

PHOTOCHEMICAL TRANSFORMATIONS OF 2,4,4,6-TETRAPHENYL-4*H*-THIOPYRAN-1,1-DIOXIDE AND SOME ITS *para*-SUBSTITUTED DERIVATIVES

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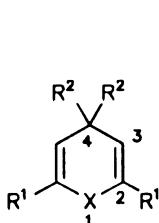
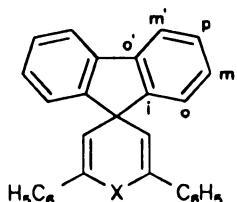
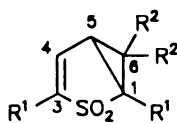
1,2,4,5-Tetrasubstituted cyclopentadienes *Vla* – *Vlf* or phenanthrene derivative *VIII*, respectively, were obtained as the main photoproducts upon irradiation of sulfones *Ia* – *If* and *II* in acetonitrile, methanol or benzene. Bridged isomers *Va* – *Vd* were isolated from the reaction of *Ia* – *Id* carried out in acetonitrile. Probable course of the investigated photochemical transformations of 4*H*-thiopyran-1,1-dioxides is discussed.

Di- π -methane rearrangements of unsaturated carbocyclic compounds^{1,2} undoubtedly belong to the most widely studied domains of organic photochemistry. Recently, this type of photochemical transformations was also described on several heterocyclic substrates^{3 – 9}.

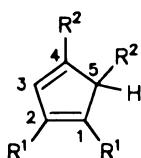
Absence of photochromic behaviour of heterocyclic sulfones type *I* and *II* in contrast to parent 4*H*-thiopyrans *III* (R^1 and R^2 is phenyl or substituted phenyl, refs^{8 – 10} or *IV*, ref.⁹) had attracted our attention to their photochemistry. Rearrangements of di- π -methane type might be expected upon irradiation of solutions of substrates *I* – *II*. However, also the possibility of SO_2 extrusion observed in series of other heterocyclic sulfones^{11,12} cannot be excluded.

Gravel and Leboeuf⁴ carried out thorough photochemical investigation of 4,4-diphenyl-4*H*-thiopyran-1,1-dioxide (*I*, $R^1 = H$ and $R^2 = C_6H_5$). They isolated in 15% yield the rearranged sulfone *V* ($R^1 = H$ and $R^2 = C_6H_5$) besides the product of simple photoaddition of methanol. In this paper, we bring evidence that with 2,4,4,6-tetrasubstituted

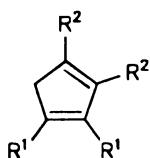
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I, $X = \text{SO}_2$ III, $X = \text{S}$ II, $X = \text{SO}_2$ IV, $X = \text{S}$ 

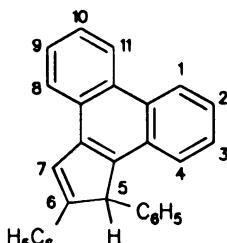
V



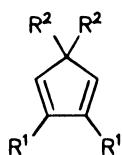
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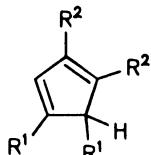
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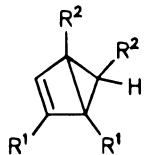
VIII



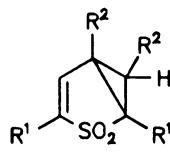
IX



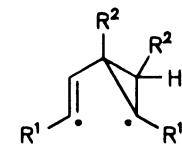
X



XI



XII



XIII

In formulae I, III, V-VII, IX-XIII:

a, $R^1 = R^2 = C_6H_5$

b, $R^1 = 4-(t-C_4H_9)C_6H_4$, $R^2 = C_6H_5$

c, $R^1 = 4-CH_3C_6H_4$, $R^2 = C_6H_5$

d, $R^1 = 4-FC_6H_4$, $R^2 = C_6H_5$

e, $R^1 = C_6H_5$, $R^2 = 4-CH_3C_6H_4$

f, $R^1 = C_6H_5$, $R^2 = 4-FC_6H_4$

g, $R^1 = C_6H_5$, $R^2 = 4-(t-C_4H_9)C_6H_4$

h, $R^1 = C_6H_5$, $R^2 = 2,2'-C_6H_4C_6H_4$

4*H*-thiopyran-1,1-dioxides *Ia* – *If* it is possible to prove and isolate both products of expected photochemical rearrangements and the SO₂ elimination from the molecule.

