Controlling the regioselectivity of the di-π-methane rearrangements of 1,2naphtho-annelated barrelene derivatives — Solution versus solid-state photochemistry

Jia Luo, Heiko Ihmels, Hans-Jörg Deiseroth, and Marc Schlosser

Abstract: The synthesis of 1,2-naphtho-annelated barrelene derivatives, namely dimethyl-7,12-dihydro-7,12-ethenobenzo[*a*]anthracene-13,14-dicarboxylate (**4a**) and dimethyl-7,14-dihydro-7,14-ethenodibenzo[*a*,*j*]-anthracene-15,16-dicarboxylate (**4b**), and the investigation of their photoreactivity in solution and in the solid state is reported. The irradiation of **4a** and **4b** resulted in regioselective di- π -methane rearrangements to give semibullvalene products; however, the product distribution is inverted upon changing the reaction medium from solution to the solid state. In solution, an α -naphtho–vinyl bridging predominates as the initial photochemical step because of the selective stabilization of the corresponding transition state, as discussed on the basis of the structures of the related biradical intermediates, whereas the solid-state photoreaction is significantly influenced by the steric constraints within the crystal lattice that only allow a β -naphtho–vinyl bridging.

Key words: di-π-methane rearrangement, barrelene derivatives, solid-state photochemistry.

Résumé : On a réalisé la synthèse de dérivés condensés 1,2-naphtobarrèlènes, à savoir le 7,12-dihydro-7,12-éthénobenzo[*a*]anthracène-13,14-dicarboxylate de diméthyle (**4a**) et le 7,14-dihydro-7,14-éthénobenzo[*a*,*j*]anthracène-15,16-dicarboxylate de diméthyle (**4b**), et on a étudié leur photoréactivité en solution et à l'état solide. L'irradiation des composés **4a** et **4b** conduit à des réarrangements di- π -méthane régiosélectifs et à la formation de produits semibullvalènes; toutefois, la distribution des produits est inversée lorsque le milieu réactionnel passe de la solution à l'état solide. En solution, un pont α -naphtovinyle prédomine comme étape photochimique initiale en raison de la stabilisation sélective de l'état de transition correspondant, tel que discuté sur la base des structures des intermédiaires biradicalaires apparentés, alors que la photoréaction à l'état solide est fortement influencée par des contraintes stériques dans le réseau cristallin qui ne permettent que la formation d'un pont β -naphtovinyle.

Mots-clés : réarrangement di-m-méthane, dérivés du barrèlène, photochimie à l'état solide.

[Traduit par la Rédaction]

Introduction

The di- π -methane rearrangement¹ of benzo-annelated derivatives of barrelene (bicyclo[2.2.2]octatriene)² and norbornadiene (bicyclo[2.2.1]heptadiene)³ has been shown to be an appropriate model reaction for the assessment of the substituent effects on the selectivity of organic photoreactions. In particular, the structural features that govern the typeselectivity, the regioselectivity, and the stereoselectivity of dibenzobarrelene photoreactions in solution^{1c–1f} and in constrained media have been evaluated in detail.⁴ Thus, in a pivotal paper,^{2a} Zimmerman et al. have shown that the irradiation of dibenzobarrelene **1a** leads to the selective for-

Received 18 December 2008. Accepted 29 January 2008. Published on the NRC Research Press Web site at canjchem.nrc.ca on 8 April 2009.

J. Luo and H. Ihmels.¹ University of Siegen, Organic Chemistry II, Adolf-Reichwein-Str. 2, 57068 Siegen, Germany. H.-J. Deiseroth and M. Schlosser. University of Siegen, Inorganic Chemistry I, Adolf-Reichwein-Str. 2, 57068 Siegen, Germany.

¹Corresponding author (e-mail: ihmels@chemie.uni-siegen.de).

mation of the dibenzosemibullvalene 2a (Scheme 1), and this remarkable regioselectivity has been rationalized in terms of the selective stabilization of one of the four possible biradicals by the electron-accepting substituent on the benzene ring. In addition, it has been shown that the nature and the position of the substituents at the benzene rings of dibenzobarrelene derivatives 1b-1f have a strong influence on the regioselectivity of the di- π -methane rearrangement (Scheme 1).^{2b,2c} Notably, both donor and acceptor substituents were shown to influence the regioselectivity of the photorearrangement of dibenzobarrelenes. At the same time, there are only a few studies with a focus on the influence of an annelated naphthalene unit on the regioselectivity of the di- π -methane rearrangement of barrelene derivatives.⁵ In particular, the competition between vinylnaphtho and vinyl-vinyl bridging in the initial step of the di-n-methane rearrangement of naphthobarrelenes was examined, and the following order of reactivity was deduced: α -naphtho-vinyl > vinyl-vinyl > β -naphtho-vinyl > benzovinyl. Nevertheless, no studies have been reported on the direct competition between photoinduced benzo-vinyl and α-naphtho-vinyl bridging in annelated barrelene derivatives. To fill this gap, we synthesized the naphtho-annelated **Scheme 1.** Substituent effects on the di- π -methane rearrangement of dibenzobarrelene derivatives.



