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Structure of Photopolymerizable(+)-(*S*)-Ethyl 3-{4-[2-*sec*-Butoxycarbonyl-(*E*)-vinyl]-phenyl}-2-cyano-(*E*)-acrylate

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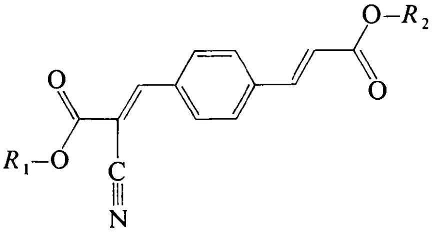
Abstract. $C_{19}H_{21}NO_4$, triclinic, $P1$, $a = 13{\cdot}163$ (3), $b = 6{\cdot}941$ (3), $c = 5{\cdot}263$ (2) Å, $\alpha = 103{\cdot}11$ (3), $\beta = 95{\cdot}69$ (3), $\gamma = 90{\cdot}14$ (3)°, $Z = 1$, $D_m = 1{\cdot}1$, $D_c = 1{\cdot}15$ Mg m^{-3}; final $R = 0{\cdot}08$. Crystals of the (+)-(*S*) enantiomer of the title compound (90% optically pure) were obtained by crystallization from 2-propanol. The skeleton of the molecule is almost completely planar and centrosymmetric. The molecules are stacked along the 7 Å axis in a motif primarily determined by C=O···phenyl interactions.

Introduction. In an attempt to accomplish asymmetric synthesis in the solid state, Addadi & Lahav (1978) have studied the photochemical behaviour of asymmetrically substituted diene molecules of the general form (I).



(I)
(II) R_1 = ethyl, R_2 = *sec*-butyl

The actual molecular formula resulted from a process of planning and crystal engineering aimed at the construction of systems suitable for dimerization and polymerization in chiral crystals (Addadi & Lahav, 1978, 1979*a*). Similar, but symmetrically substituted, diolefins have been studied by Hasegawa, Suzuki, Nakanishi & Nakanishi (1973).

In order to correlate between the stereochemical course of the lattice-controlled reaction and the structure and absolute configuration of the parent crystal, obtained from a monomer of known chirality, the crystal structure of the title compound (II) was investigated.

The intensities and refined cell dimensions were obtained on a Syntex $P\bar{1}$ diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. Of the 4079 reflexions measured, 753 were considered to be unobserved on the basis $I < 2\sigma(I)$. Lorentz and polarization corrections were applied to the net intensity counts, but no corrections were made for absorption or extinction.

The first attempt at the solution of the structure was made with *MULTAN* (Germain, Main & Woolfson, 1971) in space group $P\bar{1}$; it was assumed that the major part of the molecule was centrosymmetric and that the C≡N group and the difference between the two ester substituents at the two ends of the molecule made but a minor contribution to the diffraction data. This approach did not lead to the solution of the structure, since a large number of *E* maps did not reveal the molecular structure.

The orientation of the molecule within the unit cell was determined from a Patterson map. Thus a partial structure was obtained, except for the C≡N group and the terminal ethyl and *sec*-butyl substituents.

The partial structure was introduced into *MULTAN* with the tangent-refinement method (Karle, 1968) to improve the phases. The resulting *E* map revealed the additional heavy atoms. All the H atoms, except for those in methyl groups, were inserted in chemically reasonable positions. The structure was refined by a full-matrix least-squares technique. The heavy atoms were assigned anisotropic thermal parameters, while the H atoms were treated isotropically. The methyl H atoms of the ethyl and *sec*-butyl groups were located from difference maps. Their positions were not refined. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final *R* was 0·08. Final atomic coordinates are listed in Table 1.*

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35288 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* (× 10^4, *for* H × 10^3) *with e.s.d.'s in parentheses*

The positions of C(8) and the methyl H atoms were kept fixed during the refinement.

