# 1,3-Dipolar Cycloadditions of a Chiral Oxazolidinone with Nitrones and Nitrile Oxides

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#### Abstract

The 1,3-dipolar cycloaddition reactions of the chiral oxazolidinone (1) and nitrones are highly regioselective and only 5,5-disubstituted isoxazolidine adducts are formed. These reactions occur under equilibrating conditions to give the more stable adducts that result from addition to the exocyclic methylene of (1) from the sterically more hindered  $\pi$ -face. The *endo* adducts are generally thermodynamically favoured. In one case the novel azetidine (21) was formed from the treatment of the adduct (4a) with palladium hydroxide on carbon under a hydrogen atmosphere. The major adducts from the reaction of (1) and nitrile oxides (16a,b) had the expected stereochemistry, addition of the 1,3-dipole having occurred from the less hindered  $\pi$ -face of the exocyclic methylene of (1). The stereochemistry of many of these products has been elucidated by single-crystal X-ray structural determinations.

As part of a continuing program we have been interested in the asymmetric synthesis of novel non-proteinogenic amino acids using the chiral oxazolidinones  $(1)^1$  and (2).<sup>1-3</sup> We have recently reported that (1) and (2) undergo highly *exo*-diastereoselective Diels-Alder reaction with dienes to give chiral carbocyclic amino acid derivatives in high enantiomeric purities.<sup>1,4</sup> Other workers have demonstrated that (2) undergoes diastereoselective 1,2-addition reactions with alkyl radicals<sup>5</sup> and nitronate anions,<sup>6</sup> and cyclopropanation reactions.<sup>7</sup> In this paper we report the structure and stereochemistry of the products from the

<sup>3</sup> Beckwith, A. L. J., Pyne, S. G., Dikic, B., Chai, C. L. L., Gordon, P. A., Skelton B. W., Tozer, M. J., and White, A. H., Aust. J. Chem. 1993, 46, 1425.

<sup>4</sup> Pyne, S. G., Dikic, B., Gordon, P. A., Skelton B. W., and White, A. H., *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1505; Pyne, S. G., Safaei-G., J., Hockless, D. C. R., Skelton, B. W., Sobolev, A. N., and White, A. H., *Tetrahedron*, 1994, **50**, 941.

<sup>5</sup> Beckwith, A. L. J., and Chai, C. L. L., J. Chem. Soc., Chem. Commun., 1990, 1087.

<sup>6</sup> Crossley, M. J., and Tansey, C. W., Aust. J. Chem., 1992, 45, 479.

<sup>7</sup> Chinchilla, R., Najera, C., Garcia-Granda, S., and Menendez-Valazquez, A., *Tetrahedron Lett.*, 1993, **34**, 5799.

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<sup>&</sup>lt;sup>1</sup> Pyne, S. G., Dikic, B., Gordon, P. A., Skelton B. W., and White, A. H., Aust. J. Chem., 1993, 46, 73.

<sup>&</sup>lt;sup>2</sup> Zimmermann J., and Seebach, D., *Helv. Chim. Acta*, 1987, **70**, 1104.

1,3-dipolar cycloaddition reactions of (1) with nitrones and nitrile oxides.<sup>8</sup> The stereochemistry of many of these products has been elucidated by single-crystal X-ray structural determinations.



#### **Results and Discussion**

When a solution of oxazolidinone (1) and nitrone (3a)  $(1 \cdot 1 \text{ mol. equiv.})$  in dichloromethane was stirred at room temperature for 7 days, a 70:30 mixture of two diastereometric cycloaddition products, (4a) and (5a) was formed in 94% yield (Table 1). The same two diastereomeric products were produced in a ratio of 62:38 when this reaction (see Scheme 1) was performed at  $60^{\circ}$ C over 3 days. The diastereoisomers could be readily separated by fractional crystallization. <sup>1</sup>H n.m.r. analysis of both diastereoisomers indicated that these reactions were highly regioselective and that both diastereoisomers had the 5,5-disubstituted isoxazolidine rather than the 4,4-disubstituted isoxazolidine structure. However, the relative stereochemistry of these compounds could not be determined from n.m.r. experiments. The stereochemistry of the major diastereoisomer (4a) was unequivocally established by a single-crystal X-ray structural determination (Fig. 1). The X-ray structural analysis indicated that the stereochemistry of (4a) arises from addition of nitrone (3a) to the  $\pi$ -face of the exocyclic 4-methylene group of (1), anti to the C2 phenyl substituent, via an endo-type transition state.

To determine the stereochemistry at C3 of the minor diastereoisomer, a 73:27 mixture of the minor (5a) and major (4a) diastereoisomers was reduced (Scheme 2) with sodium borohydride to give a 72:28 mixture of diastereomeric alcohols. Treatment of this mixture with (R)-(-)- $\alpha$ -methoxy- $\alpha$ -trifluoromethylbenzeneacetyl chloride<sup>9</sup> and pyridine gave a mixture of four diastereomeric  $\alpha$ -methoxy- $\alpha$ trifluoromethylbenzeneacetates (10)-(13). The ratio of (12)+(13) to (10)+(11)



<sup>8</sup> Padwa, A., '1,3 Dipolar Cycloaddition Chemistry' Vol. 1, Ch. 2; Vol. 2, Ch. 9 (John Wiley: New York 1984).

<sup>9</sup> Dale J. A., and Mosher, H. S., J. Am. Chem. Soc., 1973, 95, 512.

### 1,3-Dipolar Cycloadditions

Dipole	Time (days)	Temp. ( $^{\circ}C$ )	Yield (%) <sup>A</sup>	Products and diastereoselection <sup>B</sup>
(3a)	7 3	с 60	94 99	$\begin{array}{c} (4a), (5a) \\ 70:30 \\ 62:38 \end{array}$
(3b)	10 22 31 3 10 22	С С 60 60 60	36 52 69 42 49 66	$(4b), (7b) \\88:12 \\88:12 \\89:11 \\72:28 \\55:45 \\33:67$
(3c)	158	с 60	50 53	(4c), (5c), (6c), (7c) 28:44:22:6 11:30:39:20
(3d)	$2 \\ 2$	с 40	27 33	(14), minor isomer > $98:<2$ 92:8
(3e)	$1 \cdot 5$ $1 \cdot 5$	с 40	25 30	(15), minor isomers 85:15 70:15:15
(16a)	D	С	94	(17a), (18a) 85:15
(16b)	D	C	$41^{\mathbf{E}}$	(17b), (18b) 83:17

Table 1.	1,3-Dipolar	cycloaddition	products	from	the	reaction	of (1)	with	nitrones	and	nitrile
			. (	oxides							

<sup>A</sup> After purification. <sup>B</sup> Determined on the crude reaction mixture by <sup>1</sup>H n.m.r. (400 MHz). <sup>C</sup> Room temperature. <sup>B</sup> Determined on the crude reaction mixture by <sup>1</sup>H n.m.r. (400 MHz).

(4a) + (5a)



Scheme 2

was 70:30 (see Experimental section for details). Clearly the above reduction reaction had produced a mixture of (8) and its enantiomer ent-(8), and (9) and its enantiomer ent-(9). Thus epimerization at C5 had occurred in the alcohol products. When this sequence of reactions was performed on diastereomerically pure (4a), only  $\alpha$ -methoxy- $\alpha$ -trifluoromethylbenzeneacetates (10) and (11) were formed, not necessarily respectively, in a 55:45 ratio. These experiments clearly establish the stereochemistries at C3 in the major (4a) and minor (5a) diastereoisomers to be opposite. We therefore suggest that the structure of the minor diastereoisomer is (5a). Although the structure (7a) could not be ruled out for the minor isomer, the <sup>1</sup>H n.m.r. spectrum of this compound was significantly different to that of (7b), the structure of which was established by single-crystal X-ray structural analysis. The above experiments also show that (4a) was obtained in high enantiomeric purity (e.e. >98%).

When a solution of diastereomerically pure (4a) was heated at 60°C for 3 days no interconversion of (4a) into (5a) or the formation of (1) and (3a) was observed. Thus (4a) appears to be formed under kinetically controlled conditions with no interconversion of (4a) into (5a) occurring under the reaction conditions. In contrast, the cycloaddition reactions of (1) and nitrones (3b) and (3c) were found to be reversible at  $60^{\circ}$ C, and furthermore the starting compounds (1) and (3b,c) were always observed in the crude reaction mixtures. When a solution of (1) and (3b) was stirred at room temperature, an 88:12 mixture of (4b)and (7b) was obtained (Table 1). The diastereomeric ratio of (4b) to (7b) remained essentially unchanged over 31 days. The structures of (4b) and (7b)were elucidated by single-crystal X-ray structural determinations (Fig. 1). The major diastereometric product (4b) had the same relative stereochemistry as (4a)and was the expected 'endo' product. The minor diastereoisomer (7b) had the unexpected stereochemistry at C4' of the 1',3'-oxazolidinone ring, i.e. at the spiro carbon (C5). This isomer arises from addition of the nitrone (3b) to the more sterically hindered  $\pi$ -face of the exocyclic 4-methylene group of (1), via an endo-type transition state. When this reaction was performed at 60°C, however, the ratio of (4b) to (7b) changed with the reaction time and, after 22 days, (7b) was the major diastereomeric product (Table 1). When a solution of diastereometrically pure (4b) was heated at  $60^{\circ}$ C for 10 days, a 32:12:56 mixture of (4b), (7b) and (1) was obtained along with some nitrone (3b).

The above experiments clearly indicate that, while diastereoisomer (4b) is favoured kinetically, diastereoisomer (7b) is thermodynamically more stable. Indeed, molecular modelling of these diastereomeric molecules by means of BIOSYM and the INSIGHT II molecular modelling program<sup>10</sup> indicated that (7b) should be thermodynamically favoured over (4b) by about 13 kJ mol<sup>-1</sup>.

The cycloaddition of (1) and (3c) at room temperature gave four diastereomeric 5,5-disubstituted isoxazolidine products (4c), (5c), (6c) and (7c) (Table 1). The ratio of these adducts remained essentially unchanged throughout the course of the reaction (Table 1). The two major diastereoisomers could not be obtained diastereomerically pure; however, the two minor diastereoisomers (6c) and (7c) could be isolated diastereomerically pure after partial separation by column chromatography and then selective crystallizations. The single-crystal X-ray

<sup>10</sup> INSIGHT II, Version 2.3.0, Biosym Technologies, San Diego, CA, U.S.A.







Fig. 1. Molecular projections of the subjects of the single-crystal X-ray studies, normal to the common oxazolidinone plane. 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

structures of (6c) and (7c) are shown in Fig. 1. Both structures have the same stereochemistry at C4' of the 1',3'-oxazolidinone ring as (7b).\* Consequently (4c) and (5c) must have the same stereochemistry at C4' as the adducts (4a) and (4b). The stereochemistry of (4c) and (5c) was based upon <sup>1</sup>H n.m.r. analysis and molecular modelling studies (Fig. 2).<sup>10</sup> The <sup>1</sup>H n.m.r. spectrum of (5c) showed that H3 was highly shielded ( $\delta$  3.30) compared to H3 in the <sup>1</sup>H n.m.r. spectrum of (4c) ( $\delta$  4.23). Molecular modelling (Fig. 2) of these compounds showed that H3 in (5c) is in the shielding region of the phenyl ring of the *N*-benzoyl group, while H3 in (4c) is remote from such influences. Thus, on these considerations, we assign the structures (4c) and (5c). When the reaction of (1) and (3c) was

\* C4' of the 1',3'-oxazolidinone ring corresponds to the spiro carbon (C5).

performed at  $60^{\circ}$ C the ratio of the diastereomeric products favoured the adducts (6c) and (7c) over (4c) and (5c) (Table 1).



Fig. 2. Energy-minimized structures of (4c) and (5c) according to the INSIGHT II molecular modelling program.<sup>10</sup>

The reactions of (1) and the cyclic nitrone (3d) were highly diastereoselective at room temperature to  $40^{\circ}$ C, but the isolated yields of the major diastereomeric product were low (Table 1). The reactions of (1) with the homologous cyclic nitrone (3e) (see Scheme 3) were less diastereoselective and again the isolated yields of the major diastereomeric product were low (Table 1). In contrast, the reaction of (1) and (3e) at  $40^{\circ}$ C apparently gave three diastereomeric adducts; however, the stereochemistry of the two minor adducts could not be determined. The single-crystal X-ray structures of the major diastereomeric adducts (14) and (15) from these reactions are shown in Fig. 1. Both adducts have the same relative stereochemistry. The stereochemistry at C4 of the 1,3-oxazolidinone ring, i.e. at the spiro carbon, of these adducts suggests that they are the thermodynamically favoured products that have been formed from a reversible cycloaddition reaction. Both adducts arise from an *endo*-like transition state.

Treatment of (1) with benzonitrile oxide (16a) at room temperature for 2 h gave an 85:15 mixture of two diastereomeric adducts (17a) and (18a) in excellent yield (94%). The analogous reaction (Scheme 4) of (1) with acetonitrile oxide (16b) proceeded with a similar diastereoselectivity; however, the isolated yield of the major diastereomerically pure product (17b) was low (41%).

The identities of the diastereometric products (17a) and (18a), and (17b) were established by single-crystal X-ray structure determinations (Fig. 1). Both the major adducts (17a,b) had the expected regiochemistry and stereochemistry at the spiro carbon. Analogous results have been reported for the addition of nitrile oxides to structurally related  $\alpha$ -methylene- $\gamma$ -butyrolactones.<sup>11</sup> Reduction of (17a) with sodium borohydride in methanol gave the alcohol (19) in 76% enantiometric purity based upon <sup>1</sup>H n.m.r. analysis of its  $\alpha$ -methyl- $\alpha$ -trifluoromethylbenzeneacetate ester (20). Clearly ring opening of (19) is much less facile than that in (8) and (9).

To date our attempts to convert our 1,3-dipolar cycloaddition products into novel amino acid derivatives have been, in general, disappointing. However, treatment of (4a) under catalytic hydrogenation/hydrogenolysis conditions with



<sup>11</sup> Pereira, S. M., Savage, G. P., Simpson, G. W., Greenwood, R. J., and Mackay, M. F., Aust. J. Chem., 1993, 46, 1401.

palladium hydroxide on carbon under an atmosphere of hydrogen gave the unexpected cis-N-(1',4'-diphenylazetidin-2'-yl)benzamide (21) in 30% yield and N-benylbenzamide in 47% yield (see Scheme 5).