Starting sulfones *Ia* – *If* and *II* were prepared from 2,4,4,6-tetraaryl-4*H*-thiopyrans⁹ *III* and *IV* by oxidation with hydrogen peroxide in acetic acid¹³ (Table I). Relatively slow (0.5 – 1 h) photolysis accompanied by SO₂ extrusion takes place upon irradiation of benzene solutions of substrates *Ia* – *If* by high pressure mercury lamp in a quartz photoreactor. HPLC analysis of the reaction mixture shows 1,2,4,5-tetraaryl-cyclopenta-1,3-dienes *Vla* – *Vlf* besides other minor components. Among them we were able to prove by NMR the bridged 1,3,6,6-tetraaryl-2-thiabicyclo[3.1.0]hex-3-ene-1,1-dioxides *Va* – *Vf*. With sulfone *Ia*, 1,2,3,4-tetraphenylcyclopenta-1,3-diene (*VIIa*) was characterized in the reaction mixture (*Vla* : *Va* : *VIIa* – 88 : 10 : 2, according to ¹H NMR). Sulfone *II* afforded 5*H*-5,6-diphenylcyclopenta[*f*]phenanthrene (*VIII*) as the main product besides the isomer *VIIh* in preparative yield 45 and 8%, respectively. Structures *Vla* – *Vlf* and *VIII* were assigned on the basis of 2D NMR experiments. With cyclopentadienes

TABLE I

Physico-chemical and spectral characteristics of sulfones *Ia* – *If* and *II*

Com- ound	Formula (M. w.)	Calculated/Found			M. p., °C (Solvent)	Reaction time, h (Yield, %)	IR (SO ₂) $\tilde{\nu}_{\text{max}}$, cm ⁻¹
		% C	% H	% S			
<i>Ia</i>	C ₂₉ H ₂₂ SO ₂ (434.6)	80.16	5.10	7.38	194 – 195 ^a (ethanol)	0.5	1 296
		80.26	5.11	7.09		(86)	1 133
<i>Ib</i>	C ₃₇ H ₂₈ SO ₂ (546.8)	81.28	7.01	5.87	^b (ethanol–benzene)	2	1 294
		81.30	7.22	6.09		(88)	1 133
<i>Ic</i>	C ₃₁ H ₂₆ SO ₂ (462.6)	80.48	5.66	6.94	236 – 238 (ethanol–benzene)	1	1 294
		80.35	5.90	6.98		(72)	1 127
<i>Id</i>	C ₂₉ H ₂₀ SO ₂ F ₂ ^c (470.5)	74.03	4.29	6.82	204 – 205 (ethanol)	0.5	1 295
		74.01	4.41	7.07		(78)	1 130
<i>Ie</i>	C ₃₁ H ₂₆ SO ₂ (462.6)	80.48	5.66	6.94	227 – 228 (ethanol–benzene)	0.5	1 296
		80.28	5.91	6.96		(80)	1 130
<i>If</i>	C ₂₉ H ₂₀ SO ₂ F ₂ ^c (470.5)	74.03	4.29	6.82	315 – 316 (heptane)	0.5	1 300
		74.24	4.11	6.64		(77)	1 130
<i>II</i>	C ₂₉ H ₂₂ SO ₂ (432.5)	80.53	4.67	7.41	284 – 285 (heptane)	0.5	1 294
		80.56	4.61	7.64		(81)	1 133

^a Reported¹³ m.p. 192 – 193 °C; ^b the compound does not melt up to 320 °C; ^c analysis for fluorine gave irreproducible results.

VIIa and *VIIb*, they were confirmed by their synthesis through photochemical isomerization of independently prepared¹⁴ 2,3,5,5-tetraarylcyclopenta-1,3-dienes *IXa* and *IXb*.

Photoisomerization of analogously obtained¹⁴ cyclopentadiene *IXg* was used for the preparation of isomer *VIIg*. The identity of hydrocarbons *VIIa* and *VIIh* was established by comparison with independently prepared¹⁴ compounds (see Experimental).

Formation of phenanthrene derivative *VIII* might be explained by a thermal [1,5]-hydrogen rearrangement of primarily formed isomer *VIIh* leading to the aromatization of the phenanthrene system. Similar aromatization was also observed in connection with photochemical rearrangements of aryl groups in the indene series¹⁵.

Because of partial thermal isomerizations of cyclopentadienes *VI* and *VIII* during crystallization, the preparative yields decreased. Presence of other isomers *VII* and *X* in the mother liquors was established by ¹H and ¹³C NMR in agreement with the study of thermal changes¹⁴. Owing to this fact, no pure *VI* was additionally isolated by crystallization. The yields given in Table II are therefore based on the mass balance after the column chromatography. Thermal rearrangement under our experimental conditions could probably explain the minor abundance of isomers *VIIa* and *VIIh*. 1,2,4,5-Tetra-substituted cyclopentadienes *VI* are also unstable in solution in the presence of mole-

TABLE II
Photochemical transformations of sulfones *Ia*–*If* and hydrocarbons *IXa*, *IXb*, and *IXg*

