Dastidar, P., Guru Row, T. N. & Venkatesan, K. (1991). *J. Mater. Chem.* **1**(6), 1057–1059.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kanagapushpam, D., Padmanabhan, K. & Venkatesan, K. (1987). *Acta Cryst.* C**43**, 1717–1721.

Kanagapushpam, D. & Venkatesan, K. (1987). *Acta Cryst.* C**43**, 1597–1599.

Kanagapushpam, D., Venkatesan, K. & Cameron, T. S. (1988). *Acta Cryst.* C**44**, 337–340.

Motherwell, S., Sussman, J. L. & Beebe, N. H. F. (1982). *PLUTO*82. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1993). B**49**, 905–909

Crystal Structure Correlations in the Photochemistry of Dimethyl 9-Chloromethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

By Jianxin Chen, Phani Raj Pokkuluri, John R. Scheffer and James Trotter

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

(*Received* 12 *January* 1993; *accepted* 6 *May* 1993)

Abstract

A study of the photochemistry of the title 9-chloromethyldibenzobarrelene-11,12-diester (1) reveals the formation of semibullvalene derivatives [(2) and (3)] in acetone solution, with additional novel photoproducts [two isomers of dimethyl 5-chloro-10-methylene-5,5a,10,10a-tetrahydroindeno[2,1-*a*]indene-5a,10a-dicarboxylate; (4) and (5)] in other solvents, and especially in solid-state photolysis. The structures of (1), (4) and (5) have been determined by X-ray crystal analyses. Crystal data: $T = 294$ K, Cu $K\alpha$, $\lambda = 1.5418$ Å, $C_{21}H_{17}ClO_4$, $M_r = 368.82$. (1), monoclinic, $P2_1/c$, $a = 10.087$ (1), $b = 16.207$ (1), $c = 11.233$ (1) Å, $\beta = 107.64$ (1)°, $V = 1749.9$ (2) Å^3, $Z = 4$, $D_x = 1.400$ g cm^{-3}, $F(000) = 768$, $\mu = 21.4$ cm^{-1}, $R = 0.042$ for 2569 reflections. (4), triclinic, $P\bar{1}$, $a = 13.893(1)$, $b = 15.968$ (2), $c = 8.191$ (2) Å, $\alpha = 98.13$ (2), $\beta = 91.78$ (2), $\gamma = 99.54$ (1)°, $V = 1771.2$ (4) Å^3, $Z = 4$ (two molecules per asymmetric unit), $D_x = 1.383$ g cm^{-3}, $\mu = 21.2$ cm^{-1}, $R = 0.045$ for 5645 reflections. (5) [15% (4) as impurity], monoclinic, $P2_1/c$, $a = 14.777$ (1), $b = 8.581$ (1), $c = 15.192$ (1) Å, $\beta = 112.10$ (1)°, $V = 1784.8$ (3) Å^3, $Z = 4$, $D_x = 1.372$ g cm^{-3}, $F(000) = 768$, $\mu = 21.0$ cm^{-1}, $R = 0.103$ for 2874 reflections. Photolysis of (1) in acetone results in the formation, *via* the triplet excited state, of the normal di-π-methane photoproducts (2) and (3). In other solvents and in the solid state, photolysis, *via* the singlet excited state, results in the novel dibenzopentalenes, (4) and (5); the mechanism by which these products are formed probably involves photorearrangement *via* a biradical (6), followed by a non-concerted Cl-atom migration. Solid-state photolysis produces relatively larger amounts of (4) and (5), and this information may be correlated with a favorable intermolecular C···Cl contact of 4.28 Å in the crystal structure of (1).

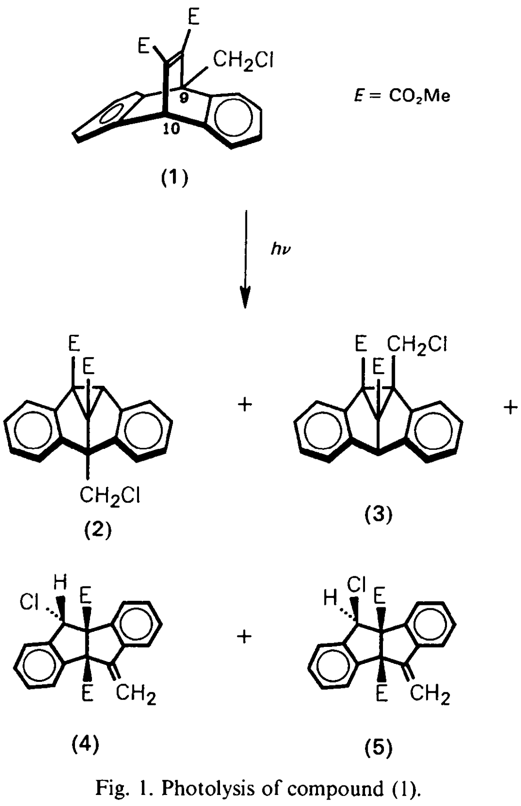

Fig. 1. Photolysis of compound (1).

