

The main product (1c) clearly demonstrates an addition/elimination reaction took place *via* a Michael-type addition at the electronically favourable position C(5) and the concomitant, well known (Finley, 1974) substitution of the C(2) methoxy group by the *N*-nucleophile (formally an amination/dealkoxylation of a vinylogous ester). As is expected from a mechanistic point of view, C(3) was not attacked, a fact which was not fully accounted for in a recent book (Hausen, 1988). However, the assumption that the nucleophilic attack may occur at position C(3) was made considering that the side chain was anchored in the lipid layer of the cell membrane of a stimulator cell, *i.e.* the position C(5) would not be available for a nucleophilic attack, and an elimination reaction at C(2) instead of a Michael-type addition reaction at C(3) was not taken into account. Thus, neither the product (1d) nor (1e) was formed, which correlates well with the experimental finding that 2,5-disubstituted *p*-benzoquinones exhibit no or only weak sensitizing properties *in vivo*.

The addition/elimination reaction proceeds surprisingly slow *in vitro* and only in the presence of a remarkable excess of the amine. Therefore, the mono-addition/elimination product (1b) could not be observed under the conditions studied.

Rotation of the methoxy methyl group was assumed to be a feature for enhanced reactivity between nucleophile and quinone (Cremer *et al.*, 1987). The result of this experiment, however, supports the assumption that methoxy groups at positions C(2) of strong quinonoid contact allergens like primin can be substituted by nucleophiles of the

receptor protein, most probably supported by enzymatic reactions *in vivo*.

References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. 1–19.
- CREMER, D., HAUSEN B. M. & SCHMALLE, H. W. (1987). *J. Med. Chem.* **30**, 1678–1681.
- FINLEY, K. TH. (1974). *The Chemistry of the Quinonoid Compounds*, Vol. 1, Part 2, edited by S. PATAI, pp. 1076–1090. London: John Wiley.
- HAUSEN, B. M. (1978). *Arch. Dermatol. Res.* **261**, 311–321.
- HAUSEN, B. M. (1979). *Mater. Med. Nordmark*, **31**, 57–76.
- HAUSEN, B. M. (1988). *Allergiepflanzen, Pflanzenallergene, Kontaktallergene*, Part 1. Landsberg, Lech: Ecomed.
- HJORTH, N., FREGERT, S. & SCHILDKNECHT, H. (1969). *Acta Derm. Venereol.* **49**, 552–555.
- JOHNSON, C. K. (1971). ORTEPII. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- SCHMALLE, H. W., JARCHOW, O. H., ADIWIDJAJA, G., KÖNIG, W. A., HEITSCH, H., RATHMANN, R., HAUSEN, B. M. & SCHULZ, K.-H. (1988). *Acta Cryst.* **C44**, 693–695.
- SCHMALLE, H. W., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K.-H. (1984). *Acta Cryst.* **C40**, 1084–1087.
- SCHOMAKER, V. & MARSH, R. E. (1983). *Acta Cryst.* **A39**, 819–820.
- SCHULZ, K.-H., GARBE, I., HAUSEN, B. M. & SIMATUPANG, M. H. (1979). *Arch. Dermatol. Res.* **264**, 275–286.
- SHELDRIK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1985). SHELXS86. In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- ULRICH, G., KLASKA, K. H., JARCHOW, O. H., SCHMALLE, H. W., KÖNIG, W. A., HEITSCH, H., RATHMANN, R., HAUSEN, B. M. & SCHULZ, K.-H. (1990). *Acta Cryst.* **C46**, 1715–1718.

Acta Cryst. (1991). **C47**, 1470–1473

Structures of Three Unsymmetrical Diester Derivatives of Dibenzobarrelene

BY JAMES TROTTER AND FRED C. WIREKO

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

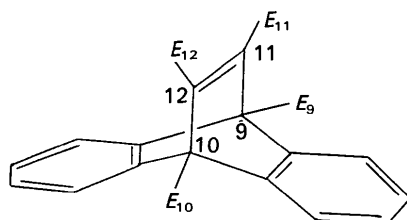
(Received 16 July 1990; accepted 13 November 1990)

