ate to 103° for (−)-1,1′-binaphthyl (Akimoto & Iitaka, 1969; Harata & Tanaka, 1973; Kuroda & Mason, 1981; Pauptit & Trotter, 1981, 1983). The present dihedral angle is comparable to that [74·4 (2)°] found in [(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene] (8,9,10-trinorborna-2,5-diene)-rhodium(I) perchlorate (Toriumi, Ito, Takaya, Souchi & Noyori, 1982) where the binaphthyl derivative is coordinated to the metal atom.

As previously shown (Harata & Tanaka, 1973), bulky substituents at the 2,2′ positions give rise to large dihedral angles. However, in this case the twist observed between the plane of each $N(CH_3)_2$ and the plane of the corresponding naphthalene ring can constitute a more efficient way of reducing the steric repulsion than the increase of the dihedral angle between the two naphthalenic rings, also taking into account that for large dihedral angles steric repulsion between an $N(CH_3)_2$ group of a naphthalene moiety and the other aromatic ring can become important.

The authors wish to thank Professor S. Merlino and Dr F. Marchetti for helpful discussions.

References

Akimoto, H. & Iitaka, Y. (1969). *Acta Cryst.* **B25**, 1491–1500.
Benson, S. C., Cai, P., Colon, M., Haiza, M. A., Tokles, M. & Snyder, J. K. (1988). *J. Org. Chem.* **53**, 5335–5341.
Gottarelli, G., Spada, G. P., Bartsch, R., Solladiè, G. & Zimmermann, R. (1986). *J. Org. Chem.* **51**, 589–592.
Harata, K. & Tanaka, J. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2747–2751.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kuroda, J. & Mason, F. (1981). *J. Chem. Soc. Perkin Trans.* 2, pp. 167–170.
Mason, S. F., Seal, R. H. & Roberts, D. R. (1974). *Tetrahedron*, **30**, 1671–1682.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Noyori, R. (1989). *Chem. Soc. Rev.* **18**, 187–208.
Noyori, R. & Takaya, H. (1985). *Chem. Scr.* **25**, 83–89.
Pauptit, R. A. & Trotter, J. (1981). *Can. J. Chem.* **59**, 1149–1152.
Pauptit, R. A. & Trotter, J. (1983). *Can. J. Chem.* **61**, 69–71.
Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
Toriumi, K., Ito, T., Takaya, H., Souchi, T. & Noyori, R. (1982). *Acta Cryst.* **B38**, 807–812.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1991). C**47**, 1261–1263

Structure of a Chiral Amide Derived from a (Vinylketenimine)tricarbonyliron(0) Complex

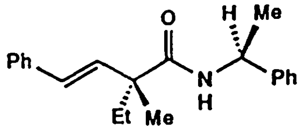
By Nathaniel W. Alcock,* Christopher J. Richards and Susan E. Thomas

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England

(*Received* 15 *August* 1990; *accepted* 5 *October* 1990)

Abstract. (2*R*)-2-Ethyl-2-methyl-4-phenyl-*N*-[(*S*)-1-phenylethyl]-(*E*)-3-butenamide, $C_{21}H_{25}NO$, M_r = 307·4, orthorhombic, $P2_12_12_1$, a = 10·071 (7), b = 19·218 (15), c = 19·406 (14) Å, V = 3756 Å^3, Z = 8, D_x = 1·09 g cm^{-3}, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ(Mo $K\alpha$) = 0·6 cm^{-1}, $F(000)$ = 1328, T = 290 K, R = 0·063 for 1600 unique observed $[I/\sigma(I) \geq 2·0]$ reflections. The two independent molecules show significant conformational differences, principally involving the (C=O)—C bond adjacent to the amide group. The molecules are linked into chains by N—H···O hydrogen bonds.

