For (I) and (II), intensities corrected for Lp; absorption corrections and secondary extinction not used; atomic scattering factors from *SHELX*76. Structures solved by direct methods with *MULTAN*11/84 (Main, Germain & Woolfson, 1984), *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1986) and *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The refined atomic coordinates and isotropic temperature factors are presented in Table 1;* important bond distances and bond angles are given in Table 2; the molecular structures and the numbering of the atoms are shown in Fig. 1. The observed values of bond lengths and bond angles of the Boc group and urethane moiety are normal (Table 2). The bond lengths of the phenacyl C=O in both molecules are similar [C(21)—O(22) = 1·225 (6) Å (I); C(14)—O(15) = 1·222 (5) Å (II)]. The ester C=O distances are slightly shorter [C(17)—O(18) = 1·192 (6) Å (I); C(10)—O(11) = 1·194 (5) Å (II)]. This small difference between phenacyl and ester C=O might be a result of the resonance effect of the phenyl ring. The urethane amide bond adopts the *trans* conformation for the two compounds with O(5)—C(6)—N(8)—C(9) torsion angles of 174·4 (2) and −178·4 (2)° respectively. The difference of dihedral angles might be due to the presence

of the phenylalanine side chain. In compound (I) the urethane N—H forms an intermolecular hydrogen bond with the phenacyl C=O of a neighbouring molecule [O(22)···H(8) = 2·207 (75) Å]. In compound (II) the crystals are stabilized by intermolecular bonds involving the urethane moieties [O(7)···H(8) = 2·114 (65) Å]. The preference of the phenacyl and urethane C=O to participate in hydrogen bonding indicates that they are better hydrogen-bond acceptors than the ester C=O group.

The *trans* amide linkage in the urethane moiety of both compounds places O(5) and H(8) in a *cis* arrangement with O(5)—H(8) = 2·308 (77) Å in (I) and 2·250 (64) Å in (II).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44164 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 2,3-Dibenzoyl-1-methylbicyclo[2.2.2]octa-2,5-diene

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Abstract. $C_{23}H_{20}O_2$, $M_r = 328·41$, monoclinic, $P2_1$, $a = 5·890$ (1), $b = 13·910$ (2), $c = 10·722$ (2) Å, $\beta = 101·01$ (2)°, $V = 862·27$ Å^3, $Z = 2$, $F(000) = 348$, D_m(by flotation) = 1·257, $D_x = 1·265$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·7107$ Å, $\mu = 0·856$ cm^{-1}, $R = 0·036$ for 1232 reflections with $I > 2\sigma(I)$. This structural study was aimed primarily at determining the conformation of the carbonyl groups. The structure could not be solved by a usual direct-methods program and a random phasing approach proved successful. Besides

the difference in conformation of the two carbonyl groups, an interesting feature, namely the indistinguishability of linkages of supposedly two types, C—CH₂—CH₂—C and C—CH=CH—C, was revealed by the structural study. This is explained in terms of a random static disorder involving the R and S isomers of the racemate material.

Introduction. The interest in the crystal structure of the title compound centres on the fact that the molecule (a) shows a selective reactivity at one of the carbonyl carbon atoms under UV irradiation. During the process of phototransformation there is apparently equal probability of abstraction of the phenyl moiety by either of the carbonyl oxygens. In that case the end product would contain a mixture of methyl 1-methyl-5-(1-phenoxy-1-phenylmethylene)bicyclo[2.2.2]oct-2-ene-6-carboxylate (b) and its 5-carboxylate isomer (c). The selective formation of the former product suggests either a restricted rotation around the C—CO bond nearer to the bridged methyl group in the excited state, or a difference in conformation of the two carbonyl carbons. The structural study was conducted to decide between the two.
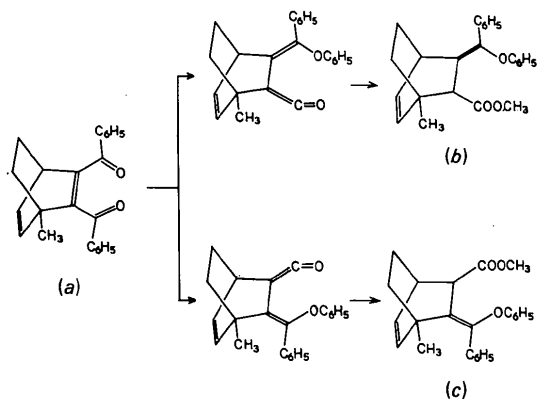
Experimental. Specimen size $0 \cdot 5 \times 0 \cdot 4 \times 0 \cdot 25$ mm. Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; 25 reflections ($10 \leq \theta \leq 20°$) for measuring lattice parameters: ω–2θ scan ranging from 1 to 25°; $0 \leq h \leq 7$, $0 \leq k \leq 16$, $-12 \leq l \leq 12$. Two reflections (020 and 111) used as standards. No decay of intensity. 1569 reflections used for structure solution and 1232 of these with $I > 2\sigma(I)$ used for refinement. No absorption correction. The structure could not be solved by MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and YZARC78 (Declercq, Germain, Baggro & Woolfson, 1978) was used successfully. Least-squares refinement on F with y coordinate of O1 kept fixed. Atomic scattering factors from International Tables for X-ray Crystallography (1974). Eleven H atoms attached to the two benzene rings and C4 (Fig. 1) were placed in

