

Crystal Structures and Solid-State Photochemistry of an Unsymmetrically Substituted Dibenzobarrelene and Its Two Photoproducts (Dibenzosemibullvalenes)

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Abstract

The photochemical rearrangement of an unsymmetrical 11,12-diester derivative of dibenzobarrelene in the solid state has been studied by crystal structure analyses of the starting material and its two regioisomeric photoproducts. The photochemical behaviour of the starting material has been examined from crystal-lattice and molecular-conformational points of view. Crystal data are: $T = 295$ K, Mo $K\alpha_1$, $\lambda = 0.70930$ Å, or Cu $K\alpha_1$, $\lambda = 1.54056$ Å; isopropyl methyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (Me/Pr), $C_{22}H_{20}O_4$, $M_r = 348.40$, triclinic, $P\bar{1}$, $a = 9.483$ (3), $b = 12.806$ (4), $c = 8.430$ (2) Å, $\alpha = 92.85$ (3), $\beta = 109.60$ (3), $\gamma = 103.05$ (3)°, $V = 930.6$ (5) Å³, $Z = 2$, $D_x = 1.243$ g cm⁻³, $\mu = 0.78$ cm⁻¹, $F(000) = 368$, $R = 0.044$ for 1741 observed reflections; 8d-isopropyl 8c-methyl 4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene-8c,8d-dicarboxylate (Me/Pr-p1), $C_{22}H_{20}O_4$, $M_r = 348.40$, monoclinic, $P2_1/a$, $a = 8.854$ (3), $b = 13.872$ (4), $c = 15.364$ (5) Å, $\beta = 105.32$ (3)°, $V = 1820$ (1) Å³, $Z = 4$, $D_x = 1.271$ g cm⁻³, $\mu = 0.81$ cm⁻¹, $F(000) = 736$, $R = 0.046$ for 1249 observed reflections; 8c-isopropyl 8d-methyl 4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene-8c,8d-dicarboxylate (Me/Pr-p2), $C_{22}H_{20}O_4$, $M_r = 348.40$, monoclinic, $P2_1/n$, $a = 15.029$ (2), $b = 8.155$ (1), $c = 14.561$ (2) Å, $\beta = 92.772$ (9)°, $V = 1782.5$ (4) Å³, $Z = 4$, $D_x = 1.298$ g cm⁻³, $\mu = 6.81$ cm⁻¹, $F(000) = 736$, $R = 0.051$ for 2065 observed reflections. The two ester carbonyl groups in Me/Pr show different degrees of conjugation to the central double bond, with the relevant bond lengths indicating some extent of electron delocalization over the α,β -unsaturated carbonyl system. One of the carbonyl groups in Me/Pr-p1 exhibits a *cis*-bisection conformation and hence conjugation with respect to the cyclopropane ring; however, no systematically induced bond-length asymmetry in the cyclopropane ring is apparent. No such conjugation of the cyclopropane ring to the π -acceptor substituents was observed in the structure of Me/Pr-p2. In general, the unsymmetrical 11,12-diester derivatives ($CO_2R_1 \neq CO_2R_2$) yield regioisomeric dibenzosemibullvalenes upon photolysis;

the product ratios of the regioisomers obtained from solution and solid-state photolysis are significantly different, with higher regioselectivities obtained in the solid-state photolysis than in solution. The photochemical pathway leading to the formation of the major product in the solid state could not be rationalized from electronic considerations based on the biradical stabilization differences (brought about by the conformational rigidity of the ester groups in the solid state) at the central vinyl C atoms. The preferred reaction pathway is consistent with steric packing factors estimated from (a) qualitative visual inspection of the local packing differences around the ester groups, (b) calculation of the van der Waals intermolecular steric energy as a result of the movement of the ester groups, and (c) superposition of the structures of major (Me/Pr-p1) and minor (Me/Pr-p2) products on the structure of the starting material in order to determine the best molecular fit.

Introduction

The di- π -methane rearrangement is a photochemical conversion of 1,4-dienes to vinylcyclopropanes *via* a radical mechanism (Zimmerman, 1980; Hixson, Mariano & Zimmerman, 1973; Zimmerman, Keck & Pflederer, 1976). The generally accepted mechanism proposed by Zimmerman (Fig. 1) involves an initial 2,4-bond formation in (1), to give a 1,4-cyclopropyldicarbonyl biradical (2). The biradical (2) then undergoes bond rearrangement to yield a 1,3-biradical (3) which subsequently closes to give the final structure (4). Dibenzobarrelenes of general structure (5) (Fig. 1) may be regarded as cyclic multichannel di- π -methane substrates and have been demonstrated to undergo the di- π -methane rearrangement both in solution (Ciganek, 1966) and in the solid state (Evans, Garcia-Garibay, Omkaram, Scheffer, Trotter & Wireko, 1986; Scheffer, Trotter, Garcia-Garibay & Wireko, 1988) *via* the triplet excited state. Photoproducts (8) and (8'), which are obtained from initial vinyl-benzo bridging at centres *E* and *E'* of (5), bear a regioisomeric relationship to each other. Consequently, the regioselective pathway leading to the formation of the major product in the

