

data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *SIR92* (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1319). Services for accessing these data are described at the back of the journal.

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4-[2,4,6-Tris(1-methylethyl)benzoyl]benzoic Acid (*S*)-(–)-Proline

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Abstract

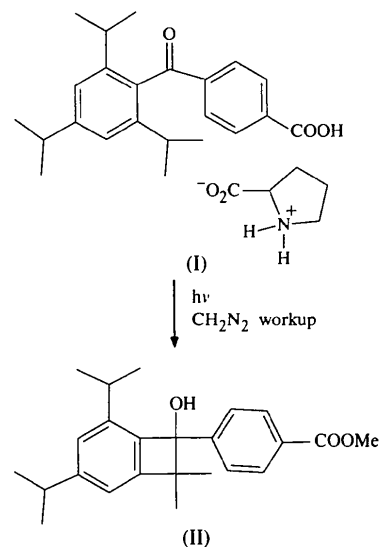
The title compound, $C_{23}H_{28}O_3 \cdot C_5H_9NO_2$, is a 1:1 complex of the benzoic acid derivative and the (*S*)-proline zwitterion, with two formula units in the asymmetric

unit (with pseudo-symmetry relationships between the separate components). The ketone carbonyl group in each benzoic acid molecule deviates slightly from a position normal to the plane of the triisopropylphenyl ring; the deviations (of about 16°) are in opposite senses in the two molecules, so that the molecules have opposite conformational chiralities, leading to a nearly racemic photoproduct on solid-state photolysis.

Comment

The photochemistry of 2,4,6-triisopropylbenzophenone has received much attention (*e.g.* Ito *et al.*, 1983; Ito & Matsuura, 1988; Wagner & Park, 1991). Although the mechanistic details of the reaction have not been fully established, the system seemed to offer excellent prospects for solid-state asymmetric synthesis by introducing ionic chiral handles (Gudmundsdottir & Scheffer, 1990; Jones, Scheffer, Trotter & Yang, 1994; Gamlin *et al.*, 1996).

Treatment of 4-[2,4,6-tris(isopropyl)benzoyl]benzoic acid with (*S*)-(–)-proline in ethanol produced a 1:1 complex, (I), whose crystal structure and photochemistry have been studied.



There are two independent formula units in the asymmetric unit. Proline is not sufficiently basic to form a salt with the carboxylic acid and hence the structure contains neutral acid molecules and proline zwitterions (rather than carboxylate anions and ammonium cations). In each of the acid molecules, the two parts of the molecule are not far from being perpendicular to each other (Figs. 1*a* and 1*b*), but there are significant deviations (from 90°) of the torsion angles about the C1—C2 and C24—C25 bonds. In the first molecule (Fig. 1*a*), the O1—C1—C2—C3 and O1—C1—C2—C7 torsion angles are $-75.0(6)$ and $106.8(5)^\circ$, respectively; in the other molecule (Fig. 1*b*), the corresponding angles

