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1,1′-Binaphthalene-2,2′-dicarbonitrile in Photochemically Sensitized Enantiodifferentiating Isomerizations

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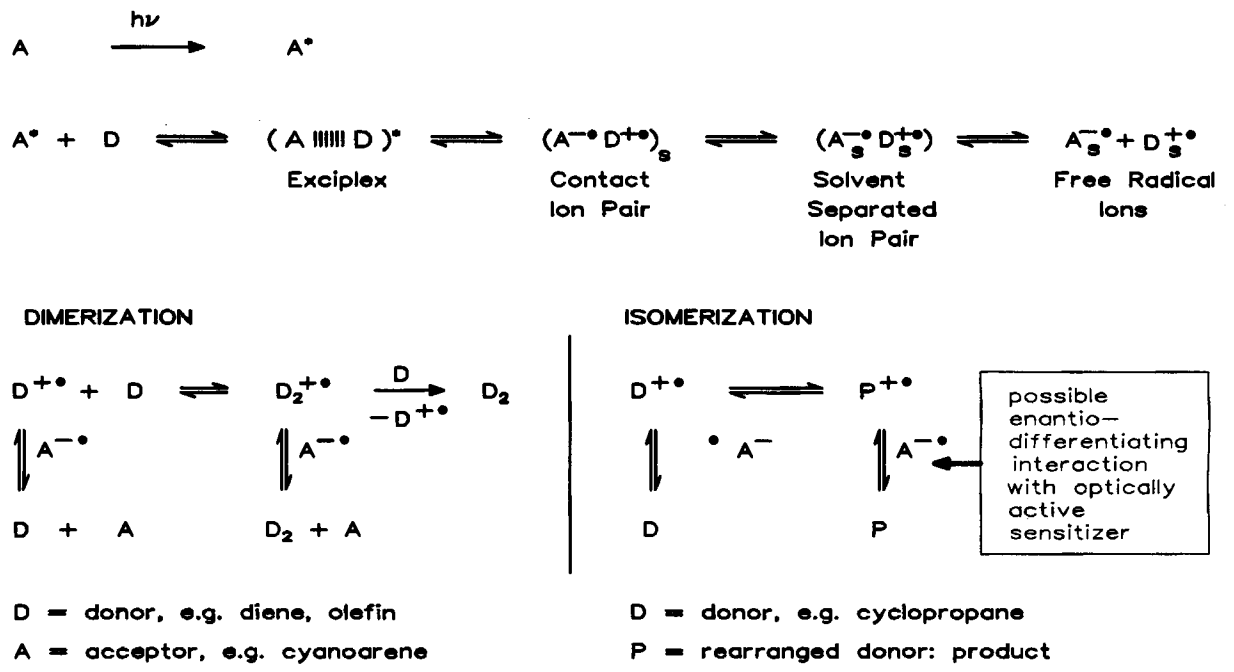
The synthesis of optically active (+)- and (−)-1,1′-binaphthalene-2,2′-dicarbonitrile (**1**) is described as well as its application in photoinduced electron transfer (PET) dimerizations and isomerizations.

Photochemically induced electron transfer (PET) reactions represent a rapidly growing field in photochemistry[2]. However, until now no report has appeared which covers the use of chiral sensitizers in charge transfer processes. In order to induce chirality in PET reactions with enantiomerically pure sensitizers, a close contact of the reaction partners (e.g. radical ion pairs, cf. Scheme 1) seems necessary. According to results reported in the literature[2c], this concept may be applied to monomolecular (e.g. isomerizations) as well as to bimolecular (e.g. dimerizations, cycloadditions) PET reactions.

During our investigations concerning binaphthalene-type acceptors[3], we synthesized optically active 1,1′-binaphthalene-2,2′-dicarbonitrile (**1**) in both enantiomeric forms. This compound was tested in a typical PET reaction (dimerization of 1,3-cyclohexadiene) and in several enantiodifferentiating photoisomerizations.