Starting compound	Solvent	Reaction time, min	Preparative yields, %			Eluent (benzene–heptane)	
			sulfone	hydrocarbon			
<i>Ia</i>	acetonitrile	10	<i>Va</i>	18	<i>Vla</i>	38	4 : 6
	methanol	20	<i>Va</i>	10	<i>Vla</i>	49	
	benzene	45	–	–	<i>Vla</i>	56 ^a	
<i>Ib</i>	acetonitrile	20	<i>Vb</i>	13	<i>Vlb</i>	31	2 : 8
	benzene	45	–	–	<i>Vlb</i>	48	
<i>Ic</i>	acetonitrile	10	<i>Vc</i>	20	<i>Vlc</i>	36	1 : 1
	benzene	30	–	–	<i>Vlc</i>	53	
<i>Id</i>	acetonitrile	18	<i>Vd</i>	12	<i>Vld</i> ^b	44	1 : 1
<i>Ie</i>	benzene	30	–	–	<i>Vle</i>	62	1 : 1
<i>If</i>	benzene	30	–	–	<i>Vlf</i> ^b	26	4 : 6
<i>II</i>	benzene	60	–	–	<i>VIII</i>	45 ^c	4 : 6
<i>IXa</i>	benzene	120	–	–	<i>Vla</i>	48	3 : 7
<i>IXb</i>	benzene	180	–	–	<i>Vlb</i>	53	2 : 8
<i>IXg</i> ^d	acetonitrile	35	–	–	<i>Vlg</i>	56	2 : 8

^a In addition to 15% of 9 : 1 mixture of isomers *Vla* and *VIIa*; ^b difluoro derivative; ^c in addition to 8% of hydrocarbon *VIIh*, m.p. 232–233 °C (heptane), ref.¹⁴ gives m.p. 232–233 °C; ^d from 0.1 g of *IXg* in acetonitrile (200 ml).

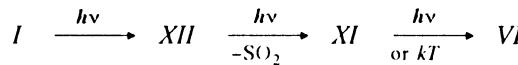
cular oxygen. Their oxidative transformation leads to mixtures of nonidentifiable products.

Observation that the photoinduced changes are faster in acetonitrile or methanol (no starting sulfone was present in the reaction mixture at 20 °C after 10 or 20 min, respectively) was used for a more detailed study of the transformations of sulfone *Ia*. Bridged photoisomer *Va* was isolated besides cyclopentadiene *VIa* in this case. HPLC study of the reaction time course indicates the existence of two parallel reaction channels. A very fast photoextrusion of SO₂ is taking place in the former. The question is whether this reaction precedes or follows the migration of the phenyl group at the position 4 to the position 3 in the parent 4*H*-thiopyran skeleton.

In the first case, the known¹⁴ 2,3,5,5-tetraphenylcyclopenta-1,3-diene (*IXa*) would be formed first and then it would give 1,2,4,5-tetraphenyl isomer *VIa* through a photochemical rearrangement of the phenyl group as mentioned above or possibly preceded by formation of its bridged precursor *XIa*. An analogous photoisomerization was observed with 2,5,5-triphenylcyclopenta-1,3-diene¹⁶. An alternative pathway would involve primary formation of bridged sulfone *XIIa* followed by SO₂ extrusion under formation of already mentioned products *XIa* and *VIa*.

Comparison of the time courses of irradiation of methanolic solutions of compounds *IXa* and *Ia* (*c* = 1.4 · 10⁻³ mol l⁻¹, 20 °C) giving the same photoproduct *VIa* shows that the transformation of sulfone *Ia* is remarkably faster (10 min) than that of hydrocarbon *IXa* (90 min).

These observations therefore bring in doubt the first assumption on the primary extrusion of SO₂ giving the intermediate *IXa*. Phototransformation of sulfones *Ia* – *II* might be therefore explained by the sequence of reaction steps.



According to contemporary knowledge on SO₂ photoextrusions^{11,12,17}, this scheme might be decomposed to more reaction steps. Biradicals *XIII* might be considered as the reactive intermediates in photolysis of compounds *I* and *II*. They might recombine to extremely labile hydrocarbons *XI* escaping identification. We consider our proposed mechanism of the formation of cyclopentadienes *VI* as an approximative one since no experimental means for its definitive confirmation are at our disposal at present. Bridged sulfones *Vb* – *Vd*, evidently formed through an alternative pathway involving di- π -methane rearrangement, were isolated besides the already mentioned products of SO₂ extrusion *VIb* – *VId* also upon irradiation of sulfones *Ib* – *Id* in acetonitrile. Successful isolation of type *V* sulfones is probably due to their slower consequent phototransformations as documented by irradiation of acetonitrile solution of pure *Vc* giving after 90 min at 20 °C according to HPLC the mixture of at least four unidentified products. Structures of bicyclic sulfones *Va* – *Vd* were verified by 2D NMR expe-

riments. ^1H NMR spectra contain (besides of aromatic protons of four phenyl groups) two doublets in the range 3.831 – 3.962 ppm and 6.855 – 6.914 ppm. Carbon chemical shifts of their corresponding carbons (32.17 – 32.48 ppm) and (129.58 – 133.03 ppm) indicate the presence of a sp^3 carbon and one olefinic methine in the molecule. Their mutual coupling $J_{\text{H-H}} = 3.5 – 3.6$ Hz confirms the vicinal arrangement. Unusually large direct spin–spin coupling $^1J = 173.3 – 173.4$ Hz is an evidence that this carbon is indeed located in a cyclopropane ring¹⁸.

