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Key indicators

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$ R factor = 0.047 wR factor = 0.129

Data-to-parameter ratio = 13.9

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

A photodimer of a 4-phenyl-4H-pyran

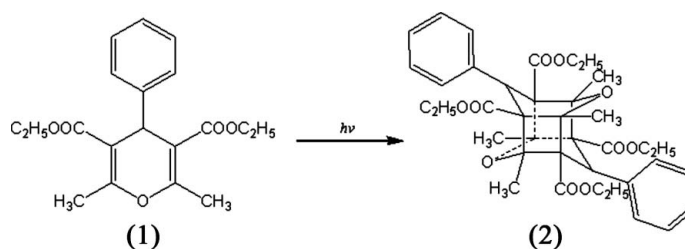
A new cage photodimer, tetraethyl 2,4,8,10-tetramethyl-6,12-diphenyl-3,9-dioxapentacyclo[6.4.0.0^{2,7}.0^{4,11}.0^{5,10}]dodecane-1,5,7,11-tetracarboxylate, $\text{C}_{38}\text{H}_{44}\text{O}_{10}$, was prepared through [2+2]-photocycloaddition of diethyl 2,6-dimethyl-4-phenyl-4H-pyran-3,5-dicarboxylate in the solid state. The molecular structure was elucidated by X-ray diffraction analysis, ^1H NMR, IR and mass spectroscopy, and elemental analysis. The molecule possesses a crystallographically imposed centre of symmetry. The crystal structure is stabilized by weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bond interactions.

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Comment

The nature of the interaction between the double bonds in 4-pyrone and 1,4-dihydropyridine systems is currently of interest. They have yielded almost exclusively head-to-tail cage dimers in the solid state and follow a double [2+2]-cycloaddition reaction pathway to give tetraasteranes (Hilgeroth *et al.*, 1998; Ahlgren & Akermark, 1974). The cage dimers of 1,4-dihydropyridine hold promise as a novel non-peptidic class of HIV protease inhibitors, and are playing an increasing role in the defeat of AIDS (Hilgeroth *et al.*, 1999). Although the photochemistry of the 4H-pyran system has not received much attention in the literature to date, we have devoted considerable effort to investigating its potential activity as an HIV protease inhibitor. In addition, there are no reports of photochemical reactions associated with a 4-phenyl-4H-pyran, especially in the solid state. Also, we wished to know whether there are steric differences between substituted 4-phenyl-4H-pyran and 1,4-dihydropyridine which would prevent dimerization, since 4-aryl-1,4-dihydropyridines are known to be remarkable inhibitors of photolysis when they are 2,6-dimethyl-substituted (Eisner *et al.*, 1970). Differences in the dimerization of these compounds could also be related to



electronic effects. At present, we cannot distinguish between these factors, but further research might answer this question. The only recorded example of a photodimer of the similar 2,6-dimethyl-4-pyrone system (Yates & Jorgenson, 1963) aroused our interest in the photodimerization of these species. Encouraged by these studies, the corresponding 2,6-dimethyl-

3,5-bis-[carboxylato(ethyl)]-4-phenyl-4*H*-pyran, (1), whose dimers could possibly be functionalized, was prepared.

Compound (1) was readily prepared by the cyclocondensation of β -dicarbonyl compounds or α,β -unsaturated ketones with aldehydes under zinc chloride catalysis (Urbahn *et al.*, 1998). By irradiation of the solid monomer, (1), with a high-pressure Hg lamp, we obtained the title compound, (2), in a yield of *ca* 30% after 8 h. The same product was also obtained by similar irradiation of a solution of (1) in acetic acid, ethanol or benzene. However, the yield of (2) was considerably lower in these cases.

The dimer, (2), is sparingly soluble in most organic solvents, but can be readily crystallized from methanol and dichloromethane. Single-crystal X-ray diffraction and other analytical data established the molecular structure of the new cage photodimer, (2), formed by a solid-state reaction (Fig. 1).

Compound (2) possesses a crystallographically imposed centre of symmetry. Bond distances and angles (Table 1) are within normal ranges (Allen *et al.*, 1987). The crystal structure is stabilized by weak intra- and intermolecular C—H...O hydrogen bonds (Table 2).

Experimental

For the solid-state dimerization reaction of diethyl 2,6-dimethyl-4-phenyl-4*H*-pyran-3,5-dicarboxylate, (1), the compound (0.5 g) was dissolved in dichloromethane (5 ml) and poured into the photolysis unit. The solvent was vaporized, which caused (1) to adhere uniformly to the wall of the Pyrex vessel, where the material was irradiated by a high-pressure Hg lamp located at a distance of 20 cm from the reactant. The reaction was monitored by thin-layer chromatography. After 8 h, the reactant was almost completely converted. Colourless single crystals of (2) suitable for X-ray analysis were obtained by slow evaporation of a methanol–dichloromethane solution (3:1 *v/v*) in a yield of 30% (0.15 g; m.p. 541–542 K).