Abstract. $T = 295$ K. 9-Isopropyl 11-methyl 9,10-dihydro-9,10-ethenoanthracene-9,11-dicarboxylate (Me/9-^{*i*}Pr), C₂₂H₂₀O₄, $M_r = 348.40$, monoclinic, $C2/c$, $a = 17.059$ (1), $b = 8.5405$ (3), $c = 25.894$ (1) Å, $\beta = 108.883$ (3)°, $V = 3569.5$ (3) Å³, $Z = 8$, $D_x = 1.296$ g cm⁻³, Cu $K\alpha_1$, $\lambda = 1.54056$ Å, $\mu = 6.8$ cm⁻¹, $F(000) = 1472$, $R = 0.049$ for 2542 reflections. 10-Isopropyl 11-methyl 9,10-dihydro-9,10-ethenoanthracene-10,11-dicarboxylate (Me/10-^{*i*}Pr), C₂₂H₂₀O₄, $M_r = 348.40$, monoclinic, $P2_1/a$, $a =$

15.388 (3), $b = 8.091$ (1), $c = 16.437$ (2) Å, $\beta = 117.86$ (1)°, $V = 1809.3$ (5) Å³, $Z = 4$, $D_x = 1.279$ g cm⁻³, Mo $K\alpha_1$, $\lambda = 0.70930$ Å, $\mu = 0.82$ cm⁻¹, $F(000) = 736$, $R = 0.042$ for 2286 reflections. 10-(–)-Menthyl 11-methyl 9,10-dihydro-9,10-ethenoanthracene-10,11-dicarboxylate (Me/10-Men), C₂₉H₃₂O₄, $M_r = 444.57$, orthorhombic, $P2_12_12_1$, $a = 8.462$ (1), $b = 14.383$ (2), $c = 19.988$ (3) Å, $V = 2432.7$ (5) Å³, $Z = 4$, $D_x = 1.213$ g cm⁻³, Mo $K\alpha_1$, $\lambda = 0.70930$ Å, $\mu = 0.81$ cm⁻¹, $F(000) = 952$, $R =$

0-036 for 2008 reflections. The ester groups at C11 have different orientations in the three molecules, with complete or partial conjugation with the C11=C12 bond. The photochemical behaviour of the materials is interpretable in terms of electronic stabilization effects.

Introduction. Previous solid-state structural and photochemical studies of dibenzobarrelene diesters (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990) have indicated that intermolecular steric interactions (rather than electronic effects) play a dominant role in determining the course of the di- π -methane photochemical reactions. The present paper describes three unsymmetrically 9,11- or 10,11-substituted diesters, in which electronic effects are likely to be more pronounced.



	E_{11}	E_{12}	E_9	E_{10}
Me/9-'Pr	CO ₂ Me	H	CO ₂ 'Pr	H
Me/10-'Pr	CO ₂ Me	H	H	CO ₂ 'Pr
Me/10-Men	CO ₂ Me	H	H	CO ₂ Men

Experimental. The general procedures and parameters of data collection and structure solution and refinement are summarized in Table 1 [see Garcia-Garibay *et al.* (1990) for further details]. The isopropyl group in Me/9-'Pr exhibits some disorder (0.83:0.17 occupancies); H atoms in Me/10-'Pr, and H12 in the other two compounds were refined, other H-atom parameters were fixed at idealized values. The absolute configuration of the Me/10-Men crystal used in the synthesis was derived from the known (1*R*,2*S*,5*R*) configuration of (-)-menthol (Prelog, 1953).

Discussion. Positional parameters are given in Table 2, and bond lengths and selected bond angles are given in Table 3.* The dibenzobarrelene ring systems in all three molecules (Fig. 1) have geometries and dimensions similar to those in related materials (Garcia-Garibay *et al.*, 1990). The ester groups at C11 have different orientations in the three molecules. The C12=C11—C13=O2 torsion angles (φ_1)

* Lists of structure factors, anisotropic thermal parameters, full bond angles, torsion angles and H-atom parameters, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53750 (75 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Data collection and refinement parameters*

