80. The Influence of the Axial Chirality of Dibenzo[*a,c*]cyclooctene on the Configuration of Its Photo-*Diels-Alder* Adducts

by **Ulrich Burger***, **Pierre-André Lottaz**, **Patricia Millasson**, and **Gérard Bernardinelli**

Department of Organic Chemistry and Laboratory of X-Ray Crystallography, University of Geneva, CH–1211 Geneva 4

(17.I.94)

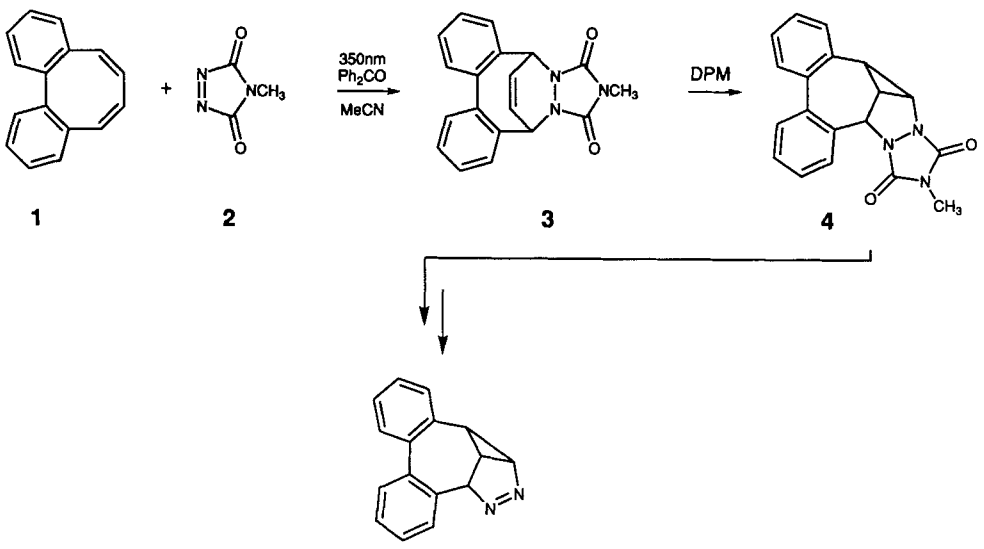
Triazole-diones and naphthoquinones are shown to add in a photochemical [4 + 2] reaction to the strongly twisted title diene **1**. With 1,4-naphthoquinone, the process is also accompanied by a [2 + 2] cycloaddition. When the pure atropisomer (–)-**1** is irradiated in presence of 2,3-dichloro-1,4-naphthoquinone (**9**), the axial chirality of the diene is preserved. Moreover, it is found to exert complete control over the chirality induced in the resulting spiro-dihydropyrane **10**. Absolute configurations are determined by X-ray crystallography. In absence of a photo-dienophile, the axially chiral, dextrorotatory 6-phenyldibenzo[*a,c*]cyclooctene ((+)-**11**) undergoes a stereospecific electrocyclization to give levorotatory 4b,6a-dihydro-5-phenylcylobuta[*l*]phenanthrene ((–)-**13**). Thus, only one out of two possible, disrotatory modes of ring closure is preferred.

Introduction. – Light induced [4 + 2]-cycloaddition reactions of 3*H*-1,2,4-triazole-3,5(4*H*)-diones to various planar and twisted π-systems have found successful application in recent years to the syntheses of complex bridged azo compounds [1–3]. The photochemical process provides a very valuable complement to the well documented thermal addition reactions of these renown dienophiles (for a review, *cf.* [4]). We have demonstrated, for instance, that the strongly twisted title diene **1** reacts readily upon photolysis with 4-methyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione **2** (MTAD) to give the formal *Diels-Alder* adduct **3**. In the dark, however, compound **1**, when heated in aprotic solvents and up to 150°, does not react with **2**. The primary photo-adduct **3** can be isomerized by a subsequent di-π-methane rearrangement (DPM) into the triazoline **4**. We have exploited this tandem of photoreactions, followed by a stepwise oxidative hydrolysis in the synthesis of 8,9-diazadibenzo[*c,e*]isobullvalene **5** [3] (*Scheme 1*).

As we were interested in the initial photo-*Diels-Alder* process, we wanted to explore further its scope and mechanistic details. Whereas the substitution pattern of dibenzo[*a,c*]cyclooctene **1** can be modified for this purpose in various ways [5], the class of 3*H*-1,2,4-triazole-3,5(4*H*)-diones allows only for structural variation of the 4-substituent. To become independent from that limitation, we decided to extend our efforts to other potential photo-dienophiles. Encouraged by the pioneering studies of *Barltrop* and *Hesp* [6], and *Wilson et al.* [7] on the photochemistry of quinones, we have chosen this class of compounds for our studies. We will show that quinones are indeed suitable photo-dienophiles. Upon irradiation they add to **1**, but thermally they are equally inert as the triazole-diones.