The structure of (21) was evident from <sup>1</sup>H and <sup>13</sup>C n.m.r. and mass and highresolution mass spectral analysis. The *cis*-stereochemistry of (21) was determined by analysis (Fig. 3) of the coupling constants for H2', H3' $\alpha$ , H3' $\beta$  and H4' in the <sup>1</sup>H n.m.r. spectrum of (21) by using the known coupling constants of *cis*and *trans*-2,3-dimethyloxetans as reference compounds.<sup>12</sup> In these four-membered heterocyclic compounds vicinal coupling constants for *cis* protons are generally larger (7.25–8.65 Hz) than those for *trans* protons (5.61–6.65 Hz). The geminal coupling constant,  $J_{3'\alpha,3'\beta}$ , in (21) is consistent with that typically found in oxetans (10.77–11.15 Hz).<sup>12</sup>



Fig. 3. Selected <sup>1</sup>H n.m.r. data for (21) in CDCl<sub>3</sub>.

A possible mechanism for the formation of (21) is given in Scheme 6. The proposed mechanism involves hydrogenolysis of (4a), followed by ring closure to the azetidinium ion (22). Carboxy-hydroxy-elimination<sup>13</sup> then gives the azetinium ion (23) to which addition of hydrogen from the less hindered  $\pi$ -face of the iminium group would give the *cis*-1,4-disubstituted product (21). Unfortunately, related azetidine products could not be isolated upon hydrogenolysis/hydrogenation of the adducts (4b) and (8).



In summary, the 1,3-dipolar cycloaddition reactions of (1) and nitrones generally occur under equilibrating conditions to give the more stable adducts that result from addition to the exocyclic methylene of (1) from the sterically more hindered  $\pi$ -face. These reactions are highly regioselective and only 5,5-disubstituted isoxazolidines are formed. The *endo* adducts are generally thermodynamically favoured. In one case the novel azetidine (21) was formed from the treatment of

<sup>12</sup> Ewing, D. F., Holbrook, K. A., and Scott, R. A., Org. Magn. Reson., 1975, 7, 554.
 <sup>13</sup> March, J., 'Advanced Organic Chemistry' 4th Edn, p. 1036 (Wiley-Interscience: New York 1992).

the adduct (4a) with palladium hydroxide on carbon under a hydrogen atmosphere. The major adducts from the reaction of (1) and nitrile oxides (16a,b) had the expected stereochemistry; addition of the 1,3-dipole occurred from the least hindered  $\pi$ -face of the exocyclic methylene of (1).

### Experimental

The nitrones (3a-c) were prepared by condensation of benzaldehyde with the appropriate N-substituted hydroxylamine.<sup>14,15</sup> Tetrahydropyridine and pyrroline N-oxides (3e,d) were prepared by oxidation of their related secondary cyclic amines with hydrogen peroxide.<sup>16</sup> All n.m.r. spectra were measured in CDCl<sub>3</sub> solution. Chemical shifts are reported in ppm downfield from tetramethylsilane as an internal reference at 0 ppm, and coupling constants are given in Hz. Proton and carbon spectra were recorded at 400 and 100 MHz, respectively. <sup>1</sup>H n.m.r. spectra of some of the compounds have been run at high temperature because at ambient temperature the n.m.r. signals were very broad due to restricted rotation about the amide C–N bound. Most <sup>1</sup>H and <sup>13</sup>C n.m.r. assignments were made from analysis of cosy and DEPT <sup>13</sup>C n.m.r. experiments, respectively. Infrared spectra were run as Nujol mulls. Melting points are uncorrected. All crystalline compounds were recrystallized from ethyl acetate/hexane.

#### 1,3-Dipolar Cycloaddition Reactions of (1) and Nitrones: General Procedure

A solution of (1) (225 mg, 0.8 mmol) and the nitrone (0.88 mmol) in dichloromethane (3 ml) under nitrogen was stirred at room temperature or  $60^{\circ}$ C in a sealed tube under an atmosphere of nitrogen for several days, as reported in Table 1. The solution was then cooled and evaporated to dryness. The crude products were purified by column chromatography on silica gel with ethyl acetate/hexane as the eluent or by fractional crystallization. The diastereoselections of these reactions were determined from <sup>1</sup>H n.m.r. (400 MHz) analysis of the crude reaction product.

# (3S,5S,7R)- and (3R,5S,7R)-6-Benzoyl-2,3,7-triphenyl-1,8-dioxa-2,6-diazaspiro[4.4]nonan-9-one (4a) and (5a)

The two diastereoisomers were separated by fractional crystallization from ethyl acetate/hexane.

(4a): m.p. 160–161°C (dec.) (Found: C, 75·8; H, 4·9; N, 5·6.  $C_{30}H_{24}N_2O_4$  requires C, 75·6; H, 5·1; N, 5·9%).  $[\alpha]_D^{27}$  -44·6 (c, 0·55 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  7·53–6·97, 20H, m; 6·95, 1H, s, H7; 4·93, 1H, dd, J 6·0, 11·4 Hz, H3; 3·32, 1H, br t, J 11·4, 12·6 Hz, H4; 2·99, 1H, dd, J 6·0, 12·6 Hz, H4. <sup>13</sup>C n.m.r.  $\delta$  170·5 (CO), 170·1 (CO), 149·2, 137, 135·9, 135·7, 130·2, 130·1, 128·9, 128·7, 128·6, 128·4, 128·3, 127·5, 127·4, 126·4, 125, 119·6, 89·6 (C 7), 88·8 (C 5), 72·1 (C 3), 47·5 (C 4).  $\nu_{max}$  1765, 1660, 1580, 1470, 1338, 1283, 1178, 1135, 1075, 1003, 743, 690 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 477 (M+H, 16%), 268 (100).

(5a): m.p. 145–146°C (dec.).  $[\alpha]_{27}^{27}$  +198·7 (c, 0·23 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  (at 55°C) 7·46–6·96, 15H, m; 6·77, 1H, s, H7; 4·29, 1H, br t, J 8·4 Hz, H3; 3·53, 1H, dd, J 7·6, 12·8 Hz, H4; 3·23, 1 H, dd, J 9·6, 12·8 Hz, H4. <sup>13</sup>C n.m.r.  $\delta$  170 (CO), 169·7 (CO), 148·1, 138·3, 135·7, 135·5, 130·6, 130·1, 128·84, 128·8, 128·44, 128·4, 128·2, 127·9, 126·7, 126·6, 124·8, 119·7, 89·5 (C7), 87·7 (C5), 69·4 (C3), 47·4 (C4).  $\nu_{max}$  1778, 1655, 1580, 1482, 133, 1160, 1010, 758, 687 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 477 (M+H, 70%), 314 (37), 268 (100).

### (3S,5S,7R)- and (3S,5S,7S)-6-Benzoyl-2-t-butyl-3,7-diphenyl-1,8-dioxa-2,6diazaspiro[4.4]nonan-9-one (4b) and (7b)

(4b): m.p. 112°C (Found: C, 74.0; H, 6.2; N, 5.8. C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub> requires C, 73.7; H, 6.2; N, 6.1%).  $[\alpha]_D^{24}$  –84.6 (c, 1 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  7.61–6.84, 15H, m; 6.95, 1H, s,

- <sup>14</sup> Heffinger, N. F., and Griffin, C. E., *Tetrahedron Lett.*, 1963, **21**, 1361.
- <sup>15</sup> Dicken, C. M., and DeShong, P., J. Org. Chem., 1982, 47, 2047.
- <sup>16</sup> Murahashi, S.-I., Shiota, T., and Imada, Y., Org. Synth., 1992, 70, 265.

H 7; 4 ·67, 1H, dd, J 6 ·0, 11 ·6 Hz, H 3; 2 ·94, 1H, br t, J 11 ·6, 12 ·6 Hz, H 4; 2 ·78, 1H, dd, J 6 ·0, 12 ·6 Hz, H 4; 0 ·95, 9H, s, 3CH<sub>3</sub>. <sup>13</sup>C n.m.r. δ 170 ·8 (CO), 170 ·3 (CO), 140, 136 ·3, 135 ·7, 130, 129 ·9, 128 ·9, 128 ·33, 128 ·27, 127 ·9, 127 ·6, 127 ·2, 126 ·3, 89 ·0 (C 7), 87 ·8 (C 5), 64 ·7 (C 3), 60 ·0 (**C**Me<sub>3</sub>), 50 ·0 (C 4), 26 ·4 (C**Me<sub>3</sub>**).  $\nu_{mex}$  1785, 1642, 1368, 1342, 1251, 1222, 1140, 1012, 761, 732, 692 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 457 (M+H, 100%).

(7b): m.p. 146–147°C.  $[\alpha]_D^{24}$  –4·0 (c, 0·4 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  (at 55°C) 7·84–6·81, 15H, m; 6·93, 1H, s, H7; 4·73, 1H, dd, J 6·0, 11·0 Hz, H3; 2·65, 1H, dd, J 11, 13·2 Hz, H4; 2·56, 1H, dd, J 6·0, 13·2 Hz, H4; 1·05, 9H, s, 3CH<sub>3</sub>. <sup>13</sup>C n.m.r.  $\delta$  170·2 (CO), 170·1 (CO), 139·6, 135·9, 134·8, 131·6, 130, 129·5, 128·7, 128·5, 128·3, 127·6, 127·2, 127·1, 88·9 (C7), 87·5 (C5), 64·6 (C3), 60·0 (**C**Me<sub>3</sub>), 48·5 (C4), 26·4 (C**Me<sub>3</sub>**).  $\nu_{max}$  1768, 1627, 1446, 1350, 1255, 1226, 1142, 1025, 721, 687 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 457 (M+H, 100%), 284 (14).

#### (38,58,7R)-, (3R,58,7R)-, (38,5R,7R)- and (3R,5R,7R)-6-Benzoyl-2-methyl-3,7-diphenyl-1,8-dioxa-2,6-diazaspiro[4.4]nonan-9-one (4c), (5c), (6c) and (7c)

(4c): <sup>1</sup>H n.m.r.  $\delta$  (in part) 7·72–6·96, 15H, m; 6·82, 1H, s, H7; 4·23, 1H, dd, J 5·6, 11·2 Hz, H3; 3·45, 1H, br t, J 12·6 Hz, H4; 2·87, 1H, dd, J 5·6, 12·8 Hz, H4; 2·63, 3H, s, CH<sub>3</sub>.

(5c): <sup>1</sup>H n.m.r.  $\delta$  (in part) 7·72–6·96, 15H, m; 6·77, 1H, s, H7; 3·30, 1H, dd, J 6·0, 12·0 Hz, H3; 3·10, 1H, br t, J 12·0 Hz, H4; 2·90, 1H, m, H4; 2·56, 3H, s, CH<sub>3</sub>.

(6c): m.p. 166–168°C (Found: C, 72·9; H, 5·4; N, 6·5.  $C_{25}H_{22}N_2O_4$  requires C, 72·5; H, 5·3; N, 6·8%).  $[\alpha]_{D5}^{D5}$  +30·2 (c, 0·42 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  (at 60°C) 7·53–7·24, 15H, m; 6·75, 1H, s, H7; 3·38, 1H, br s, H3; 2·94, 1H, dd, J 10·4, 13·0 Hz, H4; 2·84, 1H, dd, J 6·8, 13·0 Hz, H4; 2·68, 3 H, s, CH<sub>3</sub>. <sup>13</sup>C n.m.r.  $\delta$  170·2 (CO), 169·6 (CO), 137, 135·5, 135·1, 131·2, 130·1, 128·7, 128·6, 128·42, 128·41, 128·1, 127·8, 127·2, 89·1 (C7), 86·7 (C5), 72·4 (C3), 46·2 (C4), 42·8 (CH<sub>3</sub>).  $\nu_{max}$  1780, 1648, 1475, 1350, 1268, 1145, 1035, 697 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 415 (M+H, 100%), 288 (37), 210 (75).

(7c): m.p. 150–152°C.  $[\alpha]_D^{26}$ –16.7 (c, 0.15 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  (at 55°C) 7.72–6.96, 15H, m; 6.88, 1H, s, H 7; 4.28, 1H, dd, J 6.0, 11.8 Hz, H 3; 2.92, 1H, br t, J 11.8, 12.6 Hz, H 4; 2.71, 3H, s, CH<sub>3</sub>; 2.64, 1H, dd, J 6.0, 12.8 Hz, H 4. <sup>13</sup>C n.m.r.  $\delta$  170.7 (CO), 170.0 (CO), 136.0, 135.7, 134.8, 131.45, 130.1, 128.72, 128.71, 128.6, 128.5, 128.4, 127.8, 127.2, 89.5 (C7), 88.8 (C5), 73.8 (C3), 46.1 (C4), 44.3 (CH<sub>3</sub>).  $\nu_{max}$  1779, 1635, 1480, 1345, 1315, 1268, 1145, 1035, 692 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 415 (M+H, 100%), 341 (9), 288 (8), 136 (20).

# (2R,3'aR,4R)-3-Benzoyl-2-phenyltetrahydrospiro[oxazolidine-4,2'(3'H)-pyrrolo-[1,2-b]isoxazol]-5-one (14)

M.p. 142–144°C (dec.) (Found: C, 68.8; H, 5.6; N, 7.5.  $C_{21}H_{20}N_2O_4$  requires C, 69.2; H, 5.5; N, 7.7%).  $[\alpha]_{25}^{D5}$  +35.5 (c, 0.2 CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  (at 55°C) 7.42–7.25, 10H, m; 6.67, 1H, s, H2; 3.70, 1H, br s, H3'a; 3.51, 1H, m, H6'; 3.25, 1H, m, H6'; 2.87, 1H, dd, J 8.0, 13.6 Hz, H3'; 2.66, 1H, dd, J 7.6, 13.6 Hz, H3'; 2.12, 1H, m, H4'; 1.90, 2H, m, H5'; 1.71, 1H, m, H4'. <sup>13</sup>C n.m.r.  $\delta$  171.2 (CO), 169.3 (CO), 135.4, 135.1, 131.1, 130.1, 128.7, 128.5, 127.3, 127.2, 92.7 (C2'), 89.7 (C2), 65.9 (C3'a), 56.5 (CH<sub>2</sub>), 45.3 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 22.0 (CH<sub>2</sub>).  $\nu_{max}$  1772, 1646, 1380, 1268, 1150, 1025, 718, 692 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 365 (M+H, 100%), 86 (20).

