

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0420$   
 $wR(F^2) = 0.1207$   
 $S = 1.289$   
 1142 reflections  
 142 parameters  
 All H-atom parameters  
 refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.4406P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.004$

$\Delta\rho_{\max} = 0.302 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.318 \text{ e } \text{Å}^{-3}$   
 Extinction correction:  
*SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient:  
 0.1127 (65)  
 Atomic scattering factors  
 from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

(Sheldrick, 1993). Molecular graphics: *ORTEP92* (Vicković, 1994). Software used to prepare material for publication: *CSU* (Vicković, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
C1	0.7850 (2)	-0.1307 (2)	0.3971 (3)	0.0234 (5)
C3	0.6462 (2)	-0.3011 (2)	0.4055 (4)	0.0270 (5)
C5	0.6552 (2)	-0.1159 (2)	0.2010 (3)	0.0217 (5)
C7	0.6769 (2)	0.0531 (2)	0.4589 (3)	0.0253 (5)
N1	0.9048 (2)	-0.1452 (2)	0.3269 (3)	0.0284 (5)
N2	0.7559 (2)	-0.2422 (2)	0.5135 (3)	0.0319 (5)
N4	0.5880 (2)	-0.2314 (2)	0.2215 (3)	0.0279 (5)
N5	0.6647 (2)	-0.0982 (2)	-0.0328 (3)	0.0274 (5)
N6	0.5991 (2)	-0.0047 (2)	0.2794 (3)	0.0278 (5)
N8	0.7865 (2)	-0.0155 (2)	0.5254 (3)	0.0292 (5)
O3	0.6071 (2)	-0.40240 (15)	0.4647 (3)	0.0380 (5)
O7	0.6531 (2)	0.1537 (2)	0.5435 (3)	0.0350 (5)

Table 2. Selected bond lengths ( $\text{Å}$ ) and angles ( $^\circ$ )

C1—N1	1.436 (3)	C5—N5	1.435 (3)
C1—N2	1.442 (3)	C5—N4	1.439 (3)
C1—N8	1.442 (3)	C5—N6	1.448 (3)
C1—C5	1.608 (3)	C7—O7	1.232 (3)
C3—O3	1.233 (3)	C7—N6	1.348 (3)
C3—N2	1.354 (3)	C7—N8	1.357 (3)
C3—N4	1.356 (3)		
N1—C1—N2	110.7 (2)	N4—C5—N6	114.8 (2)
N1—C1—N8	110.0 (2)	N5—C5—C1	119.2 (2)
N2—C1—N8	114.7 (2)	N4—C5—C1	102.6 (2)
N1—C1—C5	118.2 (2)	N6—C5—C1	101.16 (15)
N2—C1—C5	100.9 (2)	O7—C7—N6	125.1 (2)
N8—C1—C5	102.1 (2)	O7—C7—N8	126.0 (2)
O3—C3—N2	125.2 (2)	N6—C7—N8	108.9 (2)
O3—C3—N4	125.9 (2)	C3—N2—C1	113.8 (2)
N2—C3—N4	108.9 (2)	C3—N4—C5	112.8 (2)
N5—C5—N4	109.8 (2)	C7—N6—C5	113.8 (2)
N5—C5—N6	109.4 (2)	C7—N8—C1	113.1 (2)

Table 3. Hydrogen-bonding geometry ( $\text{Å}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1a...O3 <sup>i</sup>	0.90 (3)	2.22 (3)	3.098 (3)	164 (3)
N1—H1b...O7 <sup>ii</sup>	0.89 (3)	2.15 (3)	3.039 (3)	170 (3)
N2—H2...O7 <sup>iii</sup>	0.86 (3)	2.01 (3)	2.833 (3)	159 (3)
N4—H4...N1 <sup>iv</sup>	0.92 (3)	2.09 (3)	3.005 (3)	177 (3)
N5—H5a...O3 <sup>i</sup>	0.93 (3)	2.25 (3)	3.153 (3)	165 (3)
N5—H5b...O7 <sup>ii</sup>	0.94 (3)	2.40 (3)	3.280 (3)	155 (3)
N6—H6...N5 <sup>v</sup>	0.88 (3)	2.19 (3)	3.066 (3)	177 (3)
N8—H8...O3 <sup>ii</sup>	0.85 (3)	2.49 (4)	3.236 (3)	146 (3)

Symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (iii)  $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$ ; (iv)  $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$ ; (v)  $1 - x, -y, -z$ ; (vi)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ .