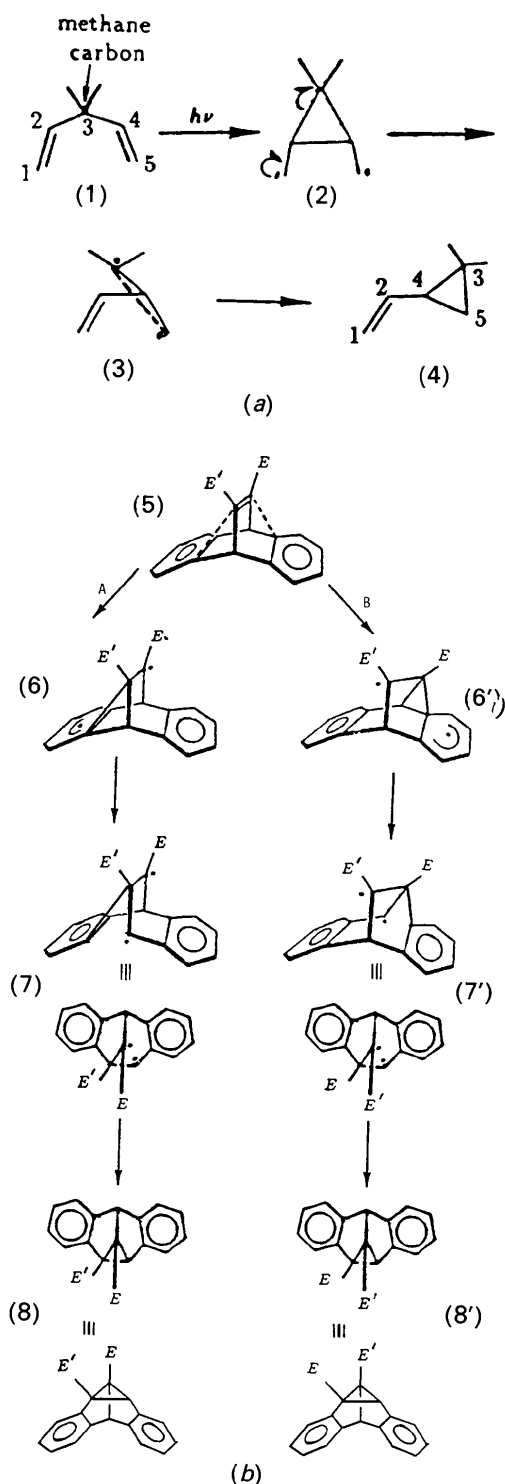


Fig. 1. (a) Schematic representation of the di- π -methane reaction mechanism. (b) Di- π -methane reaction mechanism in dibenzobarrelenes; (5) corresponds to Fig. 2(a) ($E = \text{CO}_2\text{Me}$, $E' = \text{CO}_2\text{Pr}$) and the lower drawings for (8) and (8') correspond to Figs. 2(b) and 2(c), respectively. The two additional reaction pathways, with bridging on opposite sides of molecule (5), give rise to the enantiomers of (8) and (8') (all the compounds studied in this paper are racemic).

solid state is primarily determined by the differences in the electronic and steric factors about the central vinyl C atoms and their attached ester groups.

From the electronic point of view, the regioselectivity of the rearrangement depends on the relative abilities of the ester groups to stabilize the radicals at their respective 'vinyl' C atoms following an initial vinyl-benzo bridging. If a biradical stabilization mechanism is the dominant factor determining the reaction pathway, then the major photoproduct should result from an initial vinyl-benzo bridging at the vinyl C atom bearing the ester group which is less conjugated to the central double bond. Such an initial bond formation would result in an odd-electron at the 'vinyl' C atom which bears the more conjugated ester group, a situation which is more favorable for reasons of resonance stabilization of the odd-electron (Demuth, Amrein, Bender, Braslavsky, Burger, George, Lemmer & Schaffner, 1981).

It is well known that the intrinsic reactivity of a molecule in the solid state may in some cases be less important than the nature of the packing of neighboring molecules in the crystal lattice (Cohen, Ron, Schmidt & Thomas, 1969; Cohen & Schmidt, 1964; Thomas, Morsi & Desvergne, 1977). Such packing factors may modulate or completely alter the course of an otherwise electronically favorable reaction. It is therefore reasonable to expect that the regioselectivity of the compound in the solid state might be affected by the steric packing around the ester groups in the reacting molecule and its 'fixed' lattice neighbors (Scheffer, Trotter, Garcia-Garibay & Wireko, 1988). Thus, from the crystal-packing point of view, the pathway leading to the formation of the major product in the solid state may be determined by the relative amounts of free space (Cohen, 1975; Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981) around the vinyl C atoms and their corresponding ester groups.

Predictions about the preferred reaction pathway (and hence the major product) from these two factors (electronic and crystal-lattice effects) may sometimes be contrary to one another. The two points of view were thus explored independently in an effort to gain some insight into the structural aspects of the di- π -methane rearrangement, and, if possible to derive structure-reactivity relationships for the reaction occurring in the solid state. To this end, the photochemical behavior of several differently substituted dibenzobarrelenes has been studied in solution and in the solid state. Crystal structures of some of the dibenzobarrelenes and their photoproducts (dibenzosemibullvalenes) have been determined and the relevant molecular and lattice information examined in the light of electronic and steric packing factors. Three of the compounds (a photoreactant

and its two photoproducts) are reported in this paper.

Experimental

The general procedures and parameters of data collection are summarized in Table 1. Intensities were measured at 295 K with a CAD-4F diffractometer, ω - 2θ scan (extended 25% on each side for background measurement), horizontal aperture (2.0 + $\tan\theta$) mm, vertical aperture 4 mm; three standard reflections measured periodically. Mo $K\alpha$ (graphite monochromator) or Cu $K\alpha$ (nickel-filtered) radiations were used (Table 1). Lp but no absorption corrections. The crystals scattered moderately well considering that the maximum θ values are quite high for these organic crystals; reflections with $I \geq 3\sigma(I)$ represent about 39–56% of the total number of reflections measured, data/parameter ratios are about 5–7 (Table 1). $\sigma^2(I) = S + 4(B_1 + B_2) + (0.04S)^2$, where S = scan, B_1 and B_2 background counts. The structures were determined by direct methods with the use of *MULTAN80*.*

Refinement was by full-matrix least-squares methods on F , minimizing $\sum w[|F_o| - k|F_c|]^2$, with $w = 1/\sigma^2(F)$, giving uniform values of $\sum w\Delta F^2$; H atoms were placed in calculated positions for Me/ⁱPr-p1 and were refined for Me/ⁱPr-p2 and Me/ⁱPr (except for the six terminal H atoms on the isopropyl ester group). Scattering factors were from *International Tables for X-ray Crystallography* (1974). Details of the refinements are given in Table 1.

Discussion

Final positional parameters are in Table 2,† and bond lengths and angles involving non-H atoms are in Table 3. Fig. 2 shows the stereo diagrams of the three compounds with atomic numbering. Some of the aromatic rings in all three compounds show small, but not structurally significant deviations from planarity; the maximum displacement of C atoms from the respective least-squares mean planes of the most non-planar rings are: 0.009 (3) Å for Me/ⁱPr, 0.019 (5) Å for Me/ⁱPr-p1, and 0.011 (4) Å for Me/ⁱPr-p2. The dibenzobarrelene ring skeleton in

* Programs used include locally written programs and locally modified versions of *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964), and *ORTEPII* (Johnson, 1976).