Scheme 2. Synthesis of 1,2-naphthobarrelene derivatives 4a-4c.



barrelene derivatives **4a** and **4b** and investigated their photochemical behavior. Herein, we show that the photoinduced di- π -methane rearrangements of these compounds proceed with high regioselectivity in solution and in the solid state, notably with inverse selectivities.

Results

Synthesis

The benzonaphthobarrelene 4a was obtained in 68% yield by a Diels-Alder reaction of dimethyl acetylenedicarboxylate (DMAD) with benzo[a]anthracene (3a) (Scheme 2).⁶ For the analogous synthesis of dinaphthobarrelene derivatives 4b and 4c, a mixture of the two isomeric dibenzoanthracene derivatives 3b and 3c was employed. The latter were obtained from the reaction of 1-bromonaphthalene with N-lithio-2,2,6,6-tetramethylpiperidine in THF in a ratio of 72:28, as determined by ¹H NMR spectroscopic analysis.⁷ Since the dibenzoanthracene derivatives are air and light sensitive, the product mixture was immediately made to react with DMAD to give the dinaphthobarrelenes 4b and 4c in 30% overall yield in a ratio of 71:29 (Scheme 2). Attempts to separate the two isomers 4b and 4c by column chromatography failed; however, the dinaphthobarrelene 4b was isolated by crystallization in 6% yield. At the same time, we observed a strong tendency of the two isomers 4b and 4c to co-crystallize in a 1:1 ratio.

It should be noted that all chiral products are formed without enantioselectivity. Thus, all presented chiral compounds are actually racemic mixtures.

Photoreactions

In acetone solution, the naphthobenzobarrelene **4a** (longwavelength absorption: $\lambda_{abs,max} = 292$ nm) underwent an essentially clean di- π -methane rearrangement upon irradiation ($\lambda_{ex} > 254$ nm) to give the two semibullvalene derivatives **5a**^I and **5a**^{II} in a 87:13 ratio, as determined by ¹H NMR spectroscopic analysis (Scheme 3). Although it was impossible to separate the two semibullvalenes **5a**^I and **5a**^{II} by Scheme 3. Photoreaction of benzonaphthobarrelene 4a.



column chromatography, the major photoproduct **5a**^I was isolated in 61% yield by crystallization directly from the reaction mixture. The preferential formation of the photoproduct **5a**^I in solution was also observed in MeCN and benzene solution, however, with slightly lower selectivity (Table 1). Thus, as commonly observed for free-radical reactions, there is no pronounced solvent effect on the selectivity.⁸ Moreover in all employed solvents, the product distribution did not change with varying irradiation wavelength, i.e., from $\lambda > 254$ nm (quartz glass) to $\lambda > 310$ nm (Pyrex glass). Nevertheless in MeCN and benzene, the reactions were significantly slower when the light was filtered through Pyrex glass, most likely because the Pyrex glass cuts off a significant area of the chromophore absorption.

The irradiation of crystalline samples of benzonaphthobarrelene 4a resulted in the formation of the same two semibullvalenes $5a^{I}$ and $5a^{II}$, but the selectivity was reversed compared with the photoreaction in solution, i.e., the semibullvalene 5a^{II} was formed predominantly upon solid-state photolysis (Table 1). The direct irradiation of crystals of barrelene 4a, obtained by crystallization from methanol, gave the photoproducts $5a^{I}$ and $5a^{II}$ in 22:78 ratio at 10% conversion. The conversion was improved to 41% with only a slight decrease of selectivity (25:75) by the irradiation of ground crystals, which were placed between quartz slides, i.e., by increasing the surface area exposed to the UV light. Prolonged irradiation times did not increase the conversion further, probably because of an inner-filter effect that protects the inside of the solid sample towards the light. On the other hand, the selectivity was improved to 16:84 by using ground single crystals of 4a.

The low conversion and small scale of the solid-state photoreactions often limits their potential application in synthetic organic chemistry;⁷ however, this drawback may be overcome by the performance of the photoreaction with a suspension of the finely ground substrate in a solvent in which it is insoluble.9 To test this approach, thoroughly stirred suspensions of the benzonaphthobarrelene 4a in hexane or water were irradiated. Thus, on the scale of 60.0 mg (0.16 mmol) of compound 4a, the photoreaction in hexane resulted in 90% conversion with a ratio of 33:67 between the semibullvalenes $5a^{I}$ and $5a^{II}$. In water suspension, the irradiation proceeded with lower conversion of 67%, but the selectivity was much better ($5a^{I}:5a^{II} = 14:86$). From each reaction mixture, the semibullvalene 5aII was isolated in yields as high as 37% as colorless cubes, by crystallization of the photolysate.

The product structures were identified on the basis of ¹H and ¹³C NMR spectroscopy and elemental analysis. The annelated semibullvalene structure in compounds $5a^{I}$ and $5a^{II}$ was indicated by the characteristic shifts of the cyclopropane methine protons ($5a^{I}$: δ 5.21 ppm; $5a^{II}$: δ 5.59 ppm) and the proton in the benzylic position (δ 4.64 ppm for both $5a^{I}$ and $5a^{II}$). In particular, the unambiguous structure assignment of

Medium	mb ^{<i>a,b</i>} (%)	Convn ^{<i>a,c</i>} (%)	Ratio 5a ^I /5a ^{II} a,d
Acetone solution	>97	>97	87:13
Acetonitrile solution	>97	>97	80:20
Benzene solution	89	>97 ^e	71:29
Bulk crystals ^f	97	10	22:78
Ground crystals ^{f,g}	95	41	25:75
Single crystal ^f	95	32	16:84
Hexane suspension	92	90	33:67
Water suspension	94	65 ^h	14:86

Table 1. Medium-dependent regioselectivity of the di- π -methane rearrangements of benzonaphthobarrelene **4a**.