	Me/9-'Pr	Me/10-'Pr*	Me/10-Men
Solvent	Ethanol	Ethanol	Ethanol
Dimensions (mm)	0.3 × 0.3 × 0.25	0.3 × 0.3 × 0.25	0.3 × 0.25 × 0.2
Radiation	Cu K α_1	Mo K α_1	Mo K α_1
Reflections for cell No.	25	25	25
θ range (°)	30–47	17–21	16–21
Intensity measurements†			
θ_{max} (°)	75	27.5	27.5
ω scan, ($a + b \tan \theta$), a (°)	0.70	0.60	0.65
ω scan, ($a + b \tan \theta$), b (°)	0.14	0.35	0.35
Scan speed (° min ⁻¹)	1.1–10	1.2–10	1.2–10
h	-19→21	-19→17	-10→0
k	0→10	0→10	0→18
l	-32→0	0→21	0→25
Total reflections	3657	4119	3133
Reflections with $I \geq 3\sigma(I)$	2542 (69.5%)	2286 (55.5%)	2008 (64.1%)
Structure refinements‡			
Number of parameters	248	315	302
Data/parameter ratio	10.3	8.3	10.4
Δ/σ (mean)	0.006	0.004	0.002
(maximum)	0.045	0.054	0.014
$\Delta\rho$ (e Å ⁻³)	-0.33→+0.23	-0.22→+0.18	-0.17→+0.13
$R [I \geq 3\sigma(I)]$	0.049	0.042	0.036
wR	0.054	0.046	0.037
S (goodness of fit)	2.11	1.72	1.40
R (all data)	0.075	0.095	0.073
Extinction, g	$3.9(2) \times 10^4$	—	—

* The transformation (100,010,102) produces a B -centred cell with $\beta = 89.95^\circ$, but the diffraction pattern and structure do not have orthorhombic symmetry.

† CAD-F diffractometer, three standard reflections (no significant intensity variation), no absorption corrections.

‡ Direct methods, refinement on F , $w = 1/\sigma^2(F)$; scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), and local or standard computer programs [see Garcia-Garibay *et al.* (1990) for complete references].

are $-132.1(3)$, $167.8(2)$ and $0.3(4)^\circ$ for Me/9-'Pr, Me/10-'Pr and Me/10-Men, respectively, *i.e.* anti-clinal, *anti* and *syn* conformations; the $\cos^2\varphi_1$ values (0.45, 0.96, 1.00) indicate partial conjugation of the ester group with C11=C12 in Me/9-'Pr and complete conjugation in the other two compounds. The C11—C13 bond distances, 1.477 (3), 1.470 (2) and 1.469 (3) Å, reflect these differences, when compared with the values for non-conjugated [1.497 (4) Å] and fully conjugated [1.470 (3) Å] systems (Allen, 1981). The C9/C10—C15 bond distances are considerably longer, 1.522 (3), 1.517 (3) and 1.513 (3) Å, as a result of the sp^3 hybridization at C9/C10, and the lack of any possible conjugative shortening.

The absolute configuration of the (-)-menthyl group of Me/10-Men (16*R*,17*S*,20*R* for the numbering system of Fig. 1) was assigned on the basis of the known configuration of (-)-menthol. The cyclohexane ring of the menthyl group has a chair conformation, with all three substituents equatorial (Fig. 1).

Photochemical reaction of this type of unsymmetrical dibenzobarrelene diester could result in two possible regioisomeric products, according to whether initial bond formation in the di- π -methane reaction occurs at C11 or C12 (Garcia-Garibay *et al.*, 1990). However, the only product which is obtained,

Table 2. Positional (fractional $\times 10^4$) and equivalent isotropic ($U \times 10^3 \text{ \AA}^2$) thermal parameters, with standard deviations and occupancies in parentheses