† Lists of anisotropic thermal parameters, H positions, torsion angles, bond distances and angles involving H atoms, and structure factors, together with packing diagrams, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52276 (87 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Data-collection and refinement parameters for dibenzobarrelene and dibenzosemibullvalenes

	Me/ ⁱ Pr Cyclohexane	Me/ ⁱ Pr-p1 Methylcyclohexane	Me/ ⁱ Pr-p2 Dimethyl ether
Solvent			
Dimensions (cut fragments) (mm)	0.25 × 0.3 × 0.3	0.2 × 0.25 × 0.3	0.25 × 0.3 × 0.3
Radiation	Mo $K\alpha_1$	Mo $K\alpha_1$	Cu $K\alpha_1$
Reflections for cell			
No.	25	25	25
θ range (°)	12–18	7–12	22–45
Intensity measurements			
θ_{\max} (°)	25.0	25.0	75.0
ω scan, ($a + b \tan \theta$), a (°)	0.75	0.65	0.75
ω scan, ($a + b \tan \theta$), b (°)	0.35	0.35	0.14
Scan speed (° min ⁻¹)	1.50–10.06	0.96–10.06	1.18–10.06
h	-11→10	-10→10	-18→18
k	-15→15	0→16	0→10
l	0→10	0→17	0→18
Total unique reflections	3268	3204	3667
Reflections with $I \geq 3\sigma(I)$	1741	1249	2065
%	53.3	39.0	56.3
Structure refinements			
No. of parameters refined	291	235	316
Data/parameter ratio	6.0	5.3	6.5
Δ/σ mean	0.001	0.001	0.001
maximum	0.175	0.002	0.005
$\Delta\rho$ (e Å ⁻³)	-0.19→0.21	-0.22→0.29	-0.38→0.27
R [$I \geq 3\sigma(I)$]	0.044	0.046	0.051
wR	0.049	0.048	0.057
S (goodness of fit)	1.85	1.70	2.10
R (all data)	0.105	0.179	0.103
Extinction, g	—	—	5.5 (9) × 10 ³

Me/ⁱPr is similar to that of dibenzobarrelene itself (Trotter & Wireko, 1990). The angles external to the benzene rings ρ , mean 127.2° (Fig. 3), and the intramolecular benzene-barrelene angles ϵ , mean 112.5°, are distorted to about the same extent as in dibenzobarrelene. The dibenzosemibullvalene ring skeletons in Me/ⁱPr-p1 and Me/ⁱPr-p2 are very similar. The corresponding mean values for ρ and ϵ in the product molecules where the ring fusion is between benzene and cyclopropane are 129 and 110.1°, respectively. Thus, the distortion of these angles at the fused junctions appears to be a function of ring size. In addition, the values of these angles are consistent with the observation that strain induced in the benzene ring by fusion to cycloalkanes (especially small rings) is reflected in systematic angular deformations (Allen, 1981a). Bond lengths and angles in the aromatic rings of all three compounds are close to expected values, with mean C—C_{aromatic} = 1.382, 1.386, 1.385 Å, and C—C—C_{aromatic} of 120° each for Me/ⁱPr, Me/ⁱPr-p1 and Me/ⁱPr-p2, respectively. The length of the bridging double bond (C11=C12) in Me/ⁱPr [1.334 (4) Å] is in agreement with the equivalent bridge bond length of 1.343 (5) Å in the dicarbonitrile derivative (Oliver, Fallon & Smith, 1986) but significantly longer [1.316 (4) Å] than that in dibenzobarrelene itself (Trotter & Wireko, 1990).

In the unsymmetrical diester derivatives, the ester groups are chemically and geometrically different in the degree of conjugation of the carbonyl groups to the vinyl double bond (C11=C12). For Me/ⁱPr, the dihedral angles C12—C11—C13—O2 (φ_1) and

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

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Me/Pr				
C1	9979 (3)	3397 (3)	5149 (4)	53
C2	10654 (4)	2648 (3)	4647 (4)	58
C3	9983 (4)	1565 (3)	4444 (4)	56
C4	8611 (4)	1194 (3)	4732 (4)	50
C4a	7926 (3)	1922 (2)	5213 (3)	41
C5	6617 (4)	1758 (4)	8741 (5)	77
C6	7106 (6)	2417 (7)	10315 (6)	100
C7	7776 (6)	3492 (6)	10466 (6)	100
C8	7992 (4)	3972 (4)	9116 (4)	74
C8a	7515 (3)	3335 (3)	7565 (3)	53
C9	7659 (3)	3709 (2)	5936 (3)	47
C9a	8600 (3)	3032 (2)	5411 (3)	42
C10	6430 (3)	1681 (3)	5583 (3)	45
C10a	6837 (3)	2238 (3)	7371 (4)	54
C11	6026 (3)	3350 (2)	4575 (3)	43
C12	5393 (3)	2288 (2)	4382 (3)	42
C13	5300 (3)	4146 (2)	3624 (3)	42
C14	5779 (5)	5694 (4)	2280 (6)	72
C15	3854 (3)	1663 (2)	3191 (4)	46
C16	1901 (5)	1508 (4)	441 (5)	85
C17	1136 (5)	2376 (4)	-97 (6)	123
C18	2166 (7)	955 (4)	-997 (7)	170
O1	6319 (2)	4835 (2)	3146 (2)	56
O2	3992 (2)	4197 (2)	3350 (2)	59
O3	3453 (2)	2009 (2)	1707 (2)	66
O4	3082 (3)	902 (2)	3550 (2)	95
Me/Pr-pl				
C1	6941 (5)	1662 (4)	8654 (3)	55
C2	7659 (6)	2283 (3)	8189 (4)	70
C3	7540 (6)	2144 (4)	7276 (4)	68
C4	6667 (5)	1388 (3)	6815 (3)	55
C4a	5884 (5)	787 (3)	7271 (3)	40
C5	7486 (6)	-2016 (3)	8148 (3)	63
C6	8594 (6)	-2142 (4)	8964 (4)	78
C7	8639 (6)	-1535 (4)	9685 (3)	72
C8	7559 (5)	-791 (4)	9620 (3)	58
C8a	6436 (5)	-682 (3)	8817 (3)	43
C9	5201 (5)	111 (3)	8540 (2)	42
C9a	6021 (5)	921 (3)	8189 (3)	41
C10	5032 (5)	-1037 (3)	7318 (3)	45
C10a	6400 (5)	-1281 (3)	8083 (3)	45
C11	4084 (5)	-312 (3)	7678 (3)	41
C12	4786 (5)	-25 (3)	6908 (3)	40
C13	2360 (6)	-389 (3)	7504 (3)	50
C14	131 (6)	55 (5)	7984 (4)	109
C15	3738 (5)	16 (4)	5963 (3)	49
C16	1746 (6)	981 (3)	4977 (3)	61
C17	472 (6)	1541 (4)	5210 (4)	107
C18	2409 (7)	1463 (5)	4301 (4)	123
O1	1847 (3)	50 (2)	8135 (2)	69
O2	1526 (3)	-798 (3)	6873 (2)	79
O3	2978 (3)	860 (2)	5827 (2)	59
O4	3592 (4)	-617 (2)	5411 (2)	66
Me/Pr-p2				
C1	6992 (2)	3816 (5)	9057 (2)	45
C2	7792 (3)	3184 (5)	9432 (3)	52
C3	8118 (2)	1719 (6)	9130 (3)	54
C4	7655 (2)	822 (5)	8458 (2)	46
C4a	6865 (2)	1444 (4)	8076 (2)	36
C5	5729 (3)	-1881 (5)	8378 (2)	48
C6	5135 (3)	-2481 (5)	8987 (3)	55
C7	4434 (3)	-1522 (6)	9253 (3)	57
C8	4303 (2)	44 (5)	8909 (2)	47
C8a	4890 (2)	645 (4)	8275 (2)	35
C9	5701 (2)	3367 (4)	7836 (2)	36
C9a	6533 (2)	2943 (4)	8376 (2)	36
C10	6193 (2)	656 (4)	7403 (2)	34
C10a	5600 (2)	-333 (4)	8014 (2)	34
C11	4880 (2)	2232 (4)	7785 (2)	35
C12	5595 (2)	2094 (4)	7081 (2)	34
C13	4014 (2)	3088 (5)	7539 (2)	42
C14	2552 (2)	2731 (7)	6912 (3)	59
C15	5441 (2)	2624 (4)	6105 (2)	38
C16	6096 (2)	2714 (5)	4636 (2)	45
C17	7059 (3)	2842 (8)	4417 (3)	66
C18	5577 (4)	1537 (7)	4024 (3)	63

