Tetrahedron Vol. 35, pp. 1537 to 1541
© Pergamon Press Ltd., 1979. Printed in Great Britain

0040-4020/79/0615-1537/$02.00/0

CHIRALITY AND CONFORMATIONAL CHANGES IN 4,5-DIARYLTRIPHENYLENES

A. H. A. TINNEMANS and W. H. LAARHOVEN*
Department of Organic Chemistry, Catholic University, Toernooiveld, 6525 ED Nijmegen, The Netherlands

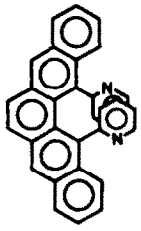
(*Received in UK 15 December 1978*)

Abstract—Line-shape analysis of temperature dependent NMR spectra of several substituted 4,5-diphenyltriphenylenes has been performed to determine the free energy of activation for rotation ($\Delta G^{\ddagger}_{rot}$) of the phenyl groups. The rotational barrier ($\Delta G^{\ddagger}_{rot}$) depends on the presence and position of substituents on the phenyl groups; it is the largest in compounds with *ortho*-substituents. The independent determined free energy of activation of racemization ($\Delta G^{\ddagger}_{rac}$) is about equal to $\Delta G^{\ddagger}_{rot}$ in 4-phenyl-5-(3,5-dimethylphenyl)triphenylene, but in 4,5-bis-(3,5-dimethylphenyl)triphenylene $\Delta G^{\ddagger}_{rac}$ is much larger than $\Delta G^{\ddagger}_{rot}$. It is concluded that the racemization does not occur via a process in which the phenyl groups remain parallel but via a molecular movement in which the phenyl groups turn around each other like cog wheels.

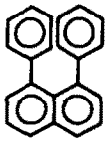
In a recent paper[1] concerning the chirality and conformational changes in 1-phenylbenzo[c]phenanthrene (1) we demonstrated that rotation of the phenyl group can occur independently of racemization. Analysis of the temperature-dependent NMR spectra of several derivatives revealed that rotation of the phenyl group can occur at one side of the benzo[c]phenanthrene moiety, for which process $\Delta G^{\ddagger}_{rot}$ is *ca.* 13.0 kcal/mol, or slightly larger when bulky substituents (I, Me, Ph) are present at C(2). During racemization the phenyl group turns around the opposite end of the benzo[c]phenanthrene skeleton in a rotatory movement. This is accompanied by a simultaneous inversion of the helical conformation. For this process $\Delta G^{\ddagger}_{rac}$ appeared to be *ca.* 16 kcal/mol.

Previously a similar study has been described[2] for N-methyl and N,N'-dimethylpyridinium derivatives, derived from 13,14-bis(2-pyridyl)pentaphene (2). The exchange processes in these compounds were ascribed to an unexpectedly facile pentaphene ring inversion, accompanied by a synchronous rotation of both pyridinium rings.

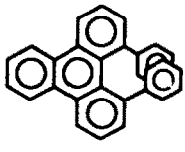
1



2



3



4

For the N-Me derivative a free energy of activation of 16.6 ± 0.1 kcal at 30° was reported. Although the conclusion about the nature of the process might be correct, it can not be derived from the experimental data, as the compounds do not contain diastereotopic protons which reflect the chirality. The data can also be interpreted by the occurrence of a rotation of the pyridine rings without racemization.

Finally, for derivatives of 1,8-diphenylnaphthalene (3) it has been shown[3] that rotational and inversional barriers are separated.

