243. Reversible Photochemistry, Absorption- and ¹H-NMR.-Spectra, and Oxidation of the [2,2]Metacyclophane-1-ene ⇄ 4,5,15,16-tetrahydropyrene System

by **R. Naef**[1]) and **Ernst Fischer**

Department of Structural Chemistry,
Weizmann Institute of Science, Rehovot, Israel

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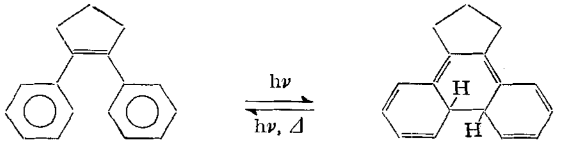
Summary. The reversible photointerconversion in the above system was investigated in a wide range of temperatures and wavelengths of irradiation. The tetrahydropyrenes are obtainable only photochemically. The unmethylated and the mono-methylated compound are oxidized with iodine quantitatively to 4,5-dihydropyrene, even at −30°. This makes it possible to estimate the absolute concentration of the tetrahydropyrenes, and thereby their molar extinction coefficients and complete electronic absorption spectra. The quantum yields in both directions do not vary appreciably with the temperature, down to −190°. This is the first case in which the photocyclization yield of a *cis*-stilbenelike compound is not attenuated on cooling, and reflects the special character of highly constrained structures. No emission was observed in solution. ¹H-NMR.-spectra of both modifications of the dimethylated compound were taken. They support the structures assumed for both modifications, and also allow an estimate of their relative concentrations.

Introduction. – Earlier reports from this [1] and other laboratories [2] described the reversible photocyclization of *cis*-stilbene and many related compounds to 4a,4b-dihydrophenanthrene (DHP) and its derivatives:

cis-stilbene DHP (2)

In all these cases the *cis* compound can undergo photoisomerization to the corresponding *trans* isomer, in addition to photocyclization. The two exceptions described so far are the systems based on 1,2-diphenylcyclopentene (**I^A**) studied extensively in this laboratory, [1], and on [2,2]-metacyclophane-1-ene (**II^A**) described by *Ramey & Boekelheide*, [3]:



I^A I^B (2)

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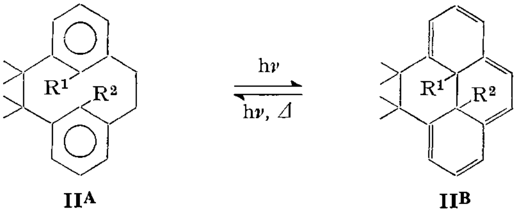
[1]) On leave of absence from the Institut für Farbenchemie der Universität Basel. R. N. gratefully acknowledges a grant from the «Stiftung für Stipendien auf dem Gebiet der Chemie», which enabled him to carry out this investigation in Rehovot.



(3)

II_a: $R^1 = R^2 = H$; II_b: $R^1 = H, R^2 = CH_3$; II_c: $R^1 = R^2 = CH_3$

(In the present paper the superscripts **A** and **B** denote the open and closed modifications, respectively, while subscripts **a**, **b**, **c** stand for the parent compound and its two methylation products.) In both compounds the *cis* structure is 'frozen', and therefore no *cis/trans* isomerization is possible, so that the respective systems are of the simple $\mathbf{A} \rightleftarrows \mathbf{B}$ type.

System $\mathbf{II^A} \rightleftarrows \mathbf{II^B}$ is of particular interest since $\mathbf{II^A}$ represents 'a rigidly constrained *cis*-stilbene moiety', [3], in which the two phenyl rings are no longer free to rotate. This strain is relieved at least partly by cyclization to $\mathbf{II^B}$, thereby greatly decreasing the energy difference between the open and the closed forms. (This difference amounts to about 30 kcal.mol^{-1} in $\mathbf{I^A} \rightarrow \mathbf{I^B}$.) We therefore extended *Boekelheide*'s preliminary investigation of these compounds [3], on a par with our study [1b] of the system $\mathbf{I^A} \rightleftarrows \mathbf{I^B}$.