Acta Crystallographica Section B
ISSN 0108-7681 ©1993

Table 1. *Crystal data, data-collection and refinement parameters for compounds* (1), (4) *and* (5)

(1) = dimethyl 9-chloromethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate. (4), (5) = two isomers of dimethyl 5-chloro-10-methylene-5,5a,10,10a-tetrahydroindeno[2,1-*a*]indene-5a,10a-dicarboxylate.

	(1)	(4)	(5)
Crystal data			
Solvent	Acetone–hexane	Ether–petroleum ether	Ether–petroleum ether
Dimensions (mm)	0.40 × 0.20 × 0.40	0.4 × 0.15 × 0.5	0.25 × 0.20 × 0.50
Formula	$C_{21}H_{17}ClO_4$	$C_{21}H_{17}ClO_4$	$C_{21}H_{17}ClO_4$
M_r	368.82	368.82	368.82
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	10.087 (1)	13.893 (1)	14.777 (1)
b (Å)	16.207 (1)	15.968 (2)	8.581 (1)
c (Å)	11.233 (1)	8.191 (2)	15.192 (1)
α (°)	90	98.13 (2)	90
β (°)	107.64 (1)	91.78 (2)	112.10 (1)
γ (°)	90	99.54 (1)	90
V (Å^3)	1749.9 (2)	1771.2 (4)	1784.8 (3)
Z	4	4	4
D_x (g cm^{-3})	1.400	1.383	1.372
$F(000)$	768	768	768
μ (cm^{-1})	21.4	21.2	21.0
Data collection (Cu $K\alpha$ radiation, λ = 1.5418 Å)			
Reflections for cell			
No.	24	24	25
2θ (°)	83–111	92–96	79–88
Intensity measurements			
2θ(max.) (°)	155	155	155
ω scan	1.05 + 0.30 tanθ	1.35 + 0.20 tanθ	1.21 + 0.25 tanθ
Scan speed (° min^{-1}) (up to 8 rescans)	32	32	32
h	$-12 \rightarrow 12$	$-17 \rightarrow 17$	$0 \rightarrow 18$
k	$0 \rightarrow 20$	$-20 \rightarrow 20$	$0 \rightarrow 10$
l	$0 \rightarrow 13$	$-10 \rightarrow 0$	$-18 \rightarrow 18$
Total No. of reflections measured	3826	7743	3951
Total No. of unique reflections	3634	7198	3801
R_{int}	0.015	0.040	0.061
Reflections with $I \geq 3\sigma(I)$	2569	5645	2874
%	70.7	78.4	75.6
Absorption, transmission factor (relative)	0.75–1.00	0.61–1.00	0.76–1.00
Structure refinements			
No. of parameters	236 (+68 H parameters)	469 (+124 H parameters)	235
Δ/σ(max.)	0.01	0.02	0.02
$\Delta\rho$ (e Å^{-3})	−0.27 to +0.21	−0.33 to +0.35	−0.93 to +0.96
R [$I \geq 3\sigma(I)$]	0.042	0.045	0.103
wR	0.062	0.063	0.152
S (goodness of fit)	1.83	2.52	5.69
R (all data)	0.067	0.062	0.121
Extinction, g	7.6 (6) × 10^{-6}	3.4 (5) × 10^{-6}	-

Introduction

Photolyses of 9,10-dimethyl- and 9-phenyldibenzobarrelene diesters result in the formation of di-π-methane semibullvalene photoproducts *via* the triplet excited states, and of cyclooctatetraenes *via* the singlet states (Pokkuluri, Scheffer & Trotter, 1993*a*,*b*). An additional major product in the solid-state photolysis of the 9,10-dimethyl diester has an unusual pentalene-type structure, which provided an important clue in deriving a mechanism for the reactions, involving a biradical intermediate and ester-group migration (Pokkuluri *et al.*, 1993*a*).