Data collection: Philips PW1100/20 software. Cell refinement: Philips PW1100/20 software. Data reduction: locally written software. Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *SHELXL93*

## References

- Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.  
 Popović, T., Sokolić, L., Modrić, N., Palković, A. & Poje, M. (1991). *Tetrahedron*, **47**, 317–322.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.  
 Vicković, I. (1988). *J. Appl. Cryst.* **21**, 987–990.  
 Vicković, I. (1994). *J. Appl. Cryst.* **27**, 437.

*Acta Cryst.* (1995). **C51**, 2595–2598

## A Precursor to Highly Unsaturated Cyclophanes: 7,19,28-Trithiatetrapoly[11.11.7.1<sup>3,23</sup>.1<sup>11,15</sup>]tritriacontacyclo[1,3(32),11(33),12,14,23-hexaene-4,9,16,22,25,30-hexayne

JOEL T. MAGUE, HARRY E. ENSLEY AND SHIVKUMAR MAHADEVAN

*Department of Chemistry, Tulane University, New Orleans, LA 70118, USA*

(Received 31 March 1995; accepted 4 July 1995)

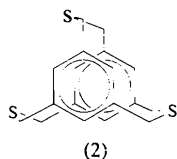
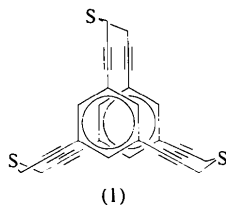
## Abstract

The title compound,  $\text{C}_{30}\text{H}_{18}\text{S}_3\cdot\text{CH}_2\text{Cl}_2$ , has an almost eclipsed conformation with the aromatic rings showing normal van der Waals contacts. The alkyne units in the bridges show some deviation from linearity as a result. The crystal contains solvent dichloromethane which was partially lost in data collection, resulting in a final effective occupancy of 0.55.

## Comment

Multiply bonded cyclophanes have been known for some time (Mitchell & Boekelheide, 1970; Boekelheide & Hollins, 1970; Boekelheide, 1973; Vögtle & Neumann, 1969; Vögtle, 1969). Recently there has been a resurgence of interest in these compounds because of the potential for their conversion to  $\text{C}_{60}$  derivatives (Vollhardt, Boese, Green, Mittendorf & Mohler, 1992). In

an effort to develop suitable routes to spheroidal molecules having extensive conjugation and a high carbon content, we have undertaken model studies of multiply bridged cyclophanes containing alkynyl units in the bridging moieties. Desulfurization of thia-bridged cyclophanes with concomitant C—C bond formation has been found to be a convenient means of generating cyclophanes possessing C=C units in the bridges (Boekelheide & Hollins, 1970), leading to the consideration that 7,19,28-trithiatetracyclo[11.11.7.1<sup>3,23</sup>.1<sup>11,15</sup>]tritriacont-1,3(32),11(33),12,14,23-hexaene-4,9,16,22,25,30-hexayne, (1) (Ensley, Magee & Mahadevan, 1995), would be a suitable model for the synthesis of extensively conjugated cyclophanes. To confirm the identity of (1), its structure was determined.