Introduction. The reaction of a homochiral (vinylketenimine)tricarbonyliron(0) complex with ethyllithium has been shown to produce only one diastereoisomer of the β,γ-unsaturated amide (I) in >95% purity (Alcock, Pike, Richards & Thomas, 1990). The crystal structure of this amide has been determined to establish the stereospecificity of the reaction. (−)-(*S*)-α-Methylbenzylamine was used as the starting material for the preparation of the iron complex and the retained chiral centre provided a reference point for identifying the chirality of the new quaternary carbon centre formed in the reaction.



(I)

* To whom correspondence should be addressed.

0108-2701/91/061261-03$03.00

Experimental. The compound was prepared as described in Alcock *et al.* (1990). Lath-shaped crystals were obtained from hexane. Data were collected with a Nicolet $P2_1$ four-circle diffractometer in ω–2θ mode. Maximum 2θ was 45° with scan range $\pm 1{\cdot}3°(2\theta)$ around the $K\alpha_1$–$K\alpha_2$ angles, scan speed 4–29° min^{-1} depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0·25 of the scan time. *hkl* ranges were 0/10, 0/20, 0/20. Three standard reflections were monitored every 200 reflections and showed a slight decrease during data collection (6%); the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 16 reflections ($16 < 2\theta < 18°$). Reflections were processed using profile analysis to give 2800 unique reflections of which 1600 were considered observed [$I/\sigma(I) \geq 2{\cdot}0$]. These were corrected for Lorentz, polarization but not absorption effects. Crystal dimensions were 0·09 × 0·13 × 0·34 mm. Systematic reflection conditions: $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$ indicate space group $P2_12_12_1$.

The structure was solved by direct methods using *SHELXTL* (Sheldrick, 1983). Anisotropic temperature factors were used for all non-H atoms. H atoms were given fixed isotropic temperature factors, $U = 0{\cdot}08$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid CH_3 units with their initial orientation taken from the strongest H-atom peaks on a difference Fourier synthesis and the positions of N—H protons were refined. The absolute structure was obtained from the known chirality at the 1′ position [C(17);C(27)]. Final refinement was on *F* by least-squares methods refining 415 parameters; despite the relatively low observation/parameter ratio, the refinement was well behaved. Largest positive and negative peaks on a final difference Fourier synthesis were of height $\pm 0{\cdot}15$ e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0{\cdot}00068$ was used and shown to be satisfactory by a weight analysis. Final $R = 0{\cdot}059$, $wR = 0{\cdot}059$, $S = 1{\cdot}35$. Maximum shift/e.s.d. in final cycle 0·6. Computing with *SHELXTL-Plus* (Sheldrick, 1988) on a DEC MicroVAX-II. Scattering factors in the analytical form and anomalous-dispersion factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic coordinates are given in Table 1 and selected bond lengths, angles and torsion angles in Table 2.*