Table 2 (cont.)

	x	y	z	U_{eq}
O1	3400 (1)	2038 (3)	7233 (2)	49
O2	3887 (2)	4526 (4)	7618 (2)	76
O3	6104 (1)	2116 (3)	5596 (1)	42
O4	4818 (2)	3418 (4)	5828 (2)	65

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

	Me/Pr	Me/Pr-pl	Me/Pr-p2
C1—C2	1.388 (4)	1.378 (6)	1.394 (5)
C1—C9a	1.380 (4)	1.386 (5)	1.378 (4)
C2—C3	1.364 (4)	1.392 (6)	1.372 (6)
C3—C4	1.386 (4)	1.382 (6)	1.382 (5)
C4—C4a	1.368 (4)	1.387 (5)	1.383 (4)
C4a—C9a	1.397 (4)	1.396 (5)	1.399 (4)
C4a—C10	1.521 (4)	—	1.515 (4)
C4a—C12	—	1.496 (5)	—
C5—C6	1.409 (7)	1.383 (6)	1.378 (5)
C5—C10a	1.389 (4)	1.387 (5)	1.379 (5)
C6—C7	1.359 (7)	1.384 (6)	1.382 (6)
C7—C8	1.373 (6)	1.392 (6)	1.383 (6)
C8—C8a	1.382 (4)	1.374 (5)	1.395 (4)
C8a—C9	1.515 (4)	1.530 (5)	—
C8a—C10a	1.383 (4)	1.394 (5)	1.399 (4)
C8a—C11	—	—	1.477 (4)
C9—C9a	1.523 (4)	1.513 (6)	1.486 (4)
C9—C11	1.536 (4)	1.543 (5)	1.541 (4)
C9—C12	—	—	1.515 (4)
C10—C10a	1.519 (4)	1.487 (5)	1.521 (4)
C10—C11	—	1.506 (5)	—
C10—C12	1.533 (4)	1.531 (5)	1.538 (4)
C11—C12	1.334 (4)	1.527 (5)	1.524 (4)
C11—C13	1.478 (4)	1.482 (6)	1.505 (4)
C12—C15	1.479 (4)	1.504 (5)	1.493 (4)
C13—O1	1.336 (3)	1.323 (5)	1.320 (4)
C13—O2	1.201 (3)	1.195 (5)	1.194 (4)
C14—O1	1.445 (4)	1.475 (5)	1.450 (4)
C15—O3	1.310 (3)	1.338 (5)	1.336 (4)
C15—O4	1.197 (3)	1.205 (5)	1.194 (4)
C16—C17	1.469 (6)	1.489 (6)	1.500 (6)
C16—C18	1.495 (7)	1.481 (7)	1.502 (6)
C16—O3	1.473 (4)	1.473 (4)	1.479 (4)
Me/Pr			
C2—C1—C9a	119.1 (3)	C10a—C10—C12	106.3 (2)
C1—C2—C3	120.7 (3)	C5—C10a—C8a	120.2 (3)
C2—C3—C4	120.5 (4)	C5—C10a—C10	127.0 (4)
C3—C4—C4a	119.4 (3)	C8a—C10a—C10	112.7 (3)
C4—C4a—C9a	120.4 (3)	C9—C11—C12	113.1 (2)
C4—C4a—C10	127.5 (3)	C9—C11—C13	120.7 (3)
C9a—C4a—C10	112.2 (3)	C12—C11—C13	126.1 (2)
C6—C5—C10a	118.3 (5)	C10—C12—C11	113.6 (2)
C5—C6—C7	120.1 (5)	C10—C12—C15	118.4 (3)
C6—C7—C8	121.9 (5)	C11—C12—C15	127.9 (2)
C7—C8—C8a	118.5 (5)	C11—C13—O1	110.6 (2)
C8—C8a—C9	126.4 (4)	C11—C13—O2	125.3 (3)
C8—C8a—C10a	121.0 (3)	O1—C13—O2	124.0 (3)
C9—C8a—C10a	112.6 (3)	C12—C15—O3	113.3 (3)
C8a—C9—C9a	105.8 (2)	C12—C15—O4	122.7 (3)
C8a—C9—C11	106.5 (2)	O3—C15—O4	124.0 (3)
C9a—C9—C11	105.7 (2)	C17—C16—C18	111.5 (4)
C1—C9a—C4a	119.9 (3)	C17—C16—O3	107.9 (3)
C1—C9a—C9	127.7 (3)	C18—C16—O3	105.7 (4)
C4a—C9a—C9	112.4 (3)	C13—O1—C14	116.2 (3)
C4a—C10—C10a	106.2 (2)	C15—O3—C16	118.9 (2)
C4a—C10—C12	105.2 (2)		
Me/Pr-pl			
C2—C1—C9a	119.0 (4)	C8a—C10a—C10	110.1 (4)
C1—C2—C3	120.9 (4)	C9—C11—C10	106.0 (3)
C2—C3—C4	120.3 (5)	C9—C11—C12	105.4 (3)
C3—C4—C4a	118.9 (4)	C9—C11—C13	125.3 (4)
C4—C4a—C9a	120.6 (4)	C10—C11—C12	60.6 (3)
C4—C4a—C12	128.8 (4)	C10—C11—C13	122.2 (4)
C9a—C4a—C12	110.6 (4)	C12—C11—C13	119.3 (3)
C6—C5—C10a	118.1 (4)	C4a—C12—C10	122.0 (3)
C5—C6—C7	120.8 (5)	C4a—C12—C15	105.4 (3)
C6—C7—C8	121.3 (4)	C4a—C12—C11	120.4 (4)
C7—C8—C8a	117.8 (4)	C10—C12—C11	59.0 (3)
C8—C8a—C9	128.6 (4)	C10—C12—C15	114.6 (3)
C8—C8a—C10a	121.2 (4)	C11—C12—C15	119.0 (3)
C9—C8a—C10a	109.9 (4)	C11—C13—O1	111.8 (4)