A perspective view of (1) is given in Fig. 1 while a view of the molecular packing is presented in Fig. 2. There are no unusual intermolecular contacts in the solid state. The two aromatic rings are each planar and additionally are coplanar within experimental error. Their mean separation of 3.591 (5) Å is consistent with a normal van der Waals contact and contrasts with the more compressed inter-ring separations of 3.192 Å in (2) (Hanson & Macaulay, 1972) and 2.809 Å in (3) (Hanson & Röhr, 1972). This can be attributed to the greater length of the bridging moieties in (1), but the result is to introduce 'bowing' of the alkyne units. Thus, for example, C7, C8 and C9 are displaced 0.059 (3), 0.169 (3) and 0.381 (4) Å, respectively, from the mean plane of the attached aromatic ring towards the opposite side of the molecule. This results in a modest nonlinearity in the alkyne groups with the angles at the alkyne C atoms generally being 2–5° less than the ideal value of 180°. The two sides of the molecule are almost eclipsed and (1) has the conformation found for (2) (Hanson & Macaulay, 1972) but without the disorder found in the latter.

Average values for the several types of bond distances and interbond angles are given in Table 2. With the exception of those angles about the  $\alpha$ -C atom of the side chain (*e.g.* C1—C7—C8) which show considerable

scatter, all show good agreement within each set. The molecular packing (Fig. 2) shows that, excepting the S atoms, (1) possesses approximate threefold symmetry. The major departure from this results from S1 being 'flipped' towards S3. The location of the solvent molecules in channels between adjacent molecules of (1) can explain the ready loss of solvent observed during data collection.

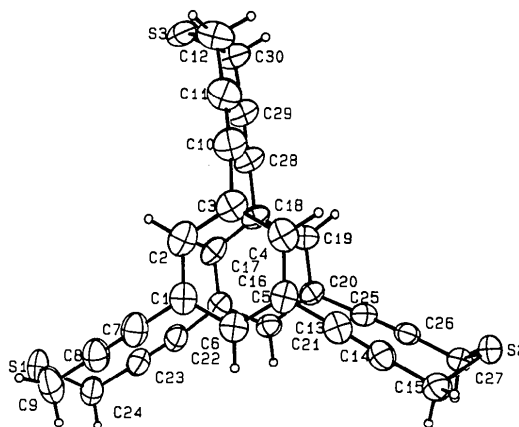


Fig. 1. A perspective view of (1). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms; H atoms are represented by arbitrarily small circles for clarity.

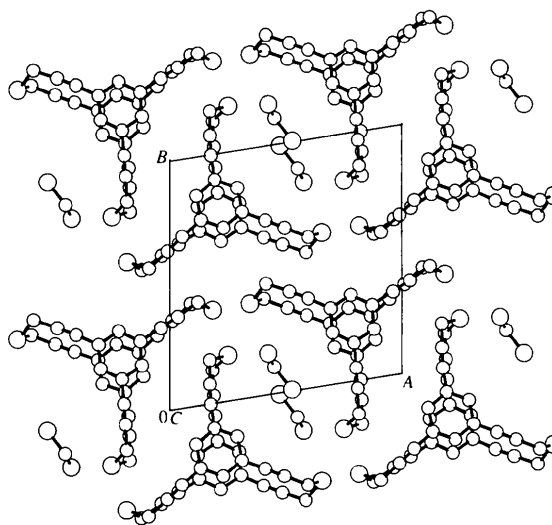


Fig. 2. The molecular packing of (1) viewed along the *c* axis.

## Experimental

Crystals of (1) were grown by cooling a solution of the compound in benzene/dichloromethane at 263 K. One was cut to size and mounted on the end of a thin glass fiber with a coat of epoxy cement.

*Crystal data*

$C_{30}H_{18}S_3 \cdot CH_2Cl_2$   
 $M_r = 559.6$   
 Triclinic  
 $P\bar{1}$   
 $a = 13.934(2) \text{ \AA}$   
 $b = 14.316(2) \text{ \AA}$   
 $c = 7.101(2) \text{ \AA}$   
 $\alpha = 97.86(1)^\circ$   
 $\beta = 103.79(2)^\circ$   
 $\gamma = 79.60(1)^\circ$   
 $V = 1346.6(8) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.380 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 11\text{--}16^\circ$   
 $\mu = 0.483 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Columnar  
 $0.53 \times 0.36 \times 0.30 \text{ mm}$   
 Colorless