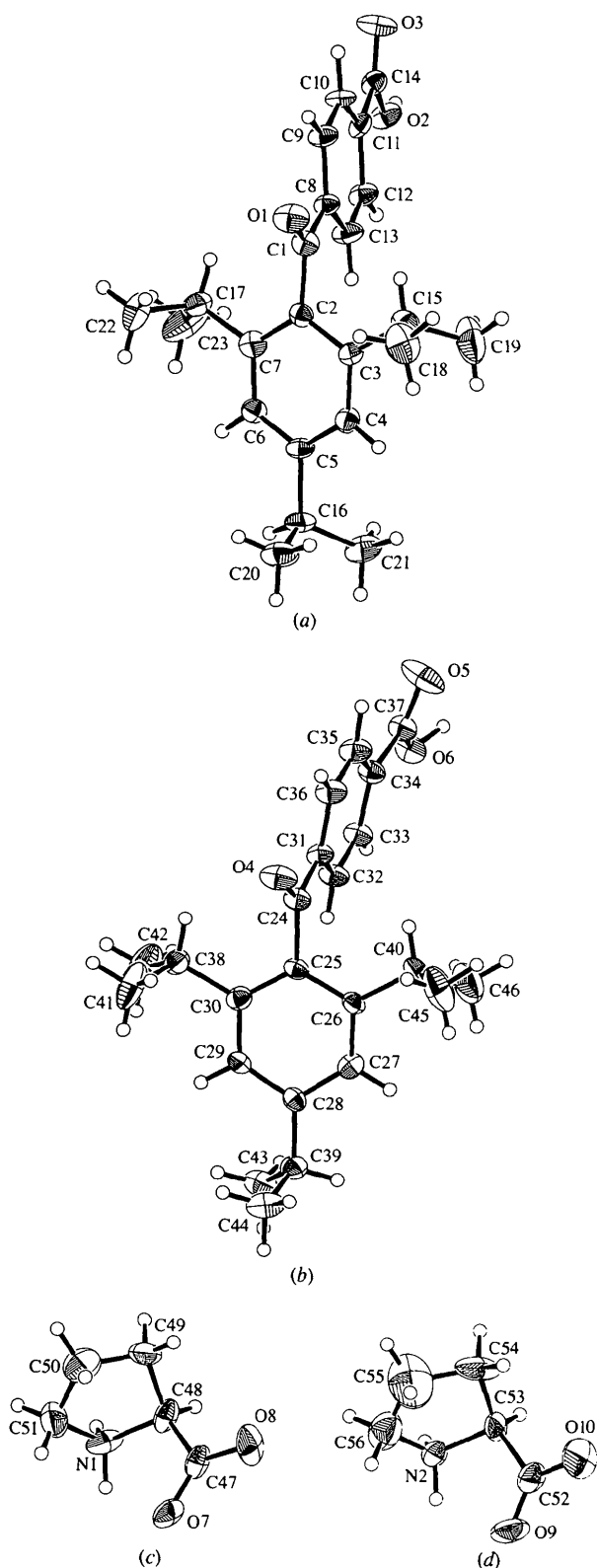


Fig. 1. Views of the acid molecules (a) and (b), and the proline zwitterions (c) and (d). Displacement ellipsoids are drawn at the 33% probability level.

are $-107.3(5)$ and $73.6(6)^\circ$. Thus, the ketone carbonyl groups are tilted from exactly perpendicular positions by about 16° , towards C15 in the first molecule (Fig. 1a), but towards C38 in the other molecule (Fig. 1b), *i.e.* the two molecules have opposite conformational chiralities.

When crystals are irradiated at $\lambda > 290$ nm at room temperature, the cyclobutanol photoproduct, (II), shows no optical activity, similar to the situation on photolysis in ethanol solution; at 233 K, the solid-state photolysis results in a slight enantiomeric excess (26%) of the (–) photoproduct (measured for the methyl ester after CH₂N₂ workup). Enantiomeric excess can be related to preferential photochemical reaction at either the *Re* face of the carbonyl group [on the left in Fig. 1, resulting in the (*R*) photoproduct] or the *Si* face [on the right, giving the (*S*) product]. Since both conformational enantiomers are present in the crystal, no strong enantiomeric preference is expected, as was observed. The slight enantiomeric excess observed at 233 K possibly results from minor effects on the reaction of slightly differing intermolecular surroundings for the two molecules.

The geometric parameters which are important in these H-atom abstraction photochemical reactions (Trotter, 1983) are d (O $\cdots\gamma$ H distance), ω (angular displacement of γ H atom from the carbonyl plane), Δ (C=O $\cdots\gamma$ H angle) and θ (γ C– γ H \cdots O angle), with ideal values < 2.72 Å, 0, 90 and 180° , respectively. For the first molecule (Fig. 1a), the more favourable geometry is on the *Si* face (on the right in Fig. 1a), with an O $\cdots\gamma$ H on C15 distance of 2.58 Å and ω , Δ and θ angles of 63, 69 and 126° , respectively (the O \cdots H distance is favourable, although the angular parameters are far from ideal; the corresponding values for the *Re* face are 3.14 Å, 47, 47 and 117°). For the other molecule (Fig. 1b), the *Re* face (on the left in Fig. 1b) has more favourable geometry, with values of 2.60 Å, 62, 69 and 125° (3.13 Å, 46, 46, 118° for the *Si* face). The C \cdots C distances involved in the formation of the new bond (C1 \cdots C15, *etc.*) are approximately the same on both sides for each molecule (2.92–2.96 Å). Hence the (*S*) photoproduct is to be expected from the first molecule (Fig. 1a) and the (*R*) photoproduct from the other molecule (Fig. 1b).