Table 3 (cont.)

C8a—C9—C9a	105.0 (3)	C11—C13—O2	124.5 (5)
C8a—C9—C11	102.4 (3)	O1—C13—O2	123.7 (5)
C9a—C9—C11	103.6 (3)	C12—C15—O3	110.0 (4)
C1—C9a—C4a	120.1 (4)	C12—C15—O4	125.2 (4)
C1—C9a—C9	129.7 (4)	O3—C15—O4	124.8 (4)
C4a—C9a—C9	109.8 (4)	C17—C16—C18	113.5 (5)
C10a—C10—C11	106.1 (3)	C17—C16—O3	106.1 (4)
C10a—C10—C12	122.1 (3)	C18—C16—O3	109.5 (4)
C11—C10—C12	60.4 (3)	C13—O1—C14	115.2 (4)
C5—C10a—C8a	120.8 (4)	C15—O3—C16	117.5 (3)
C5—C10a—C10	128.9 (4)		
Me ⁱ Pr-p2			
C2—C1—C9a	118.9 (4)	C8a—C10a—C10	109.5 (3)
C1—C2—C3	120.7 (4)	C8a—C11—C9	120.9 (3)
C2—C3—C4	120.9 (4)	C8a—C11—C12	105.7 (3)
C3—C4—C4a	118.9 (4)	C8a—C11—C13	120.6 (3)
C4—C4a—C9a	120.5 (3)	C9—C11—C12	59.2 (2)
C4—C4a—C10	129.5 (3)	C9—C11—C13	114.4 (3)
C9a—C4a—C10	109.7 (3)	C12—C11—C13	120.2 (3)
C6—C5—C10a	119.3 (4)	C9—C12—C10	105.2 (2)
C5—C6—C7	120.3 (4)	C9—C12—C11	60.9 (2)
C6—C7—C8	121.2 (4)	C9—C12—C15	119.9 (3)
C7—C8—C8a	118.7 (4)	C10—C12—C11	105.8 (2)
C8—C8a—C10a	119.6 (3)	C10—C12—C15	124.9 (3)
C8—C8a—C11	129.5 (3)	C11—C12—C15	122.5 (3)
C10a—C8a—C11	110.9 (3)	C11—C13—O1	111.2 (3)
C9a—C9—C11	122.5 (3)	C11—C13—O2	124.9 (3)
C9a—C9—C12	106.3 (3)	O1—C13—O2	123.8 (3)
C11—C9—C12	59.8 (2)	C12—C15—O3	110.7 (3)
C1—C9a—C4a	120.1 (3)	C12—C15—O4	124.2 (3)
C1—C9a—C9	129.8 (3)	O3—C15—O4	125.1 (3)
C4a—C9a—C9	110.0 (3)	C17—C16—C18	113.4 (4)
C4a—C10—C10a	103.7 (2)	C17—C16—O3	105.1 (3)
C4a—C10—C12	103.6 (3)	C18—C16—O3	109.3 (3)
C10a—C10—C12	103.4 (2)	C13—O1—C14	116.4 (3)
C5—C10a—C8a	120.8 (3)	C15—O3—C16	116.8 (3)
C5—C10a—C10	129.3 (3)		

C11—C12—C15—O4 (φ_2) are 45.6 (4) and -144.4 (3) $^\circ$, respectively, *i.e.* the stereochemistries of the C=C—C=O systems are *syn* and *anti* for the CO₂Me and Co₂ⁱPr ester groups, respectively; the shortest non-bonded intramolecular contact between the ester groups is O2...O3 = 2.918 (3) Å. The two ester groups are partially conjugated to the central double bond, but to slightly different extents ($\cos^2\varphi_1 = 0.49$, $\cos^2\varphi_2 = 0.66$). This partial conjugation in the α,β -unsaturated carbonyl system is reflected in the sp^2 — sp^2 (C11—C13 and C12—C15) single-bond lengths of 1.478 (4) and 1.479 (4) Å, respectively. The values of the bond lengths reasonably suggest some extent of electron delocalization over the α,β -unsaturated carbonyl systems; the expected bond length for complete delocalization for such a system is 1.470 (2) Å, with 1.497 (2) Å indicating no significant electron delocalization (Allen, 1981b).

There is an additional strain in the product molecules relative to the starting material as a result of the cyclopentane—cyclopropane ring fusion. Bond angles within the cyclopropane rings are within expected values. The subject of substituent-induced bond-length asymmetry in cyclopropane (Δ) and the geometry of the substituent grouping C₁—R₁—R₁₁ of Fig. 3 has received some attention in the literature (Allen, 1980, 1981b). Treatment of the geometrical data of the cyclopropane and its substituent groups in MeⁱPr-p1 and MeⁱPr-p2 along the lines of the

analysis used in the above references (using the midpoints of the cyclopropane ring bonds, M_{ij} opposite atoms C_{ij}) shows that the torsion angle τ_1 (M11—C11—C13—O2) is -11.9° and τ_2 (M12—C12—C15—O4) is 62.9° for MeⁱPr-p1, and 52.7 and 24.6° for MeⁱPr-p2 (Fig. 3). Accordingly, the C13=O2 bond in MeⁱPr-p1 shows a *cis*-bisection conformation with respect to the cyclopropane ring and the carbonyl group is expected to be conjugated to the cyclopropane ring, whereas C15=O4 should show no such conjugative ability; upper limits for effective conjugation are estimated at $\pm 15^\circ$ (Allen, 1980). No such conjugation of the Δ ring to the π -acceptor substituents is apparent in MeⁱPr-p2. Evidence of conjugation of cyclopropane to π -acceptor substituents as we have in MeⁱPr-p1 is sometimes reflected in systematic shortening of the distal bond and lengthening of vicinal bonds in the cyclopropane ring, but no such systematic bond-length asymmetry in the cyclopropane ring of MeⁱPr-p1 is apparent. However, the bond lengths