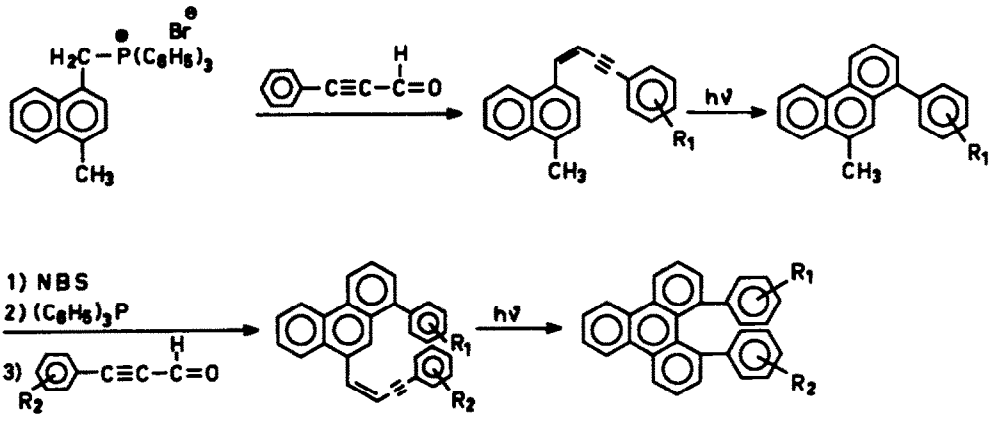
In this paper we report $\Delta G^{\ddagger}$-values for phenyl rotation and racemization in 4,5-diphenyl substituted triphenylenes (4) in which the position of the phenyl rings is comparable to the end rings in heptahelicene,[4] but is differing from them by the possibility of rotation. The compounds investigated (4–8) were obtained by application of the previously reported photocyclisation[5] of suitably substituted 1,4 - diaryl but - 1 - en - 3 - ynes (Scheme 1). Compound 8 is synthesized as reported previously.[5a] The Me substituents were introduced to simplify the analysis of the temperature dependence of the NMR spectra; in the unsubstituted compound 4 the AA'BB'C-pattern of the phenyl protons is too complex for this purpose.

The NMR spectrum of 8 in tetrachloroethylene (TCE) above 65° shows one sharp singlet for the Me groups at δ 2.04 ppm. The singlet at 6.13 ppm for the ortho-protons in the phenyl rings is broadened by meta coupling. At −27° both signals have been split up in two signals of equal intensity. The coalescence temperature (T_c) for the Me signals is +22°; for the ortho-protons +13°. Qualitatively similar results were obtained for the phenyl groups at C_5 with compound 5–7.

In Table 1 the chemical shifts are given for Me substituents and phenyl protons of compounds 4–8 at temperatures where the relevant signals of individual rotamers are sharp and well separated.

E_A and log k_o were calculated from the set of observed temperatures and their corresponding pre-exchange lifetimes τ (corr. coff. 0.995–0.998). $\Delta G^{\ddagger}$ was then obtained from the Eyring equation:

$$\Delta G^{\ddagger} = 4.57\,T(10.32 + \log \tau T) \qquad (1)$$



4 $R_1 = R_2 = H$
5 $R_1 = H$, $R_2 = 4$-methyl
6 $R_1 = H$, $R_2 = 2,4,6$-trimethyl
7 $R_1 = H$, $R_2 = 3,5$-dimethyl
8 $R_1 = R_2 = 3,5$-dimethyl

Table 1. Chemical shifts in ppm of methyl groups and phenyl protons in 4,5-diaryltriphenylenes 4–8 at the measuring temperature (T_m) indicated

Compounds	Solvent	(CH_3) in ppm	(H_{phenyl}) in ppm	T_m (in °K)
4	CS_2	-	6.41 6.32 (o)	203
5	CS_2	2.25	6.73 6.65 (o)	223
6	HCB[a]	1.44 0.76 (o)	6.57 6.50 (m)	308
7	CS_2	2.08 1.94 (m)	6.04 5.95 (o)	233
8	CS_2	2.08 1.94 (m)	6.06 5.99 (o)	240
	TCE[b]	2.12 1.96 (m)	6.16 6.06 (o)	251

[a] hexachlorobutadiene; [b] tetrachloroethylene

taking the transmission coefficient as unity because the occurrence of an intermediate is improbable. For the phenyl protons as well as the methyl groups $\Delta G^{\neq}$ was also calculated (method b) with the Eyring equation at coalescence temperature, T_c, using the approximate formulae

$$k_c = \tau_c^{-1} = (\nu_A - \nu_B)/\sqrt{2} \qquad (2)$$

in which the exchanging protons are not mutually coupled, and

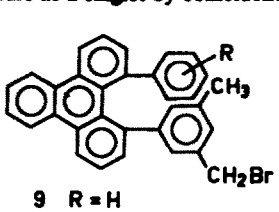
$$k_c = \tau_c^{-1} = \pi[(\nu_A - \nu_B)^2 + 6J^2AB]/\sqrt{2} \qquad (3)$$

for mutually coupled protons (H_{ortho} in 5, CH_2 in 9 and 10). The results are given in Table 2.