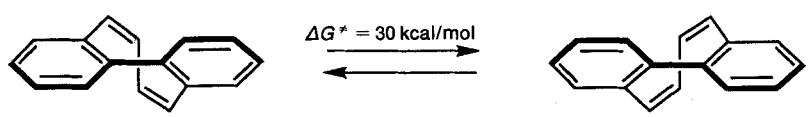
The reluctance of dibenzo[*a,c*]cyclooctene **1** to undergo thermal *Diels-Alder* reactions, undoubtedly, is due to the rigid twisted conformation of the eight-membered ring. It is known from a X-ray crystallographic analysis [8] that compound **1** has a nonconju-

Scheme 1



gated diene part, the two double bounds being nearly perpendicular to each other. According to *Rashidi-Ranjbar* and *Sandström* [9], the antipodes of this axially chiral compound can readily be separated by HPLC on swollen microcrystalline triacetylcellulose (TAC). The enantiomers are protected against racemization by a barrier of $\Delta G^{\neq} = 30$ kcal/mol. The Lund group has also calculated the CD spectrum of **1** by the CNDO/S method. It was found that the spectrum computed for the (*S*)-form shows considerable similarity with the experimental spectrum of the dextrorotatory antipode [10]. This absolute-configuration assignment, depicted in *Scheme 2*, finds corroboration in our results reported below.

Scheme 2

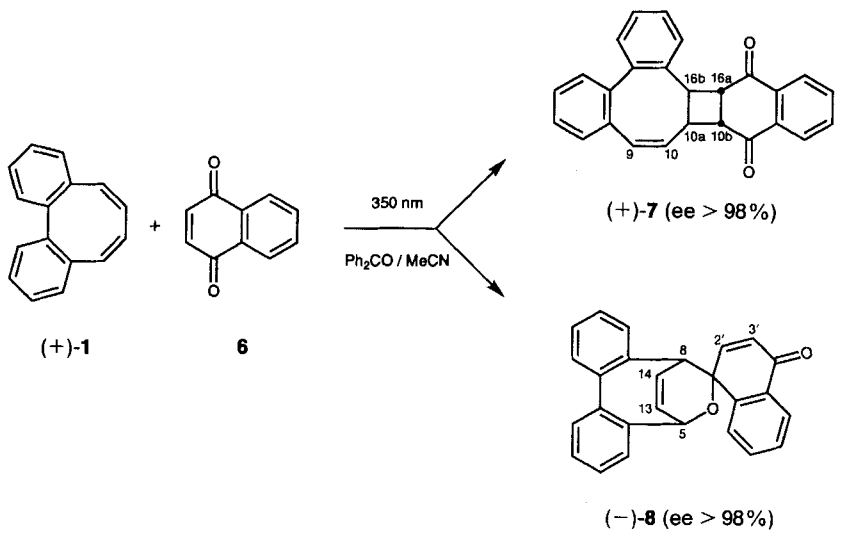


(−)-(*R*)-**1** ($[\alpha]_D = -735$) (+)-(*S*)-**1** ($[\alpha]_D = +735$)

This communication deals with the question, what influence does the axial chirality of **1** have on the stereochemical outcome of the photo-*Diels-Alder* reactions. Also, to what extent is the atropisomerism preserved, and does it induce chirality in the adducts, if new stereogenic centers are created?

Results. – When a deoxygenated solution of racemic **1** and 1,4-naphthoquinone (**6**) in MeCN or benzene was irradiated with white, visible light, two isomeric $C_{26}H_{18}O_2$ adducts were obtained in a 4:7 ratio. The minor product, isolated in 20–24% preparative yield, was found to be a cyclobutane derivative **7** resulting from the [2 + 2] addition of the diene

Scheme 3



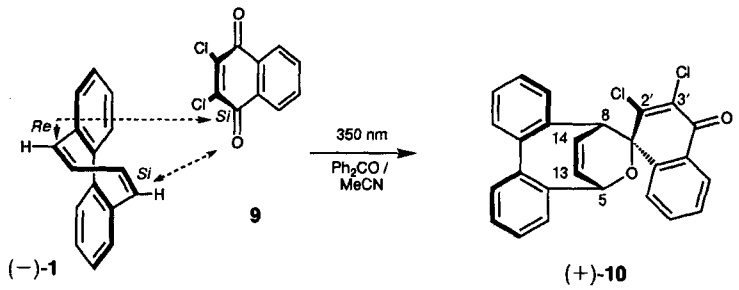
1 onto the C=C bond of naphthoquinone (*Scheme 3*). The *anti*-configuration at its four-membered ring was readily established by a ROESY experiment [11]. The major one of the photo-adducts, isolated in 35–42% preparative yield, was found to be a spiro-dihydropyrane **8**, resulting from the [4 + 2] addition of the diene to the quinonoid C=O group of **6**. We obtained the same products, **7** and **8**, again in a 4:7 ratio with the total yield ranging from 60–68%, when the photoreaction was carried out in presence of benzophenone as sensitizer and with light of 350-nm wavelength instead of visible light. Careful ^{1}H-NMR analysis of the isolated compounds **7** and **8**, with and without a chiral shift reagent ([Eu(hfc)$_3$]) present, showed both adducts to be diastereoisomerically pure racemic compounds.

