with a boat-like geometry, but rather less favourable abstraction parameters, $d = 3\cdot17$ Å, $\tau = 62°$, $\Delta = 68°$). The abstraction parameters (Table 3) are very similar to those in the chloro derivatives (Evans & Trotter, 1988), and are favourable for hydrogen abstraction, with $d \sim 2\cdot7$ Å, $\tau \sim 40°$, and Δ not far from 90°.

Although the photochemical data are not as extensive as for the chloro derivatives, the percentage cyclization for the carboxy compounds (Table 3) again appears to be relatively insensitive to reaction medium, but increases significantly (from 0 to 85%) as the cycloalkyl ring size increases. The variation with cycloalkyl ring size again correlates qualitatively with the increasing values of the biradical p-orbital angles θ_v (60–127°) and ring torsion angles (22–99°) favouring cyclization over cleavage. In addition, molecule 2 of CO_2H-5R has a $\theta_{C=O}$ angle of 25°, which favours cleavage, and is perhaps responsible for the non-observance of any cyclization product in the solid state. The amount of *trans*-OH cyclobutanol cyclization product increases markedly with increasing cycloalkyl ring size, to nearly 100% for the cyclooctyl compound in the solid state, as for the chloro derivatives (the ring-junction configurations are again probably *cis* for the cyclopentyl and *trans* for the cyclooctyl products). The increasing amount of *trans*-OH photoproducts has previously been rationalized on the basis of great steric stability of the *trans*-OH photoproduct for the larger cycloalkyl rings (Evans & Trotter, 1988). Thus the photochemistry again appears to be controlled mainly by intramolecular forces.

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Structure of Bis[(−)-menthyl] Acetylenedicarboxylate

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Abstract. $C_{24}H_{38}O_4$, $M_r = 390\cdot57$, trigonal, $P3_121$, $a = 9\cdot796$ (1), $c = 21\cdot666$ (3) Å, $V = 1800\cdot6$ (3) Å^3, $Z = 3$ (molecular symmetry C_2), $D_x = 1\cdot080$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0\cdot70926$ Å, $\mu = 0\cdot67$ cm^{-1}, $F(000) = 642$, $T = 295$ K, $R = 0\cdot040$ for 652 reflections. The molecule lies on a crystallographic twofold axis, and has a nearly linear triple C≡C bond, with the two carboxyl groups at 90° to each other; the cyclohexane ring has a chair conformation, with all substituents equatorial. Bond lengths and angles are close to expected values. The crystals undergo photoreaction, but it has not been possible to determine the details of this process.

Introduction. The production of optically active product from achiral reactant has recently been achieved by unimolecular di-π-methane photorearrangement in the solid state of a dibenzobarrelene derivative which was found to crystallize in the non-centrosymmetric space group $P2_12_12_1$ (Evans, Garcia-Garibay, Omkaram, Scheffer, Trotter & Wireko, 1986). In an effort to achieve this type of asymmetric synthesis in a controlled manner, chiral reactants (which must crystallize in a chiral space group) were synthesized. The crystal structure of one of the reagents in the syntheses, bis[(−)-menthyl] acetylenedicarboxylate, is described in the present paper. An additional point of interest is that this material itself was found to undergo photoreaction.

Experimental. Colourless rhombs, {10.1} form, dimensions about 0·4 mm, Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 10$–19°. Intensities for $\theta \le 27\cdot5°$, hkl: 0 to 11, 0 to 11, 0 to 28, ω–2θ scan width $(0\cdot65 + 0\cdot35\tan\theta)°$ at

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1–10° min^{-1}, extended 25% on each side for background measurement, three standard reflections (no decay), Lp but no absorption corrections, 1612 independent reflections measured, 652 with $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0{\cdot}04I)^2$, S = scan, B_1 and B_2 = background counts. Structure by direct methods,* with space group $P3_121$ established from the known absolute configuration of (–)-menthol, refined by full-matrix least squares on F, H atoms in calculated positions, $w = 1/\sigma^2(F)$, scattering factors from *International Tables for X-ray Crystallography* (1974), final $R = 0{\cdot}040$, $wR = 0{\cdot}043$ for 652 reflections, $S = 1{\cdot}66$, 127 parameters, $R = 0{\cdot}132$ for all 1612 reflections, $\Delta/\sigma = 0{\cdot}03$ (mean), 0·12 (maximum), maximum final difference density –0·15 to +0·10 e Å^{-3}.