#### (2R,2'R,3aR)-3'-Benzoyl-2'-phenylhexahydrospiro[2H-isoxazolo[2,3-a]pyridine-2,4'oxazolidin]-5-one (15) and Minor Isomer

The two diastereoisomers were separated by fractional crystallization from ethyl acetate/hexane and or by column chromatography on silica gel with ethyl acetate/hexane as eluent.

(15): m.p. 155–157°C (dec.) (Found: C, 69.5; H, 5.85; N, 7.1.  $C_{22}H_{22}N_2O_4$  requires C, 69.8; H, 5.9; N, 7.4%).  $[\alpha]_{27}^{27}$  +77.7 (c, 0.3 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  (at 55°C) 7.41–7.25, 10H, m; 6.63, 1H, s, H2'; 3.52, 1H, m; 2.7, 2H, m; 2.57, 1H, br s; 1.9–1.6, 6H, m; 1.25, 1H, t, J 7.2 Hz. <sup>13</sup>C n.m.r.  $\delta$  (broad signals were observed) 170.1 (CO), 169.5 (CO), 135.9, 135.5, 130.2, 130.1, 128, 127.9, 127.5, 127.4, 89.0, 86.1, 66.0, 55.2, 42.0, 28.8, 24.0,

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23.8.  $\nu_{\rm max}$  1770, 1658, 1340, 1285, 1160, 1021, 758, 690 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 379 (M+H, 100%), 288 (16), 209 (11).

Minor isomer: m.p. 46–48°C.  $[\alpha]_{\rm D}^{29}$  –10.0 (c, 0.15 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  (at 55°C) 7.35–7.00, 10H, m; 6.67, 1H, s, H2'; 3.43, 1H, m; 2.93, 1H, dd, J 6.0, 12.0 Hz; 2.68, 1H, br s; 2.58, 1H, m; 2.41, 1H, m; 1.87, 1H, m; 1.71, 4H, m; 1.27, 1H, br s. <sup>13</sup>C n.m.r.  $\delta$  (broad signals were observed) 170.1 (CO), 169.4 (CO), 136.3, 135.4, 129.9, 128.7, 128.6, 128.3, 127.3, 126.7, 103.4, 89.3 (CH), 65.8, 54.9, 42.1, 28.9, 24.6, 23.6.  $\nu_{\rm max}$  1780, 1660, 1320, 1240, 1155, 1080, 1015, 770, 680 cm<sup>-1</sup>. Mass spectrum (f.a.b. positive) m/z 379 (M+H, 15%), 247 (80), 230 (71), 188 (90).

# $(5\mathrm{S},7\mathrm{R})\text{-}$ and $(5\mathrm{R},7\mathrm{R})\text{-}6\text{-}Benzoyl\text{-}3,7\text{-}diphenyl\text{-}1,8\text{-}dioxa\text{-}2,6\text{-}diazaspiro[4.4]non-2\text{-}en-9\text{-}one$ (17a) and (18a)

To a solution of (1) (225 mg, 0.8 mmol) and triethylamine (0.11 ml, 0.8 mmol) in dry dichloromethane (10 ml) was added dropwise a solution of benzohydroxamoyl chloride (128 mg, 0.8 mmol) in dichloromethane (5 ml) under nitrogen at room temperature. After stirring for 2 h the solution was washed with water ( $2 \times 20 \text{ ml}$ ), the organic layer was dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. <sup>1</sup>H n.m.r. analysis of the crude product revealed an 85:15 mixture of diastereoisomers that were separated by column chromatography on silica gel (20% ethyl acetate/hexane) to furnish a mixture of (17a) and (18a) (300 mg, 94%).<sup>17,18</sup>

(17a): m.p. 130–132°C (Found: C, 72.6; H, 4.7; N, 7.0.  $C_{24}H_{18}N_2O_4$  requires C, 72.3; H, 4.6; N, 7.0.%).  $[\alpha]_D^{26}$  +30.2 (c, 0.5 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  7.6–7.05, 15H, m; 6.83, 1H, s, H 7; 4.13, 1 H, d, J 17.0 Hz, H 4; 4.04, 1H, d, J 17.0 Hz, H 4. <sup>13</sup>C n.m.r.  $\delta$  169.9 (CO), 168.5 (CO), 155.5 (CN), 135.2, 134.8, 130.7, 130.5, 130.4, 128.9, 128.7, 128.4, 127.9, 127.0, 126.6, 126.2, 91.9 (C5), 89.9 (C7), 43.6 (C4).  $\nu_{max}$  1768, 1655, 1385, 1305, 1255, 1020, 880, 855, 685 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 399 (M+H, 100%), 277 (15), 210 (49), 130 (53).

(18a): m.p. 222–223°C.  $[\alpha]_D^{26}$  +89.5 (c, 0.45 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  7.50–7.20, 15H, m; 6.87, 1H, s, H7; 3.86, 1H, d, J 17.6 Hz, H4; 3.54, 1H, d, J 17.6 Hz, H4. <sup>13</sup>C n.m.r.  $\delta$  169.1 (CO), 168.4 (CO), 150.6 (CN), 134.8, 134.7, 134.1, 132.3, 131.5, 131.2, 129.5, 128.1, 127.8, 126.5, 126.2, 126.0, 91.6 (C5), 89.3 (C7), 42.5 (C4).  $\nu_{max}$  1775, 1640, 1580, 1370, 1340, 1265, 1010, 880, 850, 694 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 399 (M+H, 45%), 316 (44), 288 (100).

### (5S,7R)-6-Benzoyl-3-methyl-7-phenyl-1,8-dioxa-2,6-diazaspiro[4.4]non-2-en-9-one (17b)

To a solution of (1) (225 mg, 0.8 mmol), nitroethane (150 mg, 2 mmol) and triethylamine (0.11 ml, 0.8 mmol) in dry dichloromethane (5 ml) at room temperature under nitrogen was added a solution of phenyl isocyanate (380 mg, 3.2 mmol) in dichloromethane (3 ml), by syringe over a 2.5-h period. The reaction mixture was stirred for an additional 2 h. Water (6 ml) was then added and the mixture was stirred for 3 h, and then filtered. The layers were separated and the aqueous phase was extracted with dichloromethane. The combined extracts were dried over MgSO<sub>4</sub>, and concentrated. <sup>1</sup>H n.m.r. analysis of the crude product revealed an 83:17 mixture of diastereomers. Purification of the mixture by column chromatography on silica gel (30% ethyl acetate/hexane) furnished diastereomerically pure (17b) (110 mg, 41%).<sup>19</sup>

(17b): m.p. 182–183°C (Found: C, 67.5; H, 4.9; N, 8.0.  $C_{19}H_{16}N_2O_4$  requires C, 67.8; H, 4.8; N, 8.3%).  $[\alpha]_2^{27}$  +52.0 (c, 0.2 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  7.39–7.00, 10H, m; 6.75, 1H, s, H7; 3.71, 1H, d, J 17.6 Hz, H4; 3.61, 1H, d, J 17.6 Hz, H4; 1.94, 3H, s, CH<sub>3</sub>. <sup>13</sup>C n.m.r.  $\delta$  169.8 (CO), 168.6 (CO), 154.3 (CN), 135.2, 134.9, 130.5, 130.3, 128.8, 128.4, 126.6, 126.2, 91.2 (C5), 89.8 (C7), 46.6 (C4), 12.4 (CH<sub>3</sub>).  $\nu_{max}$  1777, 1657, 1408, 1345, 1320, 1241, 1155, 1005, 740, 685 cm<sup>-1</sup>. Mass spectrum (e.s. positive) m/z 337 (M+H, 100%), 288 (40), 210 (28).

<sup>17</sup> Furniss, B. S., Hannaford, A. J., Smith, P. W. G., and Tatcheu, A. R., "Vogel's Textbook of Practical Organic Chemistry" 5th Edn, p. 1048 (Longman: London 1991).
<sup>18</sup> Liu, K.-C., Shelton, B. R., and Howe, R. K., J. Org. Chem., 1980, 45, 3916.

<sup>19</sup> Kozikowski, A. P., and Ghosh, A. K., J. Org. Chem., 1984, 49, 2762.

# (3'S,5'S)- and (3'S,5'R)-N-(5'-Hydroxymethyl-2',3'-diphenylisoxazolidin-5'-yl)benzamide (8) and (9)

To a solution of (4a) (80 mg, 0.17 mmol) in dry methanol (10 ml) and dichloromethane (2 ml) was added sodium borohydride (20 mg). After stirring 16 h at room temperature the solution was treated with acetone (3 ml) at 0°C for 10 min. The solvent was then evaporated. Water (10 ml) was added and the products were extracted into dichloromethane (2×10 ml). The extracts were dried and evaporated. Short-path column chromatography on silica gel gave a 61:39 mixture of diastereomers (8) and (9) (40 mg, 60%).

<sup>1</sup>H n.m.r. δ (major isomer, in part) 7.65–6.98, 15H, m; 6.66, 1H, br s, NH; 4.91, 1H, dd, J 7.2, 9.6, H3'; 4.20, 1H, m, CH<sub>A</sub>H<sub>B</sub>OH; 4.01, 1H, m, CH<sub>A</sub>H<sub>B</sub>OH; 3.68, 1H, br s, OH; 3.65, 1H, dd, J 7.6, 12.8 Hz, H4'; 2.60, 1H, dd, J 9.6, 12.8 Hz, H4'. <sup>1</sup>H n.m.r. δ (minor isomer, in part) δ 7.65–6.98, 15H, m; 6.89, 1H, br s, NH; 4.63, 1H, dd, J 6.0, 8.8 Hz, H3'; 4.18, 1H, m, CH<sub>A</sub>H<sub>B</sub>OH; 4.02, 1H, m, CH<sub>A</sub>H<sub>B</sub>OH; 3.27, 1H, dd, J 8.8, 13.6 Hz, H4'; 3.08, 1H, br s, OH; 2.98, 1H, dd, J 6.4, 13.6 Hz, H4'. <sup>13</sup>C n.m.r. δ (major isomer, in part) 167.19 (CO), 151.9, 140.3, 133.7, 132, 129.05, 128.9, 128.6, 127.8, 126.9, 126.7, 122.6, 115.3, 94.5, 69.5, 65.4, 45.8. <sup>13</sup>C n.m.r. δ (minor isomer, in part) δ 167.23 (CO), 149.4, 140.1, 133.7, 132.0, 129.02, 128.7, 128.6, 127.8, 126.9, 126.8, 123.5, 117.0, 93.7, 69.8, 65.6, 47.2. Mass spectrum (e.s. positive) m/z 375 (M+H, 35%), 254 (100), 180 (25).

# (S)-(-)- $\alpha$ -Methoxy- $\alpha$ -trifluoromethylbenzeneacetate Esters (10) and (11) of Alcohols (8) and (9)

A solution of (8) and (9) (10 mg, 0.03 mmol) in dichloromethane (0.5 ml) and 2 drops of dry pyridine at  $0^{\circ}$ C was treated with (R)-(-)- $\alpha$ -methoxy- $\alpha$ -trifluoromethylbenzeneacetyl chloride (12 mg, 0.04 mmol). The solution was stirred for 2 h at room temperature and then the solvent was evaporated. The residue was dissolved in dichloromethane (10 ml); the solution was washed with 5% aqueous hydrochloric acid, 10% aqueous sodium hydroxide, and then water. The organic layer was dried over MgSO<sub>4</sub>, filtered and evaporated under reduced pressure to leave an oil. Short-path column chromatography on silica gel gave a 55:45 mixture of two diastereoisomers (10) and (11) (10 mg, 61%).

<sup>1</sup>H n.m.r.  $\delta$  (major isomer, in part) 7.68–6.87, 15H, m; 6.28, 1H, s, NH; 4.99, 1H, d, J 12.0 Hz, CH<sub>A</sub>H<sub>B</sub>OR; 4.88, 1H, d, J 12.0 Hz, CH<sub>A</sub>H<sub>B</sub>OR; 4.23, 1H, t, J 8.8 Hz, H3'; 3.54, 3H, s, OCH<sub>3</sub>; 3.09, 2H, br d, J 8.0 Hz, H4'/H4'. <sup>1</sup>H n.m.r.  $\delta$  (minor isomer, in part) 7.68–6.87, 15H, m; 6.73, 1H, s, NH; 5.05, 1H, d, J 11.6 Hz, CH<sub>A</sub>H<sub>B</sub>OR; 4.87, 1H, d, J 12.0 Hz, H3'; 4.79, 1H, d, J 11.6 Hz, CH<sub>A</sub>H<sub>B</sub>OR; 3.72, 1H, dd, J 7.2, 13.0 Hz, H4'; 3.56, 3H, s, OCH<sub>3</sub>; 2.53, 1H, dd, J 10.0, 13.0 Hz, H4'.

# (3'S,5'S)-, (3'R,5'R)-, (3'S,5'R)- and (3'R,5'S)-N-(5'-Hydroxymethyl-2',3'-diphenylisoxazolidin-5'-yl)benzamide (8), ent-(8), (9), ent-(9)

The title compounds were prepared from a 73:27 mixture of (5a) and (4a) (50 mg, 0.1 mmol) by treatment with sodium borohydride as described above. Purification of the crude reaction product by column chromatography gave a 72:28 mixture (25 mg, 64%) of diastereoisomers that were identical by <sup>1</sup>H n.m.r. to the major and minor diastereoisomers, respectively, described above from (4a).

(S)-(-)- $\alpha$ -Methyl- $\alpha$ -trifluoromethylbenzeneacetate Esters (10), (11), (12) and (13) of Alcohols (8), ent-(8), (9) and ent-(9)

The title compounds were prepared from the mixture of alcohols (8), ent-(8), (9) and ent-(9) (15 mg, 0.04 mmol) as described above. Purification of the crude reaction mixture by column chromatography gave a mixture of four diastereoisomers (15 mg, 69%).