^{*a*}Determined by ¹H NMR spectroscopic analysis directly on the crude product mixture relative to *m*-dimethyl isophthalate as internal standard; error limits: $\pm 3\%$ of the given value.

^bMass balance.

^cConversion.

^{*d*}If not stated otherwise, $5a^{I}$ and $5a^{II}$ were the only detectable products.

^eApprox. 10% of unidentified byproducts were formed.

^fCrystallized from methanol solution.

^gGround crystals crushed between quartz slides.

^hApprox. 3% of unidentified byproducts were formed.

Fig. 1. Structural assignment of the benzonaphthosemibullvalene derivatives $5a^{I}$ and $5a^{II}$ by NOE (arrows indicate NOEs between the corresponding protons).



the two isomers $5a^{I}$ and $5a^{II}$ was made by NOESY NMR experiments (Fig. 1). In both cases, the substitution pattern of the cyclopropane ring, i.e., the position of the ester groups, was indicated by the NOE between the methine proton of the cyclopropane and the *ortho*-proton of the annelated benzene part (arrow a and a'). The assignment of the benzene protons was confirmed by additional NOE data, in particular by the NOE between the benzylic proton and the benzene and naphthalene protons (arrows c,d and b'-d'). Moreover, the orientation of the naphthalene unit in compounds $5a^{I}$ and $5a^{II}$ was determined by the NOE between the protons of the methyl substituent and the aromatic proton (8'-H) of the naphthalene part in isomer $5a^{I}$ (arrow b).

The photoreactivity of dinaphthobarrelene **4b** resembles the one of barrelene derivative **4a** (Scheme 4). In acetone solution, the irradiation of **4b** led to a mixture of semibullvalenes **5b^I** and **5b^{II}** in a ratio of 87:13, whereas the regioselectivity is reversed to 18:82 upon irradiation in the solid state. The product **5b^I** was obtained by crystallization in 55% yield and fully characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. Additional NOESY NMR experiments confirmed the structure of the semibullvalene derivative **5b^I** by characteristic NOE signals between an 8'-H proton of naphthalene and the cyclopropane methine proton, as well as between the benzyl proton and the 8'-H proton of naphthalene (Scheme 4). The isomer **5b^{II}** could not be isolated, but its structure was identified by NMR spectroscopic analysis directly from the product mixture. Scheme 4. Photoinduced di- π -methane rearrangement of dinaphthbarrelene 4b (arrows indicate NOEs between the corresponding protons).



Scheme 5. Reaction mechanism of the di- π -methane rearrangement of dibenzobarrlene (1g).



Discussion

The photoinduced di- π -methane rearrangement of annelated barrelenes, e.g., the parent dibenzobarrelene 2g, is initiated by a carbon-carbon bond formation between the etheno unit and an *ipso* carbon of the annelated aromatic ring to form a 1,4-biradical intermediate **BR1-g** (Scheme 5), followed by rearomatization to afford the biradical **BR2-g**, and subsequent radical recombination to the semibullvalene 2g.^{1a,1d} Depending on the substitution pattern of the substrate, up to four different regioisomeric products may be formed, and it was demonstrated that the selectivity of the initial reaction step determines the selectivity of the overall reaction (Scheme 1).^{1c} It should be noted, however, that the selectivity of a chemical reaction, in particular the di- π methane rearrangement, is mainly governed by the different reaction rates, i.e., by the energies of the different transition states rather than the ones of the corresponding reaction intermediates. Nevertheless, it is assumed that factors that stabilize one particular 1,4-biradical intermediate also stabilize the preceding transition state and thus lead to the preferen-



Scheme 6. Reaction pathways of the di- π -methane rearrangement of barrelene derivative 4a.

Scheme 7. Resonance stabilization in biradicals **BR4-a^I** and **BR4-b^I**.



tial formation of the corresponding semibullvalene isomer. According to these considerations, the regioselectivity observed in the photoreactions of the barrelene derivatives 4a and 4b may be discussed in terms of the relative stability of the possible biradical intermediates. Thus, during the di- π methane rearrangemenent of the barrelene derivative 4a, the four regioisomeric biradicals BR4-aI-BR4-aIV may be formed initially, which lead to the four isomeric benzonaphthose mibull valenes $5a^{I}-5a^{IV}$ (Scheme 6). Nevertheless, the products 5a^{III} and 5a^{IV} are not formed in detectable amounts, indicating that the intermediates BR4-aIII and BR4-a^{IV} are only generated to negligible extents. We propose that the high preference for the photoinduced vinylnaphtho bridging is governed by the significantly higher stabilization of the intermediate radicals in the naphthalene unit, compared with the stabilization in the cyclohexadienyl radical part in BR4-a^{III} and BR4-a^{IV}. Moreover, the biradicals BR4-a^I and BR4-a^{II} still contain two intact benzene rings, whose resonance energy contributes more to the overall stabilization than the one of the single naphthalene ring in BR4-a^{III} and BR4-a^{IV}.¹⁰