	x	*y*	*z*		*x*	*y*	*z*
C(1)	−3991 (15)	7158 (23)	−5341 (45)	C(2)	−3083 (8)	6898 (21)	−4482 (34)
O(3)	−2895 (3)	5257 (7)	−3255 (11)	C(4)	−2003 (5)	4351 (10)	−3601 (17)
O(5)	−1406 (4)	4813 (7)	−5048 (10)	C(6)	−1856 (5)	2807 (7)	−2114 (11)
C(7)	−938 (5)	1854 (8)	−2261 (10)	C(8)	−586	278	−1097
C(9)	323 (5)	−523 (10)	−1814 (15)	C(10)	759 (6)	−2150 (11)	−832 (19)
C(11)	232 (5)	−2889 (9)	886 (13)	C(12)	−680 (5)	−2096 (11)	1637 (17)
C(13)	−1065 (10)	−498 (10)	673 (13)	C(14)	647 (6)	−4506 (10)	2130 (15)
C(15)	1541 (5)	−5313 (11)	1965 (15)	C(16)	1823 (5)	−6887 (9)	3378 (14)
O(17)	2785 (4)	−7360 (9)	2983 (14)	O(18)	1350 (4)	−7469 (8)	4728 (13)
C(19)	3298 (8)	−8711 (2)	4584 (40)	C(20)	−2674 (6)	2307 (9)	−856 (15)
N(21)	−3321 (5)	1912 (10)	233 (15)	C(22)	4346 (9)	−7596 (27)	5826 (34)
C(23)	3476 (13)	−10493 (24)	2684 (54)	C(24)	4264 (9)	−5720 (30)	7833 (42)
H(1)	−399	845	−621	H(1′)	−443	741	−376
H(1″)	−423	588	−682	H(2)	−251 (5)	722 (11)	−550 (12)
H(2′)	−266 (6)	821 (10)	−379 (15)	H(7)	−31 (4)	232 (7)	−330 (9)
H(9)	72 (3)	−14 (6)	−301 (10)	H(10)	126 (5)	−283 (9)	−160 (12)
H(12)	−105 (6)	−282 (12)	267 (16)	H(13)	−185 (4)	19 (7)	162 (10)
H(14)	10 (3)	−501 (6)	325 (8)	H(15)	200 (4)	−521 (7)	34 (12)
H(19)	307 (10)	−879 (21)	611 (25)	H(22)	466 (12)	−876 (24)	626 (28)
H(22′)	455 (6)	−713 (13)	352 (17)	H(23)	384	−1157	346
H(23′)	396	−1000	129	H(23″)	276	−1102	154
H(24)	503	−513	850	H(24′)	390	−597	949
H(24″)	383	−466	695				

Discussion. The molecular structure and numbering system are shown in Fig. 1. Bond lengths and angles for the heavy atoms are presented in Table 2. The skeleton of the molecule is almost centrosymmetric and planar, with deviations of maximally 0·15 Å from the mean plane. The goodness of fit to a centrosymmetric molecule can be deduced from a comparison of pseudo centrosymmetrically related atoms. The average deviation from the means of these atoms is 0·06 Å. The benzene ring is rotated 6·7° about C(7)–C(8) from one ethylenic plane and −6·0° about C(11)–C(14) from the other. The *sec*-butyl group adopts an extended conformation. The molecular packing is shown in Fig. 2. The stacking motif along the 7 Å *b* axis contains

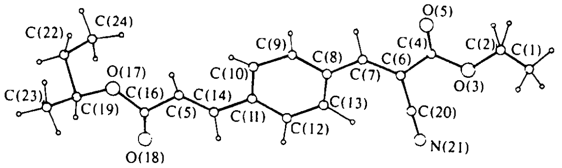

Fig. 1. The molecular structure of (II). The H atoms are assigned the same number as the C atoms to which they are attached.

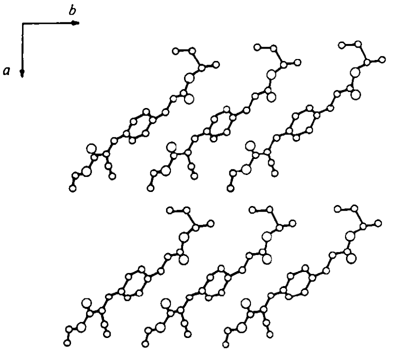

Fig. 2. The packing arrangement of (II) in the *ab* plane.

Table 2. *Bond distances* (Å) *and angles* (°) *involving the heavy atoms, with e.s.d.'s in parentheses*

C(1)–C(2)	1·27 (2)	C(11)–C(12)	1·377 (10)
C(4)–C(6)	1·467 (10)	C(15)–C(16)	1·484 (11)
C(6)–C(7)	1·380 (6)	O(17)–C(19)	1·52 (2)
C(8)–C(9)	1·370 (7)	C(20)–N(21)	1·138 (11)
C(11)–C(14)	1·501 (10)	O(3)–C(4)	1·342 (8)
C(14)–C(15)	1·306 (10)	C(6)–C(20)	1·399 (10)
C(16)–O(18)	1·127 (10)	C(8)–C(13)	1·377 (8)
C(19)–C(23)	1·44 (3)	C(10)–C(11)	1·377 (12)
C(2)–O(3)	1·442 (17)	C(12)–C(13)	1·398 (11)
C(4)–O(5)	1·235 (10)	C(16)–O(17)	1·332 (9)
C(7)–C(8)	1·428 (0)	C(19)–C(22)	1·586 (17)
C(9)–C(10)	1·443 (12)	C(22)–C(24)	1·49 (3)
C(1)–C(2)–O(3)	117·8 (14)	C(2)–O(3)–C(4)	116·6 (7)
O(3)–C(4)–O(5)	121·5 (7)	O(3)–C(4)–C(6)	112·2 (7)
O(5)–C(4)–C(6)	126·4 (6)	C(4)–C(6)–C(7)	116·1 (5)
C(4)–C(6)–C(20)	118·3 (6)	C(7)–C(6)–C(20)	125·4 (5)
C(6)–C(7)–C(8)	129·1 (3)	C(7)–C(8)–C(9)	116·2 (3)
C(7)–C(8)–C(13)	126·4 (3)	C(9)–C(8)–C(13)	117·4 (4)
C(8)–C(9)–C(10)	122·2 (7)	C(9)–C(10)–C(11)	117·6 (7)
C(10)–C(11)–C(12)	120·9 (7)	C(10)–C(11)–C(14)	121·8 (6)
C(12)–C(11)–C(14)	117·2 (7)	C(11)–C(12)–C(13)	119·5 (8)
C(8)–C(13)–C(12)	122·3 (6)	C(11)–C(14)–C(15)	128·1 (8)
C(14)–C(15)–C(16)	120·3 (7)	C(15)–C(16)–O(17)	107·5 (7)
C(15)–C(16)–O(18)	126·8 (7)	O(17)–C(16)–O(18)	125·4 (7)
C(16)–O(17)–C(19)	117·1 (8)	O(17)–C(19)–C(22)	104·3 (12)
O(17)–C(19)–C(23)	104·6 (16)	C(22)–C(19)–C(23)	110·7 (12)
C(6)–C(20)–N(21)	178·0 (8)	C(19)–C(22)–C(24)	115·8 (11)

