# SOLID-STATE PHOTOREACTIVITY OF ORTHO-DISTYRYLAROMATIC COMPOUNDS

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Abstract: While 2,2'-distyrylbiphenyl (**1**) shows no solid-state photoreactivity, the tert.-butyl substituted derivative **2** is quantitatively transformed into the intramolecular [2+2]cycloadduct **4**. In contrast, 1,2-distyrylbenzene (**5**) exhibits a strong tendency toward photopolymerization in the crystalline state, while the tert.-butylated derivative **7** proves to be photostable.

Crystalline bis(β-arylvinyl)arenes have received considerable interest as substrates for topochemically controlled photodimerization and photopolymerization reactions [1]. While most of the recent work has been focussed on the development of novel para- and meta-substituted diolefinic monomers for photocycloaddition polymerizations [1a], the aptitude of ortho-disubstituted compounds in topochemical rearrangement reactions is widely unexplored. This is mainly due to their unique tendency toward intramolecular valence isomerizations upon irradiation in solution [2], caused by the specific substrate geometry, which also seem to compete with the intermolecular processes in the crystalline state and therefore to impede control of the topochemical reaction paths. We now report on the intramolecular topochemical transformations of 2,2'-distyrylbiphenyl (**1**) and its derivative **2** which show a close analogy to their photochemical behavior in solution [2a-d,l]. In contrast hereto, the photolysis of 1,2-distyrylbenzene (**5**) in the crystalline state represents the first example of a photocycloaddition polymerization of an o-bis(β-arylvinyl)benzene.

| **1** | R = H |
| **2** | R = tert. butyl |

| **3** | R = H |
| **4** | R = tert. butyl |
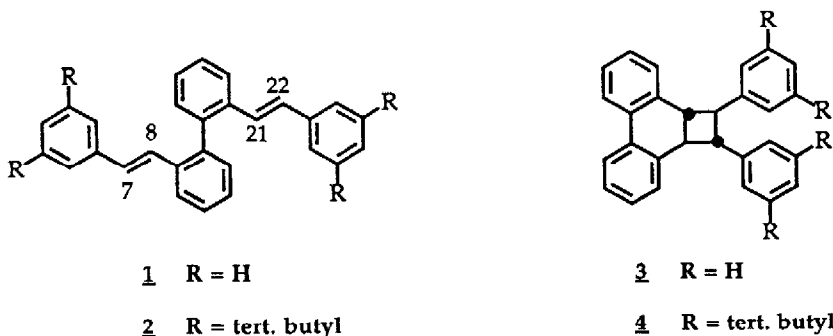
Irradiation of a microcrystalline suspension of **2** in water (125 watt mercury high-pressure lamp with pyrex filter, λ > 300 nm, 3 d, room temperature) yields quantitatively the all-trans cyclobutane derivative **4**; the same photoproduct is also formed selectively when the reaction takes place in solution (43% conversion after 30 min) or in the film (generated by spin coating, conversion rate depending on film thickness and stiffness). Surprisingly, the unsubstituted parent compound **1**, which exhibits an analogous photoreactivity in solution [2a-d] or in the immobilized phase [3] with even higher conversion rates (100% conversion to **3** after 30 min in solution), is completely photostable in the solid state.

The difference in the topochemical behavior can be explained by the molecular alignment of **1** and **2** in the single crystal: in the case of **1**, according to crystal structure analysis, the two stilbene moieties of the molecule

are twisted by an angle of 114.9° against each other; also, the intramolecular and intermolecular distances between the olefinic double bonds are far above the maximum interaction radius of 4.0 - 4.1 Å (Table 1). In single crystals derived from **2**, the angle of torsion in the central biphenyl unit, despite of the voluminous tert.-butyl substitutents attached to the terminal phenyl rings, only amounts to 59.1°, thus allowing for the intramolecular approach of the reactive vinylene units and for the observed intramolecular [2+2] cycloaddition. It has to be emphasized that independent from the reaction conditions (crystal, film, solution), only the all-trans cyclobutane derivatives **3** and, respectively, **4** are formed.
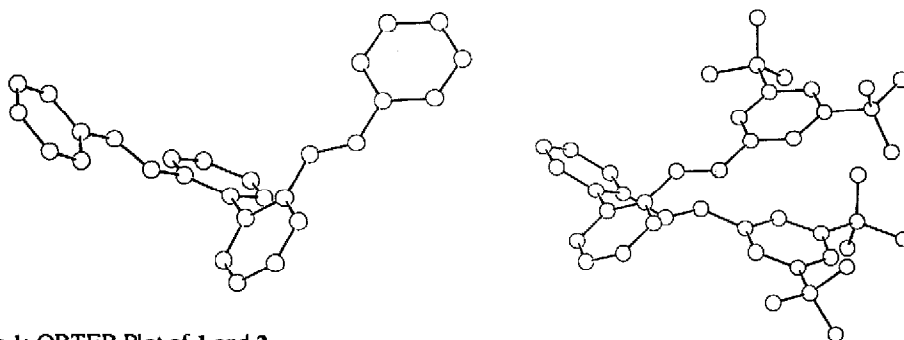