It was demonstrated that the di- π -methane rearrangemenent of the unsubstituted 1,2-naphthobarrelene is introduced by a highly selective vinyl–naphtho bridging that takes place *exclusively* between a vinyl carbon atom and the C1 position (α position) of the naphthalene.³ These observations have been explained by a higher extent of delocalization within the aromatic part of the corresponding 1,4-biradical. The same argument may be employed to rationalize the enhanced formation of the products $5a^{I}$ and $5b^{I}$ resulting from initial bridging to the C1 carbon upon irradiation of annelated barrelene derivatives 4a and 4b. In contrast to the intermediate **BR4-a^{II}**, the biradicals **BR4-a^I** and **BR4-b^I** exhibit two resonance structures with a complete benzene ring providing additional aromatic stabilization. Moreover, one of the resonance forms, indicated as **BR4'**, reveals a particular stabilization as the radical is located both in allylic and benzylic position (Scheme 7).

Notably, the solid-state photoreaction of the annelated barrelene derivatives 4a and 4b yields the semibullvalene derivative 5a^{II} and 5b^{II} as the main products. Apparently, the stereoelectronic factors that determine the regioselectivity of the di- π -methane rearrangement of **4a** and **4b** in solution are no longer effective in the solid state. Since it has been demonstrated that solid-state photoreactions often proceed on a reaction pathway that avoids steric interactions with neighboring molecules,11 it may be assumed that interor intra-molecular steric factors determine the solid-state reactivity of 4a and 4b rather than electronic effects. To investigate this aspect, an X-ray diffraction analysis was performed with single crystals of compound 4a. The benzonaphthobarrelene 4a crystallizes in the monoclinic space group of $P2_1/c$ (a = 11.3159 Å, b = 11.8742 Å, c = 14.586 Å; $\beta = 104.55^{\circ}$), with each unit cell containing two pairs of enantiomers of the barrelene molecules. Most notably, significant close contacts between two molecules were detected. The two different views of the molecular arrangement in the solid state given in Fig. 2 reveal that the benzene unit of one molecule (black in Fig. 2) is partially positioned between the vinyl unit and the naphthalene part of a neighboring molecule (Fig. 2, white, red, blue, respectively). In this arrangement, the closest contacts between the two molecules were identified between one carbonyl carbon atom of an ester group (Fig. 2, red) and an ortho-hydrogen atom of the benzene ring (Fig. 2a, C…H: 289 pm), and between the carbonyl oxygen atom of the same ester functionality and the bridgehead hydrogen atom (Fig. 2a, O...H: 262 pm). These distances correspond essentially to the sum of the van der Waals radii of the respective atoms (C.-.H: 290 pm, O…H: 272 pm)¹² and may thus result in significant intermolecular steric repulsion during the solid-state rearrangement of compound 4a. In particular, the movement of one of the ester functionalities, namely the one at the C16 position (Fig. 2, red), in the course of a di- π -methane rearrangement appears to be significantly hindered. To achieve the vinyl-naphtho bridging to give **BR4-a**^I, this ester group needs to pass the proximate benzene unit of the neighboring molecule, and the close contacts described above clearly indicate that this pathway is essentially blocked. At the same time, the other ester group (Fig. 2, blue) is free to move as there are no significant contacts with the proximate molecule (>350 pm; not shown), so that an almost unhindered vinyl-naphtho bridging is possible in the solid state to afford biradical **BR4-a^{II}**. Notably, both vinyl-benzo bridging pathways leading to the semibullvalene products 5a^{III} and 5a^{IV} are not sterically hindered in the crystal. Thus, in the absence of steric constraints in the crystal, the solid-state photoreaction is determined by the same electronic factors as in isotropic solution.

Fig. 2. Structure of the benzonaphthobarrelene 4a in the solid state (dashed lines indicate closest contacts between two neighboring molecules).



Table 2. Crystallographic data and details of the structure determination for 4a.

Parameter	Value	
Molecular formula	C ₂₄ H ₁₈ O ₄	
Formula mass	M = 370.38 g/mol	
Colour	Colourless	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ /c (No. 14)	
Unit cell dimensions	$a = 11.3159(9)$ Å, $b = 11.8742(7)$ Å, $c = 14.586(1)$ Å, $\beta = 104.55(1)^{\circ}$	
Volume	$V = 1897.0(3) \text{ Å}^3$	
Formula units/unit cell	Z = 4	
Calculated density	$\rho = 1.297 \text{ g/cm}^3$	
Diffractometer	IPDS (STOE)	
Wave length	$\lambda = 0.710~73$ (Mo-K α)	
Monochromator	Graphite	
Crystal size	$0.29 \text{ mm} \times 0.28 \text{ mm} \times 0.17 \text{ mm}$	
Measuring temperature	T = 296(2) K	
Scan type	φ - scan	
Measured θ -range	$2.24^\circ \le \theta \le 28.14^\circ$	
Index ranges	$-15 \le h \le 14, -15 \le k \le 15, -19 \le l \le 19$	
Reflections collected	20 010	
Independent reflections	4 614	
Observed reflections	21 51 [<i>I</i> >2σ(<i>I</i>)]	
Data averaging ^a	$R_{\rm int} = 0.0664, R_{\sigma} = 0.0739$	
Completeness to θ_{max}	99.5%	
Absorption coefficient	$\mu = 0.088 \text{ mm}^{-1}$	
Extinction coefficient	$\varepsilon = 0.0079(9)$	
Structure solution	Direct methods (ref. 12)	
Structure refinement	Full-matrix least-squares on F^2 (ref. 12)	
Number of parameters	256	
Number of restraints	0	
GooF on F^2	0.794	
<i>F</i> (000)	776	
Weighting scheme ^b	A = 0.0458, B = 0	
Fig. of merit ^{<i>a</i>} $[I > 2\sigma(I)]$	$R_1 = 0.0396, wR_2 = 0.0791$	
Fig. of Merit ^a [all data]	$R_1 = 0.1071, wR_2 = 0.0936$	
Residual electron density	$-0.143 \le \rho \le 0.194 \text{ e/Å}^3$	