Extension of this study to the 9-chloromethyl derivative [(1), Fig. 1] reveals normal triplet-state semibullvalene photoproducts [(2) and (3)], but novel singlet-state products [(4) and (5)]; the present X-ray analyses of (1), (4) and (5) indicate that the structures of (4) and (5) are consistent with a biradical intermediate, which, however, undergoes Cl-atom (rather than ester-group) migration.

Experimental

The materials were synthesized and characterized as previously described (Chen, Pokkuluri, Scheffer & Trotter, 1991). The crystal and molecular structures of reactant (1) and photoproducts (4) and (5) were determined by single-crystal X-ray diffraction analysis. The general procedures and parameters of data collection are summarized in Table 1. Intensities were measured with a Rigaku AFC-6 diffractometer and Cu $K\alpha$ radiation. Lp and absorption corrections (ψ scan) were applied. The structures were solved by direct methods using *TEXSAN* (Molecular Structure Corporation, 1990).

For (4), there are two molecules per asymmetric unit; one ester group in one molecule exhibits disorder, and the terminal atom was modelled as two half-occupied sites, C(16′) and C(16″) [an intermolecular C(16″)···C(16″) contact of about 2.2 Å indicates that this site cannot be occupied in two neighboring molecules]. (5) is a minor photoproduct of the photolysis of (1), and as a result of difficulty in its separation from the major dibenzopentalene, (4), the best sample of (5) was only 85% pure (as shown by gas chromatography), with the impurity being compound (4). X-ray analysis of one of these impure crystals of (5) proceeded reasonably satisfactorily, but with a high final R value, and with some residual electron-density peaks of $\sim$1 e Å^{-3} (see *Discussion*).

Discussion

Final positional parameters are in Table 2,* and selected bond lengths and angles in Table 3. Fig. 2 shows views of the molecules of (1), (4) and (5).

The structure and dimensions of the molecule of the dibenzobarrelene diester, (1), are very similar to those of other derivatives (Pokkuluri *et al.*, 1993*a*,*b*). The bond angles external to the aromatic rings, mean 126.4°, and the inter-annular benzene–barrelene angles, mean 113.2°, are distorted to about the same extent as in the other derivatives. The C(11)—C(12)

---

* Lists of anisotropic thermal parameters, hydrogen positions, bond lengths and angles, and structure factors, together with molecular and packing diagrams, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71111 (117 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0634]