When the experiment at 350 nm was repeated with enantiomerically pure (+)-**1**, we obtained in specific manner the [2 + 2] adduct and the [4 + 2] adduct, as single enantiomers, *i.e.* (+)-**7** and (−)-**8**, respectively. The ee values, determined by ^{1}H-NMR using the chiral shift reagent [Eu(hfc)$_3$] are > 98% for each. The counterexperiment performed with (−)-**1** gave the image set of enantiomers, (−)-**7** and (+)-**8**. An analytical sample of **1**, recovered from an experiment run to 54% of completion, had all its axial chirality preserved.

We have ascertained the constitution of **8** by X-ray analysis. Actually, a monocrystal of (−)-**8** was used for that purpose. This analysis (*vide infra*) clearly reveals that the aromatic ring of the naphthoquinonoid moiety of **8** is oriented *anti* to the etheno bridge, but it does not, of course, provide information about the absolute configuration of the adduct.

To gain further insight, we have examined the photoaddition of 2,3-dichloro-1,4-naphthoquinone (**9**) to the title diene **1**. In both, the benzophenone-sensitized reaction at 350 nm, and in the unsensitized reaction with visible light, the chlorinated quinone **9** turned out to be more selective than the parent naphthoquinone **6**. Only the [4 + 2] adduct **10** was obtained from the photoreaction (*Scheme 4*).

Scheme 4



When optically pure (−)-**1** was allowed to react at 350 nm with **9** in MeCN and in presence of benzophenone as sensitizer, we obtained, once again, in an enantiospecific manner (> 98% ee) the dextrorotatory adduct (+)-**10**.

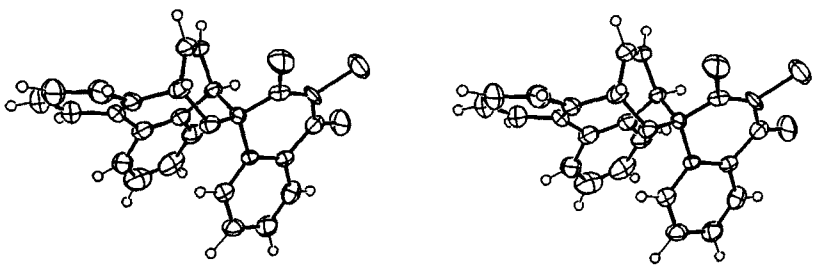


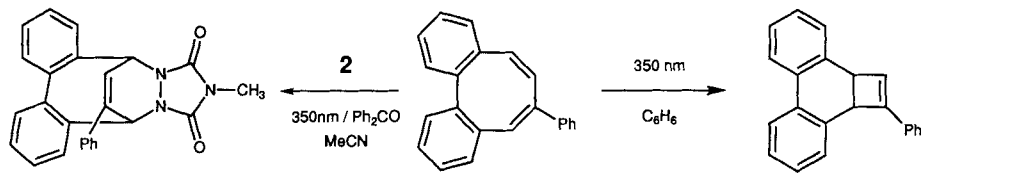
Figure. *Stereoscopic view of (+)-***10**

The presence of the two Cl-atoms now allowed the determination of the absolute configuration of (+)-**10** by X-ray crystallography. It is seen from the stereoscopic view (*Fig.*), that the axial chirality of the starting material is preserved in the 2,2′-bridged-biphenyl moiety of the photoadduct (+)-**10**. Moreover, the axial chirality of **1** exerts complete control over the chirality induced in the three new stereogenic centers. The aromatic ring of the dichloro-naphthoquinonoid moiety is oriented *anti* to the etheno bridge, as was the case for the Cl-free adduct **8**. Clearly, as is depicted in *Scheme 4*, the O-atom of the dienophile binds from the *Si*-face to the diene, whereas the C-atom of the quinonoid C=O group binds towards the *Re*-side of the diene.

The first [4 + 2] photoadduct of dibenzo[*a*,*c*]cyclooctene (**1**) we had encountered [3], *i.e.* the MTAD adduct **3** (*Scheme 1*), has a 2,2′-disubstituted biphenyl moiety resembling that of **10**. Compound **3** could, therefore, exist, at least in principle, in two atropisomeric forms. Molecular modelling using the SPARTAN program package [12], suggests however, that the barrier of racemization is to low (9.8 kcal/mol) for allowing resolution of the enantiomers. By ^{1}H- and ^{13}C-NMR in presence of [Eu(hfc)$_3$], we see a single set of resonances for compound **3** prepared from racemic **1**. Nevertheless, by lifting the C_2-symmetry of the diene, one can show that the photoaddition of MTAD is still controlled by the axial chirality in a similar way as has been found above for the naphthoquinone addition. To this purpose, we have synthesized racemic 6-phenyldibenzo[*a*,*c*]cyclooctene **11** and resolved its enantiomers by MPLC on TAC. When an MeCN soln. of (+)-**11** and

MTAD was photolyzed to 50% conversion at 350 nm in presence of benzophenone, we obtained in a stereospecific reaction (> 98% ee by NMR with [Eu(hfc)$_3$]) the dextrorotatory adduct (+)-**12**. At that conversion, the subsequent di-π-methane rearrangement mentioned in the *Introduction* (*Scheme 1*) did not amount to more than 5% of the total material balance (*Scheme 5*).