^{*a*}Definition of *R* factors see ref.13

 ${}^{b}w = 1/[\sigma^{2}(F_{0}^{2}) + (AP)^{2} + BP)], P = (F_{0}^{2} + 2F_{c}^{2})/3$

Summary and conclusion

In summary, we have shown that the di- π -methane rearrangement of 1,2-naphtho annelated barrelene derivatives 4a and **4b** proceeds with high regioselectivity. Most notably, a drastic change of the selectivity was observed upon changing from isotropic solution to the solid state. Whereas in solution, the course of the reaction is mainly governed by the selective stabilization of the corresponding transition states, which lead to the primary biradical intermediates **BR4**, the solid-state photoreaction is significantly influenced by the steric constraints within the crystal lattice. To be stressed is the fact that in the case of 4a, the major products from both reactions, i.e., in solution and in the solid state, could be isolated in reasonable yields. Considering the importance of the annelated semibullvalene derivatives as synthons in organic synthesis,^{1f} the presented systems may be employed along these lines as a useful source for the selective synthesis of complex 1,2-naphtho-annelated polycyclic aromatic compounds.1f

Experimental section

General

NMR spectra: Bruker Avance 400 (¹H NMR: 400 MHz; ¹³C NMR: 100 MHz) and a Varian NMR System 600 (¹H NMR: 600 MHz; ¹³C NMR: 150 MHz). ¹H NMR chemical shifts refer to δ_{TMS} 0.0 ppm. ¹³C NMR chemical shifts refer to solvent signals (CDCl₃: δ 77.0 ppm). Melting points: Büchi 510K apparatus (uncorrected). Mass spectra: Hewlett-Packard HP 5968 (EI, 70 eV). Elemental analyses: KEKAtech EuroEA combustion analyzer by Mr. H. Bodenstedt, Organic Chemistry I, University of Siegen. Benzo[*a*]anthracene⁵ and benzotetracenes⁶ were prepared according to literature procedures. All the other reagents and solvents were obtained from Acros Organics and Sigma-Aldrich and used as received.

Dimethyl-7,12-dihydro-7,12-ethenobenzo[a]anthracene-13,14-dicarboxylate (4a)

Under nitrogen-gas atmosphere, a suspension of benzo[a]anthracene (5.89 g, 25.8 mmol), DMAD (9.18 mL, 75.0 mmol), and AlCl₃ (0.2 g) in xylene (15 mL) was heated at 140 °C for 5 days. The mixture was cooled to room temperature (RT) and diluted with ethyl acetate (100 mL). The organic phase was extracted with 2N aq. HCl (50 mL) and brine (50 mL), and subsequently separated, dried with Na₂SO₄. The solvent was removed in vacuo and the residue was purified by column chromatography (SiO₂; EtOAc/hexane = 1:2, v/v; $R_f = 0.45$) to give an orange oil, which was solidified upon treatment with methanol to give dimethyl-7,12-dihydro-7,12-ethenobenzo[a]anthracene-13,14-dicarboxylate (4a) as ¹H NMR spectroscopically pure light yellow granules (6.47 g, 17.5 mmol, 68%). An analytical sample was prepared by recrystallization from methanol as clusters of colorless prisms, mp 142–144 °C. UV (CHCl₃): λ_{max} (log ε) = 245 (4.40), 270 (3.85), 281 (3.90), 292 (3.92), 329 (3.27). ¹H NMR (400 MHz, CDCl₃) δ: 3.79 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃), 5.64 (s, 1H, CH), 6.32 (s, 1H, CH), 6.98– 7.01 (m, 2H, ar-CH), 7.39-7.47 (m, 3H, ar-CH), 7.53-7.61 (m, 3H, ar-CH), 7.81 (d, J = 8 Hz, ar-CH), 8.27 (d, J = 8 Hz, ar-CH). ¹³C NMR (100 MHz, CDCl₃) & 48.2 (CH₃), 52.4 (overlapped CH₃ and CH), 53.6 (CH), 122.0 (ar-CH), 122.5 (6,11-CH), 123.7 (ar-CH), 123.8 (ar-CH), 125.1 (ar-CH), 125.2 (two ar-CH overlapped), 125.6 (ar-CH), 126.4 (ar-CH), 128.7 (ar-CH), 129.0 (C_q), 131.7 (C_q), 141.2 (C_q), 142.6 (C_q), 144.0 (C_q), 144.8 (C_q), 146.8 (C_q), 149.0 (C_q), 165.8 (C=O), 166.2 (C=O). EI-MS (70 eV): 370 [M⁺]. Elemental analysis calcd. (%) for C₂₄H₁₈O₄ (370.40): C 77.82, H 4.90; found C 77.62, H 4.86.