In the present paper we describe results obtained with the three compounds $\mathbf{II^A_a}$, $\mathbf{II^A_b}$, $\mathbf{II^A_c}$ and their corresponding photocyclization products $\mathbf{II^B_a}$, $\mathbf{II^B_b}$, $\mathbf{II^B_c}$.

We are greatly indebted to Professor *Boekelheide* for making this investigation possible by supplying us with samples of the three compounds, as well as with detailed information about them.

Experimental. – Our low-temperature techniques of photochemistry and spectrophotometry have been described before [1b] [4]. Light sources used were a low-pressure mercury lamp at 254 nm and a medium-pressure lamp at 313 and 546 nm. Representative light intensities were 10^{-8}, 3×10^{-7} and 7×10^{-7} Einsteins/min at 254, 313, and 546 nm, respectively. Ferri-oxalate actinometry was employed in connection with quantum yield measurements. Light intensities at 546 nm were estimated by using a Rhodamine B solution as a 'quantum converter' [6]. ^{1}H-NMR.-measurements were carried out in a *Bruker* 90 MHZ instrument combined with a *Fourier* transform system. Spectroscopic quality solvents were used. Absorption spectra were recorded on a *Cary* 14 spectrophotometer. Cells were either degassed in a high-vacuum system and then fused-off, or else flushed continuously with argon containing less than 10 ppm of oxygen.

Reversible photochemistry. – Ultraviolet irradiation causes only partial conversion of $\mathbf{II^A}$ into $\mathbf{II^B}$, since the reaction is photoreversible. (In the present context $\mathbf{II^A}$ and $\mathbf{II^B}$ stand for any of the three compounds investigated.) The photostationary state reached is governed by the equation developed by *Zimmerman et al.* [5], provided the thermal back reaction $\mathbf{II^B} \rightarrow \mathbf{II^A}$ is prevented by cooling to 0° or below [3]:

$$Q_A \cdot \varepsilon_A \cdot (C_A)_\infty = Q_B \cdot \varepsilon_B \cdot (C_B)_\infty \text{ at wavelength } \lambda \qquad (I)$$

where Q_A and Q_B are the quantum yields for processes $\mathbf{II^A} \rightarrow \mathbf{II^B}$ and $\mathbf{II^B} \rightarrow \mathbf{II^A}$, respectively, ε_A and ε_B are the molar extinction coefficients of the two modifications, and $(C_A)_\infty$ and $(C_B)_\infty$ denote the concentrations of $\mathbf{II^A}$ and $\mathbf{II^B}$ in the photostationary state established by irradiation at a wavelength λ. Fig. 1 shows the absorption spectra of the **II**^{A} and **II**^{B} modifications at 0°, the latter being obtained by the extrapolation procedures to be described later on. As is to be expected from these curves, and shown earlier [3], maximal conversion into **II**^{B} is achieved by irradiation at 254 nm, where **II**^{B} absorbs much less than **II**^{A}.