Scheme 5



(+)-**12** ($[\alpha]_D$ = +176) (+)-**11** ($[\alpha]_D$ = +295) (−)-**13** ($[\alpha]_D$ = −148 (ee > 98%))

We finally like to comment, in preliminary terms, on another photoreaction of dibenzo[*a*,*c*]cyclooctene **1** and its derivative **11**. It has been known for nearly three decades that **1**, in absence of a photo-dienophile, undergoes ring closure to give 4b,6a-dihydrocyclobuta[*l*]phenanthrene. The latter suffers subsequent cleavage into acetylene and phenanthrene during the direct photolysis, when light of short wavelength (< 300 nm) is used [13]. This dihydrocyclobuta[*l*]phenanthrene formation is an often cited and seemingly well studied example of a disrotatory electrocyclization. We have photolyzed (+)-**11** at 350 nm in benzene. Under these conditions, we obtained in 67% preparative yield the cyclization product (−)-**13** with > 98% ee determined by HPLC on *Chiracel OD-H*. From this experiment, it is clearly seen, that only one out of the two possible disrotatory modes of the cyclization is preferred under the control of the axial chirality. Efforts are in progress to determine the absolute configuration of (+)-**11** and (−)-**13**.

Discussion. – Photochemical additions of alkenes and dienes to quinones have been the subject of extensive investigations [6] [7] [14] [15]. It is well established by now, that irradiation of benzoquinones and naphthoquinones with visible light results in n,π* singlet-singlet excitation. The corresponding absorption band, normally is large with a small extinction coefficient. Intersystem crossing from the n,π* excitation to the first triplet (T_1) occurs rapidly with high efficiency, and it is from this T_1 state that most of the subsequent reactions at the quinonoid C=O group take place. The corresponding triplet energies (E_T) for the naphthoquinones **6** and **9** are 58 kcal/mol and 56 kcal/mol, respectively. These excited quinones, in contrast to the ground state, are electrophilic at the O-atoms. Consequently, C–O bond formation occurs first and can initiate the addition reactions to alkenes and dienes. These reactions give, normally, spiro-oxetanes, and spiro-dihydropyrans, respectively. Addition reactions at the C=C bond of quinones (*e.g.* the formation of **7**) are ascribed to a π,π* excitation [16]. With alkene derivatives and other π-systems having a low oxidation potential, such as enol ethers of 1,1-diphenylallenes, formation of a charge-transfer complex or an electron transfer to the T_1 state of the quinones is common and can precede the bond formation [15b] [17]. The successful interception of diradical intermediates by triplet oxygen or by SO_2 has been reported in support of the stepwise nature of this process [7]. These mechanisms account satisfacto-

rily for the formation of our spiro-dihydropyrans **8** and **10** in the case of the unsensitized reactions. Whether the orientation of the aromatic ring of the naphthoquinone reflects the initial approach, or whether it results from a thermodynamic control at the level of an intermediate diradical, is open to question. In principle, a charge-transfer complex could be invoked to account for the naphthoquinone orientation. However, no significant charge-transfer band is observed in the UV/VIS spectrum of the mixture of **1** with **6** or **9** in MeCN.

As an alternative to the excitation with visible light, the reactive T_1 state of benzoquinones and of naphthoquinones can be populated by using benzophenone (E_T = 68.6 kcal/mol) as triplet sensitizer. This accounts for the similarity of our results obtained in the direct photolyses and those of the sensitized reactions.

The authors wish to express their gratitude to Mr. *Ph. Kamalaprija* (ROESY experiments), *O. Schwalm* and *D. Stussi* (molecular modelling), and Mrs. *D. Clément* (MS). Financial support was provided by the *Swiss National Science Foundation* (grant No. 20-32645.91).

Experimental Part

General. Photolyses: *Srinivasan-Griffin* reactor (*Rayonet-RPR-100*) with *RPR* lamps, 2537 Å; double-walled quartz vessels with external cooling circuit (MeOH); *RPR* lamps, 3500 Å, and 500-W *Sylvania FFX-54* tungsten lamps (VIS); double-walled *Pyrex* vessels with external cooling circuit (MeOH). Centrifugally accelerated TLC: *Chromatotron 8924, Harrison Research*, Palo Alto. HPLC: *Kontron 325* chromatograph using *Nucleosil 5C18* and *7C18* (*Macherey-Nagel*) or *Chiracel OD-H* (*Daicel Chem. Ind.*) columns. MPLC: *Büchi B-680* chromatograph using silica gel 35–70 mesh (*Fluka*) and triacetylcellulose columns (TAC) (15–25 mesh, *Merck 16362*). Optical rotations: *Perkin-Elmer 241* polarimeter. UV Spectra (λ [nm])(log ε): *Kontron-Uvikon-860.* IR Spectra [cm^{-1}]: *Polaris-Mattson* FT-IR spectrometer. NMR Spectra: *Bruker AMX-400* (9.4 Tesla) *or Varian XL-200* (4.7 Tesla); chemical shifts in δ[ppm] relative to internal TMS; apparent scalar coupling constants J in Hz; multiplicities for ^{13}C according to DEPT or attached-proton test (APT). Explicit ^{13}C assignment is based on heteronuclear shift correlation. MS: (m/z(% relative to base peak)): *Finnigan-4023* with *INCOS* data system: electron impact, 70 eV.