A a consequence of the small $\Delta\delta$-values the accuracy of $\Delta G^{\neq}_{rot}$-values is not very high (in most cases *ca.* 1 kJ/mol). However, $\Delta G^{\neq}$-values obtained by two methods (from Me-signals) agree very well within this accuracy. It is clear that the presence of *m*-methyl groups causes a slight increase of the rotational barrier (*cf.* 7 and 8 with 5), but *meta*-substitution in only one or both phenyl rings leads to equal $\Delta G^{\neq}$-values (see 7 and 8).

o-Me substitution (in 6) leads to a larger increase than *m*-substitution. Although NMR spectra of these compounds cannot be used to decide if rotation is accompanied by inversion or occurs at one side of the triphenylene moiety, the trend of the substituent effects on the energy barrier seems more in accordance with the latter possibility.

In order to determine $\Delta G^{\neq}$-values for racemisation in this type of compounds, the products 7 and 8 were converted into the mono-bromo derivatives 9 and 10 by treatment with an equivalent amount of N-bromosuccinimide (NBS). The NMR spectrum of 9 at low temperature shows two signals for the methylene group as well as for the Me group, both in a ratio 1:2. For the methylene group the larger signal is at higher field, for the Me group at lower field. The splitting points to a conformational equilibrium, the ratio to an energy difference of *ca.* 1.7 kJ/mol between the conformers. The pattern of the methylene protons is remarkably solvent-dependent (Table 3). In CS_2 and TCE only the higher field signal shows the expected AB pattern, the lower field signal appears as a singlet by coincidence. In $CDCl_3$



9 R = H
10 R = 3,5-dimethyl

Table 2. Thermodynamic and kinetic parameters for the rotation of the phenyl substituents in compounds 4-8

Compound	Solvent	Protons used	$\Delta\delta$ (ppm)	T_c (°K)	$\Delta G^{\ddagger}_{rot}$ (method a) in kJ/mol	(kcal/mol)	$\Delta G^{\ddagger}_{rot}$ (method b)(T_c) in kJ/mol	(kcal/mol)	log k_{rot} (k in s^{-1})	E_{act} in kJ/mol	(kcal/mol)
4	CS_2	H_{ortho}	0.095								
5	CS_2	H_{ortho}	0.076	264			56.1	(13.4)			
6	HCB	H_{meta}	0.063	351			79.1	(18.9)			
		CH_3	0.685	387	78.7	(18.8)	79.9	(19.1)	14.3	87.4	(20.9)
7	CS_2	H_{ortho}	0.105	276			60.2	(14.4)			
		CH_3	0.135	289	60.7	(14.5)	62.7	(15.0)	14.5	70.7	(16.9)
8	CS_2	H_{ortho}	0.078	272			59.8	(14.3)			
		CH_3	0.147	287	60.2	(14.4)	61.9	(14.8)	14.2	67.8	(16.2)
	TCE	H_{ortho}	0.097	286			62.7	(15.0)			
		CH_3	0.162	295	61.9	(14.8)	63.2	(15.1)	14.2	69.4	(16.6)

Table 3. Variation of the methylene signal of compounds 9 and 10 with increase of temperature

Compound	Solvent	Pattern of $-CH_2-$signals (T in °C)
9	CS_2	s + AB (-50°) → s + s → s (25°)
	$CDCl_3$	AB + s (-10°) → s + s → s (50°)
	TCE	s + AB (-15°) → s + s → s (70°)
	HCB	AB + AB (15°) → s + s → s (70°)
10	CS_2	AB + AB (-50°) → AB (25°)
	HCB	AB + AB (20°) → AB (70-140°)
	TCE	AB + AB (10°) → AB (60°)

the reverse is observed. In HCB both signals show an AB pattern. For the methylene as well as the Me signals coalescence is observed on increase of temperature. As T_c and $\Delta\delta$ do not differ much from the corresponding data for the compound 7 $\Delta G^{\ddagger}_{rac}$ will have about the same value (*ca.* 60 kJ/mol). Because of the unequal population of the conformers eqns (2) and (3) can not be used, for calculation of $\Delta G^{\ddagger}_{rac}$. Before the methylene signals coalesce, their AB patterns, as far as present, simplify to singlets (Table 3). In TCE $\Delta\delta$ (14 Hz, $J_{AB} = 9.5$ Hz) for the methylene group does not differ much from the distance between the individual signals of the diastereotopic protons ($\delta_A - \delta_B = 9.2$ Hz). Therefore, $\Delta G^{\ddagger}_{rot}$ and $\Delta G^{\ddagger}_{rac}$ will not differ much for this compound. Application of eqns (3) and (1) to the coalescence of individual AB patterns (caused by racemization) gives $\Delta G^{\ddagger}_{rac} = 64 \pm 2$ kJ/mol.