<sup>1</sup>H n.m.r.  $\delta$  (major isomer, in part) 5.08, 1H, d, J 11.6, CH<sub>A</sub>H<sub>B</sub>OR; 4.80, 1H, d, J 11.6 Hz, CH<sub>A</sub>H<sub>B</sub>OR; 4.36, 1H, t, J 8.0 Hz; 3.56, 3H, s, OCH<sub>3</sub>. <sup>1</sup>H n.m.r.  $\delta$  (second most prominent diastereoisomer, in part) 4.95, 1H, d, J 11.6 Hz, CH<sub>A</sub>H<sub>B</sub>OR; 4.86, 1H, d, J

11.6 Hz,  $CH_AH_BOR$ . Mass spectrum (e.s. positive) m/z 591.7 (M+H, 35%), 470.5 (23), 102.3 (100). The other two diastereoisomers were (10) and (11).

## $(5'S)-N-(5'-Hydroxymethyl-3'-phenyl-\Delta^{2'}-isoxazolin-5'-yl)$ benzamide (19)

The title compound was prepared from (17a) (150 mg, 0.37 mmol) by treatment with sodium borohydride as described for the preparation of (8) and (9). Purification of the crude reaction product by column chromatography gave (19) (120 mg, 51%), m.p. 47–50°C.  $[\alpha]_D^{28}$  –111.2 (c, 0.2 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  7.77–7.34, 10H, m; 7.15, 1H, s, NH; 4.14, 1H, d, J 11.1 Hz, H4'; 4.00, 1H, d, J 17.4 Hz, CH<sub>A</sub>H<sub>B</sub>OH; 3.92, 1H, br d, H4'; 3.55, 1H, d, J 17.4 Hz, CH<sub>A</sub>H<sub>B</sub>OH; 3.92, 128.7, 128.6, 128.5, 127.2, 126.9, 126.8, 96.2, (C5'), 65.4 (C4'), 41.2 (CH<sub>2</sub>OH). Mass spectrum (e.s. positive) m/z 319 (M+Na, 83%), 297 (M+H, 27), 176 (100).

#### (S)-(-)- $\alpha$ -Methyl- $\alpha$ -trifluoromethylbenzeneacetate Ester (20) of Alcohol (19)

The title compound was prepared from (19) (10 mg, 0.034 mmol) as described for the preparation of (10) and (11). Short-path column chromatography gave an 88:12 mixture of two diastereoisomeric esters (15 mg, 86%).

<sup>1</sup>H n.m.r.  $\delta$  (major isomer, in part) 7.71–7.26, 15H, m; 6.71, 1H, br s, NH; 4.97, 1H, d, J 11.6 Hz, CH<sub>A</sub>H<sub>B</sub>OR; 4.83, 1H, d, J 12 Hz, CH<sub>A</sub>H<sub>B</sub>OR; 4.38, 1H, d, J 18 Hz, H4'; 3.53, 1H, d, J 18 Hz, H4'; 3.53, 3H, s, OCH<sub>3</sub>. <sup>1</sup>H n.m.r.  $\delta$  (minor isomer, in part) 7.71–7.26, 15H, m; 6.73, 1H, br s, NH; 4.90, 1H, d, J 11.2 Hz, CH<sub>A</sub>H<sub>B</sub>OR; 4.82, 1H, br d, CH<sub>A</sub>H<sub>B</sub>OR; 4.00, 1H, d, J 17.6 Hz, H4'; 3.52, 4H, m, H4', OCH<sub>3</sub>.

### (2'R,4'S)-N-(1',4'-Diphenylazetidin-2'-yl)benzamide (21)

A solution of (4a) (150 mg, 0.3 mmol) in ethyl acetate (10 ml) was stirred at room temperature under an atmosphere of hydrogen (1 atm) for 5 h in the presence of 20% palladium hydroxide on carbon (50% water) (100 mg). The catalyst was removed by filtration through Celite, and the solvent was evaporated under reduced pressure. Purification of the crude reaction mixture by column chromatography (silica gel, ethyl acetate/hexane) afforded N-(1',4'-diphenylazetidin-2'-yl)benzamide (21) (30 mg, 30%) and N-benzylbenzamide (30 mg, 47%).

(21): m.p.  $175-177^{\circ}$ C.  $[\alpha]_{D}^{26}$  +71·1 (c, 0·18 in CHCl<sub>3</sub>). <sup>1</sup>H n.m.r.  $\delta$  7·38-7·00, 15H, m; 5·27, 1H, dd, J 6·4, 9·6 Hz, H2'; 4·73, 1H, br s, NH; 4·27, 1H, dd, J 7·6, 10·4 Hz, H4'; 3·30, 1H, ddd, J 6·4, 7·6, 12·8 Hz, H3' $\alpha$ ; 2·00, 1H, ddd, J 9·6, 10·4, 12·8 Hz, H3' $\beta$ . <sup>13</sup>C n.m.r.  $\delta$  173·1 (CO), 147·3, 139·8, 137·1, 129·3, 128·8, 128·6, 128, 126·7, 125·6, 123·3, 118·6, 113·8, 60·8 (C2'), 55·9 (C4'), 40·7 (C3'). Mass spectrum (e.s. positive) m/z 329 (M+H, 100%), 182 (15). High-resolution mass spectrum m/z 329·1647±0·007 (C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O+H requires 329·1653).

N-Benzylbenzamide: m.p. 97–100°C (dec.) (lit.<sup>20</sup> 105–106°C). <sup>1</sup>H n.m.r.  $\delta$  7.8–7.3, 10H, m; 6.48, 1H, br s, NH; 4.66, 2H, d, J 5.2 Hz, CH<sub>2</sub>. <sup>13</sup>C n.m.r.  $\delta$  167.3 (CO), 138.1, 134.3, 131.5, 128.8, 128.6, 127.9, 127.6, 126.9, 44.1. Mass spectrum (e.s. positive) m/z 212 (M+H, 3%), 182 (12), 91 (100).

#### Structure Determinations

Unique diffractometer data sets were measured at c. 295 K;  $(2\theta_{\max}, \text{ as specified}; 2\theta/\theta \text{ scan} mode; monochromatic Mo K\alpha radiation, <math>\lambda 0.7107_3 \text{ Å}$ ) yielding N independent reflections,  $N_o$  of these with  $I > 3\sigma(I)$  being considered 'observed' and used in the full-matrix least-squares refinement without absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms;  $(x, y, z, U_{\text{iso}})_{\text{H}}$  were included constrained at estimated values. Conventional residuals R and  $R_{\text{w}}$  on |F| at convergence are given [statistical weights, derivative of  $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})]$ . Neutral atom complex scattering factors were used;

<sup>20</sup> Bukingham, J., 'Dictionary of Organic Compounds' Vol. 1, p. 604 (Chapman & Hall: New York 1982). Table 2. Molecular core geometries

Ph C(21)-C(26)

	(4a)	(4b)	(4L)	(6c)	(7c)	(14)	(15)	(17a)	(18a)	(17b)
					Distances (Å)					
O(1)-C(2)	1.452(9)	$1 \cdot 449(7)$	$1 \cdot 443(3)$	1.438(5)	1.446(3)	$1 \cdot 437(3)$	$1 \cdot 424(8)$	1 - 444(7)	1.450(6)	1.450/6)
O(1)-C(5)	$1 \cdot 33(1)$	1.357(7)	1.341(3)	1.340(5)	1.340(3)	1.346(3)	1.341(9)	1.330(7)	1.333(6)	1.347(6)
C(2)-C(21)	$1 \cdot 49(1)$	1.501(9)	$1 \cdot 495(4)$	$1 \cdot 503(5)$	1.487(4)	1.506(3)	1.489(9)	1.501(7)	1.500(7)	1.480(8)
C(2)-N(3)	$1 \cdot 48(1)$	$1 \cdot 450(7)$	$1 \cdot 468(3)$	1.459(5)	$1 \cdot 470(4)$	1.464(3)	1.463(8)	1.482(7)	1.478(6)	1.486(6)
N(3)-C(4)	$1 \cdot 420(9)$	$1 \cdot 444(6)$	$1 \cdot 450(3)$	$1 \cdot 454(5)$	$1 \cdot 451(3)$	$1 \cdot 448(3)$	1.43(1)	1.445(7)	1.439(6)	1.447(6)
N(3)-C(3)	$1 \cdot 41(2)$	1.383(9)	1.380(3)	1.366(4)	$1 \cdot 376(3)$	1.368(3)	1.39(1)	1.363(7)	1.354(6)	$1 \cdot 370(6)$
C(3) - O(3)	$1 \cdot 20(2)$	$1 \cdot 199(7)$	$1 \cdot 216(3)$	$1 \cdot 215(4)$	$1 \cdot 217(3)$	$1 \cdot 218(3)$	$1 \cdot 20\hat{5}(9)$	$1 \cdot 204(7)$	$1 \cdot 213(6)$	$1 \cdot 209(6)$
C(3)-C(31)	1.48(1)	1.506(9)	$1 \cdot 489(3)$	$1 \cdot 486(5)$	$1\cdot483(3)$	$1 \cdot 488(3)$	$1 \cdot 49(1)$	1.490(8)	1.502(6)	1.512(7)
C(4)-C(5)	1.53(1)	1.531(9)	$1 \cdot 517(3)$	1.527(6)	1.523(4)	1.535(3)	1.52(1)	1.523(9)	1.520(7)	1.527(7)
C(4)-C(6)	1.52(2)	1.501(9)	1.519(3)	1.519(5)	1.522(4)	1.517(3)	1.531(9)	1.508(8)	1.520(7)	1.518(7)
C(4) - O(9)	$1 \cdot 43(1)$	1.431(8)	$1 \cdot 417(3)$	$1 \cdot 414(5)$	$1 \cdot 419(3)$	$1\cdot 457(2)$	$1 \cdot 425(9)$	$1 \cdot 450(6)$	1.451(6)	1.429(6)
C(5)-O(5)	$1 \cdot 18(1)$	$1 \cdot 175(9)$	$1 \cdot 196(4)$	$1 \cdot 190(5)$	$1 \cdot 189(4)$	$1 \cdot 188(3)$	$1 \cdot 19(1)$	1.193(8)	1.188(7)	$1 \cdot 187(6)$
C(6)-C(7)	1.479(9)	1.525(8)	1.522(3)	1.508(5)	1.514(3)	1.536(3)	$1 \cdot 52(1)$	1.498(7)	$1 \cdot 477(7)$	1.473(8)
$C(7)-C^{A}$	1.50(1)	1.518(8)	1.505(3)	1.516(5)	$1 \cdot 507(3)$	1.515(3)	1.53(1)	1.462(8)	$1 \cdot 474(7)$	1.499(8)
C(7)-N(8)	1.50(1)	$1 \cdot 47(1)$	$1 \cdot 476(3)$	$1 \cdot 478(5)$	$1 \cdot 467(4)$	$1 \cdot 481(3)$	$1 \cdot 43(1)$	$1 \cdot 271(7)$	$1 \cdot 275(6)$	$1 \cdot 263(7)$
N(8)-O(9)	$1 \cdot 433(8)$	$1 \cdot 492(5)$	$1 \cdot 495(2)$	1.486(4)	$1 \cdot 483(3)$	$1 \cdot 450(2)$	1.468(8)	1.430(6)	1.430(5)	1.438(5)
N(8)-C <sup>A</sup>	1.388(8)	$1 \cdot 483(9)$	$1 \cdot 495(3)$	1.464(6)	1.463(4)	$1 \cdot 491(4)$	1.44(1)			

1,3-Dipolar Cycloadditions

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(Continued)
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Table