pronounced overlap between a C=O bond and a phenyl ring of adjacent moelcules; this C=O···phenyl interaction has been observed by Ueno, Nakanishi, Hasegawa & Sasada (1978, and references therein) in a family of symmetrically substituted diolefins.

This molecular stacking along the 7 Å axis brings parallel non-equivalent C=C bonds at a distance of 4·04 Å, which is a prerequisite for the feasibility of a $(2\pi + 2\pi)$ photocycloaddition reaction in the crystalline state (Schmidt, 1971). In fact, photodimers and photopolymers of (II) were obtained, isolated, characterized, and their absolute configuration deduced from that of the monomer crystal (Addadi & Lahav, 1978).

The thermal parameters of the atoms were found to be very high, especially those of the atoms which lie on the periphery of the molecule, and the methyl atoms of the ethyl and *sec*-butyl groups. This seems to indicate a high vibrational motion due to weak crystal forces; the high thermal parameters of the *sec*-butyl group, however, could also result from the fact that the data were measured on a non-optically-pure crystal, containing 5% of the enantiomer in the form of a solid solution (Addadi &Lahav, 1979*b*). This was not taken care of explicitly in the refinement.

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References

ADDADI, L. & LAHAV, M. (1978). *J. Am. Chem. Soc.* **100**, 2838–2844.
ADDADI, L. & LAHAV, M. (1979*a*). *Pure Appl. Chem.* **51**, 1269–1284.
ADDADI, L. & LAHAV, M. (1979*b*). *J. Am. Chem. Soc.* **101**, 2152–2156.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
HASEGAWA, M., SUZUKI, Y., NAKANISHI, H. & NAKANISHI, F. (1973). *Prog. Polym. Sci. Jpn*, **5**, 143–209.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
KARLE, J. (1968). *Acta Cryst.* B**24**, 182–186.
SCHMIDT, G. M. J. (1971). *Pure Appl. Chem.* **27**, 647–678.
UENO, K., NAKANISHI, H., HASEGAWA, M. & SASADA, Y. (1978). *Acta Cryst.* B**24**, 2034–2035.

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17-Oxosparteine

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Abstract. $C_{15}H_{24}N_2O$, orthorhombic, $P2_12_12_1$, a = 6·945 (1), b = 9·085 (1), c = 21·857 (3) Å, Z = 4, D_c = 1·20 Mg m^{-3}. The final R for 996 reflections is 0·049; R_w = 0·057. The quinolizidine skeletons (systems *A*/*B* and *C*/*D*) have the *trans–trans* configuration. The piperidine rings *A*, *B*, *C* and *D* have chair, chair, sofa and chair conformations respectively.

Introduction. 17-Oxosparteine is the first of the group of 'oxo' sparteine derivatives we have investigated. These compounds have already been examined by spectroscopic methods (Wiewiórowski & Lompa-Krzymień, 1969, 1970). From our measurements we explain the influence of the 'oxo' substituent on the conformation and molecular structure of the sparteine skeleton; *e.g.* on the N(1)–N(16) distance, the inclination of one quinolizidine skeleton to the other, and the C–N bond distance in the lactam group.

Colorless crystals of 17-oxosparteine were obtained from methanol solution. The dimensions of the crystal used for data collection were 0·4 × 0·4 × 0·3 mm. The measurements were performed on a Syntex $P2_1$ diffractometer using graphite-monochromated Cu $K\alpha$ radiation. The θ–2θ scan method was used with a variable scan speed (minimum: 2° min^{-1}; maximum: 29·3° min^{-1}), depending on the reflection intensity. A control reflection was monitored after every 57 reflections. 1090 reflections were collected, including systematic absences; 996 had intensities greater than $1{\cdot}96\sigma_I$, and were included in the refinement. Only the Lorentz and polarization corrections were applied.

The structure was solved by direct methods using the *MULTAN* program (Germain, Main & Woolfson, 1971). All nonhydrogen atoms were found on the E map based on the correct phase set. The refinement of the positions and anisotropic temperature factors of the nonhydrogen atoms was followed by the difference Fourier map, from which all H atoms were located.

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