Discussion. Final positional parameters are in Table 1, and other data have been deposited.† The molecule (Fig. 1) has C_2 symmetry, and lies on a crystallographic twofold axis at x,0,5/6, which is perpendicular to the C≡C bond. The carboxyl groups are at 90° to each other, which suggests the possibility of resonance interaction between the carboxyls and the two mutually perpendicular π systems of the triple bond. The cyclohexyl ring of the menthyl group has a chair conformation [bond torsion angles –54·0–58·1 (4), mean 56·0°], with all three substituents (methyl, isopropyl, and carboxyl) in equatorial positions. Bond lengths and angles (Table 2) are not far from expected values; C≡C = 1·176 (6) Å, and C–C≡C is nearly linear [175·6 (3)°]. The C(sp^2)–C(sp) bond adjacent to C≡C is 1·454 (4) Å, which is not significantly shortened by resonance interaction.

UV irradiation of a crystal of bis[(–)-menthyl] acetylenedicarboxylate resulted in a photoreaction to produce an oil. NMR, IR and mass spectrometric data suggested that the photoproduct was a dimer, but the data could not be interpreted in terms of a molecular structure, and attempts to obtain crystalline material for X-ray analysis were unsuccessful. Thus the details of the photochemistry remain unresolved. Possible mechanisms for the photoreaction involve intermolecular hydrogen abstraction by C(12). However, study of the crystal structure‡ reveals no distances shorter than van der Waals contacts [shortest C(12)···H distances are 3·11, 3·15, and 3·21 Å].

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Table 1. *Final positional (fractional* × 10^4) *and equivalent isotropic thermal parameters* ($U_{\rm eq}$ × 10^3 Å^2), *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	4805 (5)	2071 (5)	6577 (1)	63
C(2)	3857 (5)	1019 (4)	6038 (1)	64
C(3)	4511 (6)	1980 (5)	5446 (1)	77
C(4)	6236 (6)	2591 (5)	5367 (2)	79
C(5)	7181 (6)	3615 (5)	5907 (2)	81
C(6)	6533 (5)	2699 (5)	6507 (2)	76
C(7)	2066 (6)	277 (6)	6112 (2)	86
C(8)	1457 (6)	1417 (8)	6037 (2)	112
C(9)	1185 (7)	–1143 (8)	5688 (3)	136
C(10)	8938 (7)	4200 (8)	5841 (2)	137
C(11)	3736 (5)	1520 (5)	7605 (2)	64
C(12)	3298 (4)	428 (4)	8120 (1)	61
O(1)	4300 (3)	1096 (3)	7141 (1)	68
O(2)	3588 (6)	2640 (5)	7617 (1)	124

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

C(1)–C(2)	1·527 (5)	C(5)–C(10)	1·524 (7)
C(1)–C(6)	1·492 (6)	C(7)–C(8)	1·514 (7)
C(1)–O(1)	1·475 (4)	C(7)–C(9)	1·525 (7)
C(2)–C(3)	1·528 (5)	C(11)–C(12)	1·454 (4)
C(2)–C(7)	1·536 (6)	C(11)–O(1)	1·311 (4)
C(3)–C(4)	1·494 (7)	C(11)–O(2)	1·177 (5)
C(4)–C(5)	1·519 (6)	C(12)–C(12′)	1·176 (6)
C(5)–C(6)	1·525 (5)		

C(2)–C(1)–C(6)	112·4 (3)	C(6)–C(5)–C(10)	111·2 (4)
C(2)–C(1)–O(1)	107·6 (3)	C(1)–C(6)–C(5)	112·5 (3)
C(6)–C(1)–O(1)	107·2 (3)	C(2)–C(7)–C(8)	114·7 (4)
C(1)–C(2)–C(3)	107·4 (3)	C(2)–C(7)–C(9)	111·1 (4)
C(1)–C(2)–C(7)	113·8 (3)	C(8)–C(7)–C(9)	110·9 (5)
C(3)–C(2)–C(7)	114·0 (3)	C(12)–C(11)–O(1)	111·8 (4)
C(2)–C(3)–C(4)	112·7 (3)	C(12)–C(11)–O(2)	122·7 (4)
C(3)–C(4)–C(5)	111·7 (3)	O(1)–C(11)–O(2)	125·5 (4)
C(4)–C(5)–C(6)	109·4 (3)	C(11)–C(12)–C(12′)	175·6 (3)
C(4)–C(5)–C(10)	112·1 (4)	C(1)–O(1)–C(11)	119·2 (3)

