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*Acta Cryst.* (1984). C**40**, 1443–1445

# *cis*-1,5-Diphenyl-3-(diphenylmethylene)-4-morpholinocarbonyl-2-pyrrolidinone, $C_{34}H_{30}N_2O_3$

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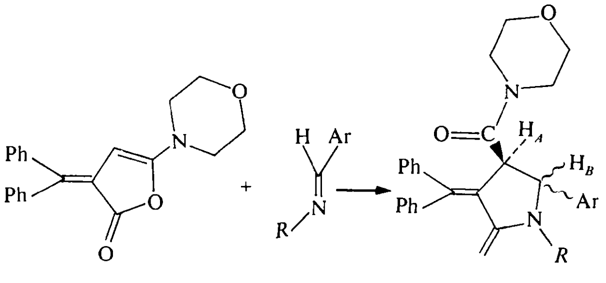
(*Received* 29 *February* 1984; *accepted* 18 *April* 1984)

**Abstract.** $M_r = 514\cdot6$, orthorhombic, *Pbca*, $a = 18\cdot262\,(5)$, $b = 23\cdot285\,(7)$, $c = 12\cdot798\,(3)$ Å, $V = 5442\,(2)$ Å$^3$, $Z = 8$, $D_x = 1\cdot256$ Mg m$^{-3}$, Cu *K*α radiation, $\lambda = 1\cdot54184$ Å, $\mu = 0\cdot648$ mm$^{-1}$, $F(000) = 2176$, $T = 293$ K, final $R = 0\cdot056$ for 2527 significant reflections. The morpholinocarbonyl and phenyl substituents at the 4 and 5 positions in the γ-lactam ring are *cis*-orientated with respect to the ring plane. All four aromatic rings are planar. The pyrrolidine ring has a C(4) envelope conformation and the morpholine ring a chair conformation. There are no intermolecular separations significantly less than the sum of the van der Waals radii.

**Introduction.** We recently reported a general synthesis of γ- and δ-lactones by the 'acyl-ene' reaction (Boyd, Monteil, Lindley & Mahmoud, 1978) and its extension to the preparation of α-(diphenylmethylene)-γ-lactones from the morpholinobutenolide (I) and aromatic aldehydes (Baydar & Boyd, 1978). We have found that imines, ArCH=N*R*, react with the butenolide in an analogous fashion, yielding α-(diphenylmethylene)-γ-lactams (II). The $^1$H NMR spectra of the crude products showed the presence of two geometrical isomers with $J_{AB}$ 8·6–9·5 and 4·0–6·0 Hz, the former predominating. We tentatively assigned the larger coupling constants to the *cis* isomers on the basis of the Karplus equation (Sternhell, 1969), but it was desirable to obtain independent confirmation since the equation does not strictly apply to strained systems, as in the present case. We therefore determined the X-ray structure of the major product (II; Ar = *R* = Ph) of the reaction of the butenolide (I) with *N*-benzylideneaniline and found that it has, indeed, the *cis* geometry.



(I) (II)

**Experimental.** Material prepared by heating under reflux morpholinobutenolide (I) (1·00 g) and *N*-benzylideneaniline (0·54 g, 1 mol) in acetonitrile for 10 min. $^1$H NMR spectrum of the reaction mixture showed presence of *cis*- and *trans*-lactams ($J_{AB} = 8\cdot6$ and 6·0 Hz respectively) in the ratio 6:1. *cis*-1,5-Diphenyl-3-(diphenylmethylene)-4-morpholinocarbonyl-2-pyrrolidinone (II, Ar = *R* = Ph) (1·14 g; 74% yield) crystallized from ethanol. Spectral parameters: $\nu_{\max}$ (Nujol) 1698 (cyclic CO), 1630 (acyclic CO), 1600 and 1120 (morpholino) cm$^{-1}$; $\delta(CF_3CO_2D)$ 2·7–3·8 (*m*,8H, morpholino), 4·74 (*d*, $H_B$), 5·87 (*d*, $H_A$)