Dimethyl-7,14-dihydro-7,14-ethenodibenzo[a,j]-anthracene-15,16-dicarboxylate (4b)

Under argon protection, a mixture of dibenzo[a,h]- and dibenzo[a,j]anthracene (28:72, 690 mg, 2.48 mmol), DMAD (0.50 mL, 4.1 mmol), and AlCl₃ (20 mg) in xylene (15 mL) was heated at 140 °C for 5 days. After cooling RT, the mixture was diluted with EtOAc (70 mL). The organic phase was extracted with 2N aq. HCl (20 mL) and brine (50 mL), and subsequently separated, dried with Na₂SO₄. The solvent was removed in vacuo and the residue was purified by column chromatography (SiO₂; EtOAc/hexane = 1:4, v/v; R_f = 0.31) to give a mixture of the two dinaphthobarrelenes 4b and 4c (4b/4c 71:29, 312 mg, 0.74 mmol, 30%). Two-fold recrystallization from EtOAc/hexane gave pure 4b as colorless needles (42 mg, 6%), mp 223-225 °C. ¹H NMR (400 MHz, CDCl₃) δ: 3.79 (s, 3H, CH₃), 3.82 (s, 3H, CH₃), 5.80 (s, 1H, CH), 7.23 (s, 1H, CH), 7.39 (d, J = 8 Hz, 2H, ar-CH), 7.55–7.59 (m, 4H, ar-CH), 7.65 (d, J = 8 Hz, 2H, ar-CH), 7.80 (d, J = 8 Hz, 2H, ar-CH). ¹³C NMR (100 MHz, CDCl₃) δ: 44.0 (CH), 52.5 (CH₃), 52.5 (CH₃), 54.8 (CH), 122.1 (ar-CH), 122.5 (ar-CH), 125.2 (ar-CH), 125.3 (ar-CH), 126.6 (ar-CH), 128.8 (ar-CH), 129.2 (C_a), 131.6 (C_q), 141.7 (C_q), 144.1 (C_q), 146.8 (C_q), 151.0 ($\dot{C_q}$), 165.7 (C=O), 166.4 (C=O). MS (m/z): 420 [M⁺]. Elemental analysis calcd. (%) for C₂₈H₂₀O₄ (420.46): C 79.98, H 4.79; found C 79.60, H 4.67.

Photoreactions

Irradiations were performed with a TQ150 middle-pressure mercury lamp (Heraeus, UV-Consulting Peschl), which was placed in a quartz cooling tube. The sample container was placed 10–15 cm in front of the lamp. The solution contained one molar equivalent of *m*-dimethyl isophthalate as internal standard for the quantitative ¹H NMR spectroscopic analysis of the photolysate.

Photolysis in solution

Solutions (10^{-3} to 10^{-2} mol/L) were placed in a 200 mL Pyrex tube (acetone) or a 50 mL quartz tube (other solvents) and purged with argon for at least 20 min. The stirred solution was irradiated for 6–13 h until the starting material was fully consumed as determined by ¹H NMR analysis. After evaporation of the solvent in vacuo, the photolysate was analyzed by ¹H NMR spectroscopy, or, in preparative experiments, recrystallized from EtOAc/hexane to obtain the major photoproduct.

Photolysis in crystalline state

15–25 μ mol of the crystalline starting material were placed in an argon-purged and sealed quartz test tube and irradiated. Afterwards, the stock solution of *m*-dimethyl iso-

phthalate was added as internal standard, and the mixture was dissolved in dichloromethane. The solvent was removed and the mixture was analyzed by ¹H NMR analysis.

Alternatively, the crystalline solids were ground to powders and sandwiched between a pair of quartz slides, which were sealed in an argon-purged polyethylene bag and irradiated. The photolysate was dissolved in dichloromethane and the stock solution of *m*-dimethyl isophthalate was added as internal standard. After the removal of solvent, the mixture was analyzed by ¹H NMR analysis.

Photolysis in suspensions

In a 20 mL quartz tube, 0.05–0.16 mmol of starting material and 10 mL of hexane or water were added. The mixture was sonicated for 10 min to destroy the larger crystals and purged with argon for 20 min. After irradiation, dichloromethane was used to dissolve (hexane) or extract (water) the photolysate. After evaporation of the solvent in vacuo the product mixture was subjected to ¹H NMR spectroscopic analysis, or redissolved in acetone/methanol to crystallize the major photoproduct.