Table 1. *Atomic coordinates* (× 10^4) *and temperature factors* (Å^2 × 10^3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
O(1)	9864 (5)	6205 (3)	1634 (3)	68 (2)
O(2)	4856 (6)	6314 (3)	1287 (3)	71 (2)
N(1)	7765 (6)	6422 (3)	1335 (4)	51 (3)
N(2)	2732 (7)	6465 (4)	1579 (4)	61 (3)
C(11)	8255 (8)	7679 (4)	1263 (5)	52 (3)
C(12)	9055 (8)	8202 (5)	1031 (5)	62 (4)
C(13)	9107 (10)	8821 (6)	1353 (6)	80 (5)
C(14)	8434 (12)	8955 (6)	1941 (6)	94 (5)
C(15)	7617 (11)	8428 (6)	2189 (5)	93 (5)
C(16)	7562 (9)	7791 (5)	1861 (5)	70 (4)
C(17)	8093 (8)	7000 (4)	884 (4)	56 (3)
C(18)	7098 (9)	− 7071 (4)	308 (4)	81 (4)
C(19)	8673 (9)	6079 (4)	1691 (4)	49 (3)
C(110)	8236 (8)	5488 (4)	2184 (5)	51 (3)
C(111)	6765 (7)	5509 (4)	2355 (5)	74 (4)
C(112)	9064 (9)	5545 (5)	2839 (4)	74 (4)
C(113)	8859 (11)	6186 (5)	3244 (5)	107 (5)
C(114)	8647 (10)	4828 (6)	1831 (5)	80 (4)
C(115)	8017 (12)	4327 (6)	1589 (6)	93 (5)
C(116)	8485 (13)	3691 (5)	1239 (6)	76 (4)
C(117)	7603 (12)	3286 (8)	865 (7)	116 (6)
C(118)	8020 (22)	2700 (9)	542 (8)	142 (9)
C(119)	9277 (21)	2501 (8)	563 (8)	121 (7)
C(120)	10183 (13)	2890 (8)	932 (7)	108 (6)
C(121)	9735 (15)	3474 (7)	1243 (6)	98 (6)
C(21)	3668 (9)	6802 (6)	2705 (5)	64 (4)
C(22)	3306 (11)	6212 (6)	3021 (7)	98 (5)
C(23)	3860 (15)	6009 (8)	3633 (8)	123 (7)
C(24)	4795 (19)	6401 (9)	3935 (8)	144 (9)
C(25)	5138 (13)	7012 (9)	3653 (7)	126 (7)
C(26)	4590 (10)	7207 (5)	3024 (5)	82 (4)
C(27)	3033 (8)	7041 (5)	2029 (5)	61 (4)
C(28)	1789 (8)	7474 (4)	2152 (5)	86 (4)
C(29)	3702 (10)	6123 (5)	1260 (5)	57 (4)
C(210)	3292 (7)	5469 (5)	866 (4)	57 (3)
C(211)	2829 (9)	4925 (4)	1399 (4)	75 (4)
C(212)	4528 (8)	5192 (5)	482 (5)	75 (4)
C(213)	4296 (10)	4546 (5)	60 (5)	115 (5)
C(214)	2227 (8)	5647 (4)	347 (5)	60 (3)
C(215)	1040 (8)	5373 (4)	288 (4)	62 (4)
C(216)	42 (8)	5559 (4)	− 229 (5)	55 (3)
C(217)	− 1218 (10)	5253 (5)	− 197 (5)	70 (4)
C(218)	− 2146 (10)	5400 (6)	− 674 (6)	80 (4)
C(219)	− 1917 (11)	5857 (5)	− 1192 (6)	83 (5)
C(220)	681 (11)	6154 (5)	− 1245 (5)	86 (4)
C(221)	262 (9)	6020 (5)	− 766 (5)	75 (4)

Discussion. Bond distances and angles in the two molecules are closely similar and correspond to standard values. However, they have significantly different conformations. This is illustrated in Fig. 1 which shows both molecules from similar viewpoints. The principal difference is in the C(n9)—C(n10) bonds with N—C—C—C torsion angles of 107·2 (10) and 55·9 (10)° respectively. This leads to molecule 1 having a much more extended overall conformation. Other torsion angles match to within about 10° between the two molecules apart from the C(n10)—ethyl bond which is *gauche* in molecule 1 and staggered in molecule 2. However, cumulatively these differences produce considerable further differences in the orientation of the N(H)(Me)(Ph) unit. Few comparable structures have been reported. Almost all structurally characterized molecules containing a quaternary carbon centre adjacent to the carbonyl of an amide are peptides and peptide analogues protected by a *tert*-butyl group [*e.g.*

---

* Lists of anisotropic thermal parameters, H-atom coordinates, full bond lengths and angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53625 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *angles and torsion angles* (°) *of molecules* 1 *and* 2

