# Crystal Structure and Photochemistry of Dimethyl 1,4-Dihydro-1,4,5,8-tetramethyl-1,4-ethenonaphthalene-2,3-dicarboxylate

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## Abstract

The photochemical rearrangement of a bridgehead-methylated 1,4-ethenonaphthalene has been studied by crystal structure analyses of (1b) and two of its photoproducts (2b and 3b). Crystal data: $T = 295$ K, Cu $K\alpha$, $\lambda = 1.54178$ Å, $C_{20}H_{22}O_4$, $M_r = 326.39$. Dimethyl 1,4-dihydro-1,4,5,8-tetramethyl-1,4-etheno-naphthalene-2,3-dicarboxylate (1b), $P2_1c$, $a = 12.643$ (1), $b = 9.288$ (1), $c = 15.153$ (1) Å, $\beta = 105.70$ (1)°, $Z = 4$, $R = 0.037$ for 1974 reflections with $I > 3\sigma(I)$. Dimethyl 2a,2b,6b,6c-tetrahydro-1,2b,3,6-tetramethylbenzo[a]cyclopropa[c,d]penta-lene-6b,6c-dicarboxylate (2b), $Pca2_1$, $a = 7.325$ (1), $b = 14.781$ (1), $c = 15.535$ (1) Å, $Z = 4$, $R = 0.045$ for 1419 reflections. Dimethyl 1,4,6,9-tetramethylbenzo-cyclooctatetraene-5,10-dicarboxylate (3b), $Pbca$, $a = 17.716$ (2), $b = 15.298$ (2), $c = 13.210$ (3) Å, $Z = 8$, $R = 0.046$ for 2265 reflections. Molecule (1b) exhibits steric strain, as a result of short intramolecular Me···Me contacts [2.963 (5) and 3.013 (5) Å]. The formation of photoproducts (2b) and (3b) can be rationalized in terms of mechanisms involving benzo-vinyl bonding, which relieves the steric crowding between methyl groups.

## Introduction

Previous photochemical and crystallographic studies of bridgehead-methylated dibenzobarrelene derivatives have shown that these compounds undergo unusual photo-rearrangements compared with their non-methylated counterparts (Pokkuluri, Scheffer & Trotter, 1990, 1993a,b,c). To determine whether such reactivity differences apply to other systems, related monobenzobarrelene derivatives have now been studied. Photolysis of solutions of diester (1a) produces the benzosemibullvalene (2a) on benzo-phenone-sensitized irradiation (*via* the triplet state) and benzocyclooctatetraene (3a) on direct irradiation (*via* the singlet state) (Scheffer & Yap, 1989; Trotter, 1989). Solution photolysis of the tetramethylated compound (1b) resulted in (2b) on sensitized and (2b) and (3b) on direct irradiation. The structures of (2b) and (3b) have now been established by crystal structure analysis and the crystal structure of (1b) has also

been determined, allowing mechanisms for the photoreaction of (1b) to be proposed.



(a) $R = $ H, $E = $ COOMe
(b) $R = $ Me, $E = $ COOMe

(1)

(2a)        (2b)