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Me/9-Pr	x	y	z	U_{eq}
C1	1195 (1)	4992 (3)	6877 (1)	42
C2	515 (2)	5706 (3)	6963 (1)	53
C3	-272 (2)	5510 (3)	6591 (1)	56
C4	-388 (1)	4609 (3)	6130 (1)	48
C4a	280 (1)	3893 (2)	6040 (1)	39
C5	286 (1)	-164 (3)	5708 (1)	49
C6	716 (2)	-1472 (3)	5965 (1)	59
C7	1504 (2)	-1317 (3)	6329 (1)	61
C8	1876 (1)	147 (3)	6446 (1)	49
C8a	1452 (1)	1461 (2)	6192 (1)	37
C9	1743 (1)	3183 (2)	6248 (1)	34
C9a	1075 (1)	4088 (2)	6413 (1)	35
C10	264 (1)	2841 (3)	5565 (1)	40
C10a	650 (1)	1298 (3)	5818 (1)	39
C11	1638 (1)	3717 (2)	5659 (1)	35
C12	872 (1)	3548 (3)	5314 (1)	39
C13	2356 (1)	4063 (3)	5478 (1)	39
C14	2820 (2)	5514 (4)	4857 (1)	71
C15	2602 (1)	3495 (2)	6651 (1)	39
C16	3654 (1)	5464 (3)	6965 (1)	50
C17 (0.83)	4277 (2)	5254 (5)	6693 (2)	92
C17' (0.17)	3860 (10)	6720 (20)	6560 (10)	80 (5)
C18 (0.83)	3569 (2)	7116 (5)	7132 (2)	86
C18' (0.17)	3600 (10)	6010 (30)	7420 (10)	90 (6)
O1	2184 (1)	5200 (2)	5101 (1)	49
O2	3005 (1)	3368 (2)	5636 (1)	54
O3	2831 (1)	4970 (2)	6605 (1)	41
O4	3007 (1)	2600 (2)	6987 (1)	71
Me/10-Pr				
C1	5119 (2)	1536 (3)	797 (2)	60
C2	4459 (2)	811 (3)	1039 (2)	74
C3	4708 (2)	592 (3)	1944 (2)	70
C4	5619 (1)	1081 (2)	2644 (2)	54
C4a	6287 (1)	1798 (2)	2406 (1)	41
C5	7428 (1)	5652 (2)	3316 (1)	45
C6	7291 (2)	7218 (3)	2923 (2)	56
C7	7028 (2)	7410 (3)	2005 (2)	58
C8	6900 (1)	6035 (2)	1455 (1)	50
C8a	7024 (1)	4478 (2)	1834 (1)	40
C9	6833 (1)	2849 (2)	1325 (1)	44
C9a	6033 (1)	2019 (2)	1477 (1)	44
C10	7334 (1)	2457 (2)	3047 (1)	37
C10a	7287 (1)	4284 (2)	2768 (1)	37
C11	7742 (1)	1779 (2)	1836 (1)	39
C12	8002 (1)	1601 (2)	2720 (1)	39
C13	8187 (1)	916 (2)	1335 (1)	42
C14	9465 (2)	-836 (4)	1453 (2)	71
C15	7697 (1)	2263 (2)	4073 (1)	45
C16	9139 (2)	2197 (4)	5532 (1)	76
C17	10065 (3)	3169 (8)	5877 (3)	128
C18	9292 (3)	357 (6)	5759 (2)	104
O1	9005 (1)	108 (2)	1890 (1)	55
O2	7834 (1)	907 (2)	508 (1)	60
O3	8660 (1)	2371 (2)	4525 (1)	61
O4	7193 (1)	2070 (3)	4439 (1)	83
Me/10-Men				
C1	3973 (3)	-2410 (2)	4998 (1)	57
C2	3645 (4)	-3353 (2)	4939 (2)	70
C3	3047 (4)	-3707 (2)	4361 (2)	69
C4	2741 (3)	-3132 (2)	3815 (1)	52
C4a	3034 (3)	-2195 (2)	3876 (1)	39
C5	5059 (3)	-708 (2)	2666 (1)	46
C6	6418 (3)	-166 (2)	2689 (1)	57
C7	6991 (3)	161 (2)	3282 (2)	60
C8	6225 (3)	-32 (2)	3872 (1)	51
C8a	4841 (3)	-552 (2)	3856 (1)	38
C9	3805 (3)	-781 (2)	4454 (1)	40
C9a	3633 (3)	-1832 (2)	4468 (1)	42
C10	2707 (3)	-1436 (1)	3345 (1)	36
C10a	4270 (3)	-903 (2)	3256 (1)	37
C11	2164 (3)	-415 (2)	4271 (1)	37
C12	1603 (3)	-756 (2)	3701 (1)	36
C13	1242 (3)	229 (2)	4687 (1)	41
C14	1193 (4)	1066 (3)	5700 (1)	82
C15	2058 (3)	-1883 (2)	2717 (1)	42
C16	-320 (3)	-2428 (2)	2187 (1)	41

Table 2 (cont.)

	x	y	z	U_{eq}
C17	-1871 (3)	-2773 (2)	2470 (1)	42
C18	-2779 (3)	-3258 (2)	1909 (1)	61
C19	-2990 (4)	-2643 (2)	1298 (1)	67
C20	-1433 (4)	-2292 (2)	1025 (1)	58
C21	-528 (3)	-1808 (2)	1588 (1)	50
C22	-1631 (5)	-1646 (3)	423 (2)	84
C23	-1686 (3)	-3364 (2)	3106 (1)	46
C24	-3240 (4)	-3455 (2)	3482 (2)	73
C25	-979 (4)	-4321 (2)	2986 (1)	68
O1	2047 (2)	482 (1)	5236 (1)	62
O2	-65 (2)	504 (1)	4564 (1)	55
O3	475 (2)	-1903 (1)	2721 (1)	43
O4	2850 (2)	-2221 (1)	2285 (1)	67