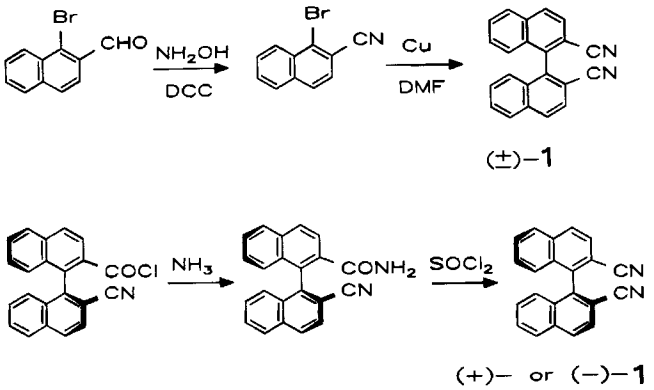
Although the synthesis of **1** is quite straightforward, only physical properties have been reported to date[4]. Racemic **1** is easily accessible from 1-bromo-2-naphthaldehyde[5], thereby avoiding use of 2,2′-diamino-1,1′-binaphthalene, which would involve the formation of carcinogenic 2-naphthylamine as a byproduct. The aldehyde is converted into 1-bromo-2-naphthalenecarbonitrile in a one-pot procedure according to the method of Vowinkel and Bartel[6]. A modified Ullmann reaction using activated copper powder in anhydrous dimethylformamide leads to racemic **1** in satisfying yield. Optically active **1** can be prepared from (*R*)- or (*S*)-1,1′-binaphthalene-2-carbonitrile-2′-carbonyl chloride. These enantiomers are intermediates in the optical resolution of 1,1′-binaphthalene-2,2′-dicarboxylic acid as described by Miyano and co-workers[7] and can be prepared accordingly. Reaction with ammonia and dehydration of the amide with thionyl chloride gives (+)- or (−)-**1** in 45–80% yield over the last three steps.

Scheme 1



  0009–2940/90/1212–2457 $ 3.50+.25/0

Scheme 2



Testing racemic **1** in the PET dimerization of 1,3-cyclohexadiene (**2**) showed it to be a very effective catalyst, compared to the conventional sensitizers 1,4-dicyanobenzene, 1,4-dicyanonaphthalene, or 9,10-dicyanoanthracene (cf. Table 1).

Scheme 3

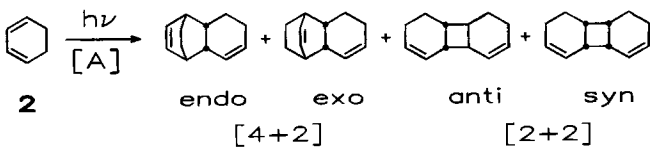


Table 1. Photosensitized dimerization of 1,3-cyclohexadiene (**2**)[a]

Sensitizer	Conversion (%)	Yields (%)[b] *endo*	*exo*	*anti*	*syn*	*endo/exo*
Benzophenone	>99	–	12	46	13	0
Phenanthrene	90	–	14	46	16	0
1,1′-Binaphthalene	53	–	9	28	10	0
1-Cyanonaphthalene	50	28	4	4	1	6.5
1,4-Dicyanonaphthalene	62	33	4	3	1	9.6
9,10-Dicyanoanthracene	39	30	3	Traces		11.2
1	96	69	7	4	2	9.5

[a] c = 0.2 mol/l; sensitizer: 0.02 mol/l; solvent. acetonitrile; irradiation time: 6 h. – [b] Absolute yields, determined by GLC.

The resulting *endo/exo* ratio of the 1,3-cyclohexadiene dimers corresponds to an electron transfer mechanism rather than to simple energy transfer sensitization[8].

In 1965 the isomerization of *cis*-1,2-diphenylcyclopropane (**3**) represented the first example of a photosensitized enantiodifferentiating reaction[9]. On the other hand, it is known that irradiation of this compound in acetonitrile in the presence of an electron acceptor involves the formation of radical cations[10].

Scheme 4

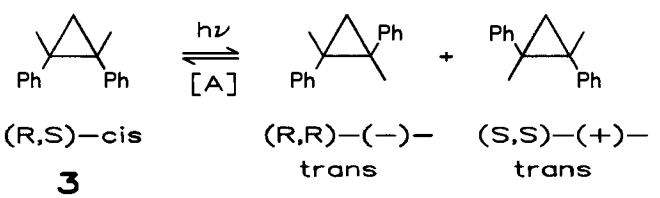


Table 2. Photosensitized isomerization of *cis*-1,2-diphenylcyclopropane (**3**)[a]

Sensitizer	Irr. time [h]	Temp. [°C]	Solvent	*cis:trans*[b]	$[\alpha]_D$	e.e.[c] [%]
(*R*)-(–)-**1**	19	Room temp.	Benzene	69:31	+9.3	2
(*R*)-(–)-**1**	19	Room temp.	CH_3CN	51:49	+0.5	0.1
(*R*)-(–)-**1**	19	–30	Toluene	67:33	+17.2	4
(*S*)-(+)-**1**	36	–15	Toluene	64:36	–14.5	3.5
(*S*)-(+)-**1**	36	–15	CH_2Cl_2	69:31	+4.0	1

[a] c = 0.1 mol/l; sensitizer: 0.01 mol/l. – [b] Determined by GLC. – [c] Calculated from $[\alpha]_D$, $[\alpha]_D$ = 418 for pure enantiomers[11].