The NMR spectrum of the methylene group in **10** at low temperature consists of two AB patterns in CS_2 as well as in HCB, again in a ratio of 1:2. By increase of temperature the signals coalesce but the AB pattern remains. Apparently, rotation occurs without racemization; T_c and $\Delta\delta$ gave an indication, that $\Delta G^{\ddagger}_{rot}$ must be about equal as found for **8** (*ca.* 62 kJ/mol). From the coalescence of Me signals in TCE, converting from three signals at δ 2.06, 1.99 and 1.89 in a ratio 3:1:2 into two singlets at δ 2.03 and 1.96 in a ratio 2:1, an equal value for $\Delta G^{\ddagger}_{rot}$ (63.0 kJ/mol) was calculated. In the solvent HCB the AB pattern does not simplify below 140°, indicating that $\Delta G^{\ddagger}_{rac}$ must be larger than 88.2 kJ/mol.

When the mechanism proposed[2] for racemisation of compounds such as **2** were appropriate for our compounds, $\Delta G^{\ddagger}_{rac}$ for **9** and **10** should be expected to be rather equal; in that mechanism parallelism of the phenyl rings is grossly maintained during inversion, and it cannot be expected that absence or presence of *m*-Me groups in one of the rings will have influence on the energy barrier of the racemisation process. Therefore, it is more likely that racemisation, accompanied by simultaneous rotation of both phenyl groups occurs in a process, in which the phenyl rings turn around each other like cog-wheels. In the transition state, where the bonds between the phenyl groups and the triphenylene moiety are in plane with the latter, the phenyl groups are mutually orthogonal. In **9** the unsubstituted phenyl group can slip along the substituted ring via such a transition state much easier than the reverse. In **10** only passage of a substituted ring can lead to racemisation. The mechanistic picture is similar to that previously given for the racemisation of 1-methyl- and 1,16-dimethylhexahelicene.[6]

EXPERIMENTAL

M.ps were determined with a Leitz m.p. microscope and are uncorrected. Uv spectra were measured in MeOH using a Cary 15 spectrophotometer, and NMR spectra were recorded either on a Varian HA-100 or a Bruker WH90 spectrometer with CS_2, tetrachloroethylene (TCE) or hexachlorobutadiene (HCB) as the solvents and TMS as the internal reference.

Chromatographic separations were done by column chromatography on silica gel (Merck; 100–230 mesh).

Photolysis experiments were carried out in a Rayonet RPR-100 reactor fitted with 300 nm fluorescence lamps. Before the irradiation all samples were purged with argon for at least 15 min.

Computer simulations of the temp. dependent NMR spectra were done using the program NMR TW2 with a PDP-11/45 computer, Vector General Display, General Purpose Graphic System Software.

For the compounds **6**, **7** and **8** the Arrhenius activation parameter, E_A and $\log k_\infty$, as well as the transition state parameter $\Delta G^{\ddagger}$ were determined by simulation of the Me signals which are broadened by the exchange reaction (method a). The simulations require three independent parameters only, viz. $(T_{2A})^{-1}$, the line-width parameter in the absence of exchange, the lifetime τ of a particular configuration and the positions of the chemical shifts at conditions of very low rotation ($\tau \to \infty$). $(T_{2A})^{-1}$ was based on measured line-width values of the Me signals at the high-temp. limit in the experimental spectra (2.5 Hz). The lifetime τ at a given temp. was found by trial and error until shape and position of the singulets matched perfectly with the experimental data.