Table 2. *Positional and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq} (Å^2)
Compound (1)				
Cl	0.33401 (8)	0.15087 (4)	0.79413 (7)	5.48 (3)
O(1)	0.0914 (2)	0.2224 (1)	0.5350 (2)	4.68 (7)
O(2)	0.0206 (2)	0.2581 (1)	0.6987 (2)	6.3 (1)
O(3)	0.1443 (2)	0.4669 (1)	0.4089 (2)	4.63 (7)
O(4)	−0.0151 (2)	0.3881 (1)	0.4553 (2)	6.19 (9)
C(1)	0.5804 (2)	0.2729 (1)	0.7746 (2)	4.16 (9)
C(2)	0.6887 (3)	0.2864 (2)	0.7243 (3)	4.8 (1)
C(3)	0.6881 (3)	0.3533 (2)	0.6492 (3)	4.9 (1)
C(4)	0.5791 (2)	0.4093 (2)	0.6230 (2)	4.4 (1)
C(4a)	0.4685 (2)	0.3951 (1)	0.6691 (2)	3.56 (8)
C(5)	0.3302 (3)	0.5517 (2)	0.8214 (3)	4.9 (1)
C(6)	0.3225 (3)	0.5628 (2)	0.9417 (3)	5.9 (1)
C(7)	0.3176 (3)	0.4960 (3)	1.0143 (3)	6.0 (1)
C(8)	0.3224 (3)	0.4153 (2)	0.9712 (2)	4.9 (1)
C(8a)	0.3307 (2)	0.4045 (1)	0.8521 (2)	3.84 (8)
C(9a)	0.4679 (2)	0.3267 (1)	0.7437 (2)	3.43 (7)
C(9)	0.3367 (2)	0.3213 (1)	0.7865 (2)	3.55 (8)
C(10a)	0.3346 (2)	0.4726 (1)	0.7777 (2)	3.89 (8)
C(10)	0.3406 (2)	0.4492 (1)	0.6486 (2)	3.74 (8)
C(11)	0.2135 (2)	0.3268 (1)	0.6650 (2)	3.55 (8)
C(12)	0.2154 (2)	0.3932 (1)	0.5949 (2)	3.65 (8)
C(13)	0.0970 (2)	0.2663 (2)	0.6364 (2)	4.09 (9)
C(14)	−0.0202 (4)	0.1636 (3)	0.4921 (4)	7.1 (2)
C(15)	0.1015 (2)	0.4141 (1)	0.4797 (2)	3.97 (8)
C(16)	0.0453 (3)	0.4878 (3)	0.2899 (3)	5.9 (1)
C(17)	0.3332 (3)	0.2477 (2)	0.8700 (2)	4.4 (1)
Compound (4)				
Cl	0.24007 (4)	0.15552 (4)	0.48086 (8)	5.11 (2)
O(1)	0.3990 (1)	0.2964 (1)	1.0107 (2)	4.47 (6)
O(2)	0.5515 (1)	0.3683 (1)	1.0232 (2)	6.41 (8)
O(3)	0.3341 (1)	0.1021 (1)	0.8312 (2)	4.73 (7)
O(4)	0.4938 (1)	0.1470 (1)	0.8892 (2)	5.07 (7)
C(1)	0.4312 (2)	0.4516 (1)	0.6883 (3)	4.6 (1)
C(2)	0.3641 (2)	0.4924 (2)	0.6157 (4)	5.2 (1)
C(3)	0.2764 (2)	0.4468 (2)	0.5447 (3)	4.9 (1)
C(4a)	0.3181 (1)	0.3184 (1)	0.6217 (2)	3.19 (6)
C(4)	0.2519 (2)	0.3596 (2)	0.5477 (3)	4.04 (8)
C(5)	0.4518 (2)	0.1051 (2)	0.4405 (3)	4.6 (1)
C(6)	0.5173 (2)	0.0888 (2)	0.3209 (4)	6.2 (1)
C(7)	0.6006 (2)	0.1480 (2)	0.3084 (4)	6.5 (1)
C(8a)	0.5571 (1)	0.2400 (1)	0.5387 (3)	3.69 (7)
C(8)	0.6224 (2)	0.2223 (2)	0.4173 (4)	5.3 (1)
C(9a)	0.4076 (1)	0.3638 (1)	0.6889 (3)	3.30 (7)
C(9)	0.5681 (1)	0.3126 (1)	0.6724 (3)	3.60 (7)
C(10a)	0.4712 (1)	0.1831 (1)	0.5463 (3)	3.37 (7)
C(10)	0.3072 (1)	0.2271 (1)	0.6503 (3)	3.27 (7)
C(11)	0.4716 (1)	0.3061 (1)	0.7566 (2)	3.10 (6)
C(12)	0.4126 (1)	0.2124 (1)	0.6912 (2)	2.93 (6)
C(13)	0.4816 (2)	0.3275 (1)	0.9445 (3)	3.89 (8)
C(14)	0.4019 (3)	0.3047 (3)	1.1891 (4)	6.3 (1)
C(15)	0.4193 (1)	0.1513 (1)	0.8167 (3)	3.51 (7)
C(16)	0.3320 (3)	0.0466 (2)	0.9571 (5)	6.3 (1)
C(17)	0.6470 (2)	0.3729 (2)	0.7092 (4)	5.1 (1)
Cl′	0.11426 (5)	0.14935 (5)	0.9709 (1)	6.53 (3)
O(1′)	0.0026 (1)	0.2774 (1)	1.4910 (2)	5.32 (7)
O(2′)	−0.1206 (2)	0.3506 (2)	1.4926 (3)	7.2 (1)
O(3′)	−0.1468 (1)	0.1293 (1)	1.3354 (3)	7.2 (1)
O(4′)	−0.0071 (1)	0.0815 (1)	1.2928 (2)	5.70 (8)
C(1′)	0.0306 (2)	0.4406 (2)	1.1841 (4)	5.0 (1)
C(2′)	0.1123 (2)	0.4848 (2)	1.1205 (4)	5.8 (1)
C(3′)	0.1820 (2)	0.4421 (2)	1.0507 (4)	5.4 (1)
C(4′)	0.1743 (2)	0.3543 (2)	1.0470 (3)	4.6 (1)
C(4a′)	0.0940 (1)	0.3103 (1)	1.1129 (3)	3.53 (7)
C(5′)	−0.1177 (2)	0.0932 (2)	0.9067 (4)	5.0 (1)
C(6′)	−0.1955 (3)	0.0729 (3)	0.7892 (4)	6.6 (1)
C(7′)	−0.2625 (2)	0.1267 (2)	0.7802 (5)	6.9 (1)
C(8′)	−0.2553 (2)	0.2013 (2)	0.8874 (4)	5.5 (1)
C(8a′)	−0.1774 (1)	0.2234 (1)	1.0060 (3)	3.95 (8)
C(9′)	−0.1592 (1)	0.2962 (1)	1.1380 (3)	3.75 (8)
C(9a′)	0.0215 (1)	0.3529 (1)	1.1764 (3)	3.49 (7)
C(10′)	0.0729 (2)	0.2180 (1)	1.1352 (3)	3.98 (8)
C(10a′)	−0.1081 (1)	0.1701 (1)	1.0133 (3)	3.64 (7)
C(11′)	−0.0638 (1)	0.2915 (1)	1.2316 (3)	3.39 (7)
C(12′)	−0.0377 (1)	0.2001 (1)	1.1637 (3)	3.41 (7)
C(13′)	−0.0667 (2)	0.3097 (2)	1.4176 (3)	4.40 (9)
C(14′)	0.0046 (4)	0.2859 (4)	1.6706 (4)	7.8 (2)
C(15′)	−0.0649 (2)	0.1331 (2)	1.2774 (4)	5.3 (1)
C(16′)	−0.1772 (5)	0.0517 (4)	1.3956 (8)	6.2 (1)
C(17′)	−0.2135 (2)	0.3574 (2)	1.1692 (4)	5.3 (1)
C(16″)	−0.0445 (5)	0.0153 (5)	1.398 (1)	7.0 (1)