Photoreaction of *cis*-**3** with 10 mol-% of (*S*)-(+)-**1** in toluene led to a 3.5% excess of (*R,R*)-(–)-*trans*-1,2-diphenylcyclopropane[11], whereas the use of (–)-**1** gave the (+) enantiomer in slight excess; the photostationary equilibrium showed a ratio of 64:36 of *cis*-:*trans*-**3**.

Addition of the radical cation quencher 1,2,4-trimethoxybenzene (TMB)[12] was carried out in order to answer the question whether complete charge transfer is involved in this reaction. Table 3 comprises the results, showing that, in toluene, TMB had no observable quenching effect with the sensitizers 1,4-dicyanonaphthalene (DCN) or **1**.

Table 3. Photosensitized isomerization of *cis*-1,2-diphenylcyclopropane (**3**): effect of 1,2,4-trimethoxybenzene (TMB)[a]

Sensitizer	Solvent	% *trans*-**2** after 21 h no TMB	0.005 M TMB	0.01 M TMB
Acetone	Acetone	38	40	40
DCN	CH_3CN	20	5	3
1	CH_3CN	46	36	27
DCN	Toluene	56	58	59
1	Toluene	40	39	39

[a] Reaction conditions: see Table 2 and Experimental.

In the more polar solvent acetonitrile, TMB quenched the reaction with DCN and **3** effectively, however, when **1** was used as sensitizer, it had only a slight influence. It might be concluded that no complete charge transfer is involved here.

Applying the same method [–14°C, toluene, 10 mol-% of (+)-**1**] as in the isomerization of **3**, 1,2-bis(4-methoxyphenyl)cyclopropane rearranged to a *cis/trans* ratio of 54:46 (determined by GLC). The resulting *cis/trans* product mixture showed an optical rotation of $[\alpha]_D$ = –8.1, corresponding to $[\alpha]_D$ = –17.7 for the *trans* isomer. The enantiomeric excess cannot be determined, since the optical rotation of the pure enantiomers of 1,2-bis(4-methoxyphenyl)-cyclopropane is not yet known.

Efforts to extend the method to the isomerization of *cis*-stilbene oxide or *cis*-2,3-diphenylaziridine led to unexpected results. Stilbene oxide did not rearrange at all, and the aziridine ring opened to benzaldehyde benzylimine. This last reaction did not occur with other electron transfer sensitizers. Investigations concerning intermolecular enantiodifferentiating photosensitized reactions are in progress.

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Experimental

(±)-1,1′-Binaphthalene-2,2′-dicarbonitrile (**1**): 10 g of copper bronze (Merck) is stirred for 10 min with 2 g of iodine in acetone (100 ml). The residue after filtration is stirred for 2 min with a mixture of acetone and conc. hydrochloric acid (200 ml, 1:1, v/v). After filtration by suction, the bright red copper powder is dried in vacuo. 7.7 g of 1-bromo-2-naphthalenecarbonitrile[6] and dry dimethylformamide (30 ml) are added to the dry metal powder. The mixture is refluxed under argon with stirring for 36 h, and, after cooling, it is poured into a beaker containing water (300 ml) and dichloromethane (300 ml). After extraction of the water phase, the combined organic phases are washed with water (3 × 100 ml) and dried with sodium sulfate. Evaporation and filtration of the residue over silica gel 60 (Merck) with dichloromethane/cyclohexane (1:1, v/v) as the eluent yield 3.2 g (63%) of fluffy, white needles, m.p. 232°C. – ^{1}H NMR ($CDCl_3$): δ = 7.16 (d, *J* = 8.4 Hz), 7.41 (d/d/d, *J* = 1.4/7.0/8.4 Hz), 7.63 (d/d/d, *J* = 1.4/7.0/8.2 Hz), 7.82 (d, *J* = 8.7 Hz), 8.00 (br. d, *J* = 8.1 Hz), 8.10 (br. d, *J* = 8.4 Hz). – ^{13}C NMR ($CDCl_3$): δ = 111.52 (C_q), 117.48 (C_q), 126.34 (CH), 126.73 (CH), 128.47 (CH), 128.69 (CH), 129.24 (CH), 130.36 (CH), 131.75 (C_q), 134.84 (C_q), 140.49 (C_q). – IR: $\tilde{\nu}$ = 3078 cm^{-1}, 3059, 3020, 2222, 1590, 1505, 1322, 870, 822, 749. – MS (70 eV): *m/z* (%) = 304 (100) [M^+], 275 (21), 138 (27), 124 (25). – Redox potential: $E^{I}_{1/2}$ = −2.16 V; $E^{II}_{1/2}$ = −2.53 V vs. Ferrocen[13].