Propiolaldehydes. The synthesis of phenylpropiolaldehyde and 3,5-dimethylphenylpropiolaldehyde have been described.[5a]

2,4,6-Trimethylphenylpropiolaldehyde was synthesized using the general procedure as described for 3,5-dimethylphenylpropiolaldehyde. Treatment of 2,4,6-trimethylacetophenone (107.4 g, 0.66 mol) with PCl_5 (146 g, 0.70 mol) yielded 1 - chloro - 1 - (2,4,6 - trimethylphenyl)ethylene (67 g, 56%), b.p. 80–83° at 2.5 mmHg. This vinyl chloride was dehydrohalogenated with sodium amide in liquid ammonia [50 g Na, 0.5 g Fe(III) nitrate, *ca.* 500 ml of ammonia] yielding 2,4,6-trimethylphenylacetylene (40.9 g, 76%), b.p. 92.5–94.5° at 15 mmHg; NMR ($CDCl_3$): δ 2.24 (S, 3H, *p*-Me), 2.39 (s, 6H, *o*-Me) 3.41 (s, 1H, ≡CH), 6.82 (s, 2H, H_{mesit}). The acetylene was converted into the desired aldehyde via the corresponding diethyl acetal as described for phenylpropiolaldehyde. 2,4,6-Trimethylphenylpropiolaldehyde diethyl acetal was obtained in 57% yield, 39.5 g, b.p. 131° at 1 mmHg; NMR ($CDCl_3$): δ 1.27 (t, 6H, Me), 2.27 (s, 3H, *p*-Me), 2.40 (s, 6H, *o*-Me), 3.77 (m, 4H, CH_2), 5.57 (s, 1H, CH), 6.85 (s, 2H, H_{mesit}). Acid hydrolysis gave 2,4,6-trimethylphenylpropiolaldehyde in 69% yield, 18.8 g, b.p. 100–102° at 0.5 mmHg, m.p. 31°; NMR ($CDCl_3$): δ 2.31 (s, 3H, *p*-Me), 2.45 (s, 6H, *o*-Me), 6.91 (s, 2H, H_{mesit}), 9.49 (s, 1H, CHO).

4-Methylphenylpropiolaldehyde. Starting with 4-methylacetophenone the above procedure for the introduction of the propiolaldehyde group was used. The intermediate 1 - chloro - 1 - (*p* - tolyl)ethylene, obtained in 63% yield, b.p. 75–80° at 13 mmHg; NMR (CCl_4): δ2.23 (s, 3H, Me), 5.37 (br s, 1H, vinyl), 5.61 (br s, 1H, vinyl), 6.99 and 7.38 (AB, 4H, $J_{AB} \simeq 13.8$ Hz) was converted into 4-methylphenylacetylene in 75% yield, b.p. 71° at 20 mmHg; NMR (CCl_4): δ 2.30 (s, 3H, Me), 2.81 (s, 1H, ≡CH), 6.89 and 7.14 (AB, 4H, $J_{AB} \simeq 14$ Hz). 4-Methylphenylpropiolaldehyde diethyl acetal was obtained in 65% yield, b.p. 111° at 0.5 mmHg; (NMR (CCl_4): δ 1.23 (s, 6H, Me), 2.33 (s, 3H, *p*-Me), 3.63 (m, 4H, CH_2), 5.68 (s, 1H, CH), 7.02 and 7.26 (AB, 4H, $J_{AB} \simeq$ 13.5 Hz). Acid hydrolysis gave the desired 4-methylphenylpropiolaldehyde as an oil which was purified by steam destillation; NMR (CCl_4): δ 2.39 (s, 3H, Me), 7.17 and 7.45 (AB, 4H, $J_{AB} \simeq 14.1$ Hz), 9.33 (s, 1H, CHO).

4,5-Diaryltriphenylenes. The syntheses of 4,5-diphenyltriphenylene 4[5b] and 4,5 - *bis*(3,5 - *dimethylphenyl*)*triphenylene* 8[5a] have been described.

1 - (2,4,6 - *Trimethylphenyl*) - 4 - (1 - *phenyl* - 9 - *phenanthryl*)*but* - 1 - *en* - 3 - *yne*. To a soln of the triphenylphosphonium salt of 9 - bromomethyl - 1 - phenylphenanthrene[5a] (2.0 g, 3.3 mmol) and of 2,4,6 - trimethylphenylpropiolaldehyde (0.565 g, 3.3 mmol) in 50 ml of a mixture of MeOH/DMF (1:1) an excess of NaOMe was added. After stirring overnight the *trans*-isomer of the wanted product could be filtered from the soln. An analytically pure sample of the *trans*-isomer was obtained by column chromatography on silica using benzene/hexane (1:9) as eluent, followed by crystallization from abs EtOH. From the original mother liquor the solvent was evaporated and water was added. After extraction with benzene, washing of the organic layer with water, and drying over $MgSO_4$, a mixture of *cis*- and *trans*-isomers was obtained by column chromatography on silica. The pure *cis*-isomer was obtained by repeated column chromatography over silica, elution with benzene/hexane (1:19), and crystallization from MeOH. Over-all yield 1.24 g (89%).