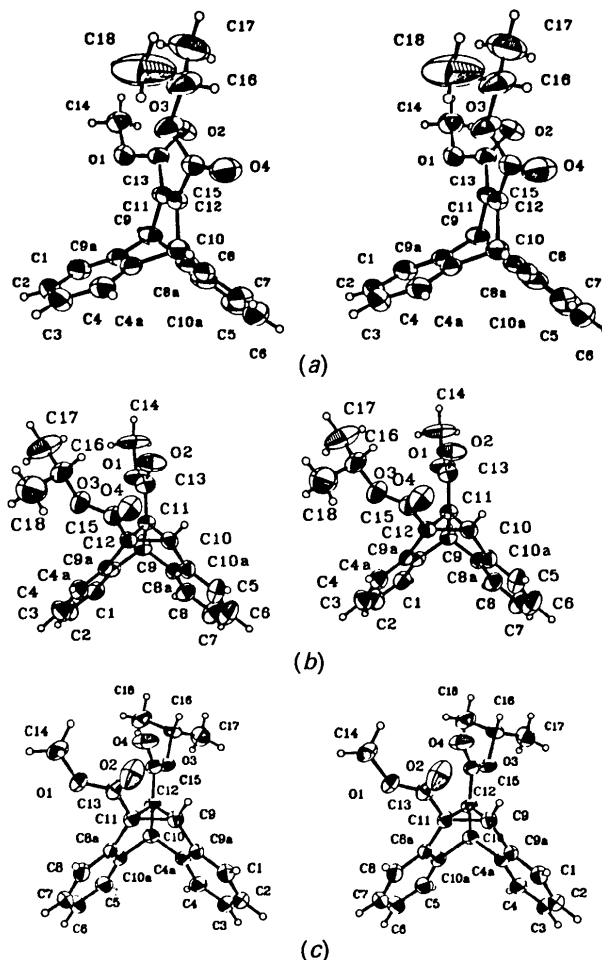


Fig. 2. Stereo diagrams (50% probability ellipsoids) and atomic numbering for (a) MeⁱPr, (b) MeⁱPr-p1 and (c) MeⁱPr-p2.

C_1-R_1 and R_1-R_{11} (Fig. 3) do seem to indicate some features of conjugation and non-conjugation. The bond lengths $C_{11}-C_{13}$ [1.482 (6) Å] and $C_{12}-C_{15}$ [1.504 (5) Å] for MeⁱPr-p1 seem to suggest that $C_{13}=O_2$ is conjugated to the cyclopropane ring while $C_{15}=O_4$ is not. Admittedly, the differences in the bond lengths are hardly significant enough to warrant any firm conclusion. It is interesting to observe that the bond lengths $C_{11}-C_{13}$ [1.505 (4) Å] and $C_{12}-C_{15}$ [1.493 (4) Å] of MeⁱPr-p2 do not differ from each other, as would be expected from the torsion angles τ_1 and τ_2 , and both are in agreement with the expected value for a non-conjugated system. The corresponding literature values for these bond lengths in conjugated and non-conjugated systems are 1.484 (4) and 1.506 (6) Å, respectively (Allen, 1980).

There are no exceptionally short intermolecular contacts in the crystal structures of these compounds although a few contacts are below the sum of the van der Waals radii of the atoms involved: $O_4 \cdots H_4$ 2.54, $H_4 \cdots H_{17c}$ 2.39 and $H_{17a} \cdots H_{18b}$ 2.27 Å in MeⁱPr-p1; $O_2 \cdots H_{14a}$ 2.58 Å in MeⁱPr-p2. No such contacts were observed in MeⁱPr.

Structure-reactivity relationships

All the dibenzobarrelenes studied so far were found to undergo the di- π -methane reaction upon irradiation in solution and in the solid state (Garcia-Garibay, 1988; Scheffer, Trotter, Garcia-Garibay & Wireko, 1988). In the unsymmetrical 11,12-diester

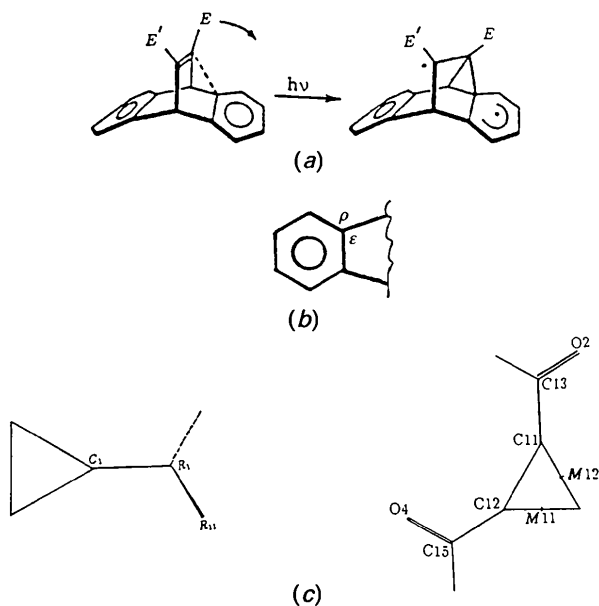
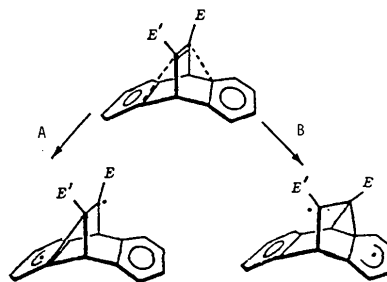


Fig. 3. (a) Movement of an ester group during vinyl-benzo bridging. (b) Definition of angles ρ and ϵ . (c) Geometry of the cyclopropane substructure.

derivatives, two products (major and minor) are usually identified. The observed product ratios for MeⁱPr obtained upon photolysis in solution and in the solid state are shown in Fig. 4, where product B is the product resulting from an initial vinyl-benzo bridging of the vinyl C atom bearing the methyl ester group and product A is the regioisomer of B. MeⁱPr-p1 (major product) and MeⁱPr-p2 (minor product) correspond to product A and product B, respectively. Regioselectivity is higher in the solid state than in solution, and this is generally the case for unsymmetrical 11,12-derivatives where the ester substituents are both alkyl groups. Two factors, odd-electron stabilization and crystal-lattice steric effects, have been explored with the view of determining which factor best explains the formation of the major product in the solid state.