calculated positions with isotropic temperature factor $B = 4 \cdot 0$ Å². Bond distances C2—C3 and C7—C8 had nearly the same value ($\sim 1 \cdot 42$ Å), intermediate between a double C=C and a single C—C bond. Three positions of hydrogen (one trigonal and two tetrahedral) for each of the said four carbons were calculated. A difference Fourier map showed positive electron density clouds at each of these 12 calculated positions; $\frac{1}{2}$ H was assumed at each. One methyl hydrogen was located from a difference Fourier map and two others calculated. The weighting scheme was $w = [\sigma_c^2(F) + 0 \cdot 000625 F^2]^{-1}$ where $\sigma_c(F)$ was based on counting statistics. Refinement converged $[(\Delta/\sigma)_{max} = 0 \cdot 610]$ at $R = 0 \cdot 036$, $wR = 0 \cdot 041$ with $S = 1 \cdot 004$. Final difference Fourier map showed max. and min. peak heights of $0 \cdot 1$ and $-0 \cdot 2$ e Å⁻³ respectively. All calculations carried out on Burroughs 6700 computer; XRAY ARC program system (World List of Crystallographic Computer Programs, 1973) locally adapted for the B6700.

Discussion. The refined positional parameters of the non-hydrogen atoms are presented in Table 1. Bond distances and angles are given in Table 2.* The view of the molecule projected down the a axis (Fig. 1) clearly shows that while C17=O2 is s-trans with respect to C5=O6, C10=O1 is in an s-cis conformation. Such a difference in disposition is also evident from the values of the torsion angles O1—C10—C5—C6 14·8, O2—C17—C6—C5 −100·5°. This difference in conformation of the two carbonyls allows a favourable overlap of O1 and C18, thereby minimizing the energy

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* Tables of observed and calculated structure factors, anisotropic thermal parameters and coordinates of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44203 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
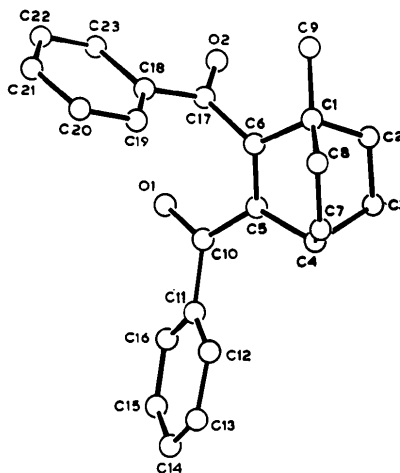

Fig. 1. An asymmetric unit of the structure viewed down the a axis.

Table 1. *Final positional parameters for non-hydrogen atoms with e.s.d.'s in parentheses and their equivalent isotropic temperature factors*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
O1	0·1949 (4)	0·4019*	0·5644 (2)	4·410
O2	0·3369 (4)	0·4786 (2)	0·8458 (2)	4·581
C1	0·6685 (5)	0·6215 (2)	0·7342 (2)	3·684
C2	0·5114 (6)	0·7094 (2)	0·7011 (3)	4·054
C3	0·4113 (5)	0·7145 (2)	0·5690 (3)	4·026
C4	0·4871 (5)	0·6299 (2)	0·4957 (3)	3·668
C5	0·4279 (4)	0·5385 (2)	0·5595 (2)	2·862
C6	0·5193 (4)	0·5352 (2)	0·6839 (2)	2·944
C7	0·7512 (5)	0·6358 (2)	0·5178 (3)	4·309
C8	0·8506 (5)	0·6306 (3)	0·6490 (3)	4·410
C9	0·7824 (5)	0·6173 (3)	0·8736 (3)	5·484
C10	0·2758 (4)	0·4598 (2)	0·4989 (2)	3·082
C11	0·2201 (5)	0·4483 (2)	0·3575 (2)	3·066
C12	0·3765 (5)	0·4712 (2)	0·2792 (2)	3·500
C13	0·3176 (6)	0·4535 (2)	0·1489 (3)	4·099
C14	0·1085 (6)	0·4144 (3)	0·0974 (2)	4·653
C15	−0·0458 (6)	0·3912 (3)	0·1731 (3)	4·932
C16	0·0097 (5)	0·4074 (3)	0·3035 (2)	3·993
C17	0·4743 (5)	0·4600 (2)	0·7763 (2)	3·127
C18	0·6116 (5)	0·3698 (2)	0·7911 (2)	3·065
C19	0·7978 (5)	0·3580 (2)	0·7299 (2)	3·443
C20	0·9318 (5)	0·2758 (2)	0·7497 (3)	3·891
C21	0·8796 (5)	0·2044 (2)	0·8284 (3)	4·137
C22	0·6937 (6)	0·2152 (2)	0·8902 (3)	4·391
C23	0·5601 (5)	0·2975 (2)	0·8715 (2)	3·673