+           +

(3a)        (3b)
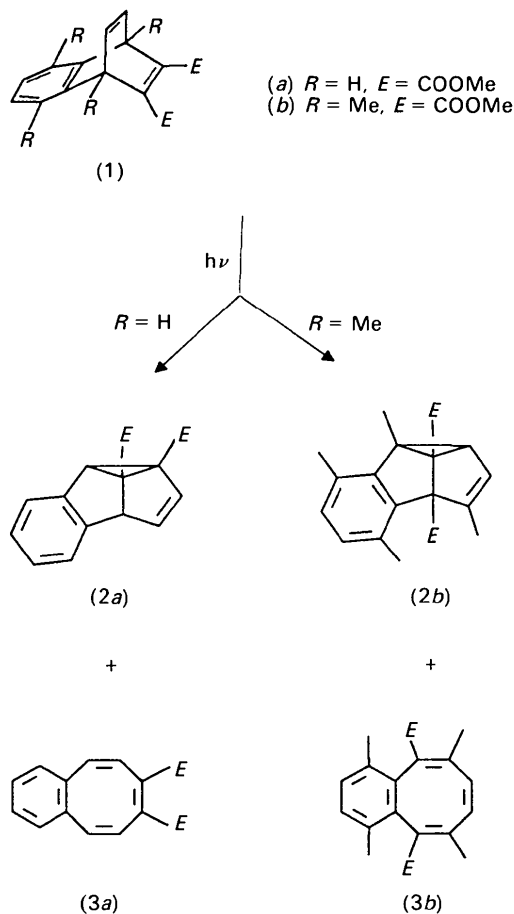
## Experimental

Unit-cell parameters and X-ray intensities, measured on a Rigaku AFC6-S diffractometer, are summarized in Table 1. All three structures were solved by direct methods and refined by full-matrix least-squares procedures with $w = 1/\sigma^2(F)$. All non-H atoms in the three structures were refined anisotropically. For (1b) and (3b), H atoms were located from difference maps and positional and isotropic thermal parameters

were refined. The C15 and C16 H atoms in (3b) are disordered over two sets of sites; these H atoms were placed in calculated positions, based on the difference map, and one site occupancy factor for each group was refined, to 0.56/0.44 for C15 H atoms and 0.59/0.41 for C16. For (2b), H atoms were placed in calculated positions and not refined. For (2b), refinement of the opposite polarity gave no significant difference in R factors. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV) and computer programs as supplied in *TEXSAN* (Molecular Structure Corporation, 1989). Details of the refinements are given in Table 1.

## Discussion

Final positional parameters are given in Table 2, selected molecular parameters in Table 3 and other data have been deposited.*

The structure and dimensions of the molecule of the ethenonaphthalene diester (1b) are quite similar to those of related di- and monobenzobarrelenes (Pokkuluri, Scheffer & Trotter, 1993a,b; Trotter, 1989). The bond angles external to the aromatic ring, mean 126.3 (2)°, are distorted to about the same extent as in the other derivatives. The C2—C3 and C9—C10 distances, 1.321 (4) and 1.304 (5) Å, correspond to double bonds (Fig. 1). The two ester groups are rotated out of the plane of the C2=C3 double bond, so that there is only partial conjugation with the C=O bonds of the ester groups; C=C—C=O torsion angles are −62.5 (3)° at the C2 ester group [$\cos^2$(angle) = 0.21] and 132.3 (3)° at the C3 group [$\cos^2$(angle) = 0.45]. The C—$CO_2$Me bond lengths [1.493 (3) and 1.485 (3) Å] are in accordance with this difference in the amount of conjugation (although the bond-length difference is not statistically significant). A major difference between the molecules of (1a) (Trotter, 1989) and (1b) is steric strain in (1b) as a result of the proximity of the substituent methyl groups. The C11···C18 and C16···C17 non-bonded distances (Fig. 1) are 2.963 (5) and 3.013 (5) Å, respectively, much shorter than the normal van der Waals distance of 4 Å; the repulsion between the methyl groups results in distortion of the bond angles, with C—C—Me increased to 127.4 (2)° at the aromatic C atoms and 119.3 (2)° at the bridgehead C atoms. The bridgehead-aromatic ring C—C bonds are also stretched, the C1—C8A and C4—C4A bond lengths being 1.566 (3) and 1.561 (3) Å, respectively.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR0027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal data, data collection and refinement parameters*