and the second se										
	(4a)	(4b)	(12)	(6c)	(7c)	(14)	(15)	(17a)	(18a)	(17b)
				Angl	es (degrees)					
C(2)-O(1)-C(5)	112.2(6)	$111 \cdot 8(4)$	$111 \cdot 8(2)$	$111 \cdot 8(3)$	$111 \cdot 7(2)$	$111 \cdot 7(2)$	112.5(5)	$112 \cdot 2(4)$	$111 \cdot 8(4)$	113.0(4
O(1)-C(2)-N(3)	102.6(6)	$104 \cdot 3(4)$	$103 \cdot 9(2)$	$104 \cdot 0(3)$	$103 \cdot 7(2)$	$104 \cdot 1(2)$	$103 \cdot 2(5)$	$103 \cdot 1(4)$	$103 \cdot 7(4)$	102.0(4
O(1)-C(2)-C(21)	109.4(7)	$107 \cdot 3(6)$	$108 \cdot 4(2)$	$108 \cdot 3(3)$	110.8(2)	109.7(2)	109.7(5)	$110 \cdot 1(4)$	$109 \cdot 1(4)$	109.5(4
N(3)-C(2)-C(21)	$113 \cdot 2(6)$	116.5(6)	115.0(2)	$115 \cdot 3(3)$	$114 \cdot 0(3)$	$114 \cdot 9(2)$	115.3(6)	113.5(5)	$115 \cdot 1(4)$	$114 \cdot 2(4)$
C(2)-N(3)-C(4)	110.5(5)	$111 \cdot 6(5)$	$111 \cdot 8(2)$	$112 \cdot 5(3)$	$111 \cdot 9(2)$	$112 \cdot 4(2)$	113.0(5)	112.3(5)	$111 \cdot 5(4)$	112.3(4
C(2)-N(3)-C(3)	$114 \cdot 8(7)$	116.0(5)	115.9(2)	118.6(3)	116.8(2)	117.5(2)	$124 \cdot 1(6)$	116.9(4)	$117 \cdot 2(4)$	$124 \cdot 1(4$
C(4)-N(3)-C(3)	$123 \cdot 8(6)$	$128 \cdot 0(5)$	$130 \cdot 2(2)$	$128 \cdot 4(3)$	$129 \cdot 7(2)$	$128 \cdot 7(2)$	122.9(5)	$129 \cdot 1(4)$	129.0(4)	$123 \cdot 1(4$
N(3)-C(3)-O(3)	119.7(7)	119.7(6)	$119 \cdot 1(2)$	$119 \cdot 2(3)$	$119 \cdot 3(3)$	$120 \cdot 2(2)$	$122 \cdot 5(7)$	119.7(5)	120.8(4)	$121 \cdot 2(5)$
N(3)-C(3)-C(31)	117.7(8)	119.3(5)	119.8(2)	$118 \cdot 9(3)$	$119 \cdot 2(2)$	$118 \cdot 2(2)$	114.3(6)	$118 \cdot 5(5)$	117.5(4)	115.8(4
O(3)-C(3)-C(31)	122.4(8)	$121 \cdot 0(7)$	120.9(3)	$121 \cdot 9(3)$	$121 \cdot 3(2)$	$121 \cdot 5(2)$	$123 \cdot 3(7)$	121.9(5)	$121 \cdot 6(4)$	122.9(4
N(3)-C(4)-C(5)	101.8(6)	$102 \cdot 2(4)$	$101 \cdot 7(2)$	$100 \cdot 7(3)$	$101 \cdot 2(2)$	100.8(2)	100.9(5)	$101 \cdot 4(4)$	$102 \cdot 2(4)$	$101 \cdot 7(4$
N(3)-C(4)-C(6)	$121 \cdot 3(6)$	$119 \cdot 8(5)$	$118 \cdot 1(2)$	$120 \cdot 1(3)$	$117 \cdot 1(2)$	$120 \cdot 7(2)$	119.2(7)	118.9(6)	120.4(4)	117.5(4
N(3)-C(4)-O(9)	109.6(7)	110.3(6)	$112 \cdot 2(2)$	$109 \cdot 2(3)$	$113 \cdot 6(2)$	$108 \cdot 2(2)$	$108 \cdot 1(5)$	$111 \cdot 4(3)$	$111 \cdot 1(4)$	110.7(4
C(5)-C(4)-C(6)	$111 \cdot 4(7)$	$111 \cdot 4(6)$	$111 \cdot 7(2)$	$111 \cdot 8(3)$	112.5(2)	$113 \cdot 3(2)$	$113 \cdot 3(5)$	112.9(4)	$113 \cdot 0(4)$	114.8(4
C(5)-C(4)-O(9)	$108 \cdot 7(6)$	106.8(5)	106.7(2)	$108 \cdot 2(3)$	105.8(2)	$107 \cdot 1(2)$	107.5(6)	106.7(5)	$104 \cdot 8(4)$	106.6(4
C(6)-C(4)-O(9)	$103 \cdot 7(6)$	$105 \cdot 7(4)$	$106 \cdot 1(2)$	$106 \cdot 4(3)$	$106 \cdot 2(2)$	$106 \cdot 1(1)$	$107 \cdot 2(5)$	$105 \cdot 1(4)$	$104 \cdot 5(4)$	$105 \cdot 2(4$
O(1)-C(5)-C(4)	109.0(7)	$108 \cdot 7(5)$	110.8(2)	$111 \cdot 0(3)$	110.9(2)	110.3(2)	109.9(6)	110.9(5)	110.6(4)	109.8(4
O(1)-C(5)-O(5)	$124 \cdot 2(7)$	$123 \cdot 3(6)$	$121 \cdot 8(2)$	$122 \cdot 5(4)$	$122 \cdot 4(3)$	$123 \cdot 1(2)$	122.6(7)	$123 \cdot 2(5)$	$123 \cdot 8(5)$	$123 \cdot 1(5)$
C(4)-C(5)-O(5)	$126 \cdot 8(8)$	127.9(5)	127.4(2)	126.5(4)	126.6(3)	126.6(2)	127.3(7)	125.9(5)	$125 \cdot 5(5)$	$127 \cdot 1(5)$
C(4)-C(6)-C(7)	$105 \cdot 3(6)$	103.5(6)	$102 \cdot 4(2)$	$104 \cdot 5(3)$	$103 \cdot 8(2)$	$105 \cdot 5(2)$	100.9(6)	$102 \cdot 0(4)$	$102 \cdot 2(4)$	101.6(4
C(6)-C(7)-N(8)	$104 \cdot 7(6)$	$102 \cdot 1(5)$	100.5(2)	$101 \cdot 4(3)$	$101 \cdot 5(2)$	$105 \cdot 1(2)$	$101 \cdot 2(6)$	113.5(5)	$114 \cdot 5(4)$	115.3(5
$C(6)-C(7)-C^{A}$	112.6(6)	112.0(6)	$113 \cdot 3(2)$	115.6(3)	$113 \cdot 7(2)$	114.9(2)	$116 \cdot 4(6)$	$124 \cdot 2(4)$	$126 \cdot 1(4)$	$125 \cdot 1(5$
$N(8)-C(7)-C^{A}$	112.6(6)	$112 \cdot 2(5)$	$112 \cdot 2(2)$	109.5(3)	$111 \cdot 6(3)$	$103 \cdot 2(2)$	$108 \cdot 1(7)$	122.3(4)	119.4(4)	119.5(5
C(7)-N(8)-O(9)	107.8(5)	$104 \cdot 6(4)$	102.8(1)	101.6(2)	103.9(2)	$106 \cdot 2(1)$	$101 \cdot 3(6)$	109.6(4)	$108 \cdot 8(4)$	108.1(4
$C(7)-N(8)-C^{A}$	119.7(7)	$118 \cdot 3(5)$	118.3(2)	$112 \cdot 8(4)$	$112 \cdot 1(3)$	$107 \cdot 4(2)$	$111 \cdot 6(6)$		-	
$O(9)-N(8)-C^{A}$	112.3(6)	$104 \cdot 1(4)$	$103 \cdot 8(1)$	$103 \cdot 5(3)$	$103 \cdot 3(2)$	$110 \cdot 1(2)$	107.6(5)		1	
C(4)-O(9)-N(8)	109.6(7)	$109 \cdot 1(4)$	$108 \cdot 0(2)$	$104 \cdot 3(2)$	$108 \cdot 0(2)$	110.5(1)	$101 \cdot 7(5)$	$109 \cdot 0(4)$	109.5(3)	109.8(3

ı

	(4a)	(4b)	(42)	(6c)	(7c)	(14)	(15)	(17a)	(18a)	(17b)
				Plane' para	neters					
$\chi^2({ m C}(2,4,5){ m O}(1){ m N}(3))^{ m B}$	307	183	105	13.6	725	1120	59	16.5	59	336
§O(1)	-0.005(6)	0.008(7)	0.008(7)	0.003(3)	0.004(2)	-0.022(2)	-0.014(5)	0.006(4)	-0.011(4)	0.031(5)
$\delta C(2)$	0.09(1)	0.036(8)	-0.021(3)	-0.012(5)	-0.053(4)	0.005(3)	0.013(9)	-0.018(8)	0.007(6)	-0.081(6)
$\delta C(21)$	-0.97(1)	$-1 \cdot 09(1)$	$-1 \cdot 244(4)$	$-1 \cdot 223(6)$	$-1 \cdot 293(4)$	$-1 \cdot 174(3)$	$-1 \cdot 14(1)$	$-1 \cdot 242(9)$	$-1 \cdot 172(8)$	-1.384(8)
δN(3)	-0.10(1)	-0.041(7)	0.007(2)	0.007(4)	0.035(3)	0.020(2)	0.010(8)	0.004(7)	0.007(5)	0.048(5)
$\delta C(3)$	0.30(2)	0.26(1)	0.342(4)	0.185(6)	0.443(4)	0.341(3)	$0 \cdot 12(1)$	0.305(10)	0.364(8)	0.072(8)
$\delta O(3)$	0.80(2)	0.42(1)	0.67(4)	0.362(7)	0.921(5)	0.671(4)	0.08(1)	0.49(1)	0.694(9)	0.020(9)
δC(31)	-0.05(2)	0.37(1)	0.200(5)	0.133(7)	0.201(5)	0.198(4)	0.26(2)	0.37(1)	0.276(9)	0.202(10)
$\delta C(4)$	$0 \cdot 11(1)$	0.067(8)	0.001(3)	-0.008(5)	-0.044(3)	-0.044(3)	-0.042(11)	0.006(8)	-0.025(6)	-0.046(6)
8C(6)	-0.71(1)	-0.87(2)	1.333(4)	1.079(6)	$1 \cdot 008(4)$	0.917(3)	0.97(1)	$-1 \cdot 07(6)$	0.979(9)	$-1 \cdot 192(8)$
8O(9)	$1 \cdot 46(1)$	1.383(8)	$-1 \cdot 199(3)$	$-1 \cdot 239(5)$	$-1 \cdot 302(2)$	$-1 \cdot 383(3)$	$-1 \cdot 34(1)$	$1 \cdot 258(8)$	$-1 \cdot 319(6)$	$1 \cdot 140(6)$
$\delta C(5)$	-0.07(1)	-0.07(1)	-0.015(3)	0.001(5)	0.031(3)	0.064(3)	0.057(10)	-0.023(8)	0.038(7)	$(2)600 \cdot 0 - 0$
80(5)	-0.22(1)	-0.20(1)	-0.049(4)	-0.014(6)	0.099(4)	0.153(3)	0.089(12)	-0.043(10)	$0 \cdot 102(8)$	0.024(8)
$\chi^{2}(C(4,6,7)N(8)O(9))^{C}$	746	2522	2335	14103	17726	10693	2872	122	114	12
6C(4)	0.18(1)	0.080(8)	-0.013(3)	0.163(5)	-0.019(3)	0.020(2)	$0 \cdot 14(1)$	-0.054(8)	-0.044(6)	-0.014(6)
δN(3)	-0.42(1)	-0.728(9)	-0.914(3)	-0.650(5)	-0.995(4)	$-1 \cdot 027(3)$	-0.69(1)	$-1 \cdot 190(9)$	$-1 \cdot 136(6)$	$-1 \cdot 104(7)$
δC(5)	1.67(1)	$1\cdot 49(1)$	1.321(4)	1.555(6)	$1\cdot 280(4)$	$1 \cdot 268(3)$	$1 \cdot 52(1)$	$1 \cdot 106(10)$	$1 \cdot 168(8)$	$1 \cdot 201(8)$
$\delta C(6)$	-0.18(1)	-0.206(8)	-0.276(4)	$0 \cdot 106(5)$	-0.177(4)	0.089(3)	0.08(1)	0.065(9)	0.041(7)	0.010(7)
$\delta C(7)$	$0 \cdot 10(1)$	0.274(8)	0.304(3)	-0.280(4)	0.290(3)	-0.174(3)	-0.34(1)	-0.020(8)	-0.011(6)	-0.001(7)
$\delta C(71/10)$	-0.85(1)	-0.37(1)	-0.200(4)	0.315(6)	-0.278(4)	0.775(4)	-0.25(1)	-0.080(11)	-0.045(9)	0.002(11)
δN(8)	0.00(1)	-0.128(6)	-0.166(2)	0.269(4)	-0.195(3)	0.143(2)	0.283(9)	-0.010(7)	-0.013(5)	-0.007(5)
$\delta C(8/81/12/13)$	0.92(1)	0.68(1)	0.587(4)	-0.436(8)	0.640(6)	1.577(4)	$0 \cdot 16(2)$			
§O(9)	-0.08(1)	0.046(6)	0.078(2)	-0.148(3)	0.073(2)	-0.057(2)	-0.171(8)	0.026(6)	0.018(4)	0.006(4)
			Dih	edral angles	(degrees)					
$\theta(C(21-26)/plane 1)$	80.6(4)	87.8(3)	$88 \cdot 3(1)$	$80 \cdot 7(2)$	89.7(1)	79.48(9)	$78 \cdot 7(3)$	87.6(2)	76.4(2)	88.0(2)
$\theta(C(3,31)N(3)O(3)/plane 1)$	26.9(4)	$12 \cdot 6(3)$	17.9(1)	$9\cdot3(2)$	$25 \cdot 0(1)$	17.6(1)	$6 \cdot 1(3)$	$13 \cdot 1(3)$	18.2(2)	$4 \cdot 5(2)$
$\theta(C(3,31)N(3)O(3)/C(31-36))$	$60 \cdot 7(4)$	$81 \cdot 7(3)$	47.9(1)	$73 \cdot 4(2)$	49.8(1)	$66 \cdot 0(1)$	$75 \cdot 3(3)$	83.0(3)	62.5(2)	75.8(2)
$\theta$ (plane 1/plane 2)	87.9(3)	86.9(3)	$81 \cdot 6(1)$	$84 \cdot 1(1)$	86.4(1)	$86 \cdot 78(8)$	$81 \cdot 2(3)$	$77 \cdot 6(2)$	$88 \cdot 7(2)$	$87 \cdot 7(2)$
$\theta(C(4,5)O(1,5)/plane 1)$	7.9(8)	6.8(3)	$1 \cdot 6(1)$	$0\cdot 4(1)$	3.5(1)	$5 \cdot 3(1)$	$3 \cdot 4(3)$	$1 \cdot 4(3)$	3.4(2)	$1 \cdot 8(2)$
$\theta(C(71-76)/plane 2)$	75.6(4)	77.0(3)	$78 \cdot 9(1)$	$90 \cdot 0(2)$	$69 \cdot 2(1)$		a supervision	$15 \cdot 9(3)$		
$\theta(C(81-86)/plane 2)$	36.3(4)		-	1	ļ					_
<sup>A</sup> Atom pendant to ring 2.	<sup>B</sup> Plane 1;	positive de	eviations lie	towards the	reader.	<sup>C</sup> Plane 2;	positive devi	iations lie tow	/ard O(5).	