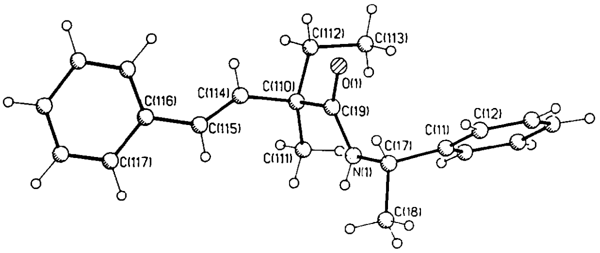
E.s.d.'s of torsion angles are 1·0°

Molecule 1		Molecule 2	
O(1)—C(19)	1·228 (10)	O(2)—C(29)	1·219 (12)
N(1)—C(17)	1·452 (11)	N(2)—C(27)	1·442 (11)
N(1)—C(19)	1·322 (11)	N(2)—C(29)	1·330 (12)
C(11)—C(17)	1·508 (12)	C(21)—C(27)	1·530 (13)
C(17)—C(18)	1·507 (12)	C(27)—C(28)	1·523 (12)
C(19)—C(110)	1·549 (12)	C(29)—C(210)	1·527 (13)
C(110)—C(111)	1·518 (11)	C(210)—C(211)	1·543 (12)
C(110)—C(112)	1·525 (12)	C(210)—C(212)	1·556 (12)
C(110)—C(114)	1·501 (14)	C(210)—C(214)	1·511 (12)
C(112)—C(113)	1·475 (14)	C(212)—C(213)	1·495 (14)
C(114)—C(115)	1·245 (16)	C(214)—C(215)	1·311 (12)
C(115)—C(116)	1·476 (16)	C(215)—C(216)	1·463 (12)
N(1)···O(2)	2·939 (10)		
N(2)···O(1*)	2·933 (10) [O(1*) at $x-1, y, z$]		
N(1)—C(17)—C(11)	113·0 (7)	N(2)—C(27)—C(21)	112·2 (8)
N(1)—C(17)—C(18)	111·5 (7)	N(2)—C(27)—C(28)	110·0 (7)
C(11)—C(17)—C(18)	110·8 (7)	C(21)—C(27)—C(28)	111·9 (8)
C(17)—N(1)—C(19)	122·6 (7)	C(27)—N(2)—C(29)	120·4 (7)
O(1)—C(19)—N(1)	122·1 (8)	O(2)—C(29)—N(2)	122·1 (8)
O(1)—C(19)—C(110)	118·5 (7)	O(2)—C(29)—C(210)	121·8 (8)
N(1)—C(19)—C(110)	119·4 (7)	N(2)—C(29)—C(210)	116·1 (8)
C(19)—C(110)—C(111)	113·2 (7)	C(29)—C(210)—C(211)	107·7 (7)
C(19)—C(110)—C(112)	107·9 (7)	C(29)—C(210)—C(212)	108·2 (7)
C(111)—C(110)—C(112)	110·4 (7)	C(211)—C(210)—C(212)	109·8 (7)
C(19)—C(110)—C(114)	105·0 (7)	C(29)—C(210)—C(214)	109·9 (7)
C(111)—C(110)—C(114)	113·0 (7)	C(211)—C(210)—C(214)	112·7 (7)
C(112)—C(110)—C(114)	106·9 (7)	C(212)—C(210)—C(214)	108·5 (7)
C(110)—C(114)—C(115)	133·2 (10)	C(210)—C(214)—C(215)	128·0 (8)
C(114)—C(115)—C(116)	130·6 (11)	C(214)—C(215)—C(216)	126·0 (8)
C(19)—N(1)—C(17)—C(11)	−82·0	C(29)—N(2)—C(27)—C(21)	−71·9
C(19)—N(1)—C(17)—C(18)	152·4	C(29)—N(2)—C(27)—C(28)	162·8
C(12)—C(11)—C(17)—N(1)	152·2	C(22)—C(21)—C(27)—N(2)	−36·5
C(16)—C(11)—C(17)—N(1)	−29·0	C(26)—C(21)—C(27)—N(2)	146·7
C(17)—N(1)—C(19)—O(1)	−3·8	C(27)—N(2)—C(29)—O(2)	−6·4
C(17)—N(1)—C(19)—C(110)	177·5	C(27)—N(2)—C(29)—C(210)	172·8
O(1)—C(19)—C(110)—C(114)	−71·6	O(2)—C(29)—C(210)—C(214)	−124·8
N(1)—C(19)—C(110)—C(114)	107·2	N(2)—C(29)—C(210)—C(214)	55·9
C(19)—C(110)—C(112)—C(113)	64·2	C(29)—C(210)—C(212)—C(213)	179·6
C(19)—C(110)—C(114)—C(115)	−115·3	C(29)—C(210)—C(214)—C(215)	−123·7
C(112)—C(110)—C(114)—C(115)	130·2	C(212)—C(210)—C(214)—C(215)	118·2
C(110)—C(114)—C(115)—C(116)	179·4	C(210)—C(214)—C(215)—C(216)	−179·5
C(114)—C(115)—C(116)—C(117)	−164·3	C(214)—C(215)—C(216)—C(217)	−175·7