| | (1b) | (2b) | (3b) |
|---|---|---|---|
| **Crystal data** | | | |
| Compound | (1b) | (2b) | (3b) |
| Formula | $C_{20}H_{22}O_4$ | $C_{20}H_{22}O_4$ | $C_{20}H_{22}O_4$ |
| $M_r$ | 326.39 | 326.39 | 326.39 |
| Dimensions | 0.5 × 0.2 × 0.05 | 0.35 × 0.35 × 0.15 | 0.4 × 0.25 × 0.15 |
| Crystal system | Monoclinic | Orthorhombic | Orthorhombic |
| Space group | $P2_1/c$ | $Pca2_1$ | $Pbca$ |
| a (Å) | 12.643 (1) | 7.325 (1) | 17.716 (2) |
| b (Å) | 9.288 (1) | 14.781 (1) | 15.298 (2) |
| c (Å) | 15.153 (1) | 15.535 (1) | 13.210 (3) |
| β (°) | 105.70 (1) | 90 | 90 |
| V (Å³) | 1713 (1) | 1682 (1) | 3580 (2) |
| Z | 4 | 4 | 8 |
| $D_c$ (g cm⁻³) | 1.27 | 1.29 | 1.21 |
| F(000) | 696 | 696 | 1392 |
| μ (cm⁻¹) | 6.7 | 6.8 | 6.4 |
| **Data collection** | | | |
| Reflections for cell | | | |
| Number | 25 | 24 | 19 |
| 2θ (°) | 25–42 | 89–112 | 68–88 |
| $2\theta_{max}$ (°) | 155.2 | 155.2 | 155.2 |
| Scan type | ω–2θ | ω–2θ | ω 2θ |
| ω scan width (°), a + b tan θ | | | |
| a | 1.21 | 1.21 | 1.10 |
| b | 0.20 | 0.20 | 0.20 |
| Scan speed* (° min⁻¹) | 32.0 | 32.0 | 16.0 |
| h | 0–16 | 0–9 | 0–22 |
| k | 0–12 | 0–20 | 0–19 |
| l | −19–19 | 0–19 | −17–0 |
| Decay (%) | 2.3 | 0.7 | 1.1 |
| Absorption | ψ scans | ψ scans | ψ scans |
| Transmission | 0.94–1.0 | 0.98–1.0 | 0.57–1.0 |
| Total unique reflections | 3730 | 1831 | 4139 |
| Reflections > 3σ(I) | 1974 | 1419 | 2265 |
| % | 52.9 | 77.5 | 54.7 |
| **Refinements** | | | |
| No. of parameters | 306 | 217 | 284 |
| Observations/ parameters | 6.45 | 6.53 | 7.97 |
| $\Delta/\sigma_{max}$ | 0.0004 | 0.007 | 0.002 |
| GOF | 1.98 | 3.90 | 2.75 |
| $\Delta\rho$ (e Å⁻³) | −0.17 to +0.14 | −0.18 to +0.20 | −0.28 to +0.30 |
| R | 0.037 | 0.045 | 0.046 |
| $R_w$ | 0.033 | 0.047 | 0.042 |
| Extinction (× 10⁶) | 1.22 | 5.85 | 0.29 |
| p factor† | 0 | 0 | 0 |

* Up to eight rescans for reflections with $I < 40\sigma(I)$.

† $\sigma^2(I) = S + 4(B_1 + B_2) + (pI)^2$, where $S$ = scan, $B_1$ and $B_2$ = background counts.

The ring system in photoproduct (2b) shows the usual additional strain as a result of the formation of the three-membered ring (Pokkuluri, Scheffer & Trotter 1993b). The external angles at the five/six-membered ring junction are increased to 129.0 (4)°; angles in the three-membered ring are in the range 58.9–61.1 (3)°. The benzocyclooctatetraene photoproduct (3b) has a molecular structure similar to that of the related dibenzo analogues (Pokkuluri, Scheffer & Trotter, 1993a,b,c), with a tub conformation for the eight-membered ring. The bond angles at the ring junction show little distortion from normal values, mean external angle 119.3 (2)°, and the angles in the

Table 2. *Positional and equivalent isotropic thermal parameters, with standard deviations in parentheses*

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

(1b)