Above mentioned photoisomerizations and the thermal isomerizations reported earlier¹⁴ allowed us to prepare two thermodynamically less stable positional isomers (*VIIa* and *IXa*) of the known¹⁹ 1,2,3,4-tetraphenylcyclopenta-1,3-diene *VIIa*. However, we were so far not able to determine the relationship of the molecular structure of these hydrocarbons to that of the only other in the literature reported tetraphenylcyclopentadiene²⁰.

EXPERIMENTAL

Temperature data were not corrected. Melting points were determined on a Boetius apparatus. Infrared spectra were measured in chloroform with a Perkin–Elmer 325 spectrometer. Spectrometer Bruker AM 400 (400.13 MHz for ^1H , 100.61 MHz for ^{13}C) was used for the measurement of NMR spectra of sulfones *I* and *II*; digital resolution was 0.18 Hz. NMR spectra of all other compounds were measured on the Varian VXR-400 instrument (399.95 MHz for ^1H , 100.577 MHz for ^{13}C , digital resolution 0.02 Hz). All measurements were performed in deuteriochloroform at 298 K; tetramethylsilane served as an internal standard. Abbreviations used in the assignment of phenyl groups: *i* – *ipso*, *o* – *ortho*, *m* – *meta*, *p* – *para*. 2D NMR experiments – COSY, delayed – COSY (ref.²¹), *J*-resolved²², (^1H , ^{13}C) – COSY and its variant optimized for the observation of long-range couplings²³ were realized using the manufacturer's software. Structure confirmation of hydrocarbons *VIIa*, *VIIb*, *VIIa*, and *VIIh* was made by comparison of ^{13}C NMR spectra with those of independently prepared standards. Similarity indices²⁴ were larger than 0.999 in all cases. NMR spectra of sulfones *Ib* – *If* and *II* were assigned by analogy with the interpreted spectra⁹ of compound *Ia*. Preparative photoexperiments were performed in an immersion quartz photoreactor. Solvents for these experiments were either of spectral grade or were purified according to the literature^{16,25}. The reaction course was followed by HPLC using the SeparonTM SGX C18 column (3 × 150 mm, 0.4 ml/min, particle size 5 μm , Tessek, The Czech Republic) in the system methanol–water 9 : 1.

Preparation of Sulfones *Ia* – *If* and *II*

Hydrogen peroxide (30%, 8 ml) was added to the solution of thiopyran derivative *III* or *IV*, respectively (5 mmol) in hot glacial acetic acid (100 ml). Reaction mixture was kept at 120 °C until transitionally formed 4*H*-thiopyran-1-oxide disappeared (HPLC analysis). Then it was cooled and poured onto ice (200 g). Crude product was filtered off and after drying it was recrystallized from a suitable solvent. Reaction times, yields, and physico-chemical properties of the products are given in Table I. Spectral characteristics of sulfones *Ia* – *If* and *II* are given in Table IV.

Photolysis of Sulfones *Ia* – *If* and *II*

Solution of sulfone *I* or *II*, respectively (0.92 mmol) in suitable solvent (400 ml) was irradiated by 400 W high-pressure mercury lamp in argon atmosphere at 20 °C. Upon consumption of the parent compound *I* or

H, respectively, (HPLC analysis) was the solvent evaporated at room temperature under reduced pressure. The products *Vla* – *Vlf*, *VIII* and *VIIh* were separated by flash chromatography on a silica gel column with benzene–heptane mixture (see Table II) as an eluent; sulfones *Va* – *Vd* were subsequently eluted with pure benzene. Obtained products were then recrystallized. Their physico-chemical properties are summarized in Table III.