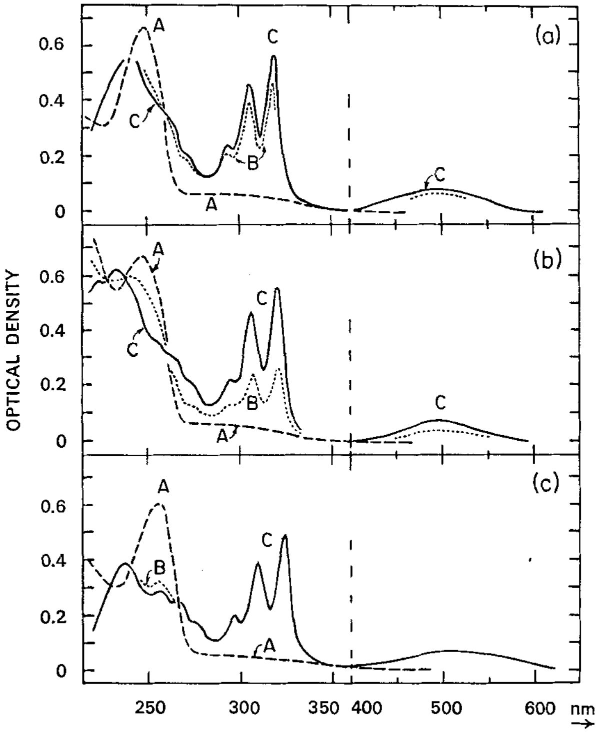


Fig. 1. *Absorption spectra of the* **A** *and* **B** *modifications of* $\mathbf{II_a}$, $\mathbf{II_b}$, $\mathbf{II_c}$. Solutions about 3×10^{-5} M in MCH/methylcyclopentane (MCP) at 0° in 10 mm cells sealed off *in vacuo*. Curves A – before irradiation (**A** modification), curves B – after 254 nm irradiation, curves C – extrapolated curves (pure **B** modification), assuming that the solutions described by curves B contain 80% B in (a) and (c), and 45% B in (b). Fig. 1a – compound $\mathbf{II_a}$; Fig. 1b – $\mathbf{II_b}$; Fig. 1c – $\mathbf{II_c}$. Note different wavelength scales

With compound $\mathbf{II_b}$ photostationary states could not be reached because of irreversible side reactions which gain importance after prolonged irradiation. In Fig. 1a and 1c curves **B** present photostationary states attained by irradiation at 254 nm. Irradiation in the visible region completely reconverts the closed **II**^{B} modification into the open **II**^{A} one, while at 313 nm, where **II**^{B} absorbs considerably more than **II**^{A}, a photostationary state containing 10–20% **II**^{B} is attained. Table 1 summarizes the photostationary states estimated for $\mathbf{II_a}$ and $\mathbf{II_c}$ according to calculations to be elaborated in a later paragraph. The composition at the photostationary state was found to be remarkably independent of the temperature at which irradiation was carried out. According to equation (I) this already indicates that the ratio Q_A/Q_B

does not vary much with the temperature. The individual Q's will be dealt-with in a later paragraph.

Table 1. *Fraction of* $\mathbf{II^B}$ *in photostationary states established by irradiation of compounds* $\mathbf{II_a}$ *and* $\mathbf{II_c}$ at 0°, at 254 and at 313 nm

Irradiation wavelength (nm)	$\mathbf{II_a^A} \rightleftarrows \mathbf{II_a^B}$	$\mathbf{II_c^A} \rightleftarrows \mathbf{II_c^B}$
313	0.10	0.20
254	0.80	0.80

Electronic Absorption Spectra. – (*Cf.* Fig. 1 and 2.) (a) *The* A *modification*: The major difference between the spectra of $\mathbf{II_a^A}$, $\mathbf{II_b^A}$, $\mathbf{II_c^A}$ and that of the analogous *cis*-stilbene is that the longwave ultraviolet peak is flat and much less intense (ε at 285 nm is about 2,600, as compared with about 10,000 in *cis*-stilbene). (b) *The* B *modification*: It is impossible to separate the **B** modification from **A**, or to achieve complete photoconversion $\mathbf{II^A} \rightarrow \mathbf{II^B}$. The absorption spectra of the pure **B** modifications have therefore to be calculated by extrapolation procedures which will be described in the following two paragraphs. These spectra (curves C in Fig. 1) are remarkably similar to those of DHP proper [1], with at least two groups of well-structured peaks in the ultraviolet, and one in the visible. The latter is red-shifted and much less intense than in DHP ($\varepsilon \approx 3{,}000$, compared with about 8,000 in DHP). Some fine structure develops in this band at low temperatures (Fig. 2).