1,3-Dipolar Cycloadditions

Table 2 (Continued)

	Table 9.	Hon-nyuroş	gen posicio	liai allu 150	uopic	displacement	paramen	CIS IOI (40)	
Atom	x	y	z	$U_{\mathrm{eq}}~(\mathrm{\AA^2})$	Atom	x	y	z	$U_{\rm eq}~({\rm \AA}^2)$
O(1)	0.4715(5)	$0.764(-)^{A}$	0.6438(2)	0.076(2)	C(5)	0.4451(7)	0.863(2)	0.6974(4)	0.066(3)
C(2)	0.3602(7)	0.627(2)	0.6161(3)	0.064(3)	O(5)	0.5183(5)	0.991(1)	0.7267(3)	0.087(2)
C(21)	0.3259(7)	0.700(2)	0.5499(3)	0.062(3)	C(6)	0.2362(6)	0.963(2)	0.7482(3)	0.053(3)
C(22)	0 • 2535(9)	0.898(2)	0.5342(4)	0.086(4)	C(7)	0.2852(6)	0.942(1)	0.8153(3)	0.050(2)
C(23)	0.229(1)	0.968(2)	0.4752(5)	0.102(4)	C(71)	0.1808(7)	1.002(2)	0.8584(3)	0.050(3)
C(24)	0·268(1)	0.836(2)	0.4269(4)	0.102(5)	C(72)	0.1844(8)	$1 \cdot 206(2)$	0.8891(4)	0.072(3)
C(25)	0.3419(9)	0·638(2)	0.4408(4)	0.097(5)	C(73)	0.082(1)	$1 \cdot 273(2)$	0.9261(4)	0.082(4)
C(26)	0.3677(7)	0.571(2)	0.5016(4)	0.072(3)	C(74)	-0.021(1)	$1 \cdot 118(2)$	0.9318(4)	0.091(4)
N(3)	0·2539(6)	0.679(1)	0.6574(3)	0·056(2)	C(75)	-0.0247(9)	0.918(2)	0.9012(4)	0.091(4)
C(3)	0·1460(8)	0.523(2)	0.6526(3)	0.065(3)	C(76)	0.0783(7)	0.851(2)	0.8651(4)	0.075(3)
O(3)	0.1485(6)	0·359(1)	0.6188(3)	0.090(3)	N(8)	0.3319(5)	0.697(1)	0.8227(3)	0.052(2)
C(31)	0.0271(6)	0.584(2)	0.6852(3)	0.056(3)	C(81)	0.4486(6)	0.648(2)	0.8602(3)	0.050(3)
C(32)	-0.0188(8)	0.428(2)	0.7269(4)	0.072(3)	C(82)	0.5304(6)	0.463(2)	0.8466(3)	0.055(3)
C(33)	-0·1308(8)	0.473(2)	0.7564(4)	0.080(3)	C(83)	0.6377(8)	0.407(2)	0.8886(4)	0.077(4)
C(34)	-0.2027(7)	0.673(2)	0.7434(4)	0.080(4)	C(84)	0.6691(8)	0.532(2)	0.9430(4)	0.077(4)
C(35)	-0·1610(8)	0.822(2)	0.7004(4)	0.075(3)	C(85)	0.5880(8)	0.713(2)	0.9552(4)	0.082(4)
C(36)	-0.0463(7)	0·783(2)	0.6700(4)	0.065(3)	C(86)	0.4817(8)	0.772(2)	0.9145(4)	0.070(3)
$\dot{C(4)}$	0 3094(7)	0.777(2)	0.7149(3)	0.052(2)	O(9)	0.3313(5)	0.599(1)	0.7613(2)	0.065(2)

Table 3. Non-hydrogen positional and isotropic displacement parameters for (4a)

<sup>A</sup> Defines origin.

Table 4.	Non-hvdrogen	positional	and	isotropic	displacement	parameters	for	(4b)	)

Atom	x	y	z	$U_{\rm eq}~({\rm \AA}^2)$	Atom	x	y	z	$U_{\rm eq}~({\rm \AA}^2)$
0(1)	0.3500(4)	0.3576(3)	$0.3094(-)^{A}$	0.070(2)	C(6)	0.5649(4)	0.5075(4)	0.1116(6)	0.051(3)
C(2)	0.2968(5)	0.3243(5)	0.1904(6)	0.060(3)	C(7)	0.6284(4)	0.6209(5)	0.1467(5)	0.048(3)
C(21)	0.2639(5)	0.2128(4)	0.1751(6)	0.057(3)	C(71)	0.7246(4)	0.6771(4)	0.0667(6)	0.049(3)
C(22)	0.3359(5)	0.1817(5)	0.1603(6)	0.068(4)	C(72)	0.8209(5)	0.7090(5)	0.1158(7)	0.070(4)
C(23)	0.3066(7)	0.0794(6)	0.1569(7)	0·079(4)	C(73)	0.9064(5)	0.7568(6)	0.0403(9)	0.091(5)
C(24)	0.2055(8)	0.0068(6)	0.1702(8)	0.092(5)	C(74)	0.8966(6)	0.7739(7)	-0·0830(9)	0.096(5)
C(25)	0.1354(7)	0.0373(7)	0.184(1)	0.116(5)	C(75)	0.8031(6)	0.7432(6)	-0.1336(7)	0.083(4)
C(26)	0.1645(6)	0.1400(6)	0.1867(8)	0.091(4)	C(76)	0.7178(5)	0.6950(5)	-0.0593(7)	0.071(4)
N(3)	0.3701(3)	0.3945(3)	0.0994(5)	0.051(2)	N(8)	0.5557(3)	0.6575(3)	0.1241(5)	0.043(2)
C(3)	0.3312(5)	0.3943(5)	-0.0182(7)	0.061(3)	C(81)	0.5650(4)	0.7439(4)	0.2013(6)	0.051(3)
O(3)	0.2447(4)	0.3305(4)	-0.0438(6)	0.094(3)	C(82)	0.6717(5)	0.8349(4)	0.1817(7)	0.067(3)
$\tilde{C}(31)$	0.3992(5)	0.4736(5)	-0.1132(6)	0.056(3)	C(83)	0.4861(5)	0.7687(5)	0.1493(7)	0.067(3)
C(32)	0.4441(6)	0.4456(6)	-0.2057(8)	0.087(5)	C(84)	0.5452(5)	0.7197(5)	0.3408(6)	0.068(4)
C(33)	0.5006(6)	0.5173(8)	-0.3026(8)	0.095(5)	O(9)	0.4535(3)	0.5690(3)	0·1596(5)	0.049(2)
C(34)	0.5088(6)	0.6105(7)	-0.3013(7)	0.091(5)	$C(01)^{B}$	0.691(3)	0.336(3)	-0.187(3)	0.18(2)
C(35)	0.4643(6)	0.6383(6)	-0.2104(8)	0.080(4)	$C(02)^{B}$	0.706(2)	0.397(2)	-0.112(2)	0.15(1)
C(36)	0.4087(5)	0.5687(5)	-0.1157(6)	0.064(3)	$O(01)^B$	0.751(2)	0.481(2)	-0.145(2)	0.150(8)
C(4)	0.4595(5)	0.4769(4)	0.1597(5)	0.049(3)	$O(02)^B$	0.727(2)	0.378(2)	-0.002(2)	0.23(1)
C(5)	0.4458(6)	0.4399(5)	0.2958(7)	0.056(3)	$C(03)^B$	0.707(4)	0.301(3)	0.005(3)	0.24(2)
O(5)	0.5051(4)	0.4751(3)	0.3787(5)	0.075(3)	C(04) <sup>B</sup>	0.725(2)	0.280(2)	0.121(4)	0.13(1)

 $^A$  Defines origin.  $\ ^B$  Site occupancy factor is  $\frac{1}{3},$  isotropic thermal parameters.

Table 5.	Non-hydrogen p	ositional and	l isotropic	displacement	parameters	for	(6c)

Atom	x	y	z	$U_{\rm eq}~({\rm \AA}^2)$	Atom	x	y	z	$U_{\rm eq}~({\rm \AA}^2)$
O(1)	0.3257(2)	0.4576(2)	0.6887(3)	0.061(1)	C(36)	0.6635(3)	0.4552(3)	0.5687(5)	0.055(1)
C(2)	0.3867(2)	0.5377(3)	0.6743(4)	0.048(1)	C(4)	0.4344(2)	0.3808(3)	0.5684(4)	0.047(1)
C(21)	0.3472(2)	0.6283(3)	0.6063(4)	0.047(1)	C(5)	0.3494(3)	0.3692(3)	0.6311(4)	0.061(1)
C(22)	0.3420(3)	0.6343(3)	0.4726(5)	0.066(2)	O(5)	0.3072(2)	0.2938(2)	0.6294(4)	0.093(1)
C(23)	0.2984(3)	0.7126(4)	0.4125(6)	0.085(2)	C(6)	0.4924(3)	0.2944(3)	0.6094(4)	0.046(1)
C(24)	0.2594(3)	0.7846(4)	0.4873(8)	0.093(3)	C(7)	0.5144(2)	0.2406(3)	0.4829(3)	0.042(1)
C(25)	0.2646(3)	0.7808(4)	0.6204(8)	0.085(2)	C(71)	0.5281(2)	0.1247(3)	0.4928(3)	0.044(1)
C(26)	0.3087(3)	0.7022(3)	0.6809(6)	0.069(2)	C(72)	0.4663(3)	0.0602(3)	0.5359(4)	0.052(1)
N(3)	0.4534(2)	0.4877(2)	0.6021(3)	0.045(1)	C(73)	0.4805(3)	-0.0450(3)	0.5510(5)	0.064(2)
C(3)	0.5263(2)	0.5394(3)	0.5879(4)	0.046(1)	C(74)	0.5554(4)	-0.0860(3)	0.5215(5)	0.072(2)
O(3)	0.5345(2)	0.6239(2)	0.6389(3)	0.071(1)	C(75)	0.6162(4)	-0.0241(4)	0.4745(5)	0.074(2)
C(31)	0.5930(2)	0.4914(3)	0.5086(4)	0.046(1)	C(76)	0.6029(3)	0.0819(4)	0.4597(5)	0.060(2)
C(32)	0.5883(3)	0.4899(3)	0.3729(4)	0.053(2)	N(8)	0.4403(2)	$0 \cdot 2612(2)$	0.4028(3)	0.051(1)
C(33)	0.6532(3)	0.4535(3)	0.2990(5)	0.060(2)	C(8)	0.4573(4)	0.2597(4)	0.2618(5)	0.076(2)
C(34)	0.7220(3)	0.4153(3)	0.3603(5)	0.061(2)	O(9)	0.4253(1)	0.3726(2)	0.4310(2)	0.0519(9)
C(35)	0.7274(3)	0.4151(3)	0.4945(5)	0.063(2)					

Table 6. Non-hydrogen positional and isotropic displacement parameters for (7b)

Atom	x	у	z	$U_{\rm eq}~({\rm \AA^2})$	Atom	x	у	z	$U_{\rm eq}~({\rm \AA}^2)$
O(1)	1.0800(1)	0.5006(2)	0.74341(6)	0.0613(7)	C(4)	0.9221(2)	0.4684(3)	0.67042(9)	0.0472(9)
C(2)	$1 \cdot 1294(2)$	0.4486(3)	0.70206(9)	0.053(1)	C(5)	0.9651(2)	0.5177(3)	0.7270(1)	0.055(1)
C(21)	$1 \cdot 2127(2)$	0.5815(3)	0.69513(9)	0.0508(9)	O(5)	0.9090(2)	0.5666(3)	0.75511(7)	0.0763(8)
C(22)	$1 \cdot 1759(3)$	0.7376(4)	0.6749(1)	0.073(1)	C(6)	0.8283(2)	0.3345(3)	0.6622(1)	0.050(1)
C(23)	$1 \cdot 2536(3)$	0.8631(4)	0.6717(1)	0.081(1)	C(7)	0.7189(2)	0.4407(3)	0.65170(9)	0.0451(9)
C(24)	$1 \cdot 3694(3)$	0.8303(5)	0.6887(1)	0.078(1)	C(71)	0.6117(2)	0.3431(3)	0.6257(1)	0.0472(9)
C(25)	$1 \cdot 4069(3)$	0.6771(5)	0.7088(1)	0.079(1)	C(72)	0.5277(2)	0·3170(3)	0.6515(1)	0.065(1)
C(26)	$1 \cdot 3291(2)$	0.5530(4)	0.7119(1)	0.064(1)	C(73)	0.4266(3)	0.2324(4)	0.6282(2)	0.087(2)
N(3)	1.0288(1)	0.4256(2)	0.65763(7)	0.0494(7)	C(74)	0.4112(3)	0.1725(4)	0.5794(2)	0.089(2)
C(3)	1.0475(2)	0.3335(3)	0.6167(1)	0.056(1)	C(75)	0.4941(3)	0.1929(4)	0.5533(1)	0.080(1)
O(3)	1.1415(1)	0.2690(2)	0.62094(7)	0.0756(8)	-C(76)	0.5953(2)	0.2804(3)	0.5765(1)	0.062(1)
C(31)	0.9562(2)	0.3252(4)	0.5670(1)	0.062(1)	N(8)	0.7464(1)	0.5722(2)	0.61763(7)	0.0460(7)
C(32)	0.9012(3)	0.4675(5)	0.5427(1)	0.078(1)	C(81)	0.6857(2)	0.7387(3)	0.6143(1)	0.0531(9)
C(33)	0.8247(3)	0.4542(8)	0.4939(2)	$0 \cdot 107(2)$	C(82)	0.5589(2)	0.7060(4)	0.5874(2)	0.068(1)
C(34)	0.8024(4)	0.303(1)	0.4701(2)	0.133(3)	C(83)	0.6961(3)	0.8241(5)	0.6661(1)	0.074(1)
C(35)	0.8580(5)	0.160(1)	0.4939(2)	0.126(3)	C(84)	0.7377(3)	0.8488(4)	0.5795(2)	0.074(1)
C(36)	0.9356(3)	0.1707(5)	0.5421(2)	0.088(2)	O(9)	0·8693(1)	0.6141(2)	0.64360(6)	0.0522(6)

Table 7. Non-hydrogen positional and isotropic displacement parameters for (7c)