Table III

Physico-chemical and spectral characteristics of compounds *Va* – *Vd*, *Vla* – *Vlg*, and *VIII*

Compound	Formula (M. w.)	Calculated/Found			M. p. ^a , °C (Solvent)	IR ^b $\tilde{\nu}_{\text{max}}$, cm ⁻¹
		% C	% H	% S		
<i>Va</i>	C ₂₉ H ₂₂ SO ₂ (434.6)	80.16 80.09	5.10 5.22	7.38 7.52	263 – 264 (ethanol)	1 300 1 340
<i>Vb</i>	C ₃₇ H ₃₈ SO ₂ (546.8)	81.28 81.59	7.01 7.12	5.87 5.71	250 – 251 (ethanol–benzene)	1 300 1 333
<i>Vc</i>	C ₃₁ H ₂₆ SO ₂ (462.6)	80.48 80.36	5.66 5.77	6.94 6.91	254 – 255 (ethanol–benzene)	1 300 1 340
<i>Vd</i>	C ₂₉ H ₂₀ SO ₂ F ₂ ^c (470.5)	74.03 74.21	4.29 4.59	6.82 6.77	205 – 206 (hexane)	1 306 1 347
<i>Vla</i>	C ₂₉ H ₂₂ (370.5)	94.02 94.29	5.98 6.22	–	155 – 156 ^d (ethanol)	1 600 1 572
<i>Vlb</i>	C ₃₇ H ₃₈ (482.7)	92.07 91.90	7.93 8.03	–	144 – 146 (ethanol–benzene)	1 596 1 572
<i>Vlc</i>	C ₃₁ H ₂₆ (398.6)	93.43 93.44	6.58 6.83	–	145 – 146 (ethanol–benzene)	1 600 1 570
<i>Vld</i>	C ₂₉ H ₂₀ F ₂ (406.5)	85.70 85.68	4.96 5.26	9.35 ^e 9.61 ^e	134 – 136 (benzene–heptane)	1 600 1 570
<i>Vle</i>	C ₃₁ H ₂₆ (398.6)	93.43 93.41	6.58 6.87	–	160 – 162 (methanol–benzene)	1 597 1 570
<i>Vlf</i>	C ₂₉ H ₂₀ F ₂ (406.5)	85.70 85.59	4.96 4.96	9.35 ^e 9.45 ^e	90 – 94 (methanol)	1 600 1 572
<i>Vlg</i>	C ₃₇ H ₃₈ (482.7)	92.07 91.87	7.93 8.14	–	170 – 171 (ethanol)	1 600
<i>VIII</i>	C ₂₉ H ₂₀ (368.5)	94.53 94.92	5.47 5.61	–	200 – 201 (ethanol)	1 596 1 570

^a Cyclopentadienes *Vla* – *Vlg* and *VIII* isomerize during melting to produce a mixture of isomers with prevailing compounds *VII*, see ref.¹⁴; ^b SO₂ or C=C stretching vibrations; ^c fluorine analysis gave irreproducible results; ^d m.p. 180 – 182 °C (after further solidification); ^e fluorine content.

TABLE IV
 ^1H , ^{13}C , and ^{19}F NMR spectra of sulfones lb – lf and II

Assignment		lb	lc	ld	le	lf	II
							δ (ppm), J (Hz)
$\text{H}-\text{R}^1$	(<i>o</i>)	7.63 m	7.58 m	7.66 m, 5.3 ^b	7.68 m	7.59 m	7.66 – 7.72 ^a m
	(<i>m</i>)	7.42 m	7.21 m	7.09 m, 8.7 ^b	7.35 – 7.45 m	7.30 – 7.38 m	7.34 – 7.40 ^a m
	(<i>p</i>)	–	–	–	7.35 – 7.45 m	7.30 – 7.38 m	7.34 – 7.40 ^a m
H-3		6.68 s	6.66 s	6.68 s	6.68 s	6.54 s	6.00 s
H-R^2	(<i>o</i>)	7.30 – 7.38 m	7.32 – 7.43 m	7.30 – 7.42 m	7.17 m	7.25 m, 5.1 ^b	7.66 – 7.72 ^a m
	(<i>m</i>)	7.30 – 7.38 m	7.32 – 7.43 m	7.30 – 7.42 m	7.26 m	7.03 m, 8.6 ^b	7.41 dd, 7.5, 7.5
	(<i>p</i>)	7.30 – 7.38 m	7.32 – 7.43 m	7.30 – 7.42 m	–	–	7.81 ^c d, 7.5
C1_3		1.31 s	2.37 s	–	2.39 s	–	7.49 dd, 7.2, 7.2
C-2		138.76	138.78	137.86	138.46	139.24	–
C-3		138.93	138.84	139.57	139.73	138.72	140.78
C-4		52.16	52.10	52.24	51.56	51.08	53.85
C-R^1	(<i>i</i>)	127.91	127.93	126.71, 3.4 ^d	131.05	130.61	130.78
	(<i>o</i>)	129.01	129.40	131.46, 8.6 ^d	129.40	129.36	129.30
	(<i>m</i>)	125.72	129.19	115.88, 21.9 ^d	128.67	128.81	128.64
	(<i>p</i>)	152.83	139.73	163.78, 250.2 ^d	129.59	129.90	129.64
C-R^2	(<i>i</i>)	142.22	142.19	141.74	139.08	137.63, 3.4 ^d	144.66
	(<i>o</i>)	128.03	128.02	127.96	127.89	129.73, 8.3 ^d	125.60, 141.9 ^e
	(<i>m</i>)	129.18	129.19	129.35	129.88	116.37, 21.7 ^d	128.67, 120.85 ^f
	(<i>p</i>)	127.64	127.92	128.17	137.61	162.33, 248.8 ^d	129.45
CH_3	31.21	21.31	–	–	21.05	–	–
CMe_3	34.73	–	–	–	–	–	–
F^g	–	–	–	–	–	–113.68	–