Electronic factors

An odd-electron stabilization mechanism predicts that the major product should result from an initial vinyl-benzo bridging at the vinyl C atom bearing the ester group (in this case C11 and the methyl ester) which is less conjugated to the central double bond. The other route (initial vinyl-benzo bridging at the more conjugated vinyl C atom) is less favorable for reasons of resonance stabilization (Demuth *et al.*, 1981). The extent of odd-electron stabilization at a particular 'vinyl' C atom can be estimated from the conjugation of the ester group with the central C=C double bond in the reactant molecule, the stabilization (Dewar, 1952) being taken as proportional to $\cos^2 \varphi$ where φ is the dihedral angle about the C—C bond between a vinyl C atom and the carbonyl C atom attached to it. The angle defines the extent to



E	E'	$\cos^2 \varphi_1$	$\cos^2 \varphi_2$	Expected Pathway	Observed Pathway	Product Ratios A : B	
						Solution	Solid
CO ₂ Me	CO ₂ ⁱ Pr	0.49	0.66	B	A	55:45	93:7

Fig. 4. Expected and observed products based on odd-electron stabilization mechanism (φ_1 , φ_2 = C=C—C=O torsion angles at E, E', respectively).

which the mean plane of the carbonyl group of the ester is out of the plane of the central double bond. The $\cos^2\phi$ values of the torsion angles, along with the expected reaction pathway leading to the formation of the major product based on the relative odd-electron stabilization considerations and the experimentally observed pathway, are presented in Fig. 4. It is clear that the argument fails to explain the results, since the predicted major product is actually observed to be the minor product. Thus, the biradical stabilization differences at the vinyl C atoms (brought about by the conformational rigidity of the ester groups in the solid state) do not appear to explain the regioselectivity of the photochemical process.

Steric factors

An alternative explanation for the observed regioselectivity involves steric considerations in the solid state. It is apparent from Fig. 3 that the initial bond formation entails a relatively large movement of the vinyl C atom and its attached ester group. Undoubtedly, there are some atomic displacements in the benzene rings and the non-bridging vinyl C atom (and its attached ester group) as well, but to a crude approximation these atoms may be regarded as relatively 'stationary'. Under these conditions, the initial bond formation may be regarded primarily as the movement of a vinyl C atom (and its attached ester group) towards a nearby 'stationary' aromatic C atom. The local steric surrounding of a particular vinyl C and its attached ester group would be an important factor in the ease of the movement necessary for the initial bond formation. The pathway leading to the formation of the major product in the solid state is expected to be an initial vinyl-benzo bridging at the vinyl C atom bearing the ester group which is less sterically hindered. Three approaches have been adopted for depicting the relative amount of free space around the ester groups: (a) qualitative visual inspection of the local packing differences around the ester groups, (b) calculation of the van der Waals intermolecular steric energy as a result of the movement of the ester groups, and (c) superposition of the structures of major and minor products on the structure of the starting material in order to determine the best molecular fit. The above three points will be considered in turn.

Examination of the crystal packing for Me^tPr* indicates that the methyl ester group is more tightly surrounded by neighboring atoms than is the isopropyl group, particularly in the direction in which the methyl ester group would have to move to form the initial vinyl-benzo bridging. This suggests that

the preferred initial bond formation would involve the vinyl C atom bearing the sterically less hindered isopropyl ester group. This is consistent with path *A* which leads to the formation of the observed major product in the solid state.

In an attempt to quantify the local packing differences around the ester groups, the motions involved in the initial vinyl-benzo bridging of each of the ester groups were simulated and the resulting intermolecular steric energy was then calculated by using a locally written program (Evans, 1986). For Me^tPr, the approach taken was as follows: a vector is defined about which a rotation is to be performed, in order to move a vinyl C atom and its attached ester group towards a nearby aromatic C atom for an initial bond formation to take place. For example, if we intend to move C11 and its attached ester group *ME* in Me^tPr into a vinyl-benzo bridging position, the vector to use would be C9 to C12 (Fig. 2a); to move C12 and its attached ester group *IS*, C10 to C11 would be defined as the vector around which a rotation would be performed. Taking the coordinates of the crystal structure of the reactant as the equilibrium position corresponding to 0° rotation, a clockwise rotation about the vector is defined as positive and an anticlockwise rotation is considered negative (see Fig. 5). The coordinates of all other atoms in the molecule are fixed and only the vinyl atom and its attached ester group are allowed to move; they constitute the 'mobile unit'. As the rotation is performed about the defined vector, the vinyl C atom of interest is gradually being brought into a bonding distance of a nearby aromatic C atom. In this particular example, if C10 and C11 is the vector, then a negative rotation about the vector should move C12 towards C4a while a positive rotation moves C12 towards C10a. At the same time, other atoms in the 'mobile unit', in this case the isopropyl ester, move against a 'fixed' environment. The rotation is performed in 2° increments and at each step the intermolecular steric interaction energy involving each atom in the 'mobile unit' and its neighboring atoms within a radius of 3.3 Å is calculated using the 6-12 Lennard-Jones pairwise non-bonded potential function (Hagler, Huller & Lifson, 1974). The sum of such energies for all the atoms in the 'mobile unit' constitutes the intermolecular steric energy for that ester group at that step. A similar treatment is applied to vinyl C atom C11 and its attached methoxycarbonyl group *ME*. The result of such a calculation is shown in Fig. 5, which is a plot of intermolecular steric energy versus angle of rotation. The two approaches (free space by inspection and intermolecular steric energy) are expected to complement each other since molecular displacement towards available free space corresponds to a low energy process.

* Packing diagrams have been deposited; see previous footnote.

It is worth noting that, even though the vinyl C atoms could in principle be moved into a C—C bonding distance of about 1.54 Å from a nearby aromatic C atom, it is not necessary to do so. This is because of the crude rigid-lattice approximation involved in the analysis. As a result, very large unrealistic energy values are obtained before the vinyl C atom is close to bonding with a nearby aromatic C atom. However, the displacements that have been used are large enough to show a trend which is a useful probe for intermolecular energy effects on the reaction course of the compounds under investigation.