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| O1 | 0.1018 (1) | 0.5415 (2) | 0.2206 (1) | 5.62 (8) |
| O2 | 0.1863 (1) | 0.4480 (2) | 0.1228 (1) | 5.65 (8) |
| O3 | 0.0405 (1) | 0.2035 (2) | 0.1519 (1) | 4.72 (7) |
| O4 | 0.1603 (2) | 0.0283 (2) | 0.1471 (1) | 6.7 (1) |
| C1 | 0.2995 (2) | 0.3993 (2) | 0.3611 (1) | 4.0 (1) |
| C2 | 0.2189 (2) | 0.3457 (3) | 0.2720 (1) | 3.8 (1) |
| C3 | 0.2041 (2) | 0.2049 (3) | 0.2669 (1) | 4.1 (1) |
| C4 | 0.2680 (2) | 0.1210 (3) | 0.3524 (2) | 4.5 (1) |
| C4A | 0.3906 (2) | 0.1624 (3) | 0.3636 (1) | 4.2 (1) |
| C5 | 0.4788 (2) | 0.0677 (3) | 0.3729 (1) | 5.0 (1) |
| C6 | 0.5822 (2) | 0.1299 (4) | 0.3825 (2) | 5.8 (1) |
| C7 | 0.5971 (2) | 0.2735 (4) | 0.3813 (2) | 5.5 (1) |
| C8 | 0.5106 (2) | 0.3717 (3) | 0.3718 (1) | 4.4 (1) |
| C8A | 0.4071 (2) | 0.3125 (3) | 0.3655 (1) | 4.0 (1) |
| C9 | 0.2565 (2) | 0.3355 (4) | 0.4378 (2) | 4.6 (1) |
| C10 | 0.2410 (2) | 0.1966 (4) | 0.4334 (2) | 4.9 (1) |
| C11 | 0.3068 (2) | 0.5624 (3) | 0.3697 (2) | 5.2 (1) |
| C12 | 0.1687 (2) | 0.4480 (3) | 0.1962 (1) | 3.9 (1) |
| C13 | 0.0584 (3) | 0.6548 (4) | 0.1555 (3) | 7.1 (2) |
| C14 | 0.1356 (2) | 0.1323 (3) | 0.1836 (2) | 4.4 (1) |
| C15 | -0.0286 (3) | 0.1540 (5) | 0.0646 (2) | 6.7 (2) |
| C16 | 0.2344 (3) | -0.0377 (4) | 0.3494 (3) | 6.4 (2) |
| C17 | 0.4752 (3) | -0.0938 (4) | 0.3729 (3) | 6.5 (2) |
| C18 | 0.5392 (3) | 0.5282 (4) | 0.3679 (2) | 5.8 (1) |

(2b)