Atom	x	у	z	$U_{\rm eq}~({\rm \AA}^2)$	Atom	x	y	z	$U_{\rm eq}~({\rm \AA}^2)$
O(1)	0.3258(2)	0.7039(2)	$1 \cdot 0357(2)$	0.0546(9)	C(36)	0.4136(3)	$1 \cdot 3017(3)$	$1 \cdot 1737(3)$	0.059(1)
C(2)	0.3444(3)	0.8047(3)	$1 \cdot 1575(3)$	0.046(1)	C(4)	0.2751(2)	0.8840(2)	0.9415(2)	0.039(1)
C(21)	0.2554(2)	0.7344(2)	$1 \cdot 2296(3)$	0.045(1)	C(5)	0.2891(2)	0.7452(3)	0.9138(3)	0.049(1)
C(22)	0.1238(3)	0.6727(3)	$1 \cdot 1568(3)$	0.066(2)	O(5)	0.2706(2)	0.6785(2)	0.8014(2)	0.073(1)
C(23)	0.0424(4)	0.6089(4)	$1 \cdot 2242(4)$	0.090(2)	C(6)	0.3422(2)	0.9945(3)	0.8694(3)	0.044(1)
C(24)	0.0927(5)	0.6064(4)	$1 \cdot 3657(5)$	0.096(3)	C(7)	$0 \cdot 2352(2)$	0.9763(3)	0.7321(3)	0.044(1)
C(25)	0.2219(5)	0.6671(4)	$1 \cdot 4388(4)$	0.087(2)	C(71)	0.2614(2)	$1 \cdot 1080(3)$	0.6717(2)	0.044(1)
C(26)	0.3039(3)	0.7319(3)	1.3711(3)	0.062(2)	C(72)	0.3085(3)	$1 \cdot 1188(3)$	0.5640(3)	0.054(1)
N(3)	0.3227(2)	0.9206(2)	1.0963(2)	0.0398(9)	C(73)	0.3392(3)	$1 \cdot 2422(3)$	0.5134(3)	0.063(2)
C(3)	0.3737(2)	1.0517(3)	$1 \cdot 1892(3)$	0.045(1)	C(74)	0·3196(3)	$1 \cdot 3541(3)$	0.5670(3)	0.066(2)
O(3)	0.4506(2)	1.0731(2)	$1 \cdot 3091(2)$	0.068(1)	C(75)	0.2730(3)	$1 \cdot 3447(3)$	0.6743(3)	0.068(2)
C(31)	0.3267(2)	$1 \cdot 1601(2)$	$1 \cdot 1446(2)$	0.043(1)	C(76)	0.2441(3)	$1 \cdot 2229(3)$	0.7271(3)	0.061(2)
C(32)	0.1969(3)	$1 \cdot 1246(3)$	$1 \cdot 0905(3)$	0.051(1)	N(8)	0.1264(2)	0.9439(2)	0.7787(2)	0.050(1)
C(33)	0.1553(3)	$1 \cdot 2309(3)$	1.0672(3)	0.064(2)	C(8)	0.0031(3)	0.8543(6)	0.6623(4)	0.088(2)
C(34)	0.2410(3)	$1 \cdot 3695(3)$	1.0946(3)	0.070(2)	O(9)	0.1417(1)	0.8469(2)	0.8753(2)	0.0489(8)
C(35)	0.3702(3)	$1 \cdot 4056(3)$	$1 \cdot 1462(3)$	0.074(2)	. ,	. ,			. ,

Table 8. Non-hydrogen positional and isotropic displacement parameters for (14)

Atom	<i>x</i>	y	z	$\overline{U}_{\mathrm{eq}}$ (Å <sup>2</sup> )	Atom	x	y	z	$U_{\rm eq}~({\rm \AA^2})$
O(1)	0.42359(9)	0.5498(1)	0.7429(2)	0.0447(5)	C(34)	0.1034(2)	0.7997(2)	0.3009(4)	0.0601(9)
C(2)	0.3785(1)	0.5118(2)	0.6043(3)	0.0371(6)	C(35)	0.0758(1)	0.7254(2)	0.4031(4)	0.0566(9)
C(21)	0.4335(1)	0.4866(2)	0.4621(3)	0.0389(6)	C(36)	0.1262(1)	0.6501(2)	0.4591(3)	0.0456(7)
C(22)	0.4619(2)	0.5601(2)	0.3544(4)	0.0553(8)	C(4)	0.3316(1)	0.6781(1)	0.6769(3)	0.0338(6)
C(23)	0.5149(2)	0.5364(2)	0.2308(4)	0.064(1)	C(5)	0.3953(1)	0.6387(2)	0.7970(3)	0.0408(7)
C(24)	0.5428(2)	0.4391(2)	0.2149(4)	0.0598(9)	O(5)	0.4201(1)	0.6803(1)	0.9175(2)	0.0608(6)
C(25)	0.5151(2)	0.3655(2)	0.3197(4)	0.0601(9)	C(6)	0.2612(1)	0.7250(2)	0.7656(3)	0.0370(6)
C(26)	0.4600(2)	0.3893(2)	0.4425(3)	0.0501(8)	C(7)	0.2526(1)	0.8308(2)	0.6907(3)	0.0390(6)
N(3)	0.32120(9)	0.5917(1)	0.5690(2)	0.0347(5)	N(8)	0.3313(1)	0.8544(1)	0.6187(2)	0.0417(6)
C(3)	0.2586(1)	0.5687(1)	0.4673(3)	0.0403(6)	O(9)	0.36768(8)	0.7584(1)	0.5792(2)	0.0387(4)
O(3)	0.2495(1)	0.4830(1)	0.4170(3)	0.0648(7)	C(10)	0.2402(2)	0.9141(2)	0.8172(3)	0.0508(8)
C(31)	0.2054(1)	0.6518(2)	0.4133(3)	0.0379(6)	C(11)	0.3219(2)	0.9290(2)	0.8931(4)	0.0593(9)
C(32)	0.2335(1)	0.7279(2)	0.3092(3)	0.0457(7)	C(12)	0.3781(2)	0.9072(2)	0.7501(4)	0.063(1)
C(33)	0.1825(2)	0.8007(2)	0.2525(3)	0.0562(9)					

computation used the XTAL 3.2 program system,<sup>21</sup> implemented by S. R. Hall. Individual variations in procedure or anomalous features are noted where applicable ('variata'). Pertinent results are given in Fig. 1 (20% thermal ellipsoids for the non-hydrogen atoms; arbitrary radii of 0.1 Å for hydrogen atoms) and Tables 2–12; material deposited\* comprises full atom coordinates and thermal parameters, non-hydrogen geometries, and structure factor amplitudes. The common (crystallographic) numbering adopted for the molecular core is shown in Table 2, with a common chirality for the oxazolidinone ring and substituents, the C(2)-Ph substituent lying away from the reader, and torsion N(3)–C(3)–C(31)–C(32) positive.

Where the material is optically active, the chirality adopted is drawn from the chemistry.

#### Crystal/Refinement Data

(4a).  $C_{30}H_{24}N_2O_4$ , *M* 476.5. Monoclinic, space group  $P_{21}$  ( $C_2^2$ , No. 4); *a* 10.06(1), *b* 5.79(1), *c* 21.398(7) Å,  $\beta$  95.42(7)°, *V* 1241 Å<sup>3</sup>.  $D_c$  (Z = 2) 1.28 g cm.<sup>-3</sup>; *F*(000) 500.  $\mu_{Mo}$  0.9 cm<sup>-1</sup>; specimen: 0.25 by 0.85 by 0.42 mm,  $2\theta_{max}$  50°; *N* 2401,  $N_o$  1633; *R* 0.065,  $R_w$  0.067.

'Variata'—Linewidths were very broad, and the optimum specimen from recrystallized material was used without cutting.

Atom	x	y	z	$U_{\rm eq}~({\rm \AA}^2)$	Atom	x	у	z	$U_{\rm eq}~({\rm \AA}^2)$
O(1) C(2) C(21) C(22)	$\begin{array}{c} 0.6650(5) \\ 0.6473(7) \\ 0.7464(7) \\ 0.7143(7) \end{array}$	$\begin{array}{c} 0 \cdot 0(-)^{\mathbf{A}} \\ 0 \cdot 1257(8) \\ 0 \cdot 1063(9) \\ 0 \cdot 009(1) \end{array}$	0.1005(4) 0.1783(6) 0.2766(6) 0.3653(6)	0.056(2) 0.048(3) 0.041(3) 0.050(3)	C(34) C(35) C(36) C(4)	$\begin{array}{c} 0.6922(8) \\ 0.6489(8) \\ 0.5619(8) \\ 0.4237(7) \end{array}$	$\begin{array}{c} 0.587(1) \\ 0.470(1) \\ 0.3540(9) \\ -0.007(1) \end{array}$	$\begin{array}{c} 0.4002(8) \\ 0.4722(6) \\ 0.4297(6) \\ 0.1507(5) \end{array}$	0.067(3) 0.065(3) 0.054(3) 0.044(3)
C(23) C(24) C(25) C(26) N(3)	0.8083(8) 0.9351(9) 0.9692(8) 0.8729(8) 0.4960(5)	$\begin{array}{c} -0.011(1) \\ 0.066(1) \\ 0.165(1) \\ 0.184(1) \\ 0.1184(8) \end{array}$	0.4557(6) 0.4534(7) 0.3657(8) 0.2778(6) 0.2065(4)	$\begin{array}{c} 0.064(3) \\ 0.076(4) \\ 0.072(4) \\ 0.061(3) \\ 0.041(2) \end{array}$	C(5) O(5) C(6) C(7) N(8)	$\begin{array}{c} 0.5418(8) \\ 0.5341(5) \\ 0.2857(7) \\ 0.1824(7) \\ 0.2739(6) \end{array}$	$\begin{array}{c} -0.071(1) \\ -0.1757(9) \\ 0.025(1) \\ -0.080(1) \\ -0.2064(8) \end{array}$	$\begin{array}{c} 0.0753(6) \\ 0.0090(4) \\ 0.0855(5) \\ 0.1487(7) \\ 0.1805(5) \end{array}$	$\begin{array}{c} 0.055(3) \\ 0.082(2) \\ 0.053(3) \\ 0.062(3) \\ 0.058(2) \end{array}$
C(3) O(3) C(31) C(32) C(33)	$\begin{array}{c} 0\cdot4267(8)\\ 0\cdot3026(5)\\ 0\cdot5197(7)\\ 0\cdot5591(8)\\ 0\cdot6453(8)\end{array}$	$\begin{array}{c} 0.226(1) \\ 0.2147(8) \\ 0.3545(9) \\ 0.477(1) \\ 0.593(1) \end{array}$	$\begin{array}{c} 0 \cdot 2748(6) \\ 0 \cdot 2987(4) \\ 0 \cdot 3176(6) \\ 0 \cdot 2496(6) \\ 0 \cdot 2907(7) \end{array}$	$\begin{array}{c} 0.047(3) \\ 0.070(2) \\ 0.044(3) \\ 0.061(3) \\ 0.066(3) \end{array}$	O(9) C(10) C(11) C(12) C(13)	$\begin{array}{c} 0.3927(5)\\ 0.2101(8)\\ 0.084(1)\\ -0.0161(9)\\ 0.0590(8) \end{array}$	$\begin{array}{c} -0.1229(7) \\ -0.303(1) \\ -0.383(1) \\ -0.262(1) \\ -0.147(1) \end{array}$	$\begin{array}{c} 0\cdot 2342(4)\\ 0\cdot 2664(6)\\ 0\cdot 2069(8)\\ 0\cdot 1550(8)\\ 0\cdot 0783(7)\end{array}$	$\begin{array}{c} 0.052(2) \\ 0.078(4) \\ 0.094(4) \\ 0.099(4) \\ 0.086(4) \end{array}$

Table 9. Non-hydrogen positional and isotropic displacement parameters for (15)

<sup>A</sup> Defines origin.

Table 10. Non-hydrogen positional and isotropic displacement parameters for (17a)

Atom	x	у	z	$U_{\rm eq}$ (Å <sup>2</sup> )	Atom	x	у	z	$U_{\rm eq}$ (Å <sup>2</sup> )
O(1)	0.5042(2)	$0.0(-)^{A}$	0.7281(3)	0.058(1)	C(35)	0.0625(5)	0.474(1)	0.5866(8)	0.095(4)
C(2)	0.4899(4)	0.1476(8)	0.6440(5)	0.050(2)	C(36)	0.1507(4)	0.391(1)	0.5616(6)	0.071(3)
C(21)	0.5893(3)	0.2523(8)	0.6727(5)	0.048(2)	C(4)	0.3578(4)	0.1406(8)	0.7846(5)	0.046(2)
C(22)	0.6305(4)	0.308(1)	0.8019(6)	0.071(3)	C(5)	0.4351(4)	-0.0062(9)	0.8106(5)	0.057(2)
C(23)	0.7222(5)	0.404(1)	0.8283(8)	0.086(3)	O(5)	0.4348(3)	-0.1156(7)	0.8908(4)	0.079(2)
C(24)	0.7712(6)	0.444(1)	0.725(1)	0.098(4)	C(6)	0.3486(4)	0.232(1)	0.9124(6)	0.051(2)
C(25)	0.7316(5)	0.388(1)	0.5958(9)	0.084(3)	C(7)	0.2309(3)	0.2252(8)	0.9063(5)	0.044(2)
C(26)	0.6391(4)	0.2922(9)	0.5714(6)	0.062(2)	C(71)	0.1778(4)	0.3104(8)	1.0018(5)	0.047(2)
N(3)	0.3966(3)	0.2307(7)	0.6808(4)	0.048(2)	C(72)	0.2361(4)	0.3740(9)	1.1225(5)	0.056(2)
C(3)	0.3476(4)	0.3530(8)	0.5960(5)	0.052(2)	C(73)	0.1865(5)	0.450(1)	$1 \cdot 2141(6)$	0.067(3)
O(3)	0.3829(3)	0.3917(7)	0.4990(4)	0.077(2)	C(74)	0.0772(5)	0.4624(9)	$1 \cdot 1872(6)$	0.064(3)
C(31)	0.2519(4)	0.4364(8)	0.6278(5)	0.049(2)	C(75)	0.0181(5)	0.404(1)	1.0681(6)	0.066(2)
C(32)	0.2624(6)	0.569(1)	0.7149(7)	0.075(3)	C(76)	0.0666(4)	0.3267(9)	0.9749(6)	0.059(2)
C(33)	0.1748(7)	0.654(1)	0.7388(9)	0.089(4)	N(8)	0.1803(3)	0.1348(7)	0.8104(4)	0.051(2)
C(34)	0.0754(7)	0.605(1)	0.6739(8)	0.092(4)	O(9)	0.2527(2)	0.0709(6)	0.7328(3)	0.051(1)

<sup>A</sup> Defines origin.

\* Copies are available from the Australian Journal of Chemistry, P.O. Box 89, East Melbourne, Vic. 3002.

<sup>21</sup> Hall, S. R., Flack, H. D., and Stewart, J. M., (Eds) 'The XTAL 3.2 Reference Manual', Universities of Western Australia, Geneva and Maryland, 1992.

(4b).  $C_{28}H_{28}N_2O_4.\frac{1}{3}CH_3CO_2C_2H_5, M$  485 · 9. Trigonal, space group P 3<sub>2</sub> ( $C_3^3$ , No. 145); a 15 · 023(6), c 10 · 656(6) Å, V 2084 Å<sup>3</sup>.  $D_c$  (Z = 3) 1 · 16 g cm<sup>-3</sup>; F(000) 774.  $\mu_{Mo}$  0 · 8 cm<sup>-1</sup>; specimen: 0 · 80 by 0 · 50 by 0 · 38 mm.  $2\theta_{max}$  45°; N 3193,  $N_o$  1908; R 0 · 055,  $R_w$  0 · 052.