Figure 1: ORTEP-Plot of **1** and **2**

The crystallographic data of both cis-cis- and trans-trans-1,2-distyrylbenzene (**5a**) and (**5b**), in particular the comparatively short distances between the reactive olefinic double bonds (Table 1), seem to exclude neither intramolecular nor intermolecular rearrangement pathways. Unexpectedly, the irradiation of a microcrystalline suspension of **5a** or **5b** in water (125 watt mercury high-pressure lamp with pyrex filter, λ > 300 nm, 3 d, room temperature) leads to the same product mixture consisting of 30% endo-5-exo-6-diphenylbenzobicyclo[2.1.1]

compound no.	selected C - C distances		
	C - C	intramolecular	intermolecular
1	7 - 21	5.72	5.10
	7 - 22	6.67	4.44
	8 - 21	4.40	5.14
	8 - 22	5.40	4.63
2	7 - 21	3.52	6.84
	7 - 22	3.71	6.80
	8 - 21	2.93	7.36
	8 - 22	3.54	7.82
5a	7 - 15	3.99	4.16
	7 - 16	5.04	4.36
	8 - 15	2.90	3.71
	8 - 16	3.88	4.03
5b	7 - 15	4.21	3.76
	7 - 16	5.48	3.83
	8 - 15	2.92	4.19
	8 - 16	4.18	3.85

Table 1: Selected C-C distances between the olefinic centers in **1**, **2**, **5a** and **5b**

hexane (**6**) and 70% of oligomeric and polymeric material with a molecular weight of up to 15,000 g/mol (Scheme 1). According to its NMR data, the latter contains cyclobutane moieties with, however, yet unknown regio- and stereochemistry.

Scheme 1
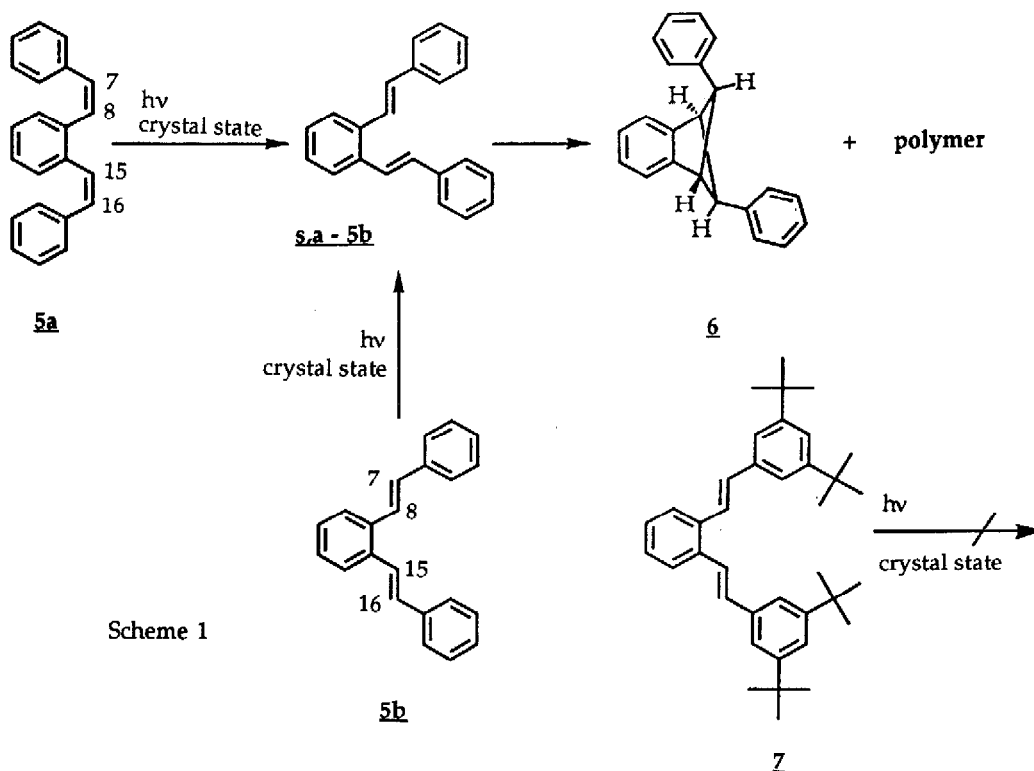
The experimental results, especially the stereoselective formation of the monomeric product **6** can be explained by assuming the presence of a rapid light-induced cis-trans isomerization and of conformational changes in the substrate crystal prior to the rearrangement processes; thereby significant amounts of the syn-anti-conformer of **5b** are formed which undergo a cross-[2+2]cycloaddition to the bicyclohexane derivative **6**. While cis-trans isomerizations in the solid state are quite common [4], this reaction is one of the first examples demonstrating the influence of conformational changes on the stereochemical course of the rearrangement reaction for ortho-bisolefinic substrates.