| | | | | |
|---|---|---|---|---|
| O1 | 0.4791 (4) | 0.6414 (2) | 0.9706 | 3.8 (1) |
| O2 | 0.7810 (4) | 0.6329 (2) | 0.9940 (3) | 4.3 (1) |
| O3 | 0.6338 (5) | 0.5313 (2) | 0.8386 (3) | 4.3 (1) |
| O4 | 0.5069 (7) | 0.5493 (2) | 0.7109 (3) | 7.2 (2) |
| C1 | 0.8565 (5) | 0.7624 (2) | 0.8555 (4) | 3.1 (2) |
| C2 | 0.8750 (6) | 0.7698 (3) | 0.7712 (4) | 3.7 (2) |
| C2A | 0.7262 (7) | 0.7275 (3) | 0.7228 (4) | 3.7 (2) |
| C2B | 0.5241 (6) | 0.7549 (3) | 0.7349 (3) | 3.4 (2) |
| C2C | 0.4828 (5) | 0.8291 (3) | 0.7971 (3) | 2.9 (2) |
| C3 | 0.3942 (5) | 0.9118 (3) | 0.7832 (4) | 3.5 (2) |
| C4 | 0.3617 (6) | 0.9662 (3) | 0.8540 (4) | 4.0 (2) |
| C5 | 0.4141 (6) | 0.9417 (3) | 0.9349 (4) | 3.9 (2) |
| C6 | 0.5130 (5) | 0.8622 (2) | 0.9502 (3) | 3.2 (2) |
| C6A | 0.5438 (5) | 0.8066 (2) | 0.8805 (3) | 2.6 (1) |
| C6B | 0.6658 (5) | 0.7221 (2) | 0.8751 (3) | 2.5 (1) |
| C6C | 0.6092 (6) | 0.6791 (2) | 0.7884 (4) | 3.2 (2) |
| C7 | 0.9848 (7) | 0.7982 (3) | 0.9223 (4) | 4.3 (2) |
| C8 | 0.3941 (7) | 0.7345 (4) | 0.6612 (4) | 4.7 (2) |
| C9 | 0.3378 (8) | 0.9453 (3) | 0.6949 (4) | 5.6 (3) |
| C10 | 0.5711 (8) | 0.8403 (3) | 1.0411 (4) | 4.6 (2) |
| C11 | 0.6536 (6) | 0.6601 (2) | 0.9539 (3) | 3.1 (2) |
| C12 | 0.4501 (8) | 0.5773 (3) | 1.0406 (4) | 5.1 (2) |
| C13 | 0.5748 (6) | 0.5810 (3) | 0.7736 (4) | 3.7 (2) |
| C14 | 0.6068 (8) | 0.4344 (3) | 0.8324 (4) | 5.3 (3) |

(3b)

| | | | | |
|---|---|---|---|---|
| O1 | 0.1456 (1) | 0.3559 (1) | 0.7151 (1) | 5.0 (1) |
| O2 | 0.2401 (1) | 0.4224 (2) | 0.6396 (2) | 7.4 (1) |
| O3 | 0.0405 (1) | 0.3256 (1) | 0.6846 (1) | 5.3 (1) |
| O4 | -0.1132 (1) | 0.3901 (2) | 0.5749 (2) | 9.5 (2) |
| C1 | 0.0042 (1) | 0.1547 (1) | 0.5639 (2) | 2.8 (1) |
| C2 | 0.0477 (1) | 0.0827 (2) | 0.5895 (2) | 3.4 (1) |
| C3 | 0.1249 (1) | 0.0892 (2) | 0.6012 (2) | 3.4 (1) |
| C4 | 0.1614 (1) | 0.1686 (1) | 0.5877 (2) | 2.8 (1) |
| C4A | 0.1188 (1) | 0.2420 (1) | 0.5611 (2) | 2.35 (9) |
| C5 | 0.1586 (1) | 0.3273 (1) | 0.5439 (2) | 2.6 (1) |
| C6 | 0.1699 (1) | 0.3586 (2) | 0.4506 (2) | 3.0 (1) |
| C7 | 0.1320 (2) | 0.3184 (2) | 0.3631 (2) | 3.8 (1) |
| C8 | 0.0585 (2) | 0.3133 (2) | 0.3504 (2) | 4.1 (1) |
| C9 | 0.0017 (1) | 0.3464 (2) | 0.4228 (2) | 3.4 (1) |
| C10 | -0.0044 (1) | 0.3127 (2) | 0.5163 (2) | 2.6 (1) |
| C10A | 0.0405 (1) | 0.2348 (1) | 0.5482 (2) | 2.37 (9) |

Table 2 (*cont.*)