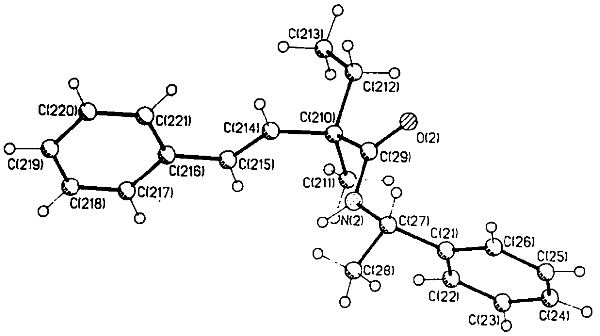
pivaloylglycyl-*N*′-methyl-L-prolinamide (Aubry, Boussard & Marraud, 1981)]. The steric requirements of such molecules are likely to be substantially different from the present example.

The molecules are linked by N—H···O hydrogen bonds into chains parallel to **a** (Fig. 2). Molecules of type (1) are oriented parallel to **b** with phenyl–phenyl interactions between those in adjacent chains. In the chains they alternate with molecules of type (2) whose lengths are aligned roughly parallel to **c**. It is possibly the difficulty of packing identical relatively bulky molecules together at the hydrogen-bonding 3 Å separation that leads to the observed stability of the compound as a mixture of two conformers.

We thank the SERC for an Earmarked studentship (CJR) and for support for the diffractometer.



Molecule 1



Molecule 2

Fig. 1. Views of the two molecules showing the atomic numbering.

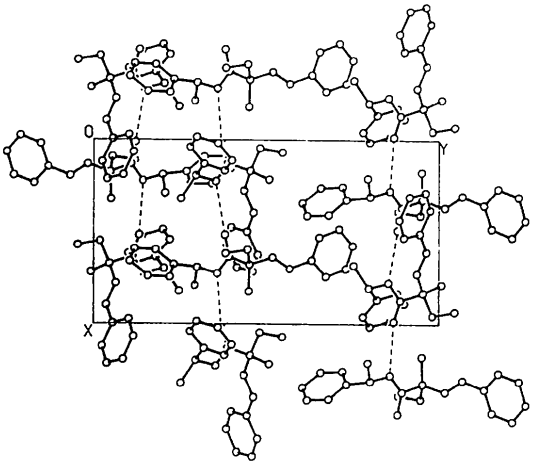


Fig. 2. Packing diagram viewed down **b** showing the hydrogen-bonded chains parallel to **a** and the different conformations of the two independent molecules.

References

Alcock, N. W., Pike, G. A., Richards, C. J. & Thomas, S. E. (1990). *Tetrahedron Asymmetry*, **1**, 531–534.

Aubry, A., Boussard, G. & Marraud, M. (1981). *Acta Cryst.* B**37**, 1474–1477.

Sheldrick, G. M. (1983). *SHELXTL Users Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Sheldrick, G. M. (1988). *SHELXTL-Plus*88 *Structure Determination Software Programs*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.