

Synthesis, Photophysical and Photochemical Properties of Four [2.2] 'Cinnamophane' Isomers; Highly Efficient Stereospecific [2 + 2] Photocycloaddition

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Anchoring two acryloyl substituents onto a paracyclophane skeleton generates four 'cinnamophane' isomers, one of which, the pseudo-*gem*, undergoes a 'topochemical' reaction in solution.

Cinnamates are under continuous investigation because of their applications as photosensitive groups in polymer materials, molecular assemblies and UV filters.¹⁻³ *Trans*-cinnamic acids and related cinnamates are known to photodimerize readily in the crystalline state according to the topochemical rule established by Schmidt and coworkers.⁴ In contrast, in fluid solutions, the major photochemical event is *trans*-*cis* isomerization,^{5a} whereas the [2 + 2] cycloaddition becomes significant only with bichromophoric systems where the two cinnamoyl groups are linked together by a spacer.^{5b} In that case, however, several intramolecular photodimers can be formed owing to the flexibility of the molecule.⁵ In the solid, it is noteworthy for cinnamates (and homologues) that adopt a β -type stacking that the dimerization yield can never exceed *ca.* 86% for statistical reasons,² even for an ideal single crystal-single crystal transformation³ where no destruction of the crystalline habit of the reactants takes place.

It appeared to us that the topochemical reaction control in the crystalline state might be transferred to solution by employing appropriately substituted [2.2]paracyclophane derivatives, since those bridged aromatic systems are well-known for their rigidly defined intraannular distances. The [2.2]paracyclophane nucleus displays eight identical aromatic sites to anchor a substituent; substituting each ring once with the same group, one can generate four isomers: the pseudo-*gem* (1), -*ortho* (2), -*para* (3) and -*meta* (4) derivatives.

Considering acryloyl substituents, the pseudo-*gem* isomer 1 seems well suited to mimic the very first stage of the stacking arrangement of the β -type structure of *trans*-cinnamic acid. A spectroscopic and photochemical study of this compound in comparison with that of its stereoisomers was thus expected to provide a deeper insight into the understanding of bimolecular interactions of the cinnamate chromophore.

In this communication, we report on the synthesis of the four new cinnamophanes 1-4 and present the preliminary results of their spectrometric and photochemical behaviour.

The cinnamophanes 1-4 were synthesized from the bis-formyl derivatives⁶ using the standard Wittig-Horner procedure which is known to afford *trans*-olefins. To a stirred suspension of NaH (1 equiv.) in cooled THF (0°C) were

successively added, dropwise, pure (EtO)₂OPCH₂CO₂R (R = Me, Et 1; Me 2-4) (1 equiv.) and a solution of (4, *x*)diformyl[2.2]paracyclophane (0.24 equiv.) in dry THF. Compounds 1-4 were isolated in good overall yields (82-88%) as white solids. Their structures were fully characterized by the usual spectroscopic methods and elemental analysis. The structure of 1 (R = Me) was confirmed by X-ray analysis† (Fig. 1). As expected, the two substituents exhibit a high degree of parallelism, the double bonds being separated by *ca.* 3.5 Å (intermolecular: *ca.* 5.0 Å). The other bond lengths and angles are in the range of those observed for related paracyclophanes.^{7c}

The UV spectra of 2 and 4 are clearly different from those of 1 and 3; 2 and 4 display a single band above 250 nm with a maximum at 320 nm whereas 1 and 3 present an intense band peaking at *ca.* 290 nm with a shoulder at *ca.* 326-330 nm (Fig. 2).

Irradiation of 1 (R = Me or Et) for 0.5 h in methanol (6.8 × 10⁻³ mol dm⁻³) solution with a high-pressure mercury lamp gave only the corresponding cyclobutane derivative 5 ([2 + 2] intramolecular cycloaddition) in quantitative yields. The photoreaction could be followed by UV spectrometry, since 5 does not absorb at 290 nm (Fig. 2) as expected; the intramolecular dimerization induced a large hypsochromic shift of the absorption band.