Crystal data

| | |
|--------------------------------|---|
| $C_{38}H_{44}O_{10}$ | $Z = 2$ |
| $M_r = 660.73$ | $D_x = 1.273 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 10.809 (2) \text{ \AA}$ | $\mu = 0.09 \text{ mm}^{-1}$ |
| $b = 11.284 (2) \text{ \AA}$ | $T = 293 (2) \text{ K}$ |
| $c = 14.314 (3) \text{ \AA}$ | Block, colourless |
| $\beta = 99.18 (3)^\circ$ | $0.30 \times 0.25 \times 0.15 \text{ mm}$ |
| $V = 1723.5 (6) \text{ \AA}^3$ | |

Data collection

| | |
|---|--|
| Rigaku R-AXIS RAPID IP diffractometer | 10246 measured reflections |
| ω scans | 3040 independent reflections |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | 1876 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.973$, $T_{\max} = 0.986$ | $R_{\text{int}} = 0.034$ |
| | $\theta_{\text{max}} = 25.0^\circ$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.073P)^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.047$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.129$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| $S = 0.97$ | $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$ |
| 3040 reflections | $\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$ |
| 219 parameters | Extinction correction: SHELXL97 |
| H-atom parameters constrained | (Sheldrick, 1997) |
| | Extinction coefficient: 0.0123 (18) |

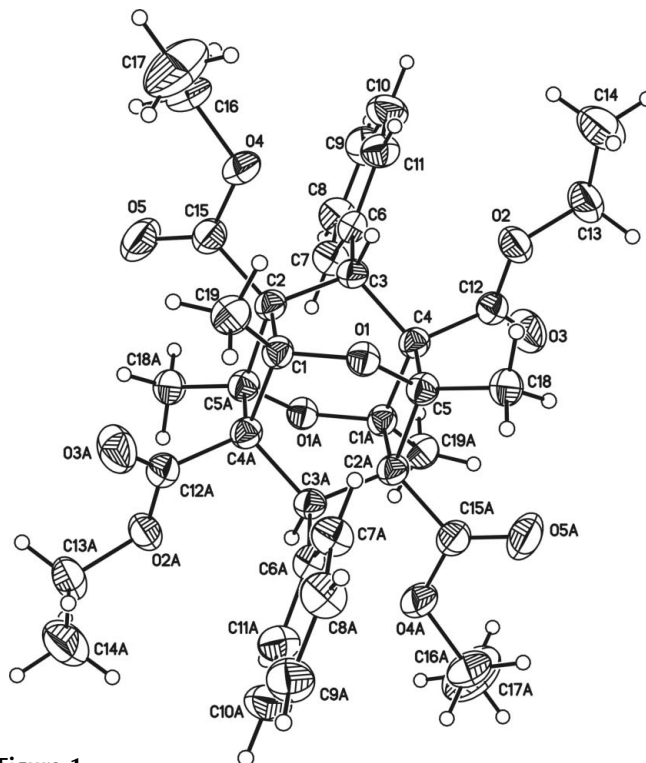


Figure 1
The molecular structure of (2), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Atoms labelled with the suffix A are at the symmetry position ($-x, 1 - y, -z$).

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|------------------------|-------------|-----------------------|-------------|
| O1—C1 | 1.428 (2) | C2—C3 | 1.538 (3) |
| O1—C5 | 1.439 (2) | C2—C5 ⁱ | 1.576 (3) |
| C1—C4 ⁱ | 1.572 (3) | C3—C4 | 1.552 (3) |
| C1—C2 | 1.587 (3) | C4—C5 | 1.569 (3) |
| C1—O1—C5 | 118.56 (14) | C2—C3—C4 | 109.72 (15) |
| O1—C1—C4 ⁱ | 112.54 (15) | C3—C4—C5 | 111.80 (16) |
| O1—C1—C2 | 112.12 (15) | C3—C4—C1 ⁱ | 114.21 (15) |
| C4 ⁱ —C1—C2 | 89.94 (14) | C5—C4—C1 ⁱ | 90.18 (14) |
| C3—C2—C5 ⁱ | 114.62 (16) | O1—C5—C4 | 112.05 (15) |
| C3—C2—C1 | 111.40 (15) | O1—C5—C2 ⁱ | 112.04 (15) |
| C5 ⁱ —C2—C1 | 89.35 (14) | C4—C5—C2 ⁱ | 90.44 (14) |

Symmetry code: (i) $-x, -y + 1, -z$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------|-------|-------------|-------------|---------------|
| C16—H16A...O5 | 0.97 | 2.24 | 2.656 (3) | 105 |
| C7—H7...O1 ⁱ | 0.93 | 2.36 | 3.080 (3) | 135 |
| C18—H18B...O5 ⁱ | 0.96 | 2.36 | 2.802 (3) | 107 |
| C13—H13B...O3 ⁱⁱ | 0.97 | 2.44 | 3.402 (3) | 171 |

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z$.

All H atoms were positioned geometrically (C—H = 0.93–0.98 \AA) and included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic, methylene and methine H atoms, or $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Data collection: RAPID-AUTO (Rigaku, 2000); cell refinement: RAPID-AUTO; data reduction: CrystalStructure (Rigaku/MS,

2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXL97*.

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