

(RRS–SSR)-2-(1-Methoxyethyl)-3-methylsuccinimide

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Abstract. $C_8H_{13}NO_3$, monoclinic, $P2_1/n$, $a = 10.191$ (5), $b = 11.592$ (6), $c = 8.358$ (4) Å, $\beta = 110.58$ (4)°, $M_r = 171.2$, $Z = 4$, $D_x = 1.23$ Mg m⁻³; $R = 0.050$ and $R_w = 0.050$ for 1702 observed reflexions. The relative configuration of the three chiral centres is *RRS* or *SSR*. The molecules build centrosymmetric dimers through N–H···O hydrogen bonds of length 2.88 (1) Å. N(1), C(2), C(3) and C(5) are coplanar, with C(4) displaced -0.134 Å from the least-squares plane.

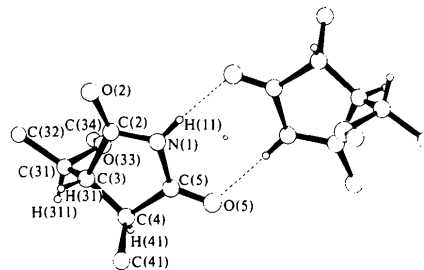
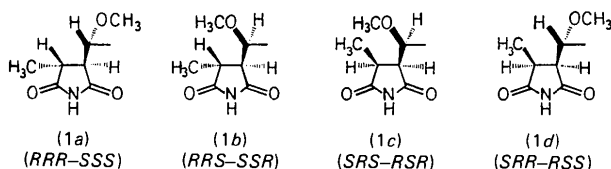


Fig. 1. The dimer of (1b).

Introduction. On treatment of the bile pigment phycocyanobilin dimethyl ester with boiling methanol, one molecule of the latter is added at the ethylidene group of the chromophore. Of the four possible diastereomeric adducts, only two are formed (Gossauer & Hinze, 1981). Methanolysis of the protein moiety of the chromoprotein C-phycocyanin and subsequent esterification of the methanol extracts leads also to these two diastereomeric adducts and additionally to phycocyanobilin dimethyl ester. All four racemic stereoisomers of 2-(1-methoxyethyl)-3-methylsuccinimide were synthesized (Gossauer & Hinze, 1980) and the relative configurations of the three chiral centres C(4), C(3) and C(31) (Fig. 1), with the exception of (1a), determined by X-ray analysis. The structures of the methanol adducts were then elucidated by stereospecific total syntheses from the corresponding monothioamides. It was established that (1a) and (1b) represent the relative configurations of the chiral centres in the methanol adducts. Inspection of structural models suggests that the five-membered ring in (1c) must be considerably strained and that a pronounced twisting of the ring must be necessary to allow C(31) and C(41) (Fig. 1) to adopt positions *cis* to one another. This paper presents the structural analysis of (1b), the following paper (Sheldrick, 1981) that of (1c).



Cell dimensions were determined by a least-squares fit to settings for 15 reflexions $\pm(hkl)$ on a Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å). Data collection was carried out in the θ - 2θ mode ($2\theta \leq 60^\circ$) with graphite-monochromated Mo $K\alpha$ radiation. No absorption correction was applied [$\mu(\text{Mo } K\alpha) = 0.048$ mm⁻¹]. After application of the observation criterion $F^2 \geq 2.0\sigma(F^2)$, 1702 unique reflexions were retained for use in the analysis. The structure was solved by direct methods and refined by full-matrix least squares with anisotropic temperature factors for the non-hydrogen atoms. The H atom positional

Table 1. Positional parameters and equivalent isotropic thermal parameters

	x	y	z	U_{eq} (Å ² × 10 ³)†
N(1)	0.8376 (1)	0.9824 (1)	0.5425 (1)	42
C(2)	0.7216 (1)	0.9946 (1)	0.5895 (2)	40
C(3)	0.6781 (1)	0.8748 (1)	0.6273 (2)	40
C(4)	0.7754 (1)	0.7920 (1)	0.5782 (2)	39
C(5)	0.8803 (1)	0.8696 (1)	0.5412 (1)	37
O(2)	0.6678 (1)	1.0864 (1)	0.5974 (1)	57
C(31)	0.6907 (1)	0.8660 (2)	0.8151 (2)	48
C(32)	0.5789 (3)	0.9320 (2)	0.8574 (4)	71
O(33)	0.8298 (1)	0.9059 (1)	0.9091 (1)	58
C(34)	0.8802 (3)	0.8779 (2)	1.0865 (2)	81
C(41)	0.7013 (2)	0.7173 (2)	0.4224 (3)	68
O(5)	0.9835 (1)	0.8406 (1)	0.5101 (1)	51