10a,10b,16a,16b-Tetrahydrodibenzo[3′,4′,5′,6′]cycloocta[1′,2′:3,4]cyclobuta[1,2-b]naphthalene-11,16-dione (**7**) *and 5,8-Dihydro-5,8-etheno-7*H*-dibenzo[c,e]oxocine-7-spiro-1′-1′*H*-naphthalen-4′-one* **8**. A soln. of (±)-**1** (49 mg, 0.24 mmol), **6** (44 mg, 0.28 mmol), and benzophenone (15 mg, 0.08 mmol) in 5 ml of MeCN was deoxygenated with Ar and irradiated at 10° for 4 h with 350-nm light. After removal of the solvent *i.v.*, the mixture was prepurified by TLC on a rotating silica-gel disk (hexane/AcOEt 9:1) to remove the sensitizer and remaining **6**. Final TLC on silica gel (0.5 mm layer, CH_2Cl_2, double development) gave **7** (20.8 mg, 24%; R_f 0.31) and **8** (36.5 mg, 42%; R_f 0.22).

The corresponding experiment without sensitizer and using visible light gave **7** (22%) and **8** (41%) after 12 h irradiation.

Data of **7**. Colourless crystals. M.p. 134–136°. IR ($CDCl_3$): 3054*w*, 3001*w*, 2938*w*, 1680*s*, 1596*m*, 1485*w*, 1278*s*, 1210*m*, 1104*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 3.36 (*ddd*, J = 9.6, 6.4, 1.4, H–C(10b)); 3.46–3.58 (*m*, H–C(16a), H–C(10a)); 3.94 (*ddd*, J = 11, 7.0, 1.4, H–C(16b)); 5.95 (*dd*, J = 11.2, 9.2, H–C(10)); 6.86 (*d*, J = 11.2, H–C(9)); 7.0–8.0 (*m*, 12 arom. H). H–C(16b) shows a strong NOE with an arom. H (determined by ROESY [11]). ^{13}C-NMR ($CDCl_3$, 100 MHz): 41.32 (CH); 46.33 (CH); 46.57 (CH); 49.69 (CH); 127.3 (CH); 127.4 (CH); 127.6 (CH); 127.7 (CH); 127.8 (CH); 127.9 (CH); 128.0 (CH); 130.3 (CH); 130.6 (CH); 130.8 (CH); 132.0 (CH); 134.2 (CH); 134.3 (CH); 134.6 (CH); 135.3 (C); 135.4 (C); 137.3 (C); 137.7 (C); 141.1 (C); 142.1 (C); 196.9 (C0); 197.3 (CO). MS: 362 (66, $M^{+\cdot}$), 347 (12), 345 (12), 229 (28), 228 (17), 226 (14), 217 (19), 216 (36), 215 (48), 204 (34), 203 (100), 202 (77), 191 (30), 178 (48), 105 (41), 104 (62), 77 (44), 76 (82), 50 (38).

Data of **8**. Colourless crystals. M.p. 166–168°. IR ($CDCl_3$): 3061*w*, 3007*m*, 2927*w*, 1728*w*, 1667*s*, 1599*m*, 1479*w*, 1380*w*, 1294*m*, 1220*m*, 1087*m*, 909*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 3.43 (*d*, J = 7.7, H–C(8)); 5.55 (*d*, J = 4.8, H–C(5)); 5.91 (*dd*, J = 9.2, 7.7, H–C(14)); 6.22 (*dd*, J = 7.4, 1.4, 1 arom. H); 6.30 (*dd*, J = 9.2, 4.8, H–C(13)); 6.32 (*d*, J = 10.4, H–C(3′)); 6.4–8.0 (*m*, 11 arom. H); 7.76 (*d*, J = 10,4, H–C(2′)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 62.44 (CH); 77.35 (CH); 78.54 (C); 119.1 (CH); 125.4 (CH); 125.9 (CH); 126.1 (CH); 127.0 (CH); 127.2 (CH); 127.3 (CH); 127.4 (CH); 127.5 (CH); 128.0 (CH); 130.1 (C); 131.0 (CH); 133.5 (CH); 134.3 (CH); 135.2

(CH); 135.8 (CH); 136.1 (C); 136.8 (C); 141.5 (C); 143.7 (C); 144.6 (C); 153.0 (CH); 184.7 (CO). MS: 362 (2, M^{+}), 205 (15), 204 (91), 203 (100), 202 (44), 158 (14), 104 (15), 102 (18). HR-MS: 362.1309 ($C_{26}H_{18}O_2$; calc. 362.1307).

