

Table 3. Selected torsion angles (°) in the title compound (e.s.d.'s about 0.3°)

C(1)–S–C(4)–C(3)	–51.7	C(4)–C(3)–C(7)–N(2)	141.2
S–C(4)–C(3)–N(1)	52.0	C(3)–C(7)–N(2)–C(8)	171.5
C(4)–C(3)–N(1)–C(2)	–51.2	C(2)–N(1)–C(5)–C(6)	–1.5
C(3)–N(1)–C(2)–C(1)	58.9		
N(1)–C(2)–C(1)–S	–66.4		
C(2)–C(1)–S–C(4)	58.5		

$0 \leq |\alpha| \leq 30^\circ$ , inclinal when  $30 \leq |\alpha| \leq 60^\circ$ , and axial when  $60 \leq |\alpha| \leq 90^\circ$ . The polar angles  $\alpha$  for S–O(1), C(3)–C(7) and N(1)–C(5) are 94.8 (4), 68.9 (4) and 32.7 (4)°, respectively. Therefore, the S=O bond and the methylcarbamoyl substituent are axially oriented, whereas the acetyl group is inclinal.

N(1) is 0.022 (4) Å above the plane formed by C(2), C(3) and C(5), showing the near-planarity of the N(1) amide arrangement. The moiety N(1), C(5), C(6), O(2) is planar [largest deviation from the least-squares plane 0.008 (4) Å for C(5)] and is at a dihedral angle of 31.4 (3)° with the least-squares plane through the six-membered ring. The *sp*<sup>2</sup>-hybridized C(7) is 0.015 (4) Å outside the plane given by C(3), C(7), O(3), N(2), which plane is at a dihedral angle of 109.4 (2)° with respect to the ring. The vicinal substituents, acetyl and methylcarbamoyl, are nearly perpendicular with a dihedral angle of 83.8 (2)° between their planes. The total geometry can best be seen from Fig. 1.

Another 4-thiapipecolic acid derivative is (3*R*,6*R*)-3-benzyl-1,4-diaza-8-thiabicyclo[4.4.0]decane-2,5-

dione (Van Poucke & Lenstra, 1982). It may be regarded as structurally related to the title compound if we disregard the fact that the bonds N(1)–C(5) and C(3)–C(7) are *trans* oriented in the former and *cis* in the latter. Indeed bond lengths and valence angles compare favourably for the majority of values (see Table 2). Notable exceptions are the shorter C–S lengths in the title compound, which is normal since they are here adjacent to S=O. Also the bonds N(1)–C(5) and N(2)–C(7) are shorter, indicating that they have more amide character than in the bicyclic counterpart. The steric crowding in the title compound forces the angles at C(3) to be relatively large. For the same reason the least-puckered side of the six-membered ring is found at C(3) and C(4) and the most puckered side at C(1) and C(2).

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## Structure of Trimethyl 8,13-Diphenyl-13-azatricyclo[8.2.1.0<sup>2,7</sup>]-trideca-2(7),3,5,11-tetraene-10,11,12-tricarboxylate, C<sub>30</sub>H<sub>27</sub>NO<sub>6</sub>

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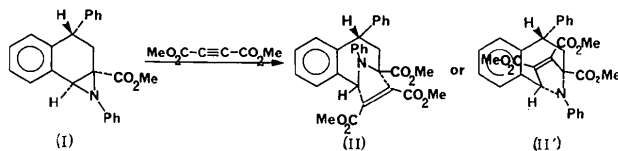
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**Abstract.** *M<sub>r</sub>* = 497.55, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 15.074 (3), *b* = 9.839 (1), *c* = 18.545 (3) Å, β = 104.39 (2)°, *V* = 2664 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.24 Mg m<sup>–3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 0.7 mm<sup>–1</sup>, *F*(000) = 1048,

*T* = 293 K, final *R* = 0.076 for 2070 independent observed reflections. The dipolar cycloaddition of dimethyl acetylenedicarboxylate to the aziridine ring leads to only one diastereoisomeric pyrroline. Its

structure indicates a stereospecific approach. The benzocondensed heptaatomic ring has an envelope conformation (N—C: 1.446 and 1.482 Å). The N—phenyl bond is shorter (N—C: 1.392 Å). The pyrrolic ring (C=C: 1.317 Å) lies in an axial configuration at the opposite side of the *N*-phenyl group with respect to the mean plane of the molecule.

