambda = 102$ nm), formerly observed for 1,4-dihydropyridines^{6,12} *IIIa*, *IIIb* (R = H, Me), has been assumed to be associated with an extension of the π -bond system in V-like photoisomers¹². Comparison of the experimental values of 564 and 666 nm with the calculated data given in Table VI enables to make a conclusion that structurally different coloured species should be responsible for the photocoloration of 4H-thiopyrans *Ia*, *Ib*. The calculated long-wave electron transition 1-1' of 3,5-bridged molecule *IVa* (567.7 nm) is evidently in better agreement with the experiment than that of di- π -methane rearranged isomer *Va* (618.0 nm). A completely different situation appears to be with the 2,2'-linked couple *IVb* and *Vb*, where the calculated value for *Vb* (647.3 nm) is not only approaching the position of the observed photochromic maximum (666 nm) but also leads to a more acceptable theoretical value of the "bridged effect" (79.6 nm) compared to that of the alternative structure *IVb* (32.0 nm). Hence, it can be suggested the photoisomers *IVa* and *Vb* are the major components of the coloured material after UV-illumination of 4H-thiopyrans *Ia*, *Ib*. This conclusion is further supported by comparison of the observed absorption curves with the corresponding theoretical spectral characteristics (Fig. 5).

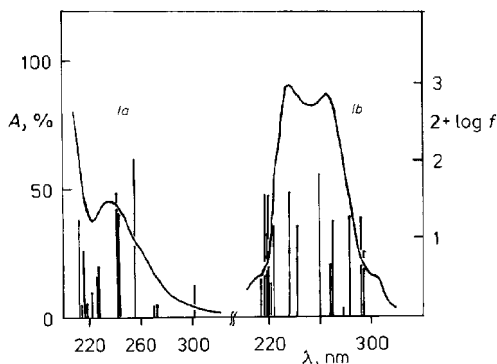


FIG. 4

Comparison of the absorption curves of 4H-thiopyrans *Ia*, *Ib* in acetonitrile with the CNDO/S-CI calculated spectra

TABLE VI

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

Compound	λ_{\max} , nm	f^a	$i\text{-}j^b$	w^c , %	λ_{\max} , nm	f^a	$i\text{-}j^b$	w^c , %
<i>Ia</i>	302.0	0.0263	1-1'	84.3	273.4	0.0291	3-3'	35.0
	271.0	0.0014	1-6'	18.7	270.7	0.0136	2-6'	20.6
	270.3	0.0050	3-4'	17.2	255.7	1.0679	1-2'	50.7
	252.3	0.0008	2-1'	43.3	243.5	0.2437	2-2'	25.4
	240.8	0.3943	1-5'	23.3	227.6	0.0442	1-5'	26.9
<i>IVa</i>	567.7	0.7619	1-1'	98.0	314.9	0.0187	1-4'	32.3
	314.3	0.0030	1-5'	52.1	302.8	0.0059	1-2'	60.0
	301.9	0.0222	2-1'	58.5	293.9	0.0433	1-7'	44.4
	285.4	0.0657	1-14'	90.0	280.9	0.1235	2-2'	89.2
	276.8	0.1161	8-1'	81.6	268.5	0.0061	1-15'	97.0
<i>Va</i>	618.0	0.3334	1-1'	97.0	337.9	0.1477	1-2'	83.9
	313.5	0.0153	1-8'	52.0	309.7	0.0985	2-1'	17.0
	306.2	0.1456	1-5'	60.2	303.0	0.3952	2-1'	29.6
	298.6	0.0988	1-7'	61.0	296.1	0.0362	1-3'	46.8
<i>VIa</i>	601.0	0.2694	1-1'	96.8	333.6	0.0638	1-3'	45.7
	327.7	0.0050	1-2'	42.4	325.0	0.1532	2-1'	73.3
	308.0	0.3124	3-1'	50.5	301.1	0.0120	1-6'	28.2
	300.0	0.2167	1-5'	37.8	298.6	0.0338	1-7'	50.3
<i>VIIa</i>	275.2	0.1509	1-1'	15.1	274.4	0.0312	1-5'	16.8
	271.2	0.4334	1-1'	44.5	270.4	0.2438	1-1'	23.7
<i>Ib</i>	295.0	0.0663	1-2'	17.0	292.9	0.2070	1-1'	28.1
	284.2	0.2063	2-1'	33.0	278.9	0.0122	1-6'	28.8
	270.3	0.1663	1-4'	24.8	269.1	0.0354	3-5'	22.1
	259.8	0.5723	2-1'	9.3	244.6	0.0108	2-2'	38.7
<i>IVb</i>	599.7	0.9208	1-1'	98.4	344.5	0.0000	2-1'	96.7
	335.4	0.0501	1-2'	81.4	327.0	0.0108	1-6'	67.8
	322.5	0.0032	1-3'	66.1	314.4	0.0513	1-7'	33.4
	308.8	0.0734	3-1'	71.6	300.2	0.0299	1-5'	30.3
	296.5	0.1679	1-8'	73.4	287.6	0.0037	2-5'	21.4
<i>Vb</i>	647.3	0.2754	1-1'	96.1	390.0	0.0900	1-2'	67.3
	355.9	0.1371	2-1'	75.4	345.7	0.0586	1-5'	50.3
	335.5	0.0223	1-3'	48.8	318.9	0.0354	1-4'	67.7
	317.4	0.0704	3-1'	38.8	314.9	0.0026	1-7'	25.1
	312.9	0.0072	1-6'	30.1	304.7	0.1502	3-1'	17.6