Bond lengths and angles in the two acid molecules and in the proline zwitterions are generally close to expected values (except for some minor anomalies in the possibly disordered proline rings). The two independent proline zwitterions are linked into a chain along the *a* axis by N–H \cdots O hydrogen bonds (Fig. 2 and Table 1); the benzoic acid molecules are attached to this chain by O(acid)–H \cdots O(proline) and O(acid) \cdots H–N(proline) hydrogen bonds, the last including intramolecular N–H \cdots O(proline) bifurcations.

The crystal structure consists of thick double slabs parallel to (001) of the acid molecules, with isopropyl groups in the middle of the slabs linked by van der

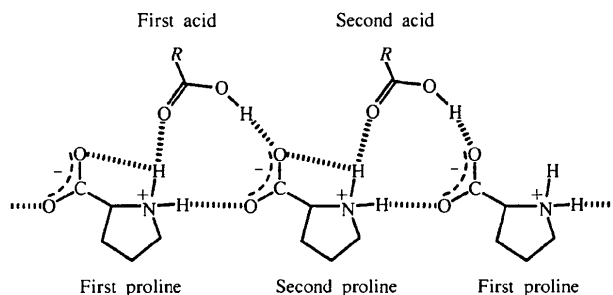


Fig. 2. Schematic of the hydrogen-bonding scheme.

Waals interactions and carboxylic acid groups situated on the surfaces of the slabs. This part of the structure conforms almost exactly to space group $P2_1/a$, with pseudo-centres of inversion between the independent (in $P2_1$) molecules at $(\frac{1}{4}, y, 0)$ ($y \sim 0.2, 0.7$; the choice of origin along the b axis is arbitrary in $P2_1$). Between these thick slabs are thinner double slabs of (*S*)-proline zwitterions, arranged in hydrogen-bonded chains along the a axis (as described above); the two independent prolines are related approximately by translation $a/2$, so that this part of the structure conforms to a subcell, $P2_1$, with $a' = a/2$ [there are no inversion centres, since all the prolines have the (*S*) configuration]. The two types of slab are linked by the acid...proline hydrogen bonds (Fig. 2) to give the overall $P2_1$ structure.

Experimental

The benzoic acid derivative was synthesized from 1,3,5-triisopropylbenzene and 4-cyanobenzoyl chloride, followed by hydrolysis. Reaction of the acid with (*S*)-proline in ethanol solution gave a 1:1 complex (details are in the supplementary material; Fu, 1994).

Crystal data

$C_{23}H_{28}O_3 \cdot C_5H_9NO_2$
 $M_r = 467.60$
 Monoclinic
 $P2_1$
 $a = 11.650(3) \text{ \AA}$
 $b = 8.530(7) \text{ \AA}$
 $c = 26.837(3) \text{ \AA}$
 $\beta = 97.60(1)^\circ$
 $V = 2644(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.175 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Rigaku AFC-6S diffractometer
 ω -2 θ scans
 Absorption correction:
 ψ scans (North, Phillips & Mathews, 1968)
 $T_{\min} = 0.882, T_{\max} = 0.938$

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$
 Cell parameters from 21 reflections
 $\theta = 23.4\text{--}29.5^\circ$
 $\mu = 0.642 \text{ mm}^{-1}$
 $T = 294 \text{ K}$
 Prism
 $0.50 \times 0.25 \times 0.10 \text{ mm}$
 Colourless

3651 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 77.73^\circ$
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 10$
 $l = -34 \rightarrow 33$

5859 measured reflections
 5559 independent reflections

3 standard reflections
 every 200 reflections
 intensity decay: 1.0%

Refinement

Refinement on F^2
 $R(F) = 0.053$
 $wR(F^2) = 0.149$
 $S = 1.66$
 5559 reflections
 613 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + 0.00063(F_o^2)^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.0062$

$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
 Extinction correction:
 Zachariasen (1967)
 Extinction coefficient:
 $0.16(4) \times 10^{-5}$
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Hydrogen-bonding geometry ($\text{\AA}, ^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O2—H73...O9 ⁱ	0.87	1.71	2.552 (4)	165
O6—H74...O7	0.99	1.56	2.523 (4)	163
N1—H1...O10 ⁱⁱ	0.96	1.75	2.671 (5)	160
N1—H2...O3 ⁱⁱⁱ	0.96	2.11	2.905 (4)	139
N2—H3...O8	0.94	1.88	2.770 (5)	159
N2—H4...O5	0.95	1.98	2.793 (4)	143
N1—H2...O7	0.96	2.26	2.647 (4)	103
N2—H4...O9	0.95	2.07	2.586 (4)	113

Symmetry codes: (i) $1-x, \frac{1}{2}+y, 1-z$; (ii) $x-1, y, z$; (iii) $-x, y-\frac{1}{2}, 1-z$.