Table 2 (*cont.*)

	x	y	z	B_{eq} (Å^2)
Compound (5)				
Cl	0.3503 (2)	−0.1106 (2)	0.0555 (2)	6.8 (1)
O(1)	0.0988 (2)	0.2754 (5)	0.1393 (3)	4.3 (2)
O(2)	0.1696 (3)	0.4810 (5)	0.1002 (3)	4.9 (2)
O(3)	0.1627 (3)	0.1588 (4)	−0.0138 (3)	4.1 (1)
O(4)	0.1189 (4)	−0.0674 (5)	0.0315 (3)	5.9 (2)
C(1)	0.3839 (4)	0.4610 (6)	0.1455 (4)	3.9 (2)
C(2)	0.4658 (4)	0.4824 (8)	0.1223 (5)	4.8 (2)
C(3)	0.5109 (4)	0.3604 (9)	0.1001 (5)	5.1 (3)
C(4)	0.4787 (4)	0.2076 (8)	0.1006 (4)	4.4 (2)
C(4a)	0.3965 (3)	0.1859 (6)	0.1247 (4)	3.3 (2)
C(5)	0.2139 (4)	−0.1578 (7)	0.2328 (4)	4.2 (2)
C(6)	0.2099 (5)	−0.2045 (9)	0.3207 (6)	5.0 (3)
C(7)	0.2298 (4)	−0.1036 (8)	0.3949 (5)	4.7 (3)
C(8)	0.2566 (4)	0.0462 (7)	0.3882 (4)	4.0 (2)
C(8a)	0.2621 (3)	0.0965 (6)	0.3040 (3)	3.1 (2)
C(9)	0.2916 (4)	0.2496 (6)	0.2814 (3)	3.6 (2)
C(9a)	0.3502 (3)	0.3095 (6)	0.1475 (3)	3.0 (2)
C(10)	0.3518 (4)	0.0364 (6)	0.1360 (4)	3.7 (2)
C(10a)	0.2386 (3)	−0.0041 (6)	0.2255 (4)	3.1 (2)
C(11)	0.2669 (3)	0.2547 (5)	0.1735 (3)	2.7 (2)
C(12)	0.2517 (3)	0.0771 (5)	0.1435 (3)	2.9 (2)
C(13)	0.1747 (4)	0.3533 (6)	0.1317 (4)	3.2 (2)
C(14)	0.0058 (4)	0.357 (1)	0.1121 (6)	6.1 (3)
C(15)	0.1695 (4)	0.0463 (6)	0.0485 (4)	3.5 (2)
C(16)	0.0849 (5)	0.143 (1)	−0.1057 (4)	5.7 (3)
C(17)	0.3050 (6)	0.3926 (8)	0.3385 (4)	6.1 (3)