* This parameter was held fixed to define the origin.

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Bond	Distance	Bond	Distance
C1—C2	1·533 (4)	C11—C12	1·396 (4)
C1—C6	1·524 (4)	C12—C13	1·395 (4)
C1—C8	1·541 (4)	C13—C14	1·363 (5)
C1—C9	1·518 (4)	C14—C15	1·368 (4)
C2—C3	1·428 (4)	C15—C16	1·392 (4)
C3—C4	1·528 (4)	C16—C11	1·385 (4)
C4—C5	1·514 (4)	C17—O2	1·227 (3)
C4—C7	1·530 (4)	C17—C18	1·486 (4)
C5—C6	1·341 (3)	C18—C19	1·391 (4)
C5—C10	1·484 (4)	C19—C20	1·383 (4)
C6—C17	1·499 (4)	C20—C21	1·374 (4)
C7—C8	1·418 (4)	C21—C22	1·392 (4)
C10—O1	1·223 (3)	C22—C23	1·382 (4)
C10—C11	1·497 (3)	C23—C18	1·395 (4)

Angle	Value	Angle	Value
C2—C1—C6	105·3 (2)	C10—C11—C16	118·2 (2)
C2—C1—C8	104·8 (2)	C12—C11—C16	118·8 (3)
C2—C1—C9	113·1 (3)	C11—C12—C13	119·7 (3)
C6—C1—C9	115·7 (2)	C12—C13—C14	120·6 (3)
C8—C1—C9	111·1 (3)	C13—C14—C15	120·4 (3)
C1—C2—C3	112·7 (3)	C14—C15—C16	120·1 (3)
C2—C3—C4	111·4 (3)	C15—C16—C11	120·4 (3)
C3—C4—C5	107·4 (2)	C6—C17—O2	118·3 (2)
C3—C4—C7	105·5 (2)	C6—C17—C18	119·9 (2)
C4—C5—C6	113·2 (2)	O2—C17—C18	121·5 (2)
C4—C5—C10	126·4 (2)	C17—C18—C19	120·7 (2)
C5—C6—C1	114·8 (2)	C17—C18—C23	119·8 (2)
C1—C6—C17	118·6 (2)	C19—C18—C23	119·4 (2)
C4—C7—C8	111·4 (3)	C18—C19—C20	120·1 (3)
C7—C8—C1	113·0 (3)	C19—C20—C21	120·3 (3)
C5—C10—O1	120·2 (2)	C20—C21—C22	120·2 (3)
C5—C10—C11	121·3 (2)	C21—C22—C23	119·9 (3)
O1—C10—C11	118·5 (2)	C22—C23—C18	120·1 (3)
C10—C11—C12	122·8 (2)		

requirement for the dissipation of the excited-state energy by abstraction of the phenyl moiety. On the other hand, the interaction between O2 and C11 would need rotations about the C10—C5 and C17—C6 bonds and is thus expected to be less favourable in terms of energy. Hence the selectivity in the photo-transformation of the molecule is evidently brought about by the conformational factor only.

An interesting feature of the structure is that the two bonds C2—C3 and C7—C8 are of the same length, intermediate between a C—C single and a C=C double bond; further, with each of these four C atoms are associated three H positions, two tetrahedral and one trigonal, each being occupied by $\frac{1}{2}$ H. Thus the two linkages C1—C2—C3—C4 and C1—C8—C7—C4, one of which is supposed to be of the type C—CH$_2$—CH$_2$—C and the other of type C—CH=CH—C, appear to be indistinguishable, each behaving like an average of the two types. This may be explained as the effect of a random static disorder in the crystal structure. There is evidently a random distribution of an equal number of two isomers, respectively R and S with respect to C1, in the structure. In the former we have C2=C3 and C7—C8; the situation is reversed in the latter. Each of the positions determined for the four atoms C2, C3, C7, C8 is an average for a pair of $\frac{1}{2}$ C. This fact is revealed by the higher values of B_{eq} for these four atoms in comparison with those of the other four atoms C1, C4, C5, C6 of the skeleton.

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