TABLE VI
(Continued)

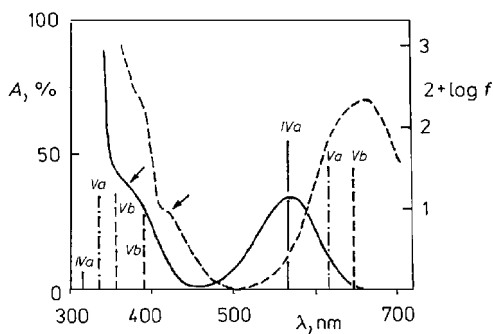
Compound	λ_{\max} , nm	f^a	$i-j^b$	w^c , %	λ_{\max} , nm	f^a	$i-j^b$	w^c , %
<i>Vib</i>	633.1	0.3087	1-1'	97.2	376.5	0.0174	1-2'	76.2
	360.3	0.1031	1-10'	8.8	333.3	0.1098	1-3'	22.5
	327.6	0.0509	1-8'	34.8	326.5	0.0119	1-3'	42.2
	316.8	0.0384	1-6'	37.2	313.2	0.0879	3-1'	44.1
<i>VIIIb</i>	293.7	0.2304	1-1'	26.4	291.3	0.0217	2-3'	15.5
	282.6	0.1107	1-5'	26.5	280.1	0.3839	1-1'	26.5
	274.8	0.5958	2-1'	35.9	270.4	0.0199	3-6'	18.2

^a Excitation from the i -th occupied Mo to the j -th unoccupied MO; ^b weight of the $i-j$ configuration; ^c 225 monoexcited configurations.

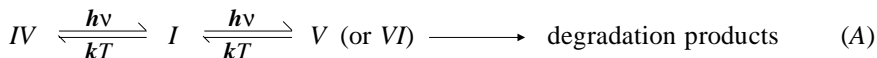
Photocolouration and Bleaching Mechanisms

As follows from the above mentioned findings, the photocolouration of 4*H*-thiopyrans *I* can hardly be described by a homogeneous mechanism independent on the 4,4-substitution patterns. The compounds like *Ia* exhibit their photochromic absorption maxima¹⁰ at 545 – 602 nm hypsochromically shifted with respect to those of analogously substituted 1,4-dihydropyridines *III* (ref.⁷). This somewhat surprising observation can be now explained considering the following scheme (A) in which the major photocolourating

FIG. 5
Comparison of the absorption curves of UV illuminated 4*H*-thiopyrans *Ia*, *Ib* (powders/MgO) with the CNDO/S-CI calculated spectra of possible photoisomers *IVa*, *Va* and *Vb*. Compound *Ia* (—); compound *Ib* (---). Arrows show parts of the curves influenced by the UV absorption of degradation products



species are the 3,5-bridged photoisomers *IV* in accordance with an intuitive suggestion of Pirelahi and co-workers⁹.



Di- π -methane rearrangements $I \rightarrow V$ and possibly also $I \rightarrow VI$ are apparently followed by degradation processes involving *VII*-like intermediates and isomeric thiopyrans^{8,10}. It might be noted the transformation $Ia \rightarrow IVa$ is photochemically allowed according to the Woodward–Hoffmann rules¹⁸ provided one of the sulfur free pairs takes on the role of an additional C=C double bond.

Contrary to this interpretation, the photocoloration of spirocyclic 4*H*-thiopyrans like *Ib* would be mainly due to the photoisomers like *V* or *VI*, similarly to spirocyclic 1,4-dihydropyridines like *IIIb* (ref.^{12,19}) (according to suggestions of Maeda and Mori⁸ and Sebek et al.¹⁰). The suppressed role of the 3,5-bridged isomers like *IV* in the photocoloration of *Ib* may be ascribed to relaxation effects associated with the coplanarity holding of the 2,2'-linked aromatic rings in *IVb*.

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