'Variata'.—Steady deterioration of the periodic standards of, ultimately, c. 6% was compensated for by appropriate scaling. The solvent comprises a disordered array about the symmetry axis.

(6c).  $C_{25}H_{22}N_2O_4$ , M 414.5. Orthorhombic, space group  $P_{21}2_{12}1$  ( $D_2^4$ , No. 19); a 16.215(6), b 12.913(5), c 10.198(5) Å, V 2135 Å<sup>3</sup>.  $D_c(Z = 4)$  1.29 g cm<sup>-3</sup>; F(000) 872.  $\mu_{Mo}$  0.9 cm<sup>-1</sup>; specimen: 0.60 by 0.45 by 0.40 mm.  $2\theta_{max}$  60°; N 3477,  $N_o$  1647; R 0.039,  $R_w$  0.036.

'Variata'.— $(x, y, z, U_{iso})_{H}$  were all refined.

(7b). C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>, *M* 456 · 6. Monoclinic, space group  $P 2_1/c$  ( $C_{2h}^5$ , No. 14); *a* 12 · 005(6), *b* 7 · 906(6), *c* 26 · 73(1) Å,  $\beta$  105 · 08(4)°, *V* 2450 Å<sup>3</sup>.  $D_c(Z = 4)$  1 · 24 g cm<sup>-3</sup>; *F*(000) 968.  $\mu_{Mo}$  0 · 8 cm<sup>-1</sup>; specimen: 0 · 75 by 0 · 38 by 0 · 21 mm.  $2\theta_{max}$  50°; *N* 4311,  $N_o$  2619; *R* 0 · 041,  $R_w$  0 · 042.

'Variata'.—(x, y, z,  $U_{\rm iso})_{\rm H}$  were all refined.

(7c).  $C_{25}H_{22}N_2O_4$ , M 414.5. Triclinic, space group  $P\bar{1}$  ( $C_1^1$ , No. 2); a 12.11(1), b 10.361(4), c 10.133(4) Å,  $\alpha$  94.91(3),  $\beta$  108.24(5)°,  $\gamma$  112.26(5)°, V 1087 Å<sup>3</sup>.  $D_c(Z=2)$  1.27 g cm<sup>-3</sup>; F(000) 436.  $\mu_{Mo}$  0.8 cm<sup>-1</sup>; specimen: 0.30 by 0.32 by 0.40 mm.  $2\theta_{max}$  50°; N 3810,  $N_o$  2424; R 0.041,  $R_w$  0.042.

'Variata'.— $(x, y, z, U_{iso})_{H}$  were all refined.

(14).  $C_{21}H_{20}N_2O_4$ , M 364.4. Orthorhombic, space group  $P_{21}2_{12}1$ ; a 16.868(4), b 13.294(2), c 8.006(2) Å, V 1795 Å<sup>3</sup>.  $D_c(Z = 4)$  1.35 g cm<sup>-3</sup>; F(000) 768.  $\mu_{Mo}$  0.9 cm<sup>-1</sup>; specimen: 0.65 by 0.60 by 0.27 mm.  $2\theta_{max}$  60°; N 2963,  $N_o$  2342; R 0.038,  $R_w$  0.040.

Table 11. Non-hydrogen positional and isotropic displacement parameters for (18a)

Atom	x	у	z	$U_{\rm eq}~({\rm \AA}^2)$	Atom	x	у	z	$U_{\rm eq}~({\rm \AA}^2)$
O(1)	0.7672(2)	0.3082(2)	0.4588(4)	0.056(1)	C(35)	0.5201(4)	0.6148(4)	0.8013(9)	0.073(3)
C(2)	0.7822(3)	0.3648(3)	0.6038(7)	0.047(2)	C(36)	0.5923(3)	0.5828(3)	0.7469(9)	0.057(2)
C(21)	0.8215(3)	0.3172(3)	0.7508(7)	0.046(2)	C(4)	0.6391(3)	0.3647(3)	0.5297(7)	0.045(2)
C(22)	0.7771(3)	0.2760(3)	0.8771(8)	0.061(2)	C(5)	0.6893(3)	0.3096(3)	0.4085(7)	0.058(2)
C(23)	0.8173(5)	0.2289(4)	1.0019(9)	0.072(3)	O(5)	0.6636(2)	0.2716(3)	0.2867(6)	0.090(2)
C(24)	0.9009(5)	0.2230(4)	0.999(1)	0.077(3)	C(6)	0.5806(3)	0.4220(4)	0.4320(7)	0.045(2)
C(25)	0.9459(4)	0.2642(4)	0.873(1)	0.074(3)	C(7)	0.5004(3)	0.3950(3)	0.5002(7)	0.042(2)
C(26)	0.9062(3)	0.3110(4)	0.7490(8)	0.059(2)	C(71)	0.4209(3)	0.4331(3)	0.4580(7)	0.052(2)
N(3)	0.7006(2)	0.3993(2)	0.6435(5)	0.042(1)	C(72)	0.4169(4)	0.5157(4)	0.4028(9)	0.069(2)
C(3)	0.6976(3)	0.4696(3)	0.7423(7)	0.046(2)	C(73)	0.3424(4)	0.5512(5)	0.359(1)	0.095(3)
O(3)	0.7598(2)	0.5031(2)	0.7923(5)	0.069(1)	C(74)	0.2735(4)	0.5021(6)	0.370(1)	0.103(4)
C(31)	0.6148(3)	0.5018(3)	0.7935(7)	0.044(2)	C(75)	0.2760(4)	0.4215(5)	0.424(1)	0.099(3)
C(32)	0.5646(3)	0.4566(4)	0.8988(8)	0.060(2)	C(76)	0.3497(3)	0.3882(4)	0.468(1)	0.077(3)
C(33)	0.4912(4)	0.4905(4)	0.9558(9)	0.072(3)	N(8)	0.5032(2)	0.3324(2)	0.6034(6)	0.055(2)
C(34)	0.4700(4)	0.5689(5)	$0.907(1)^{'}$	0.077(3)	O(9)	0.5865(2)	0.3073(2)	0.6241(5)	0.056(1)

Table 12. Non-hydrogen positional and isotropic displacement parameters for (17b)

Atom	x	y	z	$U_{\rm eq}~({\rm \AA}^2)$	Atom	x	y	z	$U_{\rm eq}~({\rm \AA^2})$
O(1)	0.6745(3)	0.3400(3)	0.4179(3)	0.050(1)	C(33)	0.6783(6)	0.0565(5)	0.0072(8)	0.075(3)
C(2)	0.7095(4)	0.2910(4)	0.3027(5)	0.040(2)	C(34)	0.7825(7)	0.0442(5)	-0.0346(7)	0.071(3)
C(21)	0.8300(4)	0.2788(4)	0.3031(5)	0.042(2)	C(35)	0.8519(6)	0.1300(5)	-0.0382(6)	0.061(2)
C(22)	0.8989(6)	0.3654(5)	0.3197(6)	0.060(2)	C(36)	0.8174(5)	0.2328(5)	0.0000(6)	0.049(2)
C(23)	1.0089(5)	0.3543(7)	0.3209(7)	0.072(3)	C(4)	0.6308(4)	0.4702(4)	0.2663(4)	0.040(2)
C(24)	1.0515(7)	0.2527(8)	0.3017(9)	0.086(3)	C(5)	0.6352(5)	0.4416(4)	0.4035(5)	0.043(2)
C(25)	0.9860(6)	0.1640(6)	0.2862(8)	0.081(3)	O(5)	0.6058(3)	0.4965(3)	0.4874(3)	0.054(1)
C(26)	0.8769(6)	0.1762(5)	0.2880(6)	0.059(2)	C(6)	0.6896(4)	0.5745(4)	0.2313(5)	0.038(2)
N(3)	0.6678(3)	0.3700(3)	0.2100(3)	0.039(1)	C(7)	0.6000(5)	0.6410(4)	0.1817(5)	0.040(2)
C(3)	0.6763(4)	0.3561(4)	0.0848(5)	0.039(2)	C(71)	0.6115(6)	0.7542(5)	0.1313(6)	0.060(2)
O(3)	0.6527(3)	0.4285(3)	0.0139(3)	0.052(1)	N(8)	0.5073(4)	0.5965(4)	0.1840(4)	0.048(2)
C(31)	0.7139(4)	0.2450(4)	0.0424(4)	0.039(2)	O(9)	0.5191(3)	0.4899(3)	0.2374(3)	0.045(1)
C(32)	0.6436(5)	0.1585(5)	0.0461(6)	0.061(2)		• /	. ,		

'Variata'.— $(x, y, z, U_{iso})_H$  were all refined.

(15).  $C_{22}H_{22}N_2O_4$ , *M* 378·4. Monoclinic, space group *P*2<sub>1</sub>; *a* 9·408(4), *b* 8·610(3), *c* 11·720(2) Å,  $\beta$  90·19(2)°, *V* 949·2 Å<sup>3</sup>.  $D_c(Z=2)$  1·32 g cm<sup>-3</sup>; *F*(000) 400.  $\mu_{Mo}$  0·9 cm<sup>-1</sup>; specimen: 0·38 by 0·27 by 0·08 mm.  $2\theta_{max}$  45°; *N* 1348,  $N_o$  951; *R* 0·045,  $R_w$  0·033.

'Variata'.—Distinction between the nitrogen atom at N(8) and possible alternative sites was made on the basis of refinement behaviour. 'Observed' criterion  $I > 2\sigma(I)$ .

(17a).  $C_{24}H_{18}N_2O_4$ , M 398.4. Monoclinic, space group  $P_{21}$ ; a 12.820(4), b 7.994(5), c 10.111(7) Å,  $\beta$  102.17(4)°, V 1013 Å<sup>3</sup>.  $D_c(Z=2)$  1.31 g cm<sup>-3</sup>; F(000) 416.  $\mu_{Mo}$  0.9 cm<sup>-1</sup>; specimen: 0.45 by 0.27 by 0.15 mm.  $2\theta_{max}$  50°; N 1922,  $N_o$  1236; R 0.039,  $R_w$  0.037. 'Variata'.—( $x, y, z, U_{iso}$ )<sub>H</sub> were all refined.

(18a).  $C_{24}H_{18}N_2O_4$ , M 398·4. Orthorhombic, space group  $P_{212121}$ ; a 16·38(1), b 15·989(7), c 7·631(3) Å, V 1998 Å<sup>3</sup>.  $D_c(Z = 4)$  1·32 g cm<sup>-3</sup>; F(000) 832.  $\mu_{Mo}$  0·9 cm<sup>-1</sup>; specimen: 0·40 by 0·11 by 0·75 mm.  $2\theta_{max}$  50°; N 2018,  $N_o$  1361; R 0·042,  $R_w$  0·043. 'Variata'.—( $x, y, z, U_{iso}$ )<sub>H</sub> were all refined.

(17b).  $C_{19}H_{16}N_2O_4$ , M 336·4. Orthorhombic, space group  $P_{21}2_{12}$ ; a 12·298(5), b 12·274(4), c 10·824(5) Å, V 1634 Å<sup>3</sup>.  $D_c(Z = 4)$  1·37 g cm<sup>-3</sup>; F(000) 704.  $\mu_{Mo}$  1·0 cm<sup>-1</sup>; specimen: 0·35 by 0·32 by 0·18 mm.  $2\theta_{max}$  50°; N 1656,  $N_o$  1262; R 0·049,  $R_w$  0·051. 'Variata'.—( $x, y, z, U_{iso}$ )<sub>H</sub> were all refined.

#### Structural Commentary

The results of the room-temperature single-crystal X-ray studies are presented above, and in summary in Fig. 1 and Table 2, which contains the molecular core geometries. In all cases, the asymmetric unit is a single molecule, with stoichiometries and connectivities consistent with the above formulations; in most cases hydrogen atoms have been located and refined in  $(x, y, z, U_{iso})$ . The crystals of (7b) and (7c), belonging to centrosymmetric space groups are racemic, presumably consequent of relative insolubility and less than 100% optical purity of the sample; the remainder crystallize in polar space groups, so that, at least within the single crystal studied, all molecules have the same chirality. Presentation of the results follows adoption of the common chirality of the parent oxazolidinone (1) with the *ad hoc* common numbering scheme given in Table 2 for the common bicyclic core; in all cases, phenyl ring C(21-26) lies away from the reader and is assigned a negative sign in the description of deviations from the associated heterocycle, while substituents of the other fused ring are assigned positive deviations if directed toward O(5). The following comments may be made.

The parent oxazolidinone ring is effectively planar throughout the series of compounds studied, the higher  $\chi^2$  values lying generally among the more precisely determined members; in no case does the deviation of any defining atom from the ring plane exceed  $0 \cdot 1_5$  Å. Distances within the ring do not vary non-trivially although it may be no accident that C(2)-N(3) in (17a,b) and (18a) exhibit the longest values associated with this parameter; the endocyclic angles are similarly uniform. The exocyclic angles at N(3) are essentially equivalent in (15) and (17b); in the remainder, in which the carbonyl disposition is reversed, they become quite unsymmetrical, C(4)-N(3)-C(3) being much the larger. At C(5), the exocyclic angle C(4)-C(5)-O(5) is slightly larger than O(1)-C(5)-O(5) throughout the series. C(6)-C(4)-O(9) varies over a range of about 3°, being smallest in (17a,b), (18a) [and, perhaps, (4a)]; variations of similar magnitude are found among the other exocyclic angles at C(4). Some variation is observed in the deviation of O(5) from the ring plane, also in that for C(21); the plane of phenyl 2 lies effectively perpendicular to the oxazolidinone ring throughout the

series. Carbonyl 3 plane lies quasi-coplanar with the ring, the maximum dihedral being  $26.9(4)^{\circ}$  in (4a), while the associated phenyl ring lies quasi-normal and quasi-parallel to the fused ring [(15) and (17b) excepted]. Angles about C(3) vary only slightly throughout the series N(3)-C(3)-C(31) being consistently just less than 120°, as might be expected from electron pair repulsion theory, while the others are slightly greater.

The other ring plane lies quasi-normal to the first, as might be expected, in most cases [excluding (17a,b) and (18a)] adopting a quasi-'envelope' conformation with C(7) the deviant atom; the fused ring in (15) is a chair, while in (14) it is a pseudo-envelope, with C(10) deviant. About C(7), the non-hydrogen angle sum is generally close to 326°, as also N(8), where [excepting (17a,b) and (18a)] the spread is rather greater (323–331°).

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