C21	-0.2208 (2)	0.3499 (2)	0.4937 (4)	0.0379 (7)
C22	-0.4045 (2)	0.3628 (2)	0.3877 (4)	0.0444 (8)
C23	-0.4859 (2)	0.4025 (2)	0.3279 (5)	0.0495 (9)
C24	-0.5871 (2)	0.4487 (2)	0.2484 (6)	0.057 (1)
C25	-0.0380 (2)	0.3371 (2)	0.5717 (4)	0.0367 (7)
C26	0.0359 (2)	0.3714 (2)	0.5833 (4)	0.0372 (7)
C27	0.1214 (2)	0.4167 (2)	0.5896 (4)	0.0401 (7)
C28	-0.1969 (2)	0.0533 (2)	0.5136 (5)	0.0483 (8)
C29	-0.1900 (2)	-0.0307 (2)	0.5070 (5)	0.0515 (9)
C30	-0.1846 (3)	-0.1337 (2)	0.4915 (5)	0.057 (1)
C11s†	0.4242 (3)	0.1656 (4)	0.3865 (8)	0.226 (2)
C12s†	0.5273 (4)	0.0055 (5)	0.254 (2)	0.517 (6)
C1s†	0.451 (1)	0.108 (1)	0.185 (2)	0.186 (7)

† Partial occupancy (see below).

*Data collection*

Enraf-Nonius CAD-4 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction: none  
 4957 measured reflections  
 4741 independent reflections  
 3731 observed reflections  
 $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.017$   
 $\theta_{\text{max}} = 24.97^\circ$   
 $h = 0 \rightarrow 16$   
 $k = -16 \rightarrow 17$   
 $l = -8 \rightarrow 8$   
 2 standard reflections  
 frequency: 120 min  
 intensity decay: 6.24%

*Refinement*

Refinement on  $F$   
 $R = 0.054$   
 $wR = 0.085$   
 $S = 3.085$   
 3731 reflections  
 325 parameters  
 H-atom parameters not refined  
 $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{\text{max}} = 0.056$   
 $\Delta\rho_{\text{max}} = 0.93 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.11 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{eq}}$
S1	-0.65619 (5)	0.37999 (7)	0.0435 (1)	0.0547 (2)
S2	0.18518 (5)	0.37536 (5)	0.3897 (1)	0.0439 (2)
S3	-0.25102 (7)	-0.18419 (5)	0.2606 (1)	0.0539 (2)
C1	-0.3104 (2)	0.2465 (2)	-0.0591 (4)	0.0437 (8)
C2	-0.2908 (2)	0.1486 (2)	-0.0468 (4)	0.0511 (9)
C3	-0.1929 (2)	0.1019 (2)	0.0041 (4)	0.0458 (8)
C4	-0.1140 (2)	0.1541 (2)	0.0420 (4)	0.0490 (9)
C5	-0.1332 (2)	0.2530 (2)	0.0299 (4)	0.0413 (8)
C6	-0.2311 (2)	0.2984 (2)	-0.0192 (4)	0.0431 (8)
C7	-0.4113 (2)	0.2955 (3)	-0.1021 (5)	0.0522 (9)
C8	-0.4944 (2)	0.3373 (3)	-0.1292 (5)	0.055 (1)
C9	-0.5961 (2)	0.3886 (3)	-0.1512 (6)	0.067 (1)
C10	-0.1762 (3)	0.0020 (2)	0.0265 (5)	0.0555 (9)
C11	-0.1721 (3)	-0.0794 (3)	0.0548 (5)	0.058 (1)
C12	-0.1710 (3)	-0.1759 (2)	0.0973 (5)	0.062 (1)
C13	-0.0534 (2)	0.3080 (2)	0.0756 (4)	0.0459 (8)
C14	0.0109 (2)	0.3575 (2)	0.1205 (4)	0.0439 (8)
C15	0.0910 (2)	0.4144 (2)	0.1804 (4)	0.0444 (8)
C16	-0.3073 (2)	0.3080 (2)	0.4505 (4)	0.0379 (7)
C17	-0.2988 (2)	0.2103 (2)	0.4611 (4)	0.0441 (8)
C18	-0.2060 (2)	0.1552 (2)	0.5109 (4)	0.0388 (7)
C19	-0.1200 (2)	0.1978 (2)	0.5512 (4)	0.0394 (7)
C20	-0.1272 (2)	0.2952 (2)	0.5421 (4)	0.0349 (7)