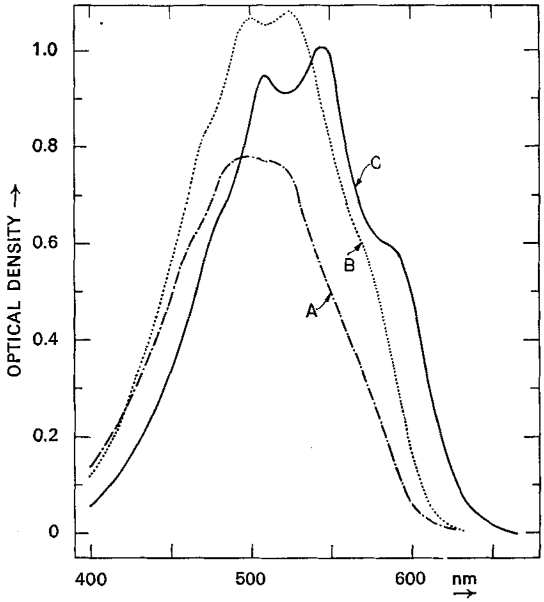
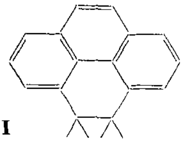


Fig. 2. *Vibrational structure of the long-wavelength absorption band of the* **B** *modification at* –*180°*. Solutions in MCH/MCP, arbitrary concentrations. Curve A – compound $\mathbf{II_a^B}$, curve B – $\mathbf{II_b^B}$, curve C – $\mathbf{II_c^B}$

The Oxidation of the $\mathbf{II^B}$ Modifications and the Extent of the Photoconversion $\mathbf{II^A \rightarrow II^B}$. – As pointed out by *Ramey & Boekelheide* [3], not only $\mathbf{II^B_a}$, but also $\mathbf{II^B_b}$ are oxidized with oxygen to 4,5-dihydropyrene, **III**. The fate of the methyl group in the latter case is not known.



III

As shown by us earlier [1b], the quantitative oxidation of the unknown DHP derivatives to known phenanthrene derivatives presents an excellent method both for identifying the DHP's and for estimating their concentration and thereby their molar extinction coefficient. Ultraviolet irradiation of $\mathbf{II^A_a}$ and $\mathbf{II^A_b}$ in methylcyclohexane (MCH) at room temperature in the presence of iodine indeed resulted in complete oxidation to **III**. For the present purpose it was necessary to carry out a *thermal* (*i.e.* not photochemical [7]) oxidation of $\mathbf{II^B_a}$ and $\mathbf{II^B_b}$, after first forming them by 254 nm irradiation of $\mathbf{II^A_a}$ and $\mathbf{II^A_b}$, respectively. To prevent thermal reversion $\mathbf{II^B \rightarrow II^A}$, such an oxidation has to be performed at 0° or below. Preliminary experiments showed that at $-20°$ oxidation with molecular oxygen is slow and incomplete with $\mathbf{II^B_a}$. The situation is even worse with $\mathbf{II^B_b}$. However, iodine, which we found to be an excellent oxidant of DHP's [1] [7] [8], causes instantaneous oxidation in both cases even at $-30°$. In a typical experiment, 3 ml of an argon-flushed MCH solution of $\mathbf{II^A_b}$ were irradiated at 254 nm in a spectrophotometric cell at $-20°$ causing partial conversion into $\mathbf{II^B_b}$ (Fig. 1b describes a similar experiment at 0°). 0.1 ml of a concentrated MCH solution of iodine were added, to give an optical density of about 0.4 at the visible peak of iodine at 525 nm. The prominent peaks of $\mathbf{II^B_b}$ at 294, 308, and 322 nm (where I_2 does not absorb) disappear immediately, and the sharp peak of **III** at 299 nm ($\varepsilon = 14{,}000$ according to our measurements, 13,000 according to [9]) forms instead. From a comparison of the height of this peak thus formed with that of the peak formed during *complete photo-oxidation* of a similar solution, as described above, one can immediately calculate the extent of photoconversion $\mathbf{II^A_b} \xrightarrow{h\nu} \mathbf{II^B_b}$ in the irradiated solution. Accordingly the solution described by curve B in Fig. 1b contains about 50% $\mathbf{II^B_b}$, and a simple extrapolation procedure [1b] leads to curve C of the pure $\mathbf{II^B_b}$ modification. Curve C in Fig. 1a was obtained in a similar fashion. From these curves, together with the known concentrations of the starting compounds, the data for $\mathbf{II^B_a}$ and $\mathbf{II^B_b}$ in Table 2 were calculated. $\mathbf{II^B_c}$ is not affected by oxygen or iodine, and the above method can therefore not be applied to it.