The *cis*-isomer m.p. 125–127°; UV_{max} (CH_3OH): 333 (log ε 4.02), 292 (4.52), 280 (4.50), 259 (4.68), [253 nm (4.65)]; NMR (CS_2): δ 1.95 (s, 6H, *o*-Me), 2.22 (s, 3H, *p*-Me), 6.05 and 6.17

(part of an AB pattern, J_{AB} = 11.7 Hz), 6.71 (br s, 2 H, H_{meta}), 6.85–7.78 (m, 1 OH), 7.99 (m, 1 H, H_8), 8.22 (s, 1 H, H_{10}), 8.58 (m, 1 H, H_4), 8.66 (m, 1 H, H_5). Found: C, 92.92; H, 6.39. Calc. for $C_{32}H_{26}$: C, 93.80; H, 6.20%.

The *trans*-isomer m.p. 141–143°; UV_{max} (CH_3OH): 344.5 (log ε 4.48), 292 (4.52), 281.5–286 flat (4.50), 260 (4.53), 251–253 flat (4.51), [238 nm (4.52)]; NMR (CS_2): δ 2.21 (s, 3 H, *p*-CH_3), 2.35 (s, 6 H, *o*-CH_3), 6.24 and 7.55 (AB, ethylene, J_{AB} = 15.9 Hz), 6.72 (s, 2 H, H_{meso}), 7.28–7.71 (m, 4 H), 7.40 (s, 5 H, Ph), 7.88 (s, 1 H, H_{10}), 8.06 (m, 1 H, H_8), 8.51 (m, 1 H, H_4), 8.57 (m, 1 H, H_5). Found: C, 93.62; H, 6.36. Calc. for $C_{32}H_{26}$: C, 93.80; H, 6.20%.

1 - (3,5 - *Dimethylphenyl*) - 4 - (1 - *phenyl* - 9 - *phenanthryl*)*but* - 1 - *en* - 3 - *yne* **12**. The Wittig synthesis of this diarylbuteanyne was performed analogously starting with the triphenylphosphonium salt of 9 - bromomethyl - 1 - phenylphenanthrene (2.5 g, 4.1 mmol) and an equiv. amount of 3,5-dimethylphenylpropiolaldehyde (0.65 g). *trans*-isomer m.p. 126–128°; UV_{max} – MeOH): 341 (log ε 4.46), 289 (4.57), [281 (4.55)], 259.5 (4.53), [252 nm (4.49)]; NMR (CS_2): δ 2.23 (s, 6 H, 2 CH_3), 6.15 and 7.57 (AB, ethylene, J_{AB} = 15.8 Hz), 6.80 (br s, 1 H, H_{para}), 6.96 (br s, 2 H, H_{ortho}), 7.40 (s, 5 H, Ph), 7.3–7.6 (m, 4 H), 7.88 (s, 1 H, H_{10}), 8.01 (m, 1 H, H_8), 8.51 (m, 1 H, H_4), 8.56 (m, 1 H, H_5). Found: C, 93.85; H, 6.22. Calc. for $C_{32}H_{24}$: C, 94.08; H, 5.92%.

1 - (4 - *Methylphenyl*) - 4 - (1 - *phenyl* - 9 - *phenanthryl*)*but* - 1 - *en* - 3 - *yne* **13** was obtained in a similar way as the foregoing compounds from the triphenylphosphonium salt of 9 - bromomethyl - 1 - phenylphenanthrene (2.1 g, 3.45 mmol) and an equivalent amount of 4-methylphenylpropiolaldehyde (0.5 g). *trans*-isomer m.p. 132–134°; UV_{max} (CH_3OH): 341 (4.48), 289 (4.59), [282 (4.58)], 259.5 (4.56), [252 (4.52)], [237 nm (4.50)]; NMR (CS_2): δ 2.32 (s, 3 H, CH_3), 6.16 and 7.57 (AB, 2 H, ethylene, J_{AB} = 15.9 Hz), 7.03 and 7.23 (AA'BB', 4 H, J_{AB} = 8.7 Hz), 7.42 (s, 5 H, Ph), 7.88 (s, 1 H, H_{10}), 8.06 (m, 1 H, H_8), 8.54 (m, 1 H, H_4), 8.60 (m, 1 H, H_5). Found: C, 94.23; H, 5.76. Calc. for $C_{31}H_{22}$: C, 94.38; H, 5.62%.