Comparing the overall energy profiles (Fig. 5), it is apparent that the profile of *ME* is relatively steeper than the profile corresponding to the movement of *IS*. A relatively shallow energy profile corresponds to a lower energy process. Therefore, the major product on the basis of this analysis should involve an initial bond formation at the vinyl C atom bearing the isopropyl ester group. Thus, the expected major product on the basis of steric arguments is consistent with the experimental data and in accord with the conclusion arrived at *via* the qualitative visual inspection of the local environments of the ester groups.

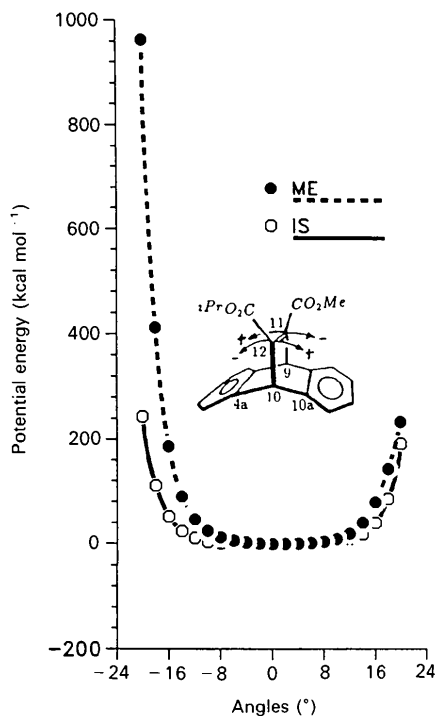


Fig. 5. Intermolecular steric energy profile for Me/Pr. The plots show that the increase in steric energy during the initial vinyl-benzo bridging step is relatively greater for bridging at the CO₂Me vinyl C atom (*ME*), so that this would be (as observed) the *less*-favorable reaction pathway (pathway *B* in Fig. 4). 1 kcal mol⁻¹ = 4.1868 kJ mol⁻¹.

A third indicator for the effect of the crystal lattice on the di- π -methane rearrangement of this class of compounds uses the idea of the reaction cavity introduced by Cohen (1975), which suggests that a reaction pathway which would lead to a product that can best be accommodated in the lattice of the starting material is usually favored in the solid state. Since the crystal structures of the major (Me/Pr-p1) and the minor (Me/Pr-p2) products arising from the photolysis of Me/Pr were determined, it was interesting to verify whether or not the reaction cavity concept is upheld in the di- π -methane rearrangement of these diesters in the solid state. One way of testing this idea in our system is to determine which of the products (major *versus* minor) better resembles the shape and size of the reactant molecule. This approach involves the superposition of the major and the minor products on the reactant molecule. Using a best molecular fit program *BMFIT* (Nyburg, 1978) a product molecule is superimposed on a reactant molecule in the crystal lattice of the starting material. It is a 'rigid' fit in that there is an atom-atom match-up between the product and the starting material without any conformation changes in the molecules. In this case the match-up is such that a particular atom number (*e.g.* C1) in the structure of

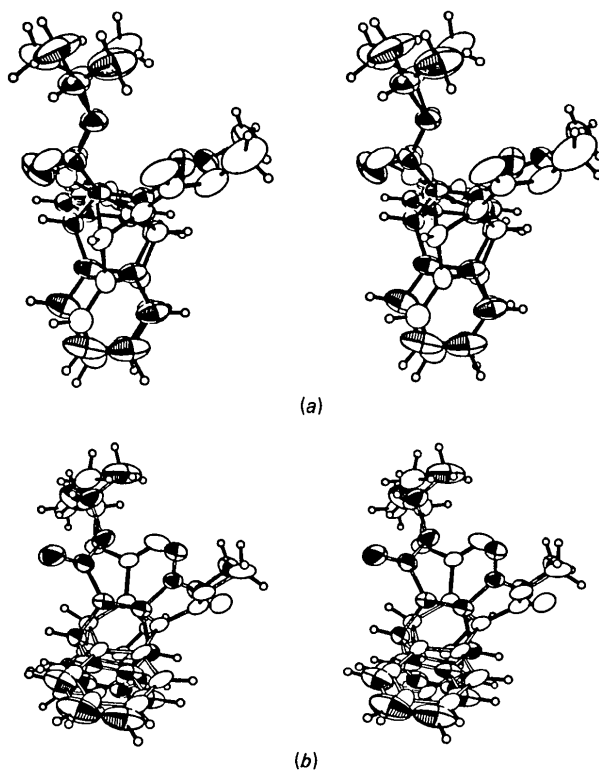


Fig. 6. Superposition of (a) Me/Pr-p1 and (b) Me/Pr-p2 on Me/Pr.

the starting material should be superimposed on an equivalent atom (C1) in the structure of the product without any conformational adjustments. It is therefore essential that equivalent atoms in the structures of the starting material and the product molecules have the same atomic numbering. Fig. 6 shows the results of such superpositions of the major product Me/¹³C-*p1* and the starting material Me/¹³C on one hand, and the minor product Me/¹³C-*p2* on the same starting material on the other. The ellipsoids of the non-H atoms of the starting material are shaded and the unshaded non-H atoms belong to the product molecule. A measure of the overlap between an atom in the product molecule and the corresponding atom in the starting material is given by the square of the distance (Δ^2) between the two atoms. The sum of all the displacements squared ($\sum\Delta^2$) gives the overall measure of fit.

It is apparent from Fig. 6 that in general the starting material and the products have rather similar shapes and common volumes of overlap. More importantly, there is a better overlap between the major product and the starting material than between the minor product and the starting material. The $\sum\Delta^2$ values are 84.6 Å² for the Me/¹³C-*p1*:Me/¹³C system and 132.8 Å² for the Me/¹³C-*p2*:Me/¹³C system. The unknown factor about this type of analysis is whether or not the conformation of the product as determined by X-ray crystallography is the same as when it was initially formed in the lattice of the starting material. For what it is worth, however, this analysis, like the previous two approaches, predicts a major product on the basis of the reaction-cavity concept, and the expected product is consistent with the experimental result.

Thus, the correlation of structural and photochemical data has shown that the odd-electron stabilization concept does not seem to explain adequately the solid-state results for these compounds. Three types of analyses – visual inspection of packing environment, potential-energy calculations, and superposition of products on starting material – do complement each other in showing that the solid-state results are explainable on the basis of steric packing factors.

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