$$\dagger U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

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

C(2)—N(1)	1.377 (2)	C(5)—N(1)	1.379 (2)
C(3)—C(2)	1.524 (2)	O(2)—C(2)	1.210 (2)
C(4)—C(3)	1.536 (2)	C(31)—C(3)	1.533 (2)
C(5)—C(4)	1.510 (2)	C(41)—C(4)	1.525 (3)
O(5)—C(5)	1.217 (2)	C(32)—C(31)	1.514 (3)
O(33)—C(31)	1.434 (2)	C(34)—O(33)	1.426 (2)
C(5)—N(1)—C(2)	113.8 (1)	C(3)—C(2)—N(1)	107.9 (1)
O(2)—C(2)—N(1)	123.8 (2)	O(2)—C(2)—C(3)	128.3 (2)
C(4)—C(3)—C(2)	104.6 (1)	C(31)—C(3)—C(2)	110.4 (1)
C(31)—C(3)—C(4)	113.7 (1)	C(5)—C(4)—C(3)	104.5 (1)
C(41)—C(4)—C(3)	114.3 (2)	C(41)—C(4)—C(5)	109.7 (1)
C(4)—C(5)—N(1)	108.4 (1)	O(5)—C(5)—N(1)	124.3 (1)
O(5)—C(5)—C(4)	127.3 (1)	C(32)—C(31)—C(3)	114.0 (2)
O(33)—C(31)—C(3)	104.5 (1)	O(33)—C(31)—C(32)	112.9 (2)
C(34)—O(33)—C(31)	115.0 (2)		

parameters were refined freely with individual isotropic temperature factors. The terminal value of R_w was 0.050 with $R = 0.050$. * Weights were given by $w = k[\sigma^2(F_o) + g(F_o^2)]^{-1}$, where g refined to 0.000380. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Table 1 lists the final non-hydrogen atom coordinates, Table 2 the bond lengths and angles. Calculations were carried out with *SHELX* (Sheldrick, 1976) and local programs. Fig. 1 was drawn with *RSPLOT* (W. S. Sheldrick).

* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35609 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Abstract. $C_8H_{13}NO_3$, monoclinic, $P2_1/c$, $a = 12.984$ (4), $b = 7.559$ (3), $c = 9.734$ (3) Å, $\beta = 97.77$ (4)°, $M_r = 171.2$, $Z = 4$, $D_x = 1.20$ Mg m⁻³; $R = 0.057$ and $R_w = 0.051$ for 1420 observed reflexions. The relative configuration of the three chiral centres is *SRS* or *RSR*. The molecules build centrosymmetric

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Discussion. Molecules of (1*b*) build centrosymmetric dimers through N(1)—H...O(5) hydrogen bonds of length 2.88 (1) Å. N(1), C(2), C(3) and C(4) are coplanar: distances from the least-squares plane are N(1) 0.002, C(2) -0.002, C(3) 0.001, C(5) -0.001 Å. C(4) is displaced -0.134, O(2) -0.008 and O(5) -0.055 Å from this plane. Bond angles at C(2) and C(3) are similar to those at C(5) and C(4) respectively. The torsion angles H(31)—C(3)—C(4)—C(41) and H(41)—C(4)—C(3)—C(31) are respectively 3(1) and 3(1)°. A torsion angle of 127.6 (2)° is observed for C(31)—C(63)—C(4)—C(41). It may, therefore, be concluded that the five-membered ring is relatively non-strained for C(31) and C(41) in a *trans* position to one another. A similar observation was made for the model compound (RRS-SSR)-2-[1-(ethylsulphonyl)ethyl]-3-methylsuccinimide (Lotter, Klein, Rüdiger & Scheer, 1977), in which C(31) and C(41) are likewise *trans* to one another. A comparison of the geometry of (1*b*) with that of (1*c*), for which C(31) and C(41) are *cis* to one another, is made in the following paper (Sheldrick, 1981).

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dimers through N—H...O hydrogen bonds of length 2.91 (1) Å. The five-membered ring is markedly twisted with C(3) and C(4) displaced respectively -0.114 and 0.180 Å from the plane of the remaining ring atoms. A torsion angle of 23.3 (2)° is observed between the *cis*-substituted C(3) and C(4).

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