The formation of the monomeric cycloadduct **6** has also been observed during the irradiation of **5** immobilized on silica gel [3], while the photolysis of **5** or of the substituted derivative **7** in solution mainly yields dimers containing two cyclobutane rings [2c,e-k]. On the other hand, crystals of **7** exhibit a high photostability, presumably because of the unfavorable alignment of the molecules in the crystal lattice.

The photochemical behavior of conjugated oligomers and polymers incorporating **1** or **5** as repeating units will be published separately [5].

References:

[1] (a) For example see: C. - M. Chung, A. Kunita, K. Hayashi, F. Nakamura, K. Saigo, M. Hasegawa, *J. Am. Chem. Soc.* **113**, 7316 (1991); b) For reviews see: W. L. Dilling, *Chem. Rev.* **83**, 1 (1983); M. Hasegawa, *Chem. Rev.* **83**, 507 (1983); M. Hasegawa, *Adv. Polym. Sci.* **42**, 1 (1982); V. Ramamurthy, K. Venkatsen, *Chem. Rev.* **87**, 433 (1987); and references cited in there.

[2] (a) C. D. Tulloch, W. Kemp, *J. Chem. Soc. (C)* **1971**, 2824; (b) W. H. Laarhoven, Th. J. H. M. Cuppen, *J. Chem. Soc., Perkin Trans. 1* **1972**, 2074; (c) P. H. G. op het Veld, W. H. Laarhoven, *J. Chem. Soc., Perkin Trans. 2* **1977**, 268; (d) A. Padwa, Ch. Doubleday, A. Mazzu, *J. Org. Chem.* **42**, 3271 (1977); (e) P. M. op den Brouw, W. H. Laarhoven, *J. Org. Chem.* **47**, 1546 (1982); (f) D. D. Morgan, S. W. Horgan, M. Orchin, *Tetrahedron Lett.* **1970**, 4347; (g) W. H. Laarhoven, J. A. M. van Broekhoven, *Tetrahedron Lett.* **1970**, 73; (h) J. Blum, M. Zimmerman, *Tetrahedron* **28**, 275 (1972); (i) M. W. Tausch, M. Elian, A. Bucur, E. Cioranescu, *Chem. Ber.* **110**, 1744 (1977); (j) W. Winter, U. Langjahr, H. Meier, J. Merkuschew, J. Juriew, *Chem. Ber.* **117**, 2452 (1984); (k) R. Zertani, H. Meier, *Chem. Ber.* **119**, 1704 (1986); (l) A. Böhm, K. Müllen, unpublished results.

[3] A. J. W. Tol, W. H. Laarhoven, *J. Org. Chem.* **51**, 1663 (1986).

[4] (a,b) M. D. Cohen, G. M. J. Schmidt, *J. Chem. Soc.* **1964**, 1996, 2000; (c) J. Bregman, K. Osaki, G. M. J. Schmidt, F. I. Sonntag, *J. Chem. Soc.* **1964**, 2021; (d) G. M. J. Schmidt, *Pure Appl. Chem.* **27**, 647,(1971); (e) F. Nakanishi, M. Hasegawa, *J. Polym. Sci.* **8**, *Part A-1* **1970**, 2151; (f) H. Takahashi, M. Sakuragi, M. Hasegawa, H. Takahashi, *J. Polym. Sci.* **10**, *Part A-1* **1972**, 1399; (g) H. G. Bührer, R. Aeschbach, T. Phillipou, J.-J. Parnaud, H.-G. Elias, *Makromol. Chem.* **157**, 13, (1972).

[5] A. Böhm, H. Mauermann, S. Stein, K. Müllen, to be published.

Experimental Data

X-ray data collection has been carried out on a four circle diffractometer (ENRAF-NONIUS). Graphite monochromatic $CuK\alpha$-Radiation ($\lambda = 1.5418\text{Å}$) has been used. The unit cell has been determined by least-square refinement of the scattering angles of 25 reflections with $\partial > 20°$.