**Introduction.** In a previous study (Vebrel, Cerutti & Carrie, 1979), we described a novel route to tricyclic aziridines (I) by reaction with monosubstituted condensed benzocyclohexane derivatives, illustrating the importance of steric and conformational factors in dipolar 1,3-cycloaddition. These reactions lead to only one type of aziridine (I), the stereochemistry of which has been determined elsewhere (Tinant, Declercq, Germain & Van Meerssche, 1982) for the methyl derivative. The *R* group always lies in an equatorial position relative to the mean plane of the benzo nucleus, and the N atom is on the same side of this plane as the axial H atom. The addition of dimethyl acetylenedicarboxylate yields only one diastereoisomer, which could possess either structure (II) or structure (II'). Contrary to what had been expected, the aziridine ring is thermally broken between the two C atoms, violating the Woodward–Hoffmann rules. The structure of the product has been determined to discover whether it corresponds to (II) or (II'), thereby establishing the stereochemistry of the reaction.



**Experimental.** Crystal (*ca* 0.3 × 0.2 × 0.2 mm) grown from ethanol; CAD-4 Nonius diffractometer; unit-cell parameters refined from 2θ angles for 25 independent reflections measured with ω–2θ scanning; 0 ≤ 2θ ≤ 120°, 0 ≤ *h* ≤ 16, 0 ≤ *k* ≤ 11, –20 ≤ *l* ≤ 20, 2070 unique reflections [*F* > 5σ(*F*)]; *R*<sub>int</sub> = 0.048. Standard reflection 402, maximal shift of 4.2% around mean intensity value (83 measurements). Lorentz and polarization corrections, absorption ignored. Direct methods, refinement on *F* values; anisotropic thermal parameters for all non-H atoms; ligand H atoms in idealized positions treated as 'riding atoms' or 'rigid groups' for CH<sub>2</sub> and CH<sub>3</sub> (C–H = 1.08 Å). Final iterations on *x*, *y*, *z* of all atoms: *R* = 0.076, *wR* = 0.078 with *w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub>) + 0.0145*F*<sub>o</sub><sup>2</sup>], 343 parameters, slope of normal probability plot = 1.12, max. shift/e.s.d. = 1.16, –0.42 ≤ Δρ ≤ 0.92 e Å<sup>–3</sup>; scattering factors of neutral C, O, N, and H atoms taken from Cromer & Mann (1968), anomalous-dispersion terms included (Cromer & Liberman, 1970). All calculations performed with programs written by Sheldrick (1976, 1981).

Table 1. Atomic coordinates (×10<sup>4</sup>) and equivalent isotropic thermal parameters (Å<sup>2</sup> × 10<sup>4</sup>)