*Compounds (+)-***7** *and (−)-***8** *from (+)-***1**. The photolysis and workup were performed according to the procedure described above for (±)-**1** starting, however, from (+)-**1** with $[\alpha]_D = +735$ [5]. Both adducts, (+)-**7** and (−)-**8** were obtained with ee > 98%, as determined by ^{1}H-NMR using [Eu(hfc)$_3$]. Compound (+)-**7**: $[\alpha]_D = +119$ ($c = 0.4$, $CHCl_3$). Compound (−)-**8**: $[\alpha]_D = -11$ ($c = 0.3$, $CHCl_3$). X-Ray analysis of (−)-**8**: see below.

*2′,3′-Dichloro-5,8-dihydro-5,8-etheno-7*H*-dibenzo[*c,e*]oxocin-7-spiro-1′-1′*H*-naphthalen-4′-one* (**10**). A soln. of (−)-**1** (41 mg, 0.20 mmol), **9** (48 mg, 0.21 mmol), and benzophenone (15 mg, 0.08 mmol) in 5 ml of MeCN was deoxygenated with Ar and irradiated at 15° for 24 h with 350-nm light. After removal of the solvent *i.v.*, the mixture was prepurified by TLC on a rotating silica-gel disk (hexane/AcOEt 19:1). Final TLC on silica gel (0.5 mm layer, hexane/AcOEt 9:1, double development) gave **10** (28.4 mg, 33%).

Data of **10**. Colourless crystal. M.p. 196–198°. IR ($CHCl_3$): 3036*w*, 2923*w*, 1672*m*, 1600*w*, 1559*w*, 1292*w*, 1206*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 3.63 (*d*, $J = 7.7$, H–C(8)); 5.81 (*d*, $J = 4.9$, H–C(5)); 5.84 (*dd*, $J = 9.6$, 7.7, H–C(14)); 6.13 (*d*, $J = 7.7$, 1 arom. H); 6.35 (*dd*, $J = 9.6$, 4.9, H–C(13)); 6.63–7.95 (*m*, 11 arom. H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 66.00 (CH); 79.65 (CH); 83.41 (C); 115.7 (CH); 125.0 (CH); 126.2 (CH); 127.3 (CH); 127.4 (CH); 127.6 (CH); 127.7 (CH); 128.3 (CH); 128.8 (CH); 130.0 (C); 131.5 (CH); 132.8 (CH); 135.1 (CH); 135.6 (CH); 135.7 (CH); 135.9 (C); 136.4 (C); 140.3 (C); 143.4 (C); 144.4 (C); 159.9 (C); 178.5 (CO). MS: $C_{26}H_{16}O_2Cl_2$ (M^{+} not found), 228 (2), 205 (13), 204 (85), 203 (100), 202 (39), 201 (8), 200 (6).

*Compound (+)-***10** *from (−)-***1**. The photolysis and workup were performed according to the procedure described above for (±)-**1**, starting, however, from (−)-**1** with $[\alpha]_D = -735$ [5]. The adduct (+)-**10** was obtained with ee > 98%, as determined by ^{1}H-NMR using [Eu(hfc)$_3$]. Compound (+)-**10**: $[\alpha]_D = +31$ ($c = 0.2$, $CHCl_3$). X-Ray analysis of (+)-**10**: see below.

*5,6,7,8-Tetrahydro-*N^{im}*-methyl-5,8-[1′-phenyletheno]dibenzo[*d,f*][1,2]diazocine-6,7-dicarboximide* (**12**) *from (+)-6-Phenyldibenzo[*a,c*]cyclooctene* (**11**). Racemic **11** (m.p. 49–51°) was obtained by *Grignard* reaction of 5,6-dihydrodibenzo[*a,c*]cycloocten-6-one [5] with PhMgBr followed by elimination of H_2O. The enantiomers (+)-**11** and (−)-**11** were separated by MPLC on TAC (EtOH/H_2O 95:5). The compounds are eluted in the order (−)-**11** ($[\alpha]_D = -295$ ($c = 0.8$, $CHCl_3$)) and (+)-**11** ($[\alpha]_D = +298$ ($c = 0.9$, $CHCl_3$)). For the synthesis of (±)-**12**, a soln. of (±)-**11** (20 mg, 0.07 mmol), **2** (16 mg, 0.14 mmol), and benzophenone (11 mg, 0.06 mmol) in 5 ml of MeCN was deoxygenated with Ar and irradiated at 15° for 2.5 h with 350-nm light. After removal of the solvent, (±)-**12** (10 mg, 36% yield) was isolated by TLC on silica gel (CH_2Cl_2/acetone 95:5).

Data of (±)-**12**. Colourless crystals. M.p. 115–116°. IR ($CDCl_3$): 3011*w*, 2921*w*, 2846*w*, 1793*w*, 1761*m*, 1702*s*, 1467*m*, 789*m*, 780*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 2.89 (*s*, 3 H); 5.72 (*d*, $J = 6.2$, 1 H); 6.11 (*s*, 1 H); 6.42 (*d*, $J = 6.2$, 1 H); 7.28–7.54 (*m*, 13 arom. H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 25.08 (CH_3); 57.88 (CH); 63.12 (CH); 124.6 (CH); 125.6 (CH); 126.8 (CH); 128.2 (CH); 128.4 (CH); 128.5 (CH); 128.9 (CH); 129.1 (CH); 131.5 (CH); 133.2 (C); 136.2 (CH); 136.4 (C); 136.5 (CH); 136.7 (C); 138.5 (C); 140.0 (C); 150.1 (CO); 150.5 (CO).