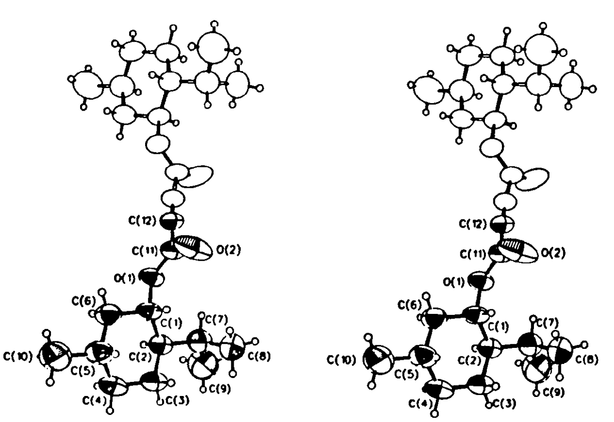

Fig. 1. Stereoview of the bis[(–)-menthyl] acetylenedicarboxylate molecule.

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* Programs used include locally written programs and locally modified versions of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964); *FORDAP* (A. Zalkin, unpublished); *ORTEP*II (Johnson, 1976).

† Lists of anisotropic thermal parameters, H-atom positions, torsion angles and structure factors, and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44688 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

‡ For packing diagram, see deposition footnote.

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N-Benzyloxycarbonyl-L-aminosuccinyl-L-phenylalaninamide (Z-L-Asu-L-Phe-NH$_2$)

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Abstract. $C_{21}H_{21}N_3O_5$, $M_r = 395\cdot42$, orthorhombic, $P2_12_12_1$, $a = 5\cdot935\,(2)$, $b = 13\cdot037\,(1)$, $c = 25\cdot992\,(2)$ Å, $V = 2011\,(1)$ Å^3, $Z = 4$, $D_x = 1\cdot31$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot5418$ Å, $\mu = 0\cdot74$ mm^{-1}, $F(000) = 832$, room temperature, final $R = 0\cdot046$ for 1343 observed reflections. The title compound adopts a type II′ β-turn conformation in the solid state, stabilized by a 4→1 intramolecular hydrogen bond between the CO of the protecting benzyloxycarbonyl group and the NH$_2$ of the terminal amide group. These results indicate that the β-turn conformation, already found in the solid state for peptides embodying the sequence Asu-Gly or Asu-Ala, is highly preferred, even when the residue next to the aminosuccinyl moiety has a bulkier side chain. In the crystal, rows of hydrogen-bonded molecules are held together by van der Waals forces between hydrophobic phenyl groups.

Introduction. In protein chemistry the succinimide ring is an intermediate in the non-enzymatic deamidation of the asparaginyl side chain (Johnson & Aswad, 1985; Clarke, 1985) and it may play, as recently suggested (O'Connor, Aswad & Clarke, 1984), an important role in the repair or degradation of proteins.

We are currently investigating structural and conformational parameters of model peptides embodying this cyclic imide structure, hereafter indicated as Asu peptides (Capasso, Mattia, Mazzarella & Zagari, 1984*a*,*b*; Capasso, Mazzarella, Sica & Zagari, 1984, 1987). Our studies have indicated that these peptides strongly prefer a type II′ β-turn conformation (Venkatachalam, 1968).

In order to investigate the role of the side chain of the residue *X* on the conformational stability of peptides containing the sequence Asu-*X*, we have synthesized and studied, by X-ray analysis, the blocked dipeptide Z-L-Asu-L-Phe-NH$_2$.

Experimental. Title compound synthesized according to procedure previously described (Schön & Rill, 1987). Crystals from methanol, $0\cdot50 \times 0\cdot05 \times 0\cdot03$ mm, Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$ radiation; lattice parameters from 25 reflections ($17 \le \theta \le 21°$); data collection: $\omega/2\theta$ scan, as suggested by peak-shape analysis; two intensity monitoring reflections (2% variation); 2226 independent reflections with $\theta \le 70°$, $0 \le h \le 7$, $0 \le k \le 15$, $0 \le l \le 31$, 1343 with $I > 2\cdot5\sigma(I)$; Lp correction, absorption ignored. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); anisotropic full-matrix (on *F*), H atoms from geometrical considerations, isotropic with

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