Table 3. *Selected bond lengths* (Å) *and torsion angles* (°) (*mean values where appropriate*)

	(1)	(4)	(5)
C═C	1.337 (3)	1.332 (3)	1.47 (1)†
C—C(arom.)	1.364–1.401 (4)	1.363–1.396 (4)	1.35–1.42 (1)
C—CO_2Me	1.489, 1.486 (3)	1.514–1.526 (3)	1.52 (1)
C—C(other)	1.517–1.546 (3)	1.454–1.593 (3)	1.47–1.58 (1)
C—Cl	1.788 (3)	1.790 (2)	1.752 (5)
C═O	1.198 (3)	1.195 (3), 1.250 (3)*	1.19 (1)
C—OMe	1.327 (3)	1.331 (3), 1.250 (3)*	1.34 (1)
O—Me	1.444 (3)	1.450 (3)	1.45 (1)

	(4)		
	Molecule 1	Molecule 2	(5)
C(4a)—C(9a)—C(11)—C(12)	9.4 (2)	−8.6 (2)	−11.6 (5)
C(9a)—C(11)—C(12)—C(10)	−19.6 (2)	19.6 (2)	19.0 (5)
C(11)—C(12)—C(10)—C(4a)	23.2 (2)	−23.7 (2)	−20.3 (5)
C(12)—C(10)—C(4a)—C(9a)	−18.4 (2)	19.4 (2)	14.7 (6)
C(10)—C(4a)—C(9a)—C(11)	5.4 (2)	−6.6 (3)	−1.8 (6)
C(8a)—C(9)—C(11)—C(12)	13.5 (2)	−10.2 (2)	−16.7 (5)
C(9)—C(11)—C(12)—C(10a)	−12.9 (2)	11.8 (2)	16.5 (4)
C(11)—C(12)—C(10a)—C(8a)	8.1 (2)	−9.8 (2)	−10.9 (5)
C(12)—C(10a)—C(8a)—C(9)	0.1 (2)	3.8 (3)	0.3 (5)
C(10a)—C(8a)—C(9)—C(11)	−8.9 (2)	4.3 (2)	10.9 (5)
C(13)—C(11)—C(12)—C(15)	−26.2 (2)	26.2 (2)	27.2 (5)
C(9)—C(11)—C(12)—C(10a)	−12.9 (2)	11.8 (2)	16.5 (4)
C(9a)—C(11)—C(12)—C(10)	−19.6 (2)	19.6 (2)	19.0 (5)
C(9)—C(11)—C(12)—C(10)	−135.2 (3)	135.5 (2)	−100.4 (4)
C(9a)—C(11)—C(12)—C(10a)	102.6 (2)	−104.1 (2)	135.9 (4)
C(12)—C(11)—C(13)—O(2)	142.9 (2)	−145.9 (3)	−138.5 (5)
C(11)—C(12)—C(15)—O(4)	−44.7 (3)	−141.4 (2)* 44.8 (3)*	−145.9 (5)

* Disordered ester group.

† See text.

distance [1.337 (3) Å] is normal for a double bond. The two ester groups are rotated out of the plane of the double bond to different extents; the C(12)—C(11)—C(13)—O(2) (adjacent to the 9-CH_2Cl substituent) and C(11)—C(12)—C(15)—O(4) dihedral angles are −111.5 (3) and +20.2 (4)°, respectively. Thus the ester group at C(11) (adjacent to CH_2Cl) is only slightly conjugated to the C(11)═C(12) double bond ($\cos^2\varphi = 0.13$), while the group at C(12) shows considerable conjugation ($\cos^2\varphi = 0.88$); the difference is doubtless due to the steric effect of the CH_2Cl substituent, which results in rotation of the C(11) ester substituent away from the favorable conjugated orientation, as in the related 9-phenyl derivative (Pokkuluri *et al.*, 1993*b*). This difference in conjugation is not reflected in the C—CO_2Me bond distances, which are essentially equal at 1.489 (3) and 1.486 (3) Å.