Table 2. Average geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

$C_r$  = ring carbon (e.g. C1),  $C_a$  = alkyne carbon (e.g. C7),  $C_{a'}$  = alkyne carbon (e.g. C8),  $C_m$  = methylene carbon (e.g. C9). The first entry in parentheses is the population standard deviation; the second is the sample standard deviation.

$C_r-C_r$	1.391 (5, 5)	$C_r-C_a-C_{a'}$	175.7 (1.7, 1.9)
$C_a-C_{a'}$	1.185 (7, 8)	$C_a-C_{a'}-C_m$	177.2 (5, 6)
$C_r-C_a$	1.435 (4, 6)	$C_a-C_m-S$	114.4 (3, 4)
$C_{a'}-C_m$	1.453 (5, 5)	$C_m-S-C_m$	102.5 (2, 3)
$C_m-S$	1.813 (7, 8)	$C_r-C_r-C_r$	120.1 (7, 7)
$C_r-C_r-C_{a'}$	120.1 (6, 7)		

General procedures for crystal orientation and unit-cell determination and refinement have been published (Mague & Lloyd, 1989). The space group  $P\bar{1}$  was assumed and confirmed by the successful refinement. In the course of the development of the structure, a molecule of solvent dichloromethane was found which was determined to have an occupancy of *ca* 0.55 based on a trial refinement of occupancy parameters. This value was fixed in the subsequent refinement. Most H atoms were seen in a difference map near the end of the refinement. All H atoms except those of the solvent molecule were placed in calculated positions (C—H = 0.95  $\text{\AA}$ ) with isotropic displacement parameters 20% larger than those of their respective parent C atoms, and updated periodically.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF* and *VAX* in *MolEN*.

We thank the Chemistry Department of Tulane University for generous financial support of the X-ray diffraction facility.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1142). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**References**

- Boekelheide, V. (1973). *Top. Curr. Chem.* **113**, 87–143.  
 Boekelheide, V. & Hollins, R. A. (1970). *J. Am. Chem. Soc.* **92**, 3512–3513.  
 Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Ensley, H. E., Mague, J. T. & Mahadevan, S. (1995). *Tetrahedron Lett.* Submitted.
- Fair, C. K. (1990). *MOLLEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Hanson, A. W. & Macaulay, E. W. (1972). *Acta Cryst.* **B28**, 1255–1260.
- Hanson, A. W. & Röhrli, M. (1972). *Acta Cryst.* **B28**, 2287–2291.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Mague, J. T. & Lloyd, C. L. (1989). *Organometallics*, **7**, 983–993.
- Mitchell, R. M. & Boekelheide, V. (1970). *J. Am. Chem. Soc.* **92**, 3510–3512.
- Vögtle, F. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 274.
- Vögtle, F. & Neumann, P. (1969). *Tetrahedron Lett.* pp. 5329–5334.
- Vollhardt, K. P. C., Boese, R., Green, J. R., Mittendorf, J. & Mohler, D. L. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 1643–1645.