^a Unresolved multiplet; ^b $J_{\text{H-F}}$, Hz; ^c H-4 (*m'*), see formula *II*; ^d $J_{\text{C-F}}$, Hz; ^e C-4 (*o'*), see formula *II*; ^f C-4 (*m'*), see formula *II*; ^g internal standard CFCl_3 .

TABLE V
¹H NMR spectra of cyclopentadienes *V*_a – *V*_g

Assignment	<i>V</i> _a	<i>V</i> _b	<i>V</i> _c	<i>V</i> _d	<i>V</i> _e	<i>V</i> _f	<i>V</i> _g
δ (ppm), <i>J</i> (Hz)							
1-H	7.333 d, 0.9	7.213 d, 0.9	7.264 d, 1.0	7.099 d, 0.9	7.074 d, 0.9	7.053 d, 0.9	7.100 d, 0.9
1-H ₅	5.256 d, 0.9	5.036 d, 0.9	5.193 d, 1.0	5.015 d, 0.9	5.032 d, 0.9	5.004 d, 0.9	5.009 d, 0.9
1-R ¹	(<i>o</i>) 7.175 – 7.313 ^a m	7.082 – 7.156 ^a m	7.096 m	7.324 m, 5.4 ^b	7.026 – 7.116 m	7.365 m	7.003 m
(<i>m</i>)	7.175 – 7.313 ^a m	7.082 – 7.156 ^a m	7.042 m	6.980 m, 8.8 ^b	7.026 – 7.116 m	7.275 m	7.060 m
(<i>p</i>)	7.175 – 7.313 ^a m	–	–	–	7.026 – 7.116 m	7.249 m	7.036 m
CH ₃	–	1.232 s	2.364 s	–	–	–	–
2-R ¹	(<i>o</i>) 7.628 m	7.358 m	7.441 m	6.959 m, 5.5 ^b	7.382 m	7.004 – 7.121 m	7.370 m
(<i>m</i>)	7.391 m	7.313 m	7.260 m	6.791 m, 8.8 ^b	7.280 m	7.004 – 7.121 m	7.267 m
(<i>p</i>)	7.283 m	–	–	–	7.247 m	7.004 – 7.121 m	7.257 m
CH ₃	–	1.331 s	2.490 s	–	–	–	–
4-R ²	(<i>o</i>) 7.569 m	7.432 m	7.441 m	7.435 m	7.349 m	7.364 m, 5.2 ^b	7.393 m
(<i>m</i>)	7.464 m	7.202 m	7.354 m	7.216 m	7.024 m	6.904 m, 8.8 ^b	7.356 m
(<i>p</i>)	7.391 m	7.082 – 7.156 ^a m	7.239 m	7.167 m	–	–	–
CH ₃	–	–	–	–	2.256 s	–	1.267 s
5-R ²	(<i>o</i>) 7.175 – 7.313 ^a m	6.994 m	7.229 – 7.272 m	7.113 m	6.996 m	7.040 m, 5.3 ^b	7.123 m
(<i>m</i>)	7.175 – 7.313 ^a m	7.082 – 7.156 ^a m	7.229 – 7.272 m	7.087 m	6.893 m	6.782 m, 8.8 ^b	7.046 m
(<i>p</i>)	7.175 – 7.313 ^a m	7.035 m	7.229 – 7.272 m	7.047 m	–	–	–
CH ₃	–	–	–	–	2.158 s	–	1.195 s

^a Unresolved multiplet; ^b *J*_{H-F}.