Table 3. Bond lengths (\AA) and selected bond angles ($^\circ$), with standard deviations in parentheses

	Me/9-Pr	Me/10-Pr	Me/10-Men
C1—C2	1.390 (3)	1.384 (4)	1.390 (5)
C1—C9a	1.386 (3)	1.382 (3)	1.379 (3)
C2—C3	1.386 (4)	1.363 (4)	1.359 (5)
C3—C4	1.379 (4)	1.393 (3)	1.393 (4)
C4—C4a	1.378 (3)	1.385 (3)	1.376 (3)
C4a—C9a	1.398 (3)	1.400 (3)	1.388 (3)
C4a—C10	1.516 (3)	1.550 (2)	1.548 (3)
C5—C6	1.383 (4)	1.393 (3)	1.390 (4)
C5—C10a	1.382 (3)	1.379 (3)	1.383 (3)
C6—C7	1.375 (3)	1.375 (3)	1.365 (4)
C7—C8	1.391 (3)	1.389 (3)	1.374 (4)
C8—C8a	1.381 (3)	1.379 (3)	1.391 (3)
C8a—C9	1.544 (3)	1.514 (2)	1.519 (3)
C8a—C10a	1.404 (3)	1.400 (2)	1.388 (3)
C9—C9a	1.549 (3)	1.522 (3)	1.519 (3)
C9—C11	1.544 (3)	1.521 (3)	1.529 (3)
C9—C15	1.522 (3)	—	—
C10—C10a	1.524 (3)	1.540 (2)	1.539 (3)
C10—C12	1.516 (3)	1.530 (2)	1.529 (3)
C10—C15	—	1.517 (3)	1.513 (3)
C11—C12	1.331 (3)	1.323 (2)	1.328 (3)
C11—C13	1.477 (3)	1.470 (2)	1.469 (3)
C13—O1	1.339 (3)	1.331 (2)	1.342 (3)
C13—O2	1.205 (3)	1.206 (2)	1.200 (3)
C14—O1	1.446 (3)	1.442 (3)	1.445 (3)
C15—O3	1.336 (2)	1.314 (2)	1.340 (3)
C15—O4	1.196 (2)	1.194 (2)	1.195 (3)
C16—C17	1.464 (5)	1.488 (4)	1.513 (3)
C16—C18	1.497 (4)	1.526 (5)	—
C16—O3	1.473 (2)	1.470 (2)	1.471 (2)
C16—C17'	1.62 (2)	—	—
C16—C18'	1.31 (2)	—	—
C16—C21	—	—	1.502 (3)
C17—C18	—	—	1.528 (3)
C17—C23	—	—	1.538 (3)
C18—C19	—	—	1.518 (4)
C19—C20	—	—	1.512 (4)
C20—C21	—	—	1.529 (4)
C20—C22	—	—	1.530 (4)
C23—C24	—	—	1.519 (4)
C23—C25	—	—	1.521 (4)
Angles in aromatic rings	119.0–120.8 (2)	118.7–121.7 (2)	118.6–121.1 (3)
External angles at aromatic ring junctions	126.1–128.8 (2)	126.0–128.7 (2)	125.7–127.9 (2)
C9—C11=C12	114.0 (2)	113.4 (2)	113.8 (2)
C10—C12=C11	114.5 (2)	115.3 (2)	114.7 (2)

both in solution and in the solid state, is that involving bond formation at C12. This is the expected product on the basis of an electronic stabilization mechanism; the C11 radical centre in the postulated biradical intermediate is a tertiary (more stable) centre, and in addition, stability can be increased further by delocalization of the odd electron over the conjugated ester group. Reaction *via* C11 would involve a (less stable) C12 secondary radical centre. Previous studies of 11,12-diester (Garcia-Garibay *et*