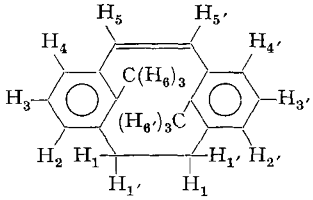
The ^{1}H-NMR.-Spectrum of $\mathbf{II^A_c}$ and $\mathbf{II^B_c}$. – The purpose of our attempts to obtain such spectra, just as in our earlier work on *cis*-2,4,6,2′,4′,6′-hexamethylstilbene [1a] was twofold: To obtain additional proof for the suggested structure of the $\mathbf{II^B}$ modifications, and to estimate the extent of photoconversion $\mathbf{II^A_c \rightarrow II^B_c}$ by means of NMR.-signals characterizing each of the two modifications. The signals assigned to

Table 2. *Wavelengths* (λ) *and extinction coefficients* (ε) *of the absorption maxima of* $\mathbf{II}_a^B$, $\mathbf{II}_b^B$, $\mathbf{II}_c^B$ in methylcyclohexane/methylcyclopentane 1:1 at 0°

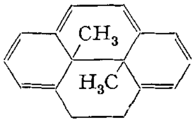
$\mathbf{II}_a^B$		$\mathbf{II}_b^B$		$\mathbf{II}_c^B$	
λ (nm)	ε	λ (nm)	ε	λ (nm)	ε
240	18,000	233	19,200	238	13,100
255	12,900	255	11,200	257	10,800
262	11,000	264	9,400	267	8,450
272	6,900	272	6,700	275	6,000
293	7,800	294	6,850	296	6,900
306	15,200	308	14,100	309	13,100
319	18,400	322	17,000	323	16,600
500	3,500	500	3,200	520	3,000

the protons of the two methyl groups are imminently suitable for the second purpose. In a typical experiment 3 ml of a 6×10^{-3} M solution of $\mathbf{II}_c^A$ in MCH were irradiated at 0° and 254 nm for 9 h. The solvent was then completely evaporated in a high-vacuum system, and the residual solid mixture of $\mathbf{II}_c^A$ and $\mathbf{II}_c^B$ dissolved in about 0.6 ml of precooled carbon tetrachloride. 0.2 ml of this solution were diluted with MCH and the absorption spectrum taken at 0°, before and after eradication of $\mathbf{II}_c^B$ with visible light. 0.4 ml of the CCl_4 solution were introduced into a NMR.-tube and its NMR.-spectrum taken at 0°, again before and after erasure of $\mathbf{II}_c^B$ with visible light. As expected, the latter spectrum was identical with the spectrum of a fresh solution of $\mathbf{II}_c^A$, as described in detail by *Ramey* [3].

Table 3. ^{1}*H-NMR.-signals and their assignments in* $\mathbf{II}_c^A$ *and* $\mathbf{II}_c^B$. For details see text. (The numbering of the protons is identical in both compounds)



$\mathbf{II}_c^A$



$\mathbf{II}_c^B$

Proton number	δ (ppm)	Shape and coupling constant (Hz)	δ (ppm)	Shape and coupling constant (Hz)
H_1, $H_{1'}$	2.26 and 2.51	2 triplets, $J_{1,1'} = 8.9$	2.1–2.6	multiplet
H_2, $H_{2'}$ H_3, $H_{3'}$ H_4, $H_{4'}$	6.58	multiplet	5.07	multiplet
H_5, $H_{5'}$	6.25	doublet, $J_{5,6} = 2.5$	4.8	doublet, $J_{5,6} = 2.7$
H_6, $H_{6'}$	.44	doublet, $J_{6,5} = 2.5$	1.89	doublet, $J_{6,5} = 2.7$

The observed signals and their suggested assignments are detailed in Table 3. The signals due to the six phenyl and two vinyl protons in $\mathbf{II}_c^A$ are shifted upfield in $\mathbf{II}_c^B$, to positions typical for olefinic protons. The reason is probably the absence of ring currents in $\mathbf{II}_c^B$, as distinct from $\mathbf{II}_c^A$. The inverse holds for the signals assigned to the six methyl protons, which are in the shielding range of the benzene ring current in $\mathbf{II}_c^A$. In $\mathbf{II}_c^B$ they appear at a much lower field, as expected for aliphatic methyl protons in the absence of ring currents. The two triplets assigned to the ethano bridge can be explained by assuming that the two geminal methylene protons take up axial and equatorial positions, respectively, with respect to the 'plane' of the molecule.