*Acta Cryst.* (1995). **C51**, 2598–2601

## Novel 2- and 5-Azido-*N*-(diphenylcarbamoyl)proline Methyl Esters. Examples of a Novel Proline Oxidation

VINCENT M. LYNCH, CHRISTOPHER HULME, PHILIP MAGNUS AND BRIAN E. DAVIS

*Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA*

(Received 14 April 1994; accepted 24 July 1995)

### Abstract

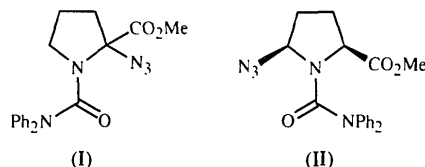
The crystal structures of two azido-substituted proline derivatives are reported. Racemic 2-azido-1-(diphenylcarbamoyl)proline methyl ester, (I), C<sub>19</sub>H<sub>19</sub>N<sub>5</sub>O<sub>3</sub>, is resolved upon crystallization from methylene chloride–diethyl ether. The azido moieties are nonlinear with N–N–N angles of 173 (1) and 170.3 (2)° for (I) and (II) [*cis*-5-azido-*N*-(diphenylcarbamoyl)proline methyl ester, C<sub>19</sub>H<sub>19</sub>N<sub>5</sub>O<sub>3</sub>], respectively. Close intramolecular contacts between the carbonyl O atom of the amide and the central N atom of the azido group are found. The contact distances between N7 and O14 are 2.780 (14) and 2.815 (2) Å for (I) and (II), respectively.

### Comment

Proline is the only imino acid found to occur naturally in mammalian proteins. The phenomenon of *cis*–*trans* isomerism found in prolyl amides plays an important role in the secondary structure of proteins (Andres & MacDonald, 1993). In fact, the designs of several reverse-turn mimetics have been based on this important imino acid (Baldwin, Hulme, Schofield & Edwards, 1993).

Anodic amide oxidations of proline derivatives have been reported recently (Shono, 1984; Wong & Moeller, 1993), allowing the construction of bicyclic lactam rings with the potential of introducing conformational constraints in peptides.

We report here a novel oxidation of *N*-(diphenylcarbamoyl)proline methyl ester utilizing the (PhIO)<sub>n</sub>/TMSN<sub>3</sub> reagent combination (Magnus, Hulme & Weber, 1994) at 233 K, giving crystalline compounds (I) and (II). The crystal structures of two pyrrolidine analogs of (I) and (II) have been reported recently (Lynch, Hulme, Magnus & Davis, 1994).



The azido group is slightly bent in both molecules. The direction of the bend is away from the carbonyl O atom, O14, so that the central N atom, N7, is closer to the O atom than to the two remaining N atoms, N6 or N8. The exocyclic bond angles around N1 are substantially different in (I) and (II).

The C13–N1–C angles, where C is azido substituted, are 119.1 (9) and 118.35 (14)° in (I) and (II), respectively; the remaining C13–N1–C(H<sub>2</sub>) angles are 126.9 (9) and 127.35 (15)°. These facts are indicative of an electrostatic interaction between the carbonyl O atom, O14, and the azido group.

The five-membered pyrrolidinic ring is in an envelope conformation in (I) with C3 as the flap atom, displaced

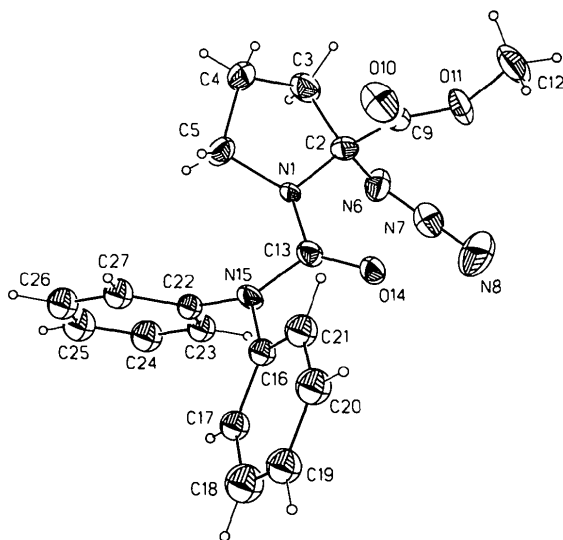


Fig. 1. View of (I) showing the atom-labelling scheme. Displacement ellipsoids are scaled to the 30% probability level. H atoms are drawn to an arbitrary scale.