TABLE VI
 ^{13}C NMR spectra of cyclopentadienes $V7a$ – $V7g$

Assignment	$V7a$	$V7b$	$V7c$	$V7d$	$V7e$	$V7f$	$V7g$
δ (ppm), J (Hz)							
Ring	1 146.89	146.15	146.42	139.02	146.11	146.59	146.51
2	150.65	150.27	150.27	139.52	150.80	149.44	150.36
3	131.48	131.84	131.76	131.02	130.50	131.20	130.78
4	140.48	140.00	135.12	150.80	140.48	140.41	132.37
5	61.89	61.91	61.79	62.01	61.47	61.08	61.45
1-R^1	(<i>i</i>) 136.04	133.24	133.56	131.93 ^a , 3.4 ^d	132.32 ^b	136.00	134.74
(<i>o</i>)	129.00	125.85	128.45	130.10, 8.0 ^d	127.83	128.44	129.03
(<i>m</i>)	127.88	125.55	128.80	115.40, 21.4 ^d	128.11	128.39	127.76
(<i>p</i>)	126.55	149.26 ^c	136.80 ^f	162.00, 247.0 ^d	126.39 ^c	127.34	126.32
2-R^1	(<i>i</i>) 138.00	138.47	133.22	132.06 ^a , 3.4 ^d	136.53 ^b	135.75	140.40
(<i>o</i>)	125.86	124.74	128.35	130.54, 7.7 ^d	128.52	128.94	128.50
(<i>m</i>)	128.38	128.09	128.35	111.05, 21.4 ^d	128.30	128.00	128.29
(<i>p</i>)	126.85	150.04 ^g	136.06 ^h	161.65, 246.4 ^d	127.08 ^c	126.74	127.04
4-R^2	(<i>i</i>) 136.31	135.12	138.34	145.64	136.57	131.07, 3.3 ^d	136.62
(<i>o</i>)	128.49	128.46	125.81	125.85	125.80	127.38, 7.8 ^d	125.30
(<i>m</i>)	128.34	128.38	128.64	128.43	129.01	115.51, 21.6 ^d	125.49
(<i>p</i>)	127.18	126.68	126.70	127.03	135.72 ⁱ	161.91, 247.2 ^d	149.65 ^j
5-R^2	(<i>i</i>) 134.95	133.63	139.94	134.73	136.23	133.51, 3.4 ^d	136.29
(<i>o</i>)	128.49	128.40	128.35	128.21	129.11	129.91, 8.0 ^d	127.87
(<i>m</i>)	128.29	128.35	129.04	128.62	129.23	115.42, 21.3 ^d	125.39
(<i>p</i>)	126.46	126.33	126.36	126.65	134.95 ^k	161.43, 244.6 ^d	148.99 ^l

^{a,b,c} Can be interchanged; ^d J_{C-F} ; ^e CH_3 δ 31.27, $CMes_3$ δ 34.41; ^f CH_3 δ 21.15; ^g CH_3 δ 31.36, $CMes_3$ δ 34.59; ^h CH_3 δ 21.25; ⁱ CH_3 δ 21.14; ^j CH_3 δ 31.30; ^k CH_3 δ 34.48; ^l CH_3 δ 21.06; ^m CH_3 δ 31.24, $CMes_3$ δ 34.29.

NMR Data of 5*H*-5,6-Diphenylcyclopenta[*I*]phenanthrene (*VIII*)

¹H NMR spectrum: 5.436 d, 1 H (H-5, *J* = 1.3); 7.080 m, 1 H (*p*-Ph5); 7.160 m, 2 H (*m*-Ph5); 7.207 m, 1 H (*p*-Ph6); 7.229 m, 2 H (*o*-Ph5); 7.298 m, 2 H (*m*-Ph6); 7.387 ddd, 1 H (H-3, *J* = 8.1, 6.9, and 1.3); 7.481 ddd, 1 H (H-2, *J* = 8.4, 6.9, and 1.4); 7.631 m, 2 H (*o*-Ph6); 7.680 ddd, 1 H (H-9, *J* = 8.2, 7.0, and 1.2); 7.713 ddd, 1 H (H-10, *J* = 8.7, 7.0, and 1.5); 7.796 d, 1 H (H-7, *J* = 1.3); 7.860 ddd, 1 H (H-4, *J* = 8.1, 1.4, and 0.5); 8.315 ddd, 1 H (H-8, *J* = 8.2, 1.5, and 0.3); 8.665 ddd, 1 H (H-1, *J* = 8.4, 1.3, and 0.5); 8.737 ddd, 1 H (H-11, *J* = 8.7, 1.2, and 0.3).

¹³C NMR spectrum: 57.45 d (C-5); 123.35 d (C-11); 123.40 d (C-1); 123.82 d (C-4); 124.60 d (C-8); 124.67 d (C-7); 125.22 d (C-2); 126.17 d (C-10); 126.56 d (*o*-Ph6); 126.60 d (C-9); 126.68 d (*p*-Ph5); 126.71 d (C-3); 127.32 d (*p*-Ph6); 127.34 s (C-11b); 128.46 d (*o*-Ph5); 128.49 d (*m*-Ph6); 128.81 d (*m*-Ph5); 128.85 s (C-11a); 129.41 s (C-4a); 130.74 s (C-7b); 135.14 s (*i*-Ph5); 138.94 s (C-4b); 139.44 s (C-6); 143.09 s (*i*-Ph6); 153.22 s (C-7a). Spectral properties of cyclopentadienes *VIIa* – *VIIf* and sulfones *Va* – *Vd* are given in Tables V and VI and VII and VIII, respectively.