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Table 1. *Atomic parameters of non-hydrogen atoms*

| | $x$ | $y$ | $z$ | $U_{eq}$(Å$^2$ × $10^3$)† |
|---|---|---|---|---|
| N(1) | 0·4903 (1) | 0·1973 (1) | 0·1581 (2) | 45 (1) |
| C(2) | 0·4954 (2) | 0·2494 (1) | 0·2098 (3) | 53 (2) |
| C(3) | 0·4604 (2) | 0·2933 (1) | 0·1426 (2) | 48 (2) |
| C(4) | 0·4125 (2) | 0·2623 (1) | 0·0658 (2) | 44 (2) |
| C(5) | 0·4503 (2) | 0·2018 (1) | 0·0590 (2) | 48 (2) |
| C(11) | 0·5348 (2) | 0·1488 (1) | 0·1802 (3) | 52 (2) |
| C(12) | 0·5615 (2) | 0·1386 (2) | 0·2801 (3) | 69 (2) |
| C(13) | 0·6066 (2) | 0·0915 (2) | 0·2980 (4) | 80 (3) |
| C(14) | 0·6248 (2) | 0·0545 (2) | 0·2190 (4) | 82 (3) |
| C(15) | 0·5974 (2) | 0·0634 (2) | 0·1208 (4) | 78 (3) |
| C(16) | 0·5526 (2) | 0·1105 (2) | 0·1005 (3) | 64 (2) |
| O(21) | 0·5227 (1) | 0·2568 (1) | 0·2955 (2) | 71 (2) |
| C(31) | 0·4729 (2) | 0·3504 (1) | 0·1440 (2) | 51 (2) |
| C(311) | 0·5314 (2) | 0·3785 (1) | 0·2069 (3) | 55 (2) |
| C(312) | 0·5163 (2) | 0·4285 (2) | 0·2629 (3) | 68 (2) |
| C(313) | 0·5713 (3) | 0·4566 (2) | 0·3174 (3) | 88 (3) |
| C(314) | 0·6414 (3) | 0·4365 (2) | 0·3140 (4) | 100 (4) |
| C(315) | 0·6572 (2) | 0·3879 (2) | 0·2579 (4) | 93 (3) |
| C(316) | 0·6029 (2) | 0·3586 (2) | 0·2046 (3) | 74 (2) |
| C(321) | 0·4311 (2) | 0·3886 (1) | 0·0725 (3) | 55 (2) |
| C(322) | 0·3550 (2) | 0·3921 (2) | 0·0756 (3) | 73 (2) |
| C(323) | 0·3180 (2) | 0·4261 (2) | 0·0035 (4) | 89 (3) |
| C(324) | 0·3559 (3) | 0·4565 (2) | −0·0711 (4) | 93 (3) |
| C(325) | 0·4306 (3) | 0·4539 (2) | −0·0732 (4) | 97 (3) |
| C(326) | 0·4679 (2) | 0·4210 (2) | −0·0008 (3) | 77 (3) |
| C(41) | 0·3348 (2) | 0·2566 (1) | 0·1083 (2) | 47 (2) |
| O(42) | 0·3264 (1) | 0·2517 (1) | 0·2025 (2) | 63 (1) |
| N(43) | 0·2776 (1) | 0·2562 (1) | 0·0421 (2) | 53 (2) |
| C(44) | 0·2813 (2) | 0·2598 (2) | −0·0724 (3) | 64 (2) |
| C(45) | 0·2170 (2) | 0·2920 (2) | −0·1127 (3) | 86 (3) |
| O(46) | 0·1495 (1) | 0·2671 (1) | −0·0793 (2) | 78 (2) |
| C(47) | 0·1463 (2) | 0·2695 (3) | 0·0290 (4) | 108 (4) |
| C(48) | 0·2054 (2) | 0·2388 (3) | 0·0810 (3) | 100 (3) |
| C(51) | 0·3977 (2) | 0·1531 (1) | 0·0406 (3) | 54 (2) |
| C(52) | 0·3606 (2) | 0·1270 (2) | 0·1222 (4) | 74 (2) |
| C(53) | 0·3080 (3) | 0·0854 (2) | 0·1001 (6) | 107 (4) |
| C(54) | 0·2940 (3) | 0·0703 (2) | −0·0024 (9) | 125 (5) |
| C(55) | 0·3319 (3) | 0·0954 (2) | −0·0827 (5) | 110 (4) |
| C(56) | 0·3836 (2) | 0·1367 (2) | −0·0613 (3) | 76 (3) |

† $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j$.