The observed signals thus adequately support the proposed structure of $\mathbf{II}_c^B$, and therefore indirectly also that of $\mathbf{II}_a^B$ and $\mathbf{II}_b^B$.

The extent of photoconversion $\mathbf{II}_c^A \xrightarrow{h\nu} \mathbf{II}_c^B$ was determined from the ratio of the methyl signals assigned to the two modifications. In the experiment described above, the conversion thus calculated was 55 ± 5%. From a combination of this result with the optical spectra of the solutions, the optical spectrum of pure $\mathbf{II}_c^B$ could be calculated by extrapolation. The resulting spectral data are given in Fig. 1c and in the last column in Table 2, and agree with those reported by *Ramey* [3]. (The latter estimated the extent of photoconversion by a different procedure, suggested by us in an earlier paper [10].) The only exception is the 520 nm band where we find $\varepsilon = 3{,}000$, while Ramey reported 2,000.

The Quantum Yields of the Photointerconversions $\mathbf{II}^A \rightleftarrows \mathbf{II}^B$ in the Temperature Range 0° to –190°. – In all stilbene derivatives and analogues investigated so far, we found the quantum yield of ring closure, $Q(\mathbf{A} \rightarrow \mathbf{B})$ or in short Q_A, to fall off at low temperatures [1b] [8], while the quantum yield of the reverse reaction, $Q(\mathbf{B} \rightarrow \mathbf{A})$ or Q_B, remained either constant or also fell off at still lower temperatures. In view of the constrained structure of $\mathbf{II}^A$ it was of particular interest to check this point with the three compounds of the present series.

The quantum yields in both directions were measured in the usual way, using deaerated vacuum-sealed cells containing 3 ml of solutions in a 1:1 mixture of MCH and methylcyclopentane, and employing ferri-oxalate actinometry. The calculations were based on the molar extinction coefficients of the **B** modifications estimated as described above, and therefore include a correspondingly large uncertainty. In those cases where photostationary states could be established without parallel partial decomposition, *Zimmerman*'s exact method for photoreversible systems was used [5] [11]. In the other cases yields were estimated from the initial rates of photoconversion. Irradiation at 546 nm did not involve these difficulties, but instead the uncertainty of the actinometry is larger. In view of all these factors we believe that the Q's given in Tables 4 and 5 are uncertain to ± 20% of their values. The values for Q_B at 254 nm were estimated from Q_A and the composition of the photostationary state achieved by irradiation at 254 nm, using equation (I). These estimations involve the ratio $(C_A/C_B)_\infty$ which, for low or high degrees of photoconversion, is very sensitive to the estimated $(C_B)_\infty$. Thus, if for $\mathbf{II}_a^A \xrightarrow{254} \mathbf{II}_a^B$ we assume a photostationary state containing 90% **B** instead of the 80% used in calculating the third column of

Table 4. *Temperature dependence of the quantum yields* Q_A *of the photocyclisation of [2,2]metacyclophane-1-enes* $\mathbf{II}_a^A$, $\mathbf{II}_b^A$, $\mathbf{II}_c^A$ (*ca.* 3 · 10^{-5} M in MCH/MCP 1:1)

Temp. °C	Irradiation wavelength (nm)	$\mathbf{II}_a^A$	$\mathbf{II}_b^A$	$\mathbf{II}_c^A$
0	313	0.43	0.47	–
	254	0.50	0.53	–
– 50	313	0.29	0.39	0.65
	254	0.45	–	–
–100	313	0.41	0.37	0.54
	254	0.44	0.41	0.69
–140	313	0.47	–	0.52
	254	–	–	–
–180	313	0.43	0.27	0.54
	254	0.39	0.33	0.60
–190	313	0.38	0.34	0.49
	254	0.33	0.36	0.55