*Compound (+)-***12** *from (+)-***11**. Compound (+)-**12** ($[\alpha]_D = +176$ ($c = 0.25$, $CHCl_3$)) was obtained in ee > 98% by the corresponding experiment starting with (+)-**11**.

*4b,6a-Dihydro-5-phenylcyclobuta[*l*]phenanthrene* (**13**). A soln. of **11** (20 mg, 0.07 mmol) in 5 ml of benzene was deoxygenated with Ar and irradiated at 10° for 2 h with 350-nm light. Product **13** (13.4 mg, 67% yield) was isolated by TLC on a rotating disk (silica gel, hexane). The two enantiomers (+)-**13** ($[\alpha]_D = +150$ ($c = 0.2$, $CHCl_3$)) and (−)-**13** ($[\alpha]_D = -148$ ($c = 0.2$, $CHCl_3$)) can be separated by HPLC on a *Chiracel-OD-H* column (hexane/i-PrOH 99:1).

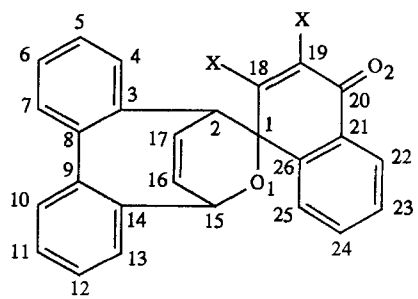
Data of **13**. Colourless crystals. M.p. 183–185°. IR ($CDCl_3$): 3008*w*, 1594*w*, 1202*s*, 902*s*, 777*w*, 733*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 4.32 (*dd*, $J = 4.6$, 1.3, 1 H); 4.75 (*d*, $J = 4.6$, 1 H); 6.40 (*d*, $J = 1.3$, 1 H); 7.21–7.95 (*m*, 13 arom. H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 41.18 (CH); 44.56 (CH); 123.4 (CH); 123.7 (CH); 125.6 (CH); 126.6 (CH); 127.0 (CH); 127.6 (CH); 127.7 (CH); 128.0 (CH); 128.3 (CH); 128.7 (CH); 130.5 (CH); 131.0 (C); 132.0 (C); 133.5 (CH); 134.1 (C); 135.0 (C); 136.9 (C); 149.6 (C). MS ($C_{22}H_{16}$): 280 (8, M^{+}), 179 (16), 178 (100), 177 (4).

*Crystallographic Data for (−)-***8** *and (+)-***10**. Cell parameters and diffracted intensities (h 0.8; k 0.11; l 0,24 and all antireflections of these) were measured at r.t. on a *STOE STADI4* diffractometer with graphite-monochromated MoK_α radiation ($l = 0.71069$ Å) for (−)-**8** and on a *Nonius CAD4* diffractometer with graphite-monochromated CuK_α radiation ($\gamma = 1.5418$ Å) for (+)-**10**. Two reference reflections measured every 60 min, showed variations less than 3.2 s (I). Data were corrected for *Lorentz* and polarization effects ((−)-**8** and (+)-**10**) and for absorption [18] ((+)-**10**). The structures were solved by direct methods using MULTAN 87 [19], all other calculations used XTAL [20] system and ORTEP [21] programs. The chirality/polarity of the structure (+)-**10** was refined and the absolute structure parameter [22] converges to $x = -0.01(3)$. Atomic scattering factors and anomalous dispersion terms were taken from [23]. All coordinates of the H-atoms were observed and refined. Both

compounds are isostructural, and the configuration of (−)-**8** has been fixed to be inverse to the refined absolute configuration of (+)-**10**. No stacking interaction nor short interatomic distances was observed in the molecular packing. A summary of crystal data, intensity measurement and structure refinement is given in *Table 1*. Selected geometrical parameters are reported in *Table 2*. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, 12, Union Road, Cambridge CB2 1EZ, England.

Table 1. *Summary of Crystal Data, Intensity Measurement, and Structure Refinement for Compounds (−)-8 and (+)-10*

	(−)-**8**	(+)-**10**		(−)-**8**	(+)-**10**
Formula	$C_{26}H_{18}O_2$	$C_{26}H_{16}O_2Cl_2$	A^*(min., max.)	–	1.242, 1.475
Mol. wt.	362.4	431.3	$((\sin\theta)/\gamma)_{max}$ [Å^{-1}]	0.54	0.51
Crystal system	Orthorhombic	Orthorhombic	Temp. [K]	298	298
Space group	$P2_12_12_1$	$P2_12_12_1$	No. measured reflections	2828	2615
a [Å]	7.718(1)	7.3215(8)	No observed reflections	1304	2083
b [Å]	10.686(3)	11.0749(8)	Criterion for observed	$[F_o] > 4\sigma(F_o)$	$[F_o] > 4\sigma(F_o)$
c [Å]	22.058(5)	24.387(2)	Refinement (on F)	Full-matrix	Full-matrix
V [Å^3]	1819.2(7)	1977.4(3)	No. parameters	307	320
Z	4	4	Weighting scheme	$\omega = 1/\sigma^2(F_o)$	$\omega = 1/\sigma^2(F_o)$
$F(000)$	760	888	Max. and min. $\Delta\rho$ [e·Å^{-3}]	0.51, −0.63	0.21, −0.32
D_c [g·cm^{-3}]	1.32	1.45	x		−0.01(3)
Radiation	MoK_α	CuK_α	S	1.63	3.09
μ [mm^{-1}]	0.077	3.122	R, ωR	0.052, 0.019	0.040, 0.030