($J_{AB} = 8·0$ Hz), and 7·1–7·5 (*m*, 20H, 4 × Ph); *m/e* 514 $(M)^{·+}$, 428 $(M - \text{morpholino})^{·+}$, and 400 $(M - \text{morpholinocarbonyl})^{·+}$; (found: C 79·5; H 5·8; N 5·3; $C_{34}H_{30}N_2O_3$ requires C 79·35; H 5·9; N 5·45%). Pale yellow prismatic crystals, m.p. 558–559 K, elongated along **c**, 0·4 × 0·4 × 0·7 mm; preliminary crystal data from precession photographs. Hilger & Watts Y290 diffractometer, Cu $K\alpha$ nickel-filtered radiation, 15 reflections used for accurate measurement of cell parameters. $\omega/2\theta$ step scans, 0·01° per step, count time of 1 s per step, scan range 0·68° plus $\alpha_1\alpha_2$ angular separation. Stationary background counts at both ends of each scan for 1/10th total scan time. Four reference reflections, every fifty reflections, intensity variation ± 2%. Intensity data for $0 \le \theta \le 30°$ (4 equivalents) and $30 \le \theta \le 65°$ (1 equivalent), 8249 measurements, agreement residual for 4458 equivalents of 1·3%, 3890 unique *hkl* of which 2527 had $I > 3\sigma(I)$. $0 \le h \le 21$, $0 \le k \le 27$, $0 \le l \le 13$. Lp and empirical absorption corrections from 00*l* reflections (North, Phillips & Mathews, 1968) for all data (max.variation in transmission factor of 20%). Structure solved by direct-methods program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement, using only significant reflections, isotropic, $R = 0·165$. Hydrogen atoms located by difference Fourier synthesis, subsequently placed in calculated positions assuming C—H distance of 1·0 Å, not refined. Further refinement with all non-hydrogen atoms anisotropic, no more than 21 atoms (190 parameters including scale factor) refined per cycle, final $R = 0·056$, $R_w = 0·057$. Least-squares program: modified version of that coded by D. W. J. Cruickshank and J. G. F. Smith, quantity minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 0·0007$ if $|F_o| \le 100$, otherwise $w = [1-\exp(-10\sin^2\theta/\lambda^2)]/(200 + |F_o| + 0·00001|F_o|^2)$. Max. $\Delta/\sigma = 0·8$; max., min. heights in final difference Fourier map 0·2, −0·2 e Å$^{-3}$. Scattering factors from Hanson, Herman, Lea & Skillman (1964); all computations performed on CDC 6600 computer at University of London Computer Centre.

**Discussion.** The positional and isotropic thermal parameters of the non-hydrogen atoms are listed in Table 1.* The numbering of the atoms, interatomic distances and angles are given in Fig. 1. A stereo-

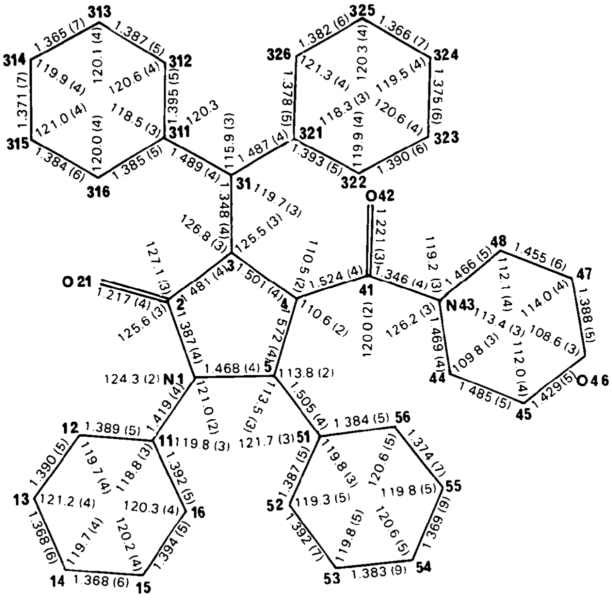

Fig. 1. A schematic drawing of the molecule showing the atomic labelling and the interatomic distances (Å) and angles (°). Pyrrolidine ring angles: N(1)–C(2)–C(3) 107·4 (3); C(2)–C(3)–C(4) 107·5 (2); C(3)–C(4)–C(5) 102·2 (2); C(4)–C(5)–N(1) 103·7 (2); C(5)–N(1)–C(2) 112·5 (2)°. Other angles not shown in the figure: N(1)–C(11)–C(12) 121·4 (3); C(5)–C(51)–C(56) 118·4 (3); C(4)–C(41)–O(42) 118·5 (3); O(42)–C(41)–N(43) 121·5 (3); C(3)–C(31)–C(311) 124·1 (3); C(31)–C(311)–C(316) 121·2 (3); C(31)–C(321)–C(326) 119·8 (3); C(31)–C(321)–C(322) 121·9 (3).