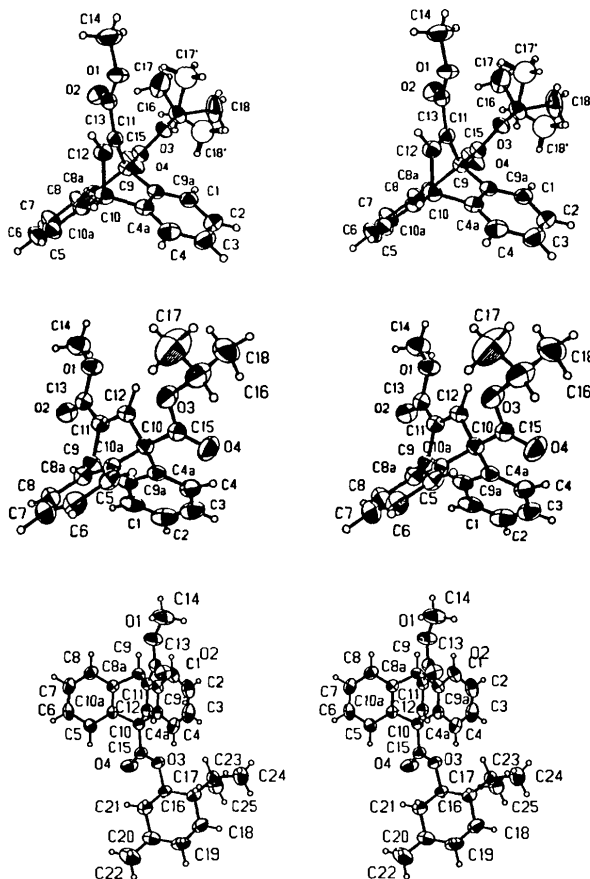


Fig. 1. Stereoviews of the molecules of Me/9-Pr (top), Me/10-Pr (centre) and Me/10-Men (bottom).

Acta Cryst. (1991). **C47**, 1473–1476

Structure of 4-Bromo-4'-fluorobiphenyl

BY W. B. GLEASON* AND MYLES BROSTROM

Corporate Research Laboratories, 3M Company, 3M Center, St Paul, MN 55144, USA

M. C. ETTER

Department of Chemistry, University of Minnesota, Minneapolis, MN 55144, USA

AND R. B. JOHNSON

Rochelle Crystal Corporation at the College of St Catherine, St Paul, MN 55105, USA

(Received 9 August 1990; accepted 13 November 1990)

Abstract. $C_{12}H_8BrF$, $M_r = 251.1$, monoclinic, $P2_1/c$, $a = 9.709$ (2), $b = 13.311$ (2), $c = 17.487$ (5) Å, $\beta =$

* To whom correspondence should be addressed at: Department of Biochemistry, University of Minnesota, Minneapolis, MN 55455, USA.

al., 1990) have indicated that electron stabilization was not the controlling factor in the photochemical reactions of those materials, but that intermolecular steric effects were dominant. A qualitative study of intermolecular contacts in the present unsymmetrical esters indicates that bond formation at C12 is favourable. The initial step in the reaction [see Fig. 4 of Garcia-Garibay *et al.* (1990)] is believed to involve $C11 \cdots C8a$ or $C9a$, or $C12 \cdots C4a$ or $C10a$ bond formation; this step results in large motion of a bulky ester group bonded to C11 or C12, which is impeded by intermolecular steric repulsions in the crystal. Since there is no ester group at C12 in the present compounds, reaction at C12 is favoured by these steric effects. It seems likely though that the electron stabilization effect is the dominant factor in determining the photochemical reaction pathway for these unsymmetrical diesters (since solution and solid-state products are identical).

We thank Professor J. R. Scheffer and Dr M. Garcia-Garibay for crystals and collaborative photochemical studies, the Natural Sciences and Engineering Research Council of Canada for financial support, and the University of British Columbia Computing Centre for assistance.

References

- ALLEN, F. H. (1981). *Acta Cryst.* **B37**, 890–900.
 GARCIA-GARIBAY, M., SCHEFFER, J. R., TROTTER, J. & WIREKO, F. C. (1990). *Acta Cryst.* **B46**, 431–440.
 PRELOG, V. (1953). *Helv. Chim. Acta*, **36**, 308–319.

116.29 (5)°, $V = 2026.2$ Å³, $Z = 8$, $D_x = 1.64$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 39.7$ cm⁻¹, $F(000) = 992$, $T = 298$ (1) K, $R = 0.043$ for 1776 observed reflections. This crystal is isostructural with 4,4'-dibromobiphenyl and has inter-ring dihedral angles