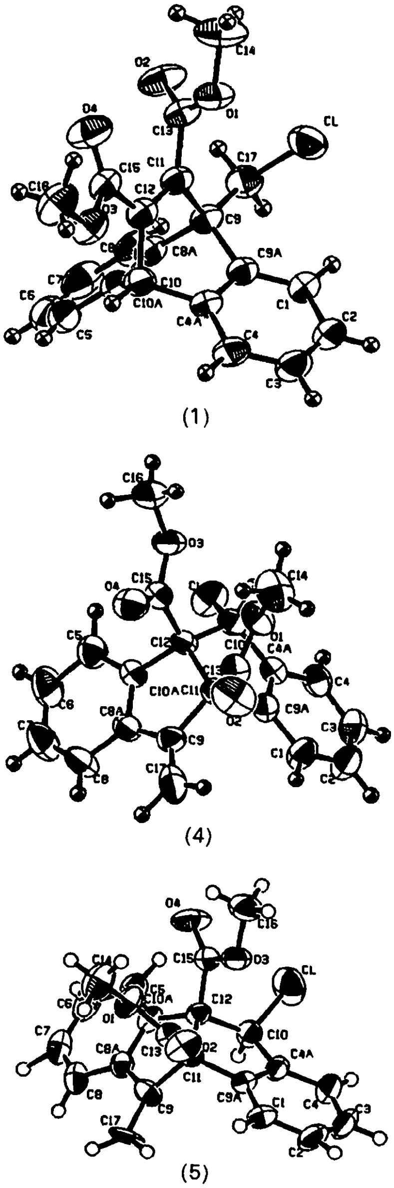

Fig. 2. Views (50% thermal ellipsoids) of (1), (4) (unprimed molecule; primed molecule is quite similar), and (5) [for (4) and (5), the enantiomers of Figs. 1 and 3; crystals are racemates]; stereo versions are shown in the supplementary material. The dibenzobarrelene numbering system of (1) is retained for (4) and (5).

The crystal structure analysis of photoproduct (4) posed a minor problem of disorder of one of the ester groups in one of the two independent molecules; this disorder involves two orientations related by 180° rotation about the C—CO_2Me bond, giving two half-occupied sites for the terminal Me group, and apparently equal C—O bond distances (closely spaced oxygen sites could not be resolved).

The analysis for photoproduct (5) was more problematic, since the material could be obtained only with about 15% of compound (4) as impurity. Nevertheless, the crystal structure of (5) has been determined with reasonable accuracy. The only apparently anomalous features involve the exocyclic methylene group, where C=CH_2 is 1.47 (1) Å (Table 3), more nearly equal to a single (rather than a double) bond length, and the bonds at C(9) show some apparent deviation from exact planarity [angle sum = 356°, compared with 360° in (4)]. However, the ^1H NMR spectrum does not show any methyl resonance, other than that for the two ester groups, which rules out the possibility of a single bond. The thermal parameter of the exocyclic methylene C atom, C(17), is also somewhat anomalous [U_{11} = 0.132 (6), U_{22} = 0.071 (4), U_{33} = 0.023 (2) $Å^2$].* These anomalous features could result from partial occupancy of the molecular site by an impurity molecule of (4) or by a molecule of (5), each rotated 180° with respect to the major orientation of (4). Roughly parallel orientation of a C=CH_2 group (1.33 Å, 85% occupancy) and a C—Cl group (1.79 Å, 15% occupancy) would give CH_2 and Cl sites separated by about 0.5 Å, and a weighted C—X bond length of about 1.48 Å (close to the observed 1.47 Å); at the Cl site (85%), 15% of CH_2 occupancy would give C—X about 1.76 Å [close to the observed C—Cl length of 1.75 *cf.* 1.79 Å in (1) and (4)]. Since the partially occupied sites are close together, and the exact nature of the possible disorder is uncertain, further refinement of this model was not attempted.

The general structures and dimensions of the molecules of (4) and (5) are very similar to each other, but considerably different from the dibenzopentalene derived from photolysis of the 9,10-dimethyl diester (Pokkuluri *et al.*, 1993*a*). In the latter dibenzopentalene, the central bond in the ring system is a C=C double bond, so that the ring system is nearly planar. In (4) and (5), the central bond is a C—C single bond, so that the molecules are folded about C(11)—C(12), these bonds being quite long, 1.58–1.59 Å, presumably as a result of ring strain. The C—CO_2Me substituents are about 26° from eclipsed configurations (Table 3), and all are rotated about 40° out of the rough C(13)—C(11)—C(12)—C(15) plane. The five-membered rings in (4) and (5) are

---

* Depository material.

significantly non-planar. The rings without Cl substituents are C(11) evelopes; the rings with Cl substituents are more non-planar, with a C(12) envelope in (5) and half-chair conformations in (4).