Dimethyl-4b,10b-dihydrobenzo[5,6]cyclopropa[3,4]pentaleno[1,2-a]naphthalene-4c,10d-dicarboxylate (5a¹)

Prepared by photoreaction in acetone solution. Yield 61%, colorless needles, mp 177–179 °C. UV (CHCl₃): λ_{max} (log ε) = 246 (4.44), 281 (3.73), 328 (2.97). ¹H NMR (400 MHz, CDCl₃) &: 3.76 (s, 3H, CH₃), 3.83 (s, 3H, CH₃), 4.64 (s, 1H, CH), 5.21 (s, 1H, CH), 7.00-7.08 (m, 2H, ar-CH), 7.17 (d, J = 7 Hz, 1H, ar-CH), 7.33–7.44 (m, 4H, ar-CH), 7.64–7.68 (m, 2H, ar-CH), 7.75 (d, J = 8 Hz, 1H, ar-CH). ¹³C NMR (100 MHz, CDCl₃) δ: 49.7 (CH₃), 52.4 (CH), 52.9 (CH), 55.5 (CH₃), 58.4 (C_q), 66.8 (C_q), 120.2 (ar-CH), 121.3 (ar-CH), 123.5 (ar-CH), 125.0 (ar-CH), 125.7 (ar-CH), 126.6 (ar-CH), 126.8 (ar-CH), 127.4 (ar-CH), 127.7 (C_a), 128.8 (ar-CH), 129.5 (ar-CH), 130.3 (C_a), 133.1 (C_q), 134.8 (C_q), 147.8 (C_q), 150.0 (C_q), 169.6 (C=O), 169.6 (C=O). MS (m/z): 370 [M⁺]. Elemental analysis calcd. (%) for $C_{24}H_{18}O_4$ (370.40): C 77.82, H 4.90; found C 77.74, H 4.81.

Dimethyl-4b,10c-dihydro-benzo[5,6]cyclopropa[1,2h]naphthalene-4c,10e-dicarboxylate (5a^{II})

Prepared by photoreaction in water suspension. Yield 37%, colorless cuboids, mp 173-175 °C. ¹H NMR (600 MHz, CD₃Cl) δ: 3.75 (s, 3H, CH₃), 3.91 (s, 3H, CH₃), 4.64 (s, 1H, CH), 5.59 (s, 1H, CH), 6.98-7.04 (m, 2H, ar-CH), 7.28 (d, J = 8 Hz, 1H, ar-CH), 7.34 (d, J = 8 Hz, 1H, ar-CH), 7.38 (d, J = 9 Hz, 1H, ar-CH), 7.34 (d, J = 8 Hz, 1H, ar-CH), 7.44 (dd, J = 7 Hz, 1H, ar-CH), 7.59 (dd, J =7 Hz, 1H, ar-CH), 7.62 (d, J = 8 Hz, 1H, ar-CH), 7.62 (d, J = 8 Hz, 1H, ar-CH), 7.78 (d, J = 8 Hz, 1H, ar-CH), 8.14 (d, J = 8 Hz, 1H, ar-CH). ¹³C NMR (150 MHz, CD₃Cl) δ : 50.1 (CH₃), 52.4 (CH), 52.9 (CH), 53.7 (CH₃), 67.8 (C_a), 68.7 (C_a), 121.4 (ar-CH), 123.3 (ar-CH), 123.7 (ar-CH), 125.7 (two overlapped ar-CH), 126.7 (ar-CH), 127.0 (ar-CH), 127.3 (ar-CH), 127.8 (ar-CH), 128.8 (ar-CH), 129.8 (C_q), 133.2 (C_q), 134.9 (C_q), 145.3 (C_q), 148.9 (C_q), 168.6 (C=O), 169.4 (C=O), one C_q signal is overlapped. MS (m/z): 370 [M⁺]. Elemental analysis calcd. (%) for $C_{24}H_{18}O_4$ (370.40): C 77.82, H 4.90; found C 77.98, H 4.81.

Dimethyl-6d,12*b*-*dihydro-cyclopropa*[3,4]*pentaleno-*[1,2*a*;6,5-*c*']*dinaphthalene-6c*,12*d*-*dicarboxylate* (5*b*^I)

Prepared by photoreaction in acetone solution. Yield 55%, white granules, mp 217-218 °C. ¹H NMR (600 MHz, CDCl₃) &: 3.78 (s, 3H, CH₃), 3.89 (s, 3H, CH₃), 5.13 (s, 1H, CH), 5.34 (s, 1H, CH), 7.30–7.38 (m, 4H, ar-CH), 7.41 (d, J = 8 Hz, 1H, ar-CH), 7.46 (dd, J = 7 Hz, 1H, ar-CH), 7.59 (d, J = 8 Hz, 1H, ar-CH), 7.64 (two overlapped doublet, J = 8 Hz, 2H, ar-CH), 7.68–7.71 (m, 2H, ar-CH), 8.10 (d, J = 8 Hz, 1H, ar-CH). ¹³C NMR (100 MHz, CDCl₃) δ : 48.5 (CH), 52.4 (CH₃), 53.0 (CH₃), 56.3 (CH₃), 58.8 (C₀), 67.4 (C_a), 120.0 (ar-CH), 120.1 (ar-CH), 123.5 (ar-CH), 124.3 (ar-CH), 125.0 (ar-CH), 125.3 (ar-CH), 126.6 (ar-CH), 126.6 (ar-CH), 127.5 (Cq), 128.3 (ar-CH), 128.4 (ar-CH), 128.8 (ar-CH), 129.4 (ar-CH), 129.8 (Cq), 130.5 (Cq), 130.7 (C_q), 132.5 (C_q), 133.1 (C_q), 146.9 (C_q), 148.0 (C_q), 169.6 (C=O), 169.7 (C=O). MS (m/z): 420 [M+]. Elemental analysis calcd. (%) for C₂₈H₂₀O₄ (420.46): C 79.98, H 4.79; found C 79.47, H 4.71.