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| C11 | -0.0801 (2) | 0.1442 (2) | 0.5549 (3) | 4.3 (1) |
| C12 | 0.2460 (2) | 0.1734 (2) | 0.6009 (3) | 4.5 (2) |
| C13 | 0.1869 (1) | 0.3737 (2) | 0.6349 (2) | 3.5 (1) |
| C14 | 0.1631 (3) | 0.4019 (4) | 0.8079 (3) | 7.4 (3) |
| C15 | 0.2180 (1) | 0.4359 (2) | 0.4221 (2) | 4.6 (1) |
| C16 | -0.0456 (2) | 0.4206 (2) | 0.3809 (2) | 5.8 (2) |
| C17 | -0.0581 (1) | 0.3476 (2) | 0.5919 (2) | 3.7 (1) |
| C18 | -0.0885 (3) | 0.3553 (4) | 0.7659 (4) | 8.2 (3) |

Table 3. *Ranges or averages of bond lengths (Å) and angles (°)*

| | (1b) | (2b) | (3b) |
|---|---|---|---|
| C=C | 1.321, 1.304 (5) | 1.321 (8) | 1.316–1.342 (3) |
| C—C (aromatic) | 1.348–1.409 (5) | 1.363–1.410 (8) | 1.381–1.403 (3) |
| C—CO$_2$Me | 1.493, 1.485 (3) | 1.532, 1.489 (6) | 1.483, 1.478 (3) |
| C—C (other) | 1.501–1.566 (4) | 1.464–1.549 (6) | 1.470–1.516 (4) |
| C=O | 1.195 (3) | 1.191 (6) | 1.199 (3) |
| C—OMe | 1.337 (3) | 1.328 (6) | 1.312 (3) |
| O—Me | 1.447 (3) | 1.453 (6) | 1.446 (5) |
| Angles | | | |
| Ring junction (external) | 126.3 (2) | 129.0 (4) | 119.3 (2) |
| C—C($sp^2$)—Me | 127.4, 116.2 (2) | 123.8, 119.0 (4) | 122.1, 119.2; 126.0, 113.2 (2) |
| C—C($sp^3$)—Me | 119.3, 113.4 (2) | 120.4, 117.1 (4) | – |
| C—C—C (three-ring) | – | 58.9–61.1 (3) | – |
| C—C—C (eight-ring) | – | – | 119.9–125.2 (3) |

eight-membered ring are in the range 119.9–125.2 (2)°, with the largest values at the unsubstituted C atoms. The bond lengths in the eight-membered ring correspond to double [1.316–1.342 (3) Å], aromatic [1.403 (3) Å] and single bonds [1.470–1.500 (3) Å]. The ester groups are not far from fully conjugated with the neighbouring C=C double bond systems; C=C—C=O torsion angles are −26.5 (4)° for the C5 ester group [cos$^2$(angle) = 0.80] and 21.0 (4)° for the C10 group [cos$^2$(angle) = 0.87]. The C—CO$_2$Me bond lengths, mean 1.480 (3) Å, are (barely significantly) shorter than the lengths in (1b) [mean 1.489 (3) Å].

*Photochemistry of* (1b)