Photoisomerization of Cyclopentadienes *IXa*, *IXb*, and *IXc*

Solution of studied cyclopentadiene *IX* (ref.¹⁴) (1.1 mmol) in suitable solvent (400 ml) was irradiated by 400 W high-pressure mercury lamp in argon atmosphere at 20 °C. Upon disappearance of the starting compound *IX* (HPLC analysis) was the solvent removed under reduced pressure at room temperature. The reaction products were isolated in a similar way already described, see Tables II and III.

TABLE VII

¹H NMR spectra of sulfones *Va* – *Vd*

Assignment	<i>Va</i>	<i>Vb</i>	<i>Vc</i>	<i>Vd</i>
	δ (ppm), <i>J</i> (Hz)			
4	6.914 d, 3.6	6.864 d, 3.5	6.855 d, 3.6	6.859 d, 3.5
5	3.962 d, 3.6	3.894 d, 3.5	3.888 d, 3.6	3.831 d, 3.5
1-R ¹	(<i>o</i>) 7.165 – 7.321 ^a m	7.266 m	6.946 – 7.101 ^a m	7.058 m, 5.3 ^b
	(<i>m</i>) 7.165 – 7.321 ^a m	7.132 m	6.946 – 7.101 ^a m	6.949 m, 8.7 ^b
	(<i>p</i>) 7.165 – 7.321 ^a m	– ^c	– ^d	–
3-R ¹	(<i>o</i>) 7.165 – 7.321 ^a m	7.245 m	6.946 – 7.101 ^a m	7.143 m, 5.3 ^b
	(<i>m</i>) 7.165 – 7.321 ^a m	6.968 m	6.946 – 7.101 ^a m	6.949 m, 8.7 ^b
	(<i>p</i>) 7.165 – 7.321 ^a m	– ^e	– ^f	–
6-R ² (<i>endo</i>)	(<i>o</i>) 7.633 m	7.591 m	7.587 m	7.578 m
	(<i>m</i>) 7.302 m	7.282 m	7.281 m	7.306 m
	(<i>p</i>) 7.288 m	7.165 m	7.162 m	7.202 m
6-R ² (<i>exo</i>)	(<i>o</i>) 7.091 m	7.055 m	6.946 – 7.101 ^a m	6.978 – 7.102 m
	(<i>m</i>) 7.017 m	6.976 m	6.946 – 7.101 ^a m	6.978 – 7.102 m
	(<i>p</i>) 6.976 m	6.941 m	6.946 – 7.101 ^a m	6.978 – 7.102 m

^a Unresolved multiplet; ^b *J*_{H-H}, Hz; ^c CH₃ δ 1.224; ^d CH₃ δ 2.263; ^e CH₃ δ 1.246; ^f CH₃ δ 2.282.

TABLE VIII
 ^{13}C NMR spectra of sulfones *Va* – *Vd*

Assignment	1	<i>Va</i>	<i>Vb</i>	<i>Vc</i>	<i>Vd</i>
		δ (ppm), J (Hz)			
Ring	1	57.27	56.91	57.06	56.60
	3	143.94	143.87	143.87	143.05
	4	132.95	129.58	133.03	130.19
	5	32.17	32.43	32.26	32.48
	6	58.15	58.00	57.95	58.07
1-R ¹	(<i>i</i>)	127.89	124.86	124.74	123.71, π 0 ^c
	(<i>o</i>)	128.70	126.92	129.24	129.23, 8.5 ^c
	(<i>m</i>)	128.70	127.87	129.43	115.61, 22.0 ^c
	(<i>p</i>)	127.41	152.75 ^a	138.54 ^b	163.64, 250.2 ^c
3-R ¹	(<i>i</i>)	127.72	124.75	124.91	123.73, π 0 ^c
	(<i>o</i>)	127.23	126.92	127.06	128.24, 9.5 ^c
	(<i>m</i>)	128.70	125.30	129.49	115.91, 22.0 ^c
	(<i>p</i>)	128.45	151.50 ^d	139.79 ^c	162.86, 248.9 ^c
5-R ² (<i>endo</i>)	(<i>i</i>)	139.96	140.50	140.22	139.60
	(<i>o</i>)	132.95	135.97	133.03	132.97
	(<i>m</i>)	127.95	125.69	127.90	127.98
	(<i>p</i>)	129.65	127.28	127.30	127.50
5-R ² (<i>exo</i>)	(<i>i</i>)	135.13	135.33	135.33	134.89
	(<i>o</i>)	128.48	128.54	128.55	128.37
	(<i>m</i>)	128.06	127.87	128.05	128.20
	(<i>p</i>)	126.88	126.63	126.80	127.08

^a CMe_3 δ 34.68, CH_3 δ 31.15; ^b CH_3 δ 21.32; ^c $J_{\text{C}-\text{F}}$; ^d CMe_3 δ 34.50, CH_3 δ 31.10; ^e CH_3 δ 21.28.

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