4 - *Phenyl* - 5 - (4 - *methylphenyl*)*triphenylene* **5**. A soln of **13** in 320 mg (0.78 mmol) of **12** in 1 l. deaerated MeOH was irradiated in a Rayonet Reactor at 300 nm for 22 hr. After evaporation of the solvent the results of three consecutive runs were combined, and purified by column chromatography over silica using hexane as eluent. The white material (208 mg, 65%) was crystallized from EtOH giving **7** as white needles, m.p. 205–207°; UV_{max} (CH_3OH): 289 (log ε 4.57), 268 (4.76), 260.5 nm (4.69); NMR (CS_2): δ 8.53–8.22 (m, 4 H), 7.62–7.29 (m, 4 H), 7.05–6.68 (m, 5 H), 6.60–6.30 (m, 3 H), 5.94 (m, 2 H), 2.0 (s, 2 CH_3). Found: C, 93.81; H, 6.17. Calc. for $C_{32}H_{24}$: C, 94.08; H, 5.92%.

4 - *Phenyl* - 5 - (4 - *methylphenyl*)*triphenylene* **5**. A soln of **13** in MeOH was irradiated and worked-up under similar conditions as used in the preparation of **7**: yield 52%; m.p. 102–104° (EtOH); UV_{max} (MeOH): 289 (log ε 4.58), 269 (4.74), 258.5 nm (4.68); NMR (CS_2): δ 8.33–8.20 (m, 4 H), 7.86–7.24 (m, 4 H), 7.0–6.77 (m, 7 H), 6.44–6.15 (m, 4 H), 2.22 (s, Me). Found: C, 94.04; H, 5.86. Calc. for $C_{31}H_{22}$: C, 94.38; H, 5.62%.

4 - *Phenyl* - 5 - (2,4,6 - *trimethylphenyl*)*triphenylene* **6**. A soln of 370 mg of **11** in 1.25 l. deaerated MeOH was irradiated in a Rayonet Reactor at 300 nm for 40 hr. The solvent was evaporated from the dark yellow soln and the residue was purified by column chromatography over silica using hexane as eluent. The mixture eluted, containing mainly *cis*-**11** and **6** in a *ca.* 4:1 ratio, was dissolved in EtOH, from which soln **6** crystallized. Recrystallization from MeOH gave pure **6**, m.p. 213–219°; UV_{max} (CH_3OH): [283 (log ε 4.58)], 269 (4.75), [262 nm (4.70)]; NMR (CS_2): δ 8.50–8.2 (m, 4 H), 7.58–7.33 (m, 4 H), 7.11–6.88 (m, 5 H), 6.57–6.29 (m, 4 H), 2.17 (s, Me), 1.33 (s, Me), 0.67 (s, Me). Found: C, 93.51; H. 6.48. Calc. for $C_{33}H_{28}$: C, 93.80; H, 6.20%.

The monobromination of **7** and **8** with N-bromosuccinimide was conducted in the usual way in CCl_4 as a solvent. After filtration of the succinimide the products **9** and **10** were purified by careful elution from a short silicagel column.

REFERENCES

[1] W. H. Laarhoven, W. H. M. Peters and A. H. A. Tinnemans, *Tetrahedron* **34**, 769 (1978).

[2] D. L. Fields, T. H. Regan and R. E. Graves, *J. Org. Chem.* **36**, 2995 (1971).

[3] R. L. Clough and J. D. Roberts, *J. Am. Chem. Soc.* **98**, 1018 (1976).

[4] R. H. Martin, *Angew. Chem.* (Int. Ed.) **13**, 649 (1974).

[5a] A. H. A. Tinnemans and W. H. Laarhoven, *J. Chem. Soc.* Perkin II, 1104, 1114 (1976); [b] A. H. A. Tinnemans and W. H. Laarhoven, *J. Am. Chem. Soc.* **96**, 4617 (1974).

[6] J. H. Borkent and W. H. Laarhoven, *Tetrahedron* **34**, 2565 (1978).