Photolysis of the tetramethylated compound (1b) produces photoproducts (2b) and (3b) with substitution patterns quite different from those derived from the parent compound (1a) (which gives 2a and 3a). The factor which causes this different behaviour is most likely the steric crowding resulting from the intramolecular Me···Me contacts of 2.96 and 3.01 Å in (1b). The mechanism proposed for the formation of (3a) from (1a) involves initial intramolecular [2 + 2] photocycloaddition between the two vinyl groups, followed by electrocyclic ring opening (Bender & Brooks, 1975). The same pathway in (1b) would involve initial bond formations C2—C9 and C3—C10 (Fig. 1). This would result in methyl groups C11 and C16 moving even closer to methyl
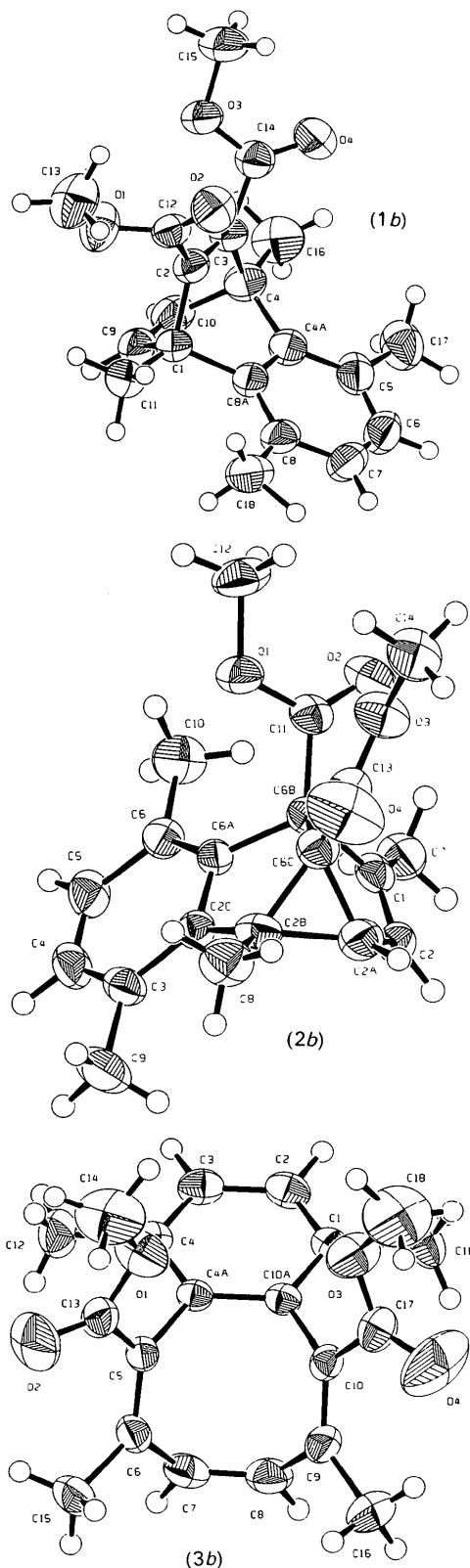
groups C18 and C17; molecular modelling calculations indicate Me⋯Me separations of *ca* 2.86 Å in the intermediate [2 + 2] cycloadduct (Jones, Scheffer, Trotter & Yap, 1993).

The formation of the experimentally observed singlet-state photoproduct (3b) can be rationalized as occurring through intramolecular photocycloaddition in (1b) between the ester-substituted double bond and the double bond of the aromatic ring, followed by electrocyclic reorganization. This mechanism relieves the steric crowding between the methyl groups, the formation of C2—C8A and C3—C4A bonds increasing the C11⋯C18 and C16...C17 contacts (to *ca* 3.1 Å). This sterically favoured pathway leads to (3b) and appears to be followed, despite the fact that it involves initial disruption of aromaticity.

The formation of photoproduct (2b) from (1b) can be analysed in a similar manner: sterically-assisted benzo-vinyl bridging (rather than the vinyl–vinyl bridging in 1a), followed by opening of the new three-membered ring to regenerate aromaticity and form a tertiary allylic radical, and final closure to give 2(b).
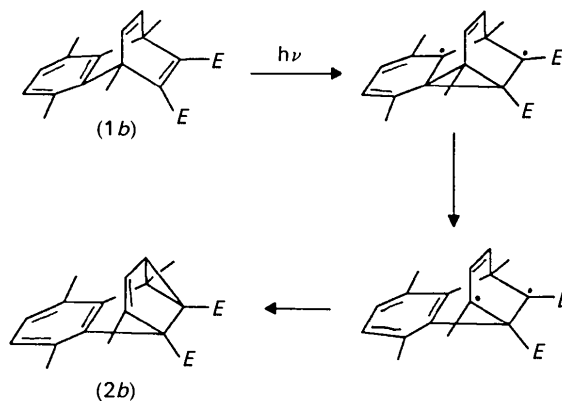
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Fig. 1. Structures of (1b), (2b) and 3(b) (50% thermal probability ellipsoids).