There are two formula units per asymmetric unit; pseudo-symmetry relationships give correlation coefficients as high as 0.72. The two carboxylic acid H atoms were fixed in positions determined from difference synthesis; other H atoms were placed in idealized sites. The absolute configuration is established from the known configuration of (*S*)-(-)-proline. High displacement parameters for atoms in the proline rings probably indicate disorder.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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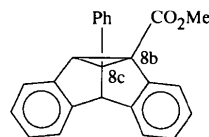
Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1301). Services for accessing these data are described at the back of the journal.

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in determining which of the two reaction pathways is more favourable. For CO₂Me/CXYMe derivatives (X = S, Y = O; X = O, Y = S), for example, initial bond formation involves the C atom bearing the CO₂Me substituent, with the intermediate biradical stabilized by resonance with the CSOMe or COSMe groups (Jones, Rattray, Scheffer & Trotter, 1995); as a result, only the 8c-thiono and 8c-thiolo dibenzosemibullvalene products are formed.



(I)

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Methyl 8c-Phenyl-4b,8b,8c,8d-tetrahydro-dibenzo[a,f]cyclopropa[c]pentalene-8b-carboxylate

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Abstract

The title molecule, C₂₄H₁₈O₂, is the sole product of photolysis of a phenyl-methoxycarbonyl-dibenzobarrelene derivative, has a dibenzosemibullvalene structure, 8c-phenyl and 8b-methoxycarbonyl substituents, and normal bond lengths and angles.

Comment

Photolysis of dibenzobarrelene (9,10-dihydro-9,10-ethenoanthracene) derivatives proceeds *via* the di- π -methane reaction to produce dibenzosemibullvalene photoproducts. For unsymmetrically substituted 11,12-derivatives, two isomeric dibenzosemibullvalene photoproducts (and their enantiomers) are possible, the proportions of the products being greatly influenced by the nature of the substituent groups (Rattray, Yang, Gudmundsdottir & Scheffer, 1993). The proposed mechanism (Zimmerman, 1991) involves initial bond formation between a vinyl (C11 or C12) and a benzo C atom, to form a biradical, with one of the radical sites at the second vinyl C atom. The polar nature and the radical-stabilizing ability of the 11,12-substituents are important

The CH₃/CO₂Me dibenzobarrelene derivative gives only the 8b-CH₃/8c-CO₂Me product, again in accord with radical stabilization by delocalization of the radical electron over the CO₂Me group (Rattray *et al.*, 1993). By contrast, the only photoproduct from photolysis of the Ph/CO₂Me derivative has been shown to be the 8c-Ph/8b-CO₂Me dibenzosemibullvalene (Fig. 1); this is in accord with the greater radical-stabilizing ability of the phenyl substituent. The photoproduct molecule, (I) (Fig. 1) has a normal folded dibenzosemibullvalene skeleton, with a three-membered ring, and normal bond lengths and angles.

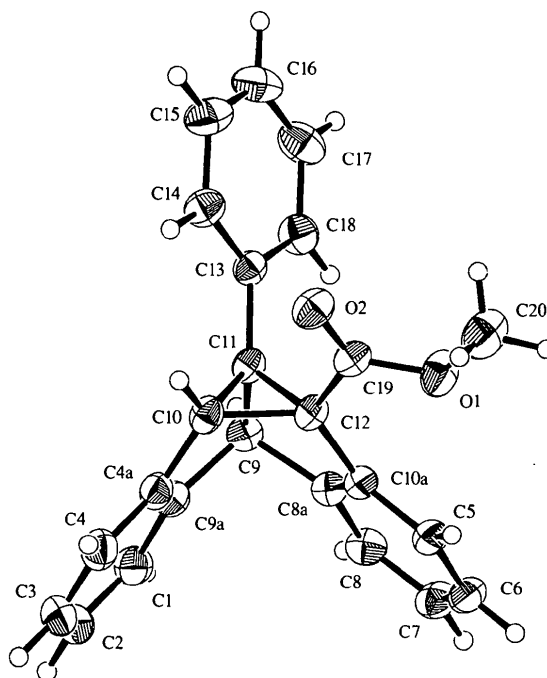


Fig. 1. View of the molecule (33% ellipsoids; dibenzobarrelene numbering system).