$$U_{eq} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C(1)	2516 (4)	2267 (6)	3784 (3)	459 (4)
C(2)	3442 (4)	2356 (6)	4189 (3)	475 (4)
C(3)	4057 (4)	1372 (6)	4082 (3)	544 (5)
C(4)	3819 (5)	308 (7)	3594 (4)	616 (5)
C(5)	2905 (5)	237 (7)	3178 (4)	635 (5)
C(6)	2288 (5)	1184 (7)	3285 (3)	566 (5)
C(7)	1754 (4)	3203 (6)	3913 (3)	501 (4)
C(8)	1914 (4)	4750 (6)	3943 (3)	480 (4)
C(9)	2733 (4)	5239 (6)	4576 (3)	437 (3)
C(10)	3815 (4)	3455 (6)	4761 (3)	447 (4)
C(11)	828 (5)	2987 (8)	3348 (5)	666 (5)
C(12)	656 (6)	3530 (10)	2645 (5)	927 (7)
C(13)	–200 (9)	3387 (13)	2155 (6)	1162 (8)
C(14)	–849 (9)	2678 (14)	2367 (9)	1279 (9)
C(15)	–744 (8)	2149 (14)	3039 (9)	1339 (9)
C(16)	166 (6)	2304 (10)	3574 (6)	1065 (7)
C(17)	3939 (4)	5295 (6)	3865 (3)	459 (4)
C(18)	3535 (5)	6355 (6)	3405 (4)	556 (5)
C(19)	3897 (5)	6810 (7)	2821 (4)	632 (6)
C(20)	4665 (6)	6232 (8)	2697 (4)	714 (6)
C(21)	5096 (5)	5182 (7)	3161 (4)	644 (5)
C(22)	4743 (4)	4720 (7)	3737 (3)	534 (5)
C(23)	2736 (4)	4462 (6)	5294 (3)	424 (4)
C(24)	3334 (4)	3462 (6)	5380 (3)	445 (4)
C(25)	2103 (5)	4830 (7)	5764 (3)	550 (4)
C(26)	3532 (5)	2379 (7)	5953 (3)	533 (5)
C(27)	677 (7)	4354 (12)	6034 (6)	1111 (8)
C(28)	3169 (7)	1553 (9)	7046 (4)	925 (7)
C(29)	2632 (5)	6743 (7)	4729 (3)	539 (4)
C(30)	3314 (7)	8698 (8)	5355 (6)	969 (6)
O(1)	2280 (4)	5692 (6)	6237 (3)	931 (6)
O(2)	4060 (4)	1473 (5)	5969 (2)	692 (4)
O(3)	1340 (3)	4113 (5)	5591 (2)	723 (5)
O(4)	3032 (3)	2562 (5)	6451 (2)	696 (5)
O(5)	1924 (4)	7351 (5)	4559 (3)	763 (5)
O(6)	3402 (3)	7295 (4)	5102 (3)	706 (5)
N	3616 (3)	4852 (5)	4466 (3)	448 (3)

Table 2. Bond lengths (Å) and torsion and dihedral angles (°)

Ring (1)			
C(1)–C(2)	1.415 (8)	C(4)–C(5)	1.403 (9)
C(2)–C(3)	1.387 (8)	C(5)–C(6)	1.366 (9)
C(3)–C(4)	1.372 (8)	C(6)–C(1)	1.398 (8)
Ring (2)			
C(11)–C(12)	1.373 (11)	C(14)–C(15)	1.323 (18)
C(12)–C(13)	1.389 (12)	C(15)–C(16)	1.488 (14)
C(13)–C(14)	1.338 (17)	C(16)–C(11)	1.354 (11)
Ring (3)			
C(17)–C(18)	1.389 (8)	C(20)–C(21)	1.398 (10)
C(18)–C(19)	1.402 (9)	C(21)–C(22)	1.384 (9)
C(19)–C(20)	1.360 (10)	C(22)–C(17)	1.410 (8)
N–C(9)	1.446 (7)	C(8)–C(9)	1.554 (7)
N–C(10)	1.482 (7)	C(10)–C(2)	1.521 (8)
N–C(17)	1.392 (7)	C(9)–C(23)	1.535 (8)
C(1)–C(7)	1.536 (8)	C(23)–C(24)	1.317 (8)
C(7)–C(8)	1.539 (8)	C(24)–C(10)	1.503 (8)
Ester groups			
C(25)–O(1)	1.202 (7)	C(29)–O(6)	1.313 (7)
C(26)–O(2)	1.190 (7)	C(27)–O(3)	1.463 (9)
C(29)–O(5)	1.194 (7)	C(28)–O(4)	1.460 (8)
C(25)–O(3)	1.319 (8)	C(30)–O(6)	1.473 (8)
C(26)–O(4)	1.341 (7)		
C(2)–C(10)–N–C(17)	59.9 (8)	C(8)–C(9)–N–C(17)	63.3 (8)
C(7)–C(8)–C(9)–N	69.0 (9)	N–C(10)–C(2)–C(1)	–54.7 (8)
C(1)–C(7)–C(8)–C(9)	–4.8 (8)	C(8)–C(7)–C(7)–C(1)–C(2)	48.6 (7)
C(9)–C(23)–C(24)–C(10)	0.4 (9)	C(26)–C(24)–C(23)–C(9)	–174.7 (8)
C(26)–C(24)–C(23)–C(25)	3.7 (7)	C(10)–C(23)–C(24)–C(25)	179.2 (8)
Mean plane (1)   C(1) to C(6)   planar to within 0.009 Å			
Mean plane (2)   C(11) to C(16)   planar to within 0.009 Å			
Mean plane (3)   C(17) to C(22)   planar to within 0.012 Å			
(1)–(2)	85.7 (3)	(1)–(3)	84.3 (3)
		(2)–(3)	52.8 (3)