Polarization-, Lorentz- and an empirical absorption correction has been applied. During the last least-square full matrix refinement, anisotropic temperature coefficients were given to C-atoms, while H-atoms at coordinates, which had been computed using the known bonding geometry, were refined in the "riding mode" with fixed isotropic temperature coefficients ($B_{Hxy} = B_{Cx} \cdot 1.3$)

Crystallographic data:

1 $C_{28}H_{22}$: Space group $P2_12_12_1$, unit cell:

$a = 14.711(1)$ Å, $b = 8.889(2)$ Å, $c = 15.832(1)$ Å, $Z = 4$, $V = 2070.1$ Å^3, $d_x = 1.150$ gcm^{-3}, $R = 4.2\%$, $R_w = 4.6\%$.

2 $C_{44}H_{54}$: Space group $P2_1/c$, unit cell:

$a = 17.149(1)$ Å, $b = 11.914(1)$ Å, $c = 18.685(3)$ Å, $\beta = 92.739(7)°$, $Z = 4$, $V = 3813.1$ Å^3, $d_x = 1.015$ gcm^{-3}, $R = 5.1\%$, $R_w = 4.6\%$.

For one of the two *tert.*-butyl groups of each styrene substituent two statistically occupied positions for each CH_3- group are found.

5a $C_{22}H_{18}$: Space group $P2_1/n$, unit cell:

$a = 13.022(1)$ Å, $b = 5.763(1)$ Å, $c = 22.217(1)$ Å, $ß = 102.364(3)°$, $Z = 4$, $V = 1628.6$ Å^3, $d_x = 1.152$ gcm^{-3}, $R = 3.3\%$, $R_w = 3.0\%$.

5b $C_{22}H_{18}$: Space group $P2_1/C$, unit cell:

$a = 14.887(5)$ Å, $b = 5.664(3)$ Å, $c = 19.182(1)$ Å, $ß = 92.815(7)°$, $Z = 4$, $V = 1615.6$ Å^3, $d_x = 1.161$ gcm^{-3}, $R = 3.8\%$, $R_w = 3.3\%$.

Atomic coordinates, bond lenghts and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.

Some spectroscopic data:

1 see ref. [2a - d], **5b** see ref. [2h - k], **6** see ref. [3]

2 mp = 127 - 128 °C; ^{1}H-NMR (200 MHz, CDCL$_3$): δ = 7.83 (d, 2H); 7.47 - 7.24 (m, 8H), 7.13 (s, 4H), 7.00 (dd, J = 16.0 Hz, 4H), 1.27 (s, 36H); ^{13}C-NMR (50 MHz, CDCl$_3$): δ = 150.8, 140.1, 137.2, 136.5, 131.0, 130.4, 127.8, 127.5, 127.1, 124.9, 121.8, 121.0, 34.8, 31.5; EI-mass-spectrum (rel. int.[%]): m/e = 582 (0.08), 404 (87.1), 178 (4.3), 57 (100).

3 ref. [2b]; ^{1}H-NMR (200 MHz, CDCl$_3$): δ = 7.83 (d, J = 7.2 Hz, 2H), 7.43 - 7.18 (m, 16H), 3,78 + 3.24 (AA'BB', 4H)

4 ^{1}H-NMR (200 MHz, CDCl$_3$): δ = 7.76 (d, J = 8.0 Hz, 2H), 7.27 (bs, 6H), 7.21 (s, 2H), 7.13 (s, 4H), 3.78 + 3.08 (AA'BB', 4H), 1.22 (s, 36H).

5a mp = 87 °C; ^{1}H-NMR (200 MHz, CDCl$_3$): δ = 7.16 (AA'BB', J = 5.5 Hz, 4H), 7.17 (s, 10H), 6.63 (dd, J = 12.2 Hz, 4H); ^{13}C-NMR (50 MHz, CDCL$_3$): δ = 137.1, 136.6, 130.8, 129.4, 129.2, 129.0, 128.1, 127.1, 127.0;

7 mp = 105 °C; ^{1}H-NMR (200 MHz, CDCl$_3$) : δ = 7.47 (s, 4H), 7.45 (AA'BB', 4H), 7.38 (s, 2H), 7.37 (dd, J= 16.0 Hz, 4H), 1.36 (s, 36H); ^{13}C-NMR (50 MHz, CDCl$_3$): δ = 151.2, 137.1, 136.3, 132.4, 127.8, 126.8, 126.1, 122.5, 121.1, 35.1 31.8; EI-mass-spectrum (rel. int. [%]): m/e = 506 (72.8), 449 (13.1), 303 (100), 203 (52.7), 57 (63.2).

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