In the crystalline state 1 (R = Me) is smoothly transformed on irradiation into 5 according to the topochemical rule. Intermolecular cycloaddition (which could result in polymer formation) is precluded because of the excessive distance between the reactive centres (*ca.* 5.0 Å). The structure of 5 was fully established by the usual spectroscopic and elemental analysis‡ and by the determination of its X-ray crystal structure.§

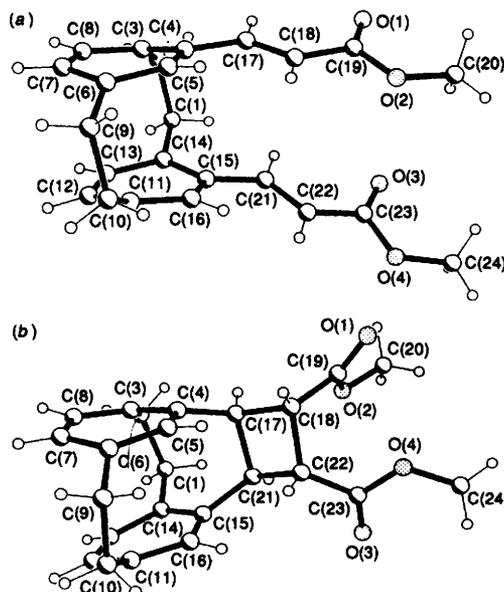
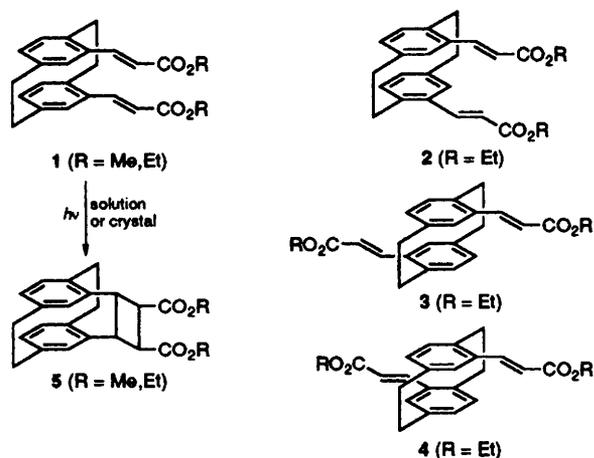


Fig. 1 The structures of compound 1 (a) and 5 (b) in the crystal. Radii are arbitrary.

The other cinnamophanes **2–4** did not give any intramolecular [2 + 2] photocycloaddition, consistent with the unfavourable arrangements of the reactive centres. Only *trans–cis* isomerization occurred, as revealed by ^1H NMR spectrometry; *e.g.*, after irradiation for 1 h in methanol ($2.6 \times 10^{-3} \text{ mol dm}^{-3}$), **3** was transformed into a 1:1 mixture of *trans–trans* and *cis–trans* isomers.

The photocycloaddition quantum yield Φ_R for **1** \rightarrow **5** (*ca.* 0.8) was found to be almost independent of the solvent (cyclohexane, 0.78; hexadecane, 0.73; MeCN, 0.82, MeOH, 0.81), the temperature (in methanol $\Phi_R = 0.81$ at 30°C and 0.84 at -90°C) and the presence of oxygen. It is the *highest* yield reported to date for any cinnamate.⁸ Remarkably, the chemical yield was found to be 100%.

Cinnamophanes **1–4** are poorly fluorescent and display structureless spectra with maxima around 450–470 nm. The excitation spectra were found to be independent of the emission wavelength and similar to the absorption spectra. The weak fluorescence quantum yields (Φ_F) (**1**, $\Phi_F = 6 \times 10^{-4}$; **2–4**, $\Phi_F = 3–6 \times 10^{-2}$) underline the occurrence of very efficient non-radiative channels for the deactivation of the singlet excited state. The fluorescence process was not found to be strongly sensitive to temperature: cooling the solution (from 20 to -90°C) led to a significant change only for **1**, for which Φ_F reached 0.18×10^{-2} at 90°C , but the value remains very low. The fluorescence decays \ddagger recorded for **2–4** (but not for **1**, too poorly fluorescent) were found to be single exponential (15–18 ns) indicating the presence of only one emitting species in the nanosecond range.