X-ray diffraction analysis of compound 4a

The conditions and parameters adopted for the determination of crystallographic data of compound 4a are listed in Table 2.

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3912. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 720890 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Acknowledgement

This paper is dedicated to Trevor Linden on the occasion of his retirement and in appreciation of his exemplary behavior on and off the ice. We thank Dr. Thomas Paululat for carrying out the NOESY experiments and for helpful discussions on spectra analysis.

References

(a) Zimmerman, H. E. In *Rearrangements in ground and excited states*; de Mayo, P., Ed.; Academic Press: New York, USA, 1980; chap. 16; (b) Liao, C.-C.; Yang, P.-H. In *Handbook of Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, Fla., USA, 1995; chap. 15; (c) Scheffer, J. R.; Yang, J. In *Handbook of Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, Fla., USA, 1995; chap. 15; (c) Scheffer, J. R.; Yang, J. In *Handbook of Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, Fla., USA, 1995; chap. 16; (d) Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065 doi:10.1021/cr910109c. PMID:11848853.; (e) Liao, C.-

C.; Peddinti, R. K. In *Handbook of Photochemistry and Photobiology*; Horspool, W. M., Lenci, F., Eds.; CRC Press: Boca Raton, Fla., USA, 2003; chap. 32; (f) Ramaiah, D.; Sajimon, M. C.; Joseph, J.; George, M. V. *Chem. Soc. Rev.* **2005**, *34*, 48. doi:10.1039/b300843f. PMID:15643489.

- (2) (a) Zimmerman, H. E.; Sulzbach, H. M.; Tollefson, M. B. J. Am. Chem. Soc. 1993, 115, 6548 doi:10.1021/ja00068a011.;
 (b) Ihmels, H.; Mohrschladt, C. J.; Grimme, J. W.; Quast, H. Synthesis 2001, 8, 1175 doi:10.1055/s-2001-15064.;(c) Rattray, G.; Yang, J.; Gudmundsdottir, A. D.; Scheffer, J. R. Tetradedron Lett. 1993, 34, 35. doi:10.1016/S0040-4039(00) 60051-5.
- (3) Snow, R. A.; Cottrell, D. M.; Paquette, L. A. J. Am. Chem. Soc. 1977, 99, 3734. doi:10.1021/ja00453a036.
- (4) (a) Garcia-Garibay, M.; Scheffer, J. R.; Watson, D. G. J. *Chem. Soc. Chem. Commun.* **1989**, 600. doi:10.1039/ c39890000600.; (b) Garcia-Garibay, M.; Omkaram, N.; Schffer, J. R.; Trotter, J.; Wirenko, F. J. Am. Chem. Soc. **1989**, 111, 4985 doi:10.1021/ja00195a066.; (c) Chen, J.; Scheffer, J. R.; Trotter, J. Tetrahedron **1992**, 48, 3251 doi:10.1016/0040-4020(92)85002-V.; (d) Benitez, M.; Bringmann, G.; Dreyer, M.; Garcia, H.; Ihmels, H.; Waidelich, M.; Wissel, K. J. Org. Chem **2005**, 70, 2315 doi:10.1021/ jo047878j.; (e) Ding, J.; Desikan, V.; Han, X. X.; Xiao, T.

L.; Ding, R. F.; Jenks, W. S.; Armstrong, D. W. Org. Lett. 2005, 7, 335. doi:10.1021/ol047599i. PMID:15646991.

- (5) (a) Zimmerman, H. E.; Bender, C. O. J. Am. Chem. Soc. 1969, 91, 7516 doi:10.1021/ja01054a053.; (b) Zimmerman, H. E.; Bender, C. O. J. Am. Chem. Soc. 1970, 92, 4366. doi:10.1021/ja00717a038.
- (6) Platt, K. L.; Oesch, F. J. Org. Chem. 1981, 46, 2601. doi:10. 1021/jo00325a041.
- (7) *Photochemistry in organized and constrained media*; Ramamurthy, V., Ed.; VCH: NY, USA, 1991.
- (8) Reichardt, C. Solvents and solvent effects on organic chemistry; Wiley-VCH: Weinheim, Germany, 2003; chap. 5.
- (9) (a) Toda, F. *Top. Curr. Chem.* 2005, 254, 1 doi:10.1007/ b98357.; (b) Scheffer, J. R.; Wang, K. *Synthesis* 2001, 8, 1253. doi:10.1055/s-2001-15056.
- (10) Dewar, M. I. S.; de Liano, C. J. Am. Chem. Soc. 1969, 91, 789. doi:10.1021/ja01032a001.
- (11) Ramamurthy, V.; Venkatesan, K. Chem. Rev. 1987, 87, 433. doi:10.1021/cr00078a009.
- (12) Bondi, A. J. Phys. Chem. 1964, 68, 441. doi:10.1021/ j100785a001.
- (13) Sheldrick, G. M. SHELX-97 [computer program]; University of Göttingen, Göttingen, Germany, 1997.