**Discussion.** Atomic parameters are given in Table 1.\* Bond lengths (Table 2) and angles reveal no unusual features.

The benzo (ring 1) and phenyl groups (rings 2 and 3) are close to planar with mean C—C = 1.39 Å. Rings (1) and (2) in *peri* interaction adopt an orthogonal conformation [dihedral angle: 85.7 (3)°], the C(7)—ring (2) bond being purely equatorial [1.2 (3)°, relative to mean plane 1 (see Table 2)]. The N atom displays three different N—C bonds, the shortest N—C(17) [1.392 (7) Å] joining the *N*-phenyl group to the heptaatomic ring (Fig. 1); this large ring has an envelope conformation, the point of it being the N atom (1.07 Å from the mean plane 1); C(8) and C(3) lie closer to the plane (0.76 and 0.60 Å). The ethylene adduct [C(23)=C(24): 1.317 (8) Å] lies in axial configuration with respect to the benzo ring (1) (Fig. 1) and on the other side of this plane. The relative disposition of H(7) and N is thus inverted with respect to the original aziridine (I). The structure clearly corresponds to the diastereoisomer (II').

This structure determination indicates that the acetylene approaches the aziridine ring (I) from the side in which the H atom is directed and that after the triangular ring opens, the N atom is displaced to the opposite side of the ring.

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39503 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

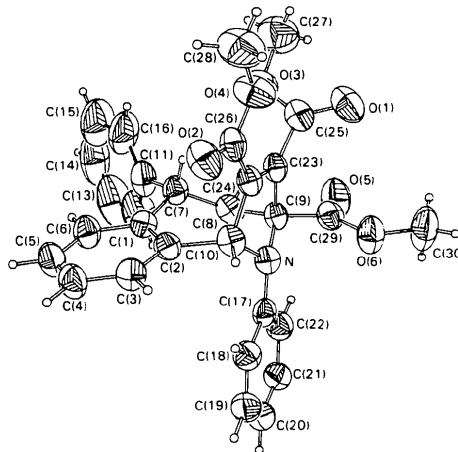


Fig. 1. Thermal-ellipsoid plot (50% probability) of pyrroline molecule (II'), showing the atom-numbering scheme.

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### *trans*-Cinnamoyl Peroxide, C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>

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**Abstract.**  $M_r = 294.13$ , monoclinic,  $P2_1$ ,  $a = 14.64$  (2),  $b = 9.10$  (2),  $c = 5.63$  (1) Å,  $\beta = 93.0$  (2)°,  $U = 749.00$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.305$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 0.760$  mm<sup>-1</sup>,  $F(000) = 308$ ,  $T =$

$ca$  293 K. Final  $R = 0.069$  for 604 unique reflexions. In the crystal the molecule takes up an extended conformation, its two acyloxy groups lying in approximately orthogonal planes. The  $\alpha,\beta$ -unsaturated carbonyl