$C_{22}H_{12}N_2$ (304.3) Calcd. C 86.82 H 3.97 N 9.20
Found C 86.56 H 3.93 N 9.14

(S)-(+)- or (R)-(−)-1,1′-Binaphthalene-2,2′-dicarbonitrile (**1**): 1,1′-Binaphthalene-2-carbonitrile-2′-carbonyl chloride, prepared from 8.6 mmol of the (*S,S*)-acetonitrile clathrate or the (*R,S*)-ethanol clathrate of 2′-[(1-phenylethyl)aminocarbonyl]-1,1′-binaphthalene-2-carboxylic acid[7], is cooled to 0°C and mixed with 50 ml of ice-cold conc. ammonia. The mixture is stirred vigorously until the dark lumps have disappeared. After stirring at room temp. for at least 24 h, the resulting brownish precipitate is collected by filtration and dried in a desiccator. The amide may be recrystallized from cyclohexane {$[\alpha]_D$ = −66.8 (*c* = 1.59, $CHCl_3$) from (*R,S*)-clathrate, $[\alpha]_D$ = +66.9 (*c* = 0.85, $CHCl_3$) from (*S,S*)-clathrate}. – The mixture of 0.4 g of the crude amide with 5 ml of pure thionyl chloride is refluxed until the evolution of gas ceases (ca. 90 min). Distillation of excess thionyl chloride and purification of the residue by filtration over silica gel with dichloromethane/cyclohexane as the eluent yield 0.20 g (50%) of light, white needles. $[\alpha]_D$ = −70.5 (*c* = 1, $CHCl_3$), from (*R,S*)-clathrate, $[\alpha]_D$ = +68.6 (*c* = 1.54, $CHCl_3$), from (*S,S*)-chlathrate. According to HPLC analysis [Daicel Chiralpak OT(+); eluent: methanol] and comparison with the racemate, both enantiomers are >99% enantiomerically pure.

Photoisomerizations: The reaction mixtures in closed pyrex tubes are irradiated with a high-pressure mercury burner (Philips HPK 125 W) in a merry-go-round-type apparatus (Hans Mangels, Bornheim) fitted with a water-cooled quartz immersion well. A solution of 0.5 mmol of the cyclopropane, the oxirane[14], or the aziridine[15] as well as 0.05 mmol of the sensitizer in 5 ml of dry solvent was purged with argon for 2 min. The *cis/trans* ratios were determined by GLC analysis (25 m HP Ultra 2 for diphenylcyclopropane, 25 m SE 30 for the other three-membered ring compounds). The reaction conditions for the dimerization of 1,3-cyclohexadiene (**2**) have been described elsewhere[3]. The cyclopropanes are prepared by the decomposition of the corresponding 1-pyrazolines[16]. Pure *cis*-1,2-diphenylcyclopropane is obtained by crystallization from pentane at −20°C, pure *cis*-1,2-bis(4-methoxyphenyl)cyclopropane is prepared by fractional distillation and recrystallization of the earlier fractions from methanol and workup of the mother liquors.

CAS Registry Numbers

(±)-**1**: 129680-07-5 / (+)-**1**: 129783-81-9 / (−)-**1**: 129783-80-8 / **2**: 592-57-4 / **3**: 1138-48-3 / 1-bromo-2-naphthalenecarbonitrile: 20176-08-3 / (*R*)-1,1′-binaphthalene-2-carbonitrile-2′-carbonyl chloride: 129207-26-7 / (*S*)-1,1′-binaphthalene-2-carbonitrile-2′-carbonyl chloride: 125662-30-8 / (*R*)-1,1′-binaphthalene-2-carbonitrile-2′-amide: 129680-08-6 / (*S*)-1,1′-binaphthalene-2-carbonitrile-2′-amide: 129680-09-7 / *endo*-1,3-cyclohexadiene dimer: 703-35-5 / *exo*-1,3-cyclohexadiene dimer: 703-36-6 / (*R,R*)-(−)-*trans*-1,2-diphenylcyclopropane: 129783-82-0 / (*S,S*)-(+)-*trans*-1,2-diphenylcyclopropane: 129783-83-1 / 1,2-bis(4-methoxyphenyl)cyclopropane: 3718-51-2

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