Compound (1) undergoes a normal di-π-methane rearrangement when photolysed in acetone solution, to form the dibenzosemibullvalene photoproducts, (2) and (3) (Fig. 1). In contrast, in other solvents *e.g.* chloroform, and in the solid state, photolysis results in the formation of additional photoproducts, which have now been characterized as the dibenzopentalene derivatives (4) and (5) (Figs. 1 and 2); the amounts of (4) and (5) are greatest in the solid-state photolysis (Chen *et al.*, 1991). Products (2) and (3) are likely formed *via* the triplet excited state, and (4) and (5) *via* the singlet state, since no traces of the latter products are found in acetone (a triplet sensitizer). The formation of (4) and (5) may be rationalized by postulating a biradical intermediate, similar to the biradical proposed in the formation of a dibenzopentalene in the photolysis of the 9,10-dimethyl diester (Pokkuluri *et al.*, 1993*a*). The proposed mechanism (Fig. 3) involves rearrangement of (1), *via* the S_1 excited state, to biradical (6); (6) then undergoes homolysis of the C—Cl bond to produce a Cl atom and radical (7), which has an exocylic methylene group. Recombination of the radical pair then results in epimers (4) and (5). Such β-C—Cl bond fission of 1,4-biradicals has been proposed in other photochemical reactions (Wagner, Lindstrom, Sedon & Ward, 1981). The mechanism thus involves a non-concerted Cl-atom migration, rather than the previously observed ester migration (Pokkuluri *et al.*, 1993*a*).

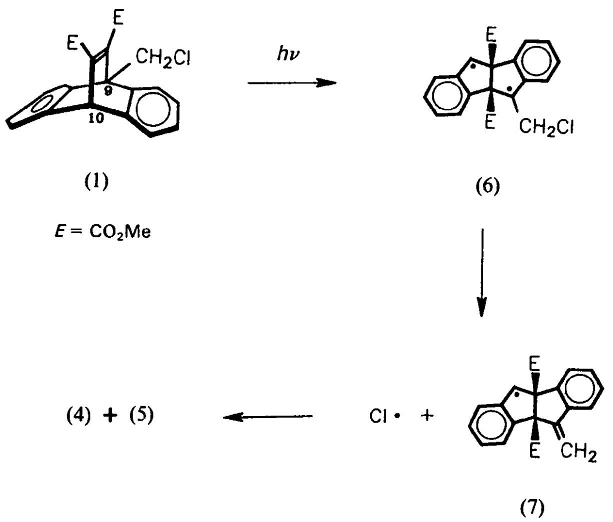

Fig. 3. Proposed reaction mechanism, involving intermediate biradical (6) and Cl-atom migration, in the formation of photoproducts (4) and (5).

In the crystal structure of (1) there is an intermolecular Cl···C(10) contact of 4.28 Å. Although this is not particularly short (van der Waals radii sum = 3.55 Å), it does suggest the possibility of an intermolecular Cl-atom transfer in the solid-state photolysis, since C(10) becomes the chlorine-bearing C atom of the photoproducts, (4) and (5). The larger amounts of these photoproducts in the solid-state photolysis may be related to the favorable reaction pathway provided by the C···Cl contacts. Intermolecular Cl-atom transfer has been proposed previously in the solid-state reaction of a chlorinated cyclohexadienone (Décoret, Vicens & Royer, 1985).

No ester-migration pentalenes or cyclooctatetaene derivatives were observed in the photolysis of (1).

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

References

Chen, J., Pokkuluri, P. R., Scheffer, J. R. & Trotter, J. (1991). *J. Photochem. Photobiol.* **57**, 21–26.

Décoret, C., Vicens, J. & Royer, J. (1985). *J. Mol. Struct.* **121**, 13–22.

Molecular Structure Corporation (1990). *TEXRAY. TEXSAN Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Pokkuluri, P. R., Scheffer, J. R. & Trotter, J. (1993*a*). *Acta Cryst.* B**49**, 107–116.

Pokkuluri, P. R., Scheffer, J. R. & Trotter, J. (1993*b*). *Acta Cryst.* B**49**, 754–760.

Wagner, P. J., Lindstrom, M. J., Sedon, J. H. & Ward, D. R. (1981). *J. Am. Chem. Soc.* **103**, 3842–3849.