(−)-**8** X = H
(+)-**10** X = Cl

Table 2. *Selected Bond Lengths* [Å], *Bond Angles, and Torsional Angles* [°] *for Compounds (−)-8 and (+)-10*. Arbitrary numbering as shown above.

	(−)-**8**	(+)-**10**		(−)-**8**	(+)-**10**
O(1)–C(1)	1.46(1)	1.434(7)	O(1)–C(1)–C(2)	107.7(7)	109.6(5)
O(1)–C(15)	1.44(1)	1.470(8)	C(18)–C(1)–C(26)	111.2(8)	108.7(5)
O(2)–C(20)	1.23(1)	1.215(8)	C(1)–C(2)–C(3)	112.7(7)	108.5(5)
C(1)–C(2)	1.54(1)	1.573(9)	C(1)–C(2)–C(17)	107.9(8)	107.8(5)
C(1)–C(18)	1.51(2)	1.539(9)	C(3)–C(2)–C(17)	115.2(9)	117.6(6)
C(1)–C(26)	1.53(1)	1.519(8)	C(2)–C(3)–C(8)	126.3(9)	127.5(6)
C(2)–C(3)	1.51(1)	1.506(9)	C(3)–C(8)–C(9)	129.8(9)	128.7(6)
C(2)–C(17)	1.53(1)	1.519(9)	C(8)–C(9)–C(14)	128.7(9)	129.1(7)
C(3)–C(8)	1.44(1)	1.42(1)	C(9)–C(14)–C(15)	123.7(8)	122.8(6)
C(8)–C(9)	1.50(1)	1.53(1)	O(1)–C(15)–C(14)	110.6(8)	111.2(5)
C(9)–C(14)	1.39(2)	1.39(1)	O(1)–C(15)–C(16)	113.5(7)	115.3(5)
C(14)–C(15)	1.55(2)	1.51(1)	C(14)–C(15)–C(16)	104.9(9)	105.9(6)
C(15)–C(16)	1.51(1)	1.499(9)	C(15)–C(16)–C(17)	121.8(9)	120.3(6)
C(16)–C(17)	1.31(2)	1.32(1)	C(2)–C(17)–C(16)	117.0(9)	118.5(6)
C(18)–C(19)	1.33(2)	1.310(9)	C(1)–C(18)–C(19)	121(1)	120.7(6)

Table 2 (cont.)

	(−)-**8**	(+)-**10**		(−)-**8**	(+)-**10**
C(18)–Cl(1)	–	1.711(7)	C(18)–C(19)–C(20)	121(1)	122.7(6)
C(19)–C(20)	1.45(2)	1.492(9)	C(19)–C(20)–C(21)	120(1)	113.3(6)
C(19)–Cl(2)	–	1.735(7)	C(20)–C(21)–C(26)	118.3(9)	121.1(5)
C(20)–C(21)	1.46(2)	1.495(9)	C(1)–C(26)–C(21)	119.5(8)	118.2(5)
C(21)–C(26)	1.41(1)	1.405(8)			
C(15)–O(1)–C(1)–C(2)	45(1)	−40.7(7)	C(15)–C(16)–C(17)–C(2)	12(2)	−10(1)
O(1)–C(1)–C(2)–C(3)	66(1)	−68.2(6)	C(15)–C(16)–C(17)–C(2)	12(2)	−10(1)
C(1)–C(2)–C(3)–C(18)	−70(1)	72.3(8)	C(1)–O(1)–C(15)–C(16)	0(1)	−3.7(9)
C(2)–C(3)–C(8)–C(9)	−20(2)	17(1)	C(26)–C(1)–C(18)–C(19)	−31(1)	38.5(8)
C(3)–C(8)–C(9)–C(14)	45(2)	−44(1)	C(1)–C(18)–C(19)–C(20)	10(2)	−10(1)
C(8)–C(9)–C(14)–C(15)	−22(2)	23(1)	C(18)–C(19)–C(20)–C(21)	14(2)	−18.4(9)
C(9)–C(14)–C(15)–O(1)	56(1)	−57.7(8)	C(19)–C(20)–C(21)–C(26)	−13(2)	16.4(9)
C(1)–O(1)–C(15)–C(14)	−117.5(8)	116.9(6)	C(20)–C(21)–C(26)–C(1)	−10(1)	13.5(9)
O(1)–C(1)–C(2)–C(17)	−62.1(9)	60.2(6)	C(18)–C(1)–C(26)–C(21)	31(1)	−39.0(8)
C(1)–C(2)–C(17)–C(16)	35(1)	−35.3(9)			

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