Table 5. *Temperature dependence of the quantum yields* Q_B *of the photochemical ring opening of the 4,5,15,16-tetrahydropyrenes* $\mathbf{II}_a^B$, $\mathbf{II}_b^B$, $\mathbf{II}_c^B$ (*ca.* 3 · 10^{-5} M in MCH/MCP 1:1)

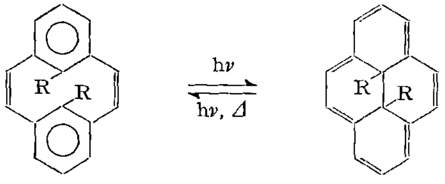
Temp. °C	Irradiation wavelength (nm)	$\mathbf{II}_a^B$	$\mathbf{II}_b^B$	$\mathbf{II}_c^B$
0°	546	0.58	0.63	0.51
	313	–	0.57	0.47
	(254)	(0.20)	–	(0.45)
– 50	546	0.46	0.61	0.39
	313	0.48	0.55	0.41
	(254)	(0.18)	–	–
–100	546	0.62	0.55	0.39
	313	0.66	0.55	0.34
	(254)	(0.18)	–	(0.41)
–140	546	0.60	–	0.39
	313	0.42	–	0.32
	(254)	(0.12)	–	–
–180	546	–	0.64	0.27
	313	–	0.47	0.34
	(254)	(0.16)	–	(0.35)
–190	546	–	–	0.32
	313	0.58	0.57	0.26
	(254)	(0.13)	–	(0.32)

Table 5, the resulting Q_B at 254 nm and 0° increases to 0.31, while all the remaining Q's decrease by about 10% of their value.

The most prominent features of the data given in Tables 4 and 5 are the absence of any serious effect of the temperature on the quantum yields in both directions, and the rather low values for Q. As mentioned above, this is the first case of a photocyclization in *cis*-stilbene-like compounds which is not attenuated sharply at low temperatures.

Luminescence. – Neither the **A** nor the **B** modifications of all three compounds show any luminescence in solution, down to −190°. A rather weak emission, peaked around 445 nm, was observed from solid $\mathbf{II}_c^A$. Again, this is the first case of a *cis*-stilbene-like compound not exhibiting fluorescence in solution even at −190°.

Discussion. – The constrained structure of the [2,2]metacyclophane-1-enes is responsible for the major differences between the photoreversible $\mathbf{II}^A \rightleftarrows \mathbf{II}^B$ system and the closely related *cis*-stilbene ⇄ DHP and related systems: the absence of fluorescence, and of any variation of the photocyclization quantum yield with temperature. Whatever the nature of the energy barrier in the photocyclizations described by us before [1] [7] [8], such an energy barrier clearly does not exist in the present system, and one is tempted to blame the more or less free rotation of the phenyl rings in *cis*-stilbenes, which is frozen-out in the metacyclophane-enes. In this context one should mention that the distance between the two carbon atoms involved in the photocyclization is 2.6 Å in [2,2]metacyclophane-diene $\mathbf{IV}^A$, [12a], and 2.7 Å in [2,2]metacyclophane [12b]. We may assume that in $\mathbf{II}_a^A$ this distance has some intermediate value, say 2.65 Å, considerably less than the 3.4 Å found [13] in diphenylcyclopentene (system 2). In view of the rigid structure of this molecule, the molecular geometry in the excited state cannot be very different from that in the ground state. Also, the excess of energy of the closed, **B**, modification over that of the open, **A**, modification in the present system should by virtue of the internal strain be considerably smaller than in *cis*-stilbene (system 1) or diphenylcyclopentene (system 2). This assumption is supported by the observation [14] that in the even more constrained [2,2]metacyclophane-diene $\mathbf{IV}^A$, thermodynamic equilibrium with $\mathbf{IV}^B$ is established, and the energy difference is about 3 kcal.mol^{-1} in favor of $\mathbf{IV}^B$! This should at least partly be due to the internal strain in $\mathbf{IV}^A$. The absence of fluorescence confirms that photocyclization remains the major path of energy degradation of the dissolved excited molecule $\mathbf{II}^A$ even at the lowest temperature studied.