As virtually no temperature effect was observed on fluorescence efficiency (down to 183 K) and photocycloaddition, the latter has negligible activation energy whatever the nature of the excited state responsible for the reaction.

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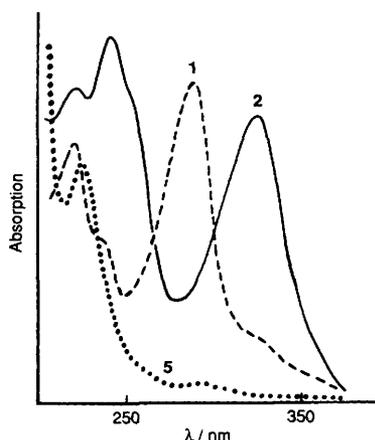


Fig. 2 Electronic absorption spectra of **1**, **2** and **5** in methanol at room temperature

Footnotes

† *Crystal data* for **1**: $\text{C}_{24}\text{H}_{24}\text{O}_4$, monoclinic, space group $P2_1$, $a = 7.180(2)$, $b = 11.803(2)$, $c = 11.617(2)$ Å, $\beta = 103.06(3)^\circ$, $V = 959.0(4)$ Å³, $Z = 2$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu = 0.09 \text{ mm}^{-1}$, $D_c = 1.304 \text{ Mg m}^{-3}$, $T = 163 \text{ K}$. A total of 3781 intensities (2314 unique) were measured to $2\theta 50^\circ$ on a Stoe-Stadi-4 diffractometer with a Siemens LT-2 low-temperature attachment. The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included with a riding model. The final $wR(F^2)$ for all reflections was 0.127, with a conventional $R(F)$ of 0.051, for 255 parameters.

‡ Photoproduct **5**: 100% yield, mp 197°C . ^1H NMR (CDCl_3): δ 6.49 (2H, dd, J 7.8, 1.7 Hz), 6.23 (2H, d, J 7.8 Hz), 6.19 (2H, d, J 1.7 Hz), 4.72–4.70 (2H, m, cyclobutane ring), 3.78 (6H, s), 3.19–3.15 (2H, m, ethane bridge). Satisfactory elemental analysis was obtained. UV (methanol) λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1}$) 196 (54 575), 226(sh) (15 740), 244 (5321), 258(sh) (1367).

§ *Crystal data* for **5**: $\text{C}_{24}\text{H}_{24}\text{O}_4$, monoclinic, space group $P2_1/c$, $a = 7.715(3)$, $b = 14.741(5)$, $c = 17.083(5)$ Å, $\beta = 102.99(3)^\circ$, $V = 1893.1(11)$ Å³, $Z = 4$, $D_c = 1.321 \text{ Mg m}^{-3}$, $T = 153 \text{ K}$. Other details as above, with the following differences: 4490 intensities (4365 unique), $2\theta_{\text{max}} 55^\circ$, $wR(F^2)$ 0.267, $R(F)$ 0.087, 255 parameters. The rather high R values are associated with residual electron density (max. $1.6 \text{ e } \text{Å}^{-3}$) near C(20) and C(24), probably indicating a slight disorder.

Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material can be obtained on quoting the full literature citation and the reference numbers CSD 400778 (**1**), CSD 400777 (**5**). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ The fluorescence decays were measured by single photon timing. The authors thank Professor F. De Schryver for kindly providing us with the DECAN (1.0) program for decay curves analysis (T. de Roeck, N. Boens, J. Dockx, copyright 1991).

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- P. L. Egerton, E. Pitts and A. Reiser, *Macromolecules*, 1981, **14**, 95. The photodimerization quantum yield of α -cinnamic acid in the crystal was reported to be *ca.* 0.7.