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* Lists of anisotropic thermal parameters, hydrogen-atom coordinates and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39417 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

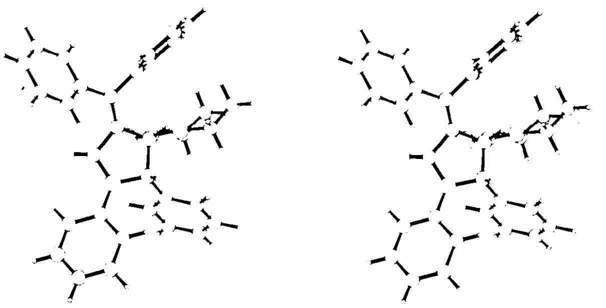

Fig. 2. A stereodrawing of the molecule viewed perpendicular to the lactam ring plane.

drawing of the molecule viewed perpendicular to the plane defined by atoms N(1), C(2) and C(3) is given in Fig. 2, and clearly shows the *cis*-axial configuration of the hydrogen atoms at C(4) and C(5). The morpholinocarbonyl group at C(4) and phenyl ring at C(5) are thus equatorial and the torsion angle C(41)—C(4)—C(5)—C(51) is 29·6 (4)°.

The conformation of the lactam ring is given by the pseudorotational phase parameters (Altona, Geise & Romers, 1968) $\Delta = -49{\cdot}3\ (10)°$ and $\varphi_m = 25{\cdot}9\ (10)°$, where the torsion angle C(3)—C(4)—C(5)—N(1) is taken as $\varphi_0$. These parameters indicate that the C(4) envelope conformation is predominant; C(4) and C(5) are displaced by −0·457 (5) and −0·058 (5) Å respectively from the plane defined by N(1), C(2) and C(3). All four aromatic rings are planar within experimental error and the morpholino ring adopts a chair conformation with an asymmetry parameter (Duax & Norton, 1975) of $\Delta C_s^{N(43)} = 2{\cdot}7°$. In the diphenylmethylene moiety at C(3) the two phenyl rings are orientated at a dihedral angle of 93·8 (2)° with respect to one another. The phenyl rings at N(1) and C(5) are inclined by dihedral angles of 25·9 (1) and 62·2 (1)° respectively with respect to the N(1), C(2), C(3) plane.

Our thanks are due to the Governors of Chelsea College for a research studentship (to AEB).

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*Acta Cryst.* (1984). C**40**, 1445–1449

# Grantianine, $C_{18}H_{23}NO_7$: a Pyrrolizidine Alkaloid

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(*Received* 25 *January* 1984; *accepted* 11 *April* 1984)

**Abstract.** $M_r = 365{\cdot}1$, monoclinic, $P2_1$, $a = 12{\cdot}93\ (1)$, $b = 6{\cdot}32\ (1)$, $c = 10{\cdot}78\ (1)$ Å, $\beta = 102{\cdot}73\ (9)°$, $V = 859{\cdot}3$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}411$, $D_m = 1{\cdot}40\ (2)$ Mg m$^{-3}$, $\bar{\lambda}$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}07$ mm$^{-1}$, $F(000) = 388$, room temperature. Final $R = 0{\cdot}059$ for 1321 observed reflections. Grantianine, a retronecine-derived pyrrolizidine alkaloid, has the carbonyl bonds of the ester functions on opposite sides of the 11-membered macrocycle with an angle of 139·6 (5)° between the bonds. The $\gamma$-butyrolactone ring is *trans*-fused to the macrocycle across bond C(13)—C(14). The exocyclic methyl group at C(24) is in a quasi-axial orientation.

**Introduction.** The present analysis is part of a study of natural and synthetic pyrrolizidine alkaloids (PA's) which are structurally interesting. Grantianine is a rare PA and was originally isolated from *Crotalaria grantiana* (Adams, Carmack & Rogers, 1942). Recently it has been found to be the major alkaloid isolated from *Crotalaria globifera* seeds obtained from inland