$\mathbf{IV}^A$ $\mathbf{IV}^B$

On the other hand, the quantum yields are still far from unity and therefore, in the absence of fluorescence, additional deactivation paths of the excited metacyclophaneene molecules must exist. If we assume that photocyclization proceeds via the excited singlet state, as apparently it does in *cis*-stilbene [1b] [15], we remain with two possible deactivation paths: intersystem crossing to a non-reactive triplet state, which undergoes radiationless conversion to the ground state (no phosphorescence), or radiationless transition from the singlet excited state to the ground state. The present results do not allow a decision between the two possibilities. The absence of phosphorescence indicates that detection of a possible triplet with ESR., or flash methods [16] may be difficult, although these methods will eventually be tried out with the present systems. The same holds for the photochemical ring opening reaction $\mathbf{II}^{\mathbf{B}} \rightarrow \mathbf{II}^{\mathbf{A}}$.

The authors are indebted to Prof. *V. Boekelheide* for providing samples of the three compounds investigated, to Mrs. *T. Wismonski-Knittel* for advice and help in the NMR. and quantum yield investigation, and to Mrs. *Nelly Castel* for technical assistance. *R.N.* acknowledges a grant from the «*Stiftung für Stipendien auf dem Gebiet der Chemie*», Basel.

REFERENCES

[1] a) *D. Gegiou, K. A. Muszkat & E. Fischer*, Chem. Commun. 447 (1965); b) *K. A. Muszkat & E. Fischer*, J. chem. Soc. (B), 662 (1967); c) *A. Bromberg, K. A. Muszkat & E. Fischer*, Israel J. Chemistry *10*, 765 (1972).

[2] a) *W. M. Moore, D. D. Morgan & F. R. Stermitz*, J. Amer. chem. Soc. *85*, 829 (1963); b) *F. B. Mallory & C. W. Mallory*, J. Amer. chem. Soc. *94*, 6041 (1972), and previous papers listed therein; c) *E. V. Blackburn, C. E. Loader & C. J. Timmons*, J. chem. Soc. (C), 166 (1970).

[3] a) *C. E. Ramey*, Ph. D. thesis, University of Oregon, 1968; b) *C. E. Ramey & V. Boekelheide*, J. Amer. chem. Soc. *92*, 3681 (1970).

[4] *E. Fischer*, Mol. Photochemistry *2*, 99 (1970).

[5] *G. Zimmerman, L. Chow & U. Paik*, J. Amer. chem. Soc. *80*, 3528 (1958).

[6] *C. A. Parker*, Photoluminescence of Solutions. Elsevier, London 1968.

[7] a) *T. Knittel, G. Fischer & E. Fischer*, Chem. Commun. *84* (1972); b) *T. Knittel-Wismonsky, G. Fischer & E. Fischer*, Tetrahedron Letters 2853 (1972).

[8] *T. Wismonsky, G. Fischer & E. Fischer*, forthcoming publication (J. chem. Soc., Perk. II).

[9] *C. S. Marvel & B. O. Wilson*, J. org. Chemistry *23*, 1483 (1958).

[10] *E. Fischer*, J. phys. Chemistry *71*, 3704 (1967).

[11] *S. Malkin & E. Fischer*, J. phys. Chemistry *68*, 1153 (1964).

[12] a) *C. J. Brown*, J. chem. Soc. 3278 (1953); b) *A. W. Hanson & M. Röhr*, Acta crystallogr. *B28*, 2032 (1972).

[13] X-ray crystallographic data by *J. Bernstein*, to be published.

[14] a) *H. R. Blattman*, Ph. D. thesis, E.T.H., Zürich, 1967; b) *H. R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneaux & V. Boekelheide*, J. Amer. chem. Soc. *87*, 130 (1965).

[15] *G. S. Hammond et al.* (8 coauthors), J. Amer. chem. Soc. *86*, 3197 (1964).

[16] *E. Fischer*, Pure appl. Chemistry *24*, 531 (1970).