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

Standard deviations are given in parentheses.

Cl–C(2)	1·731 (3)	O(1)–C(5)	1·366 (3)
O(1)–C(7)	1·436 (5)	O(2)–C(8)	1·245 (3)
O(3)–C(18)	1·370 (3)	O(3)–C(21)	1·433 (4)
N(1)–C(1)	1·378 (4)	N(2)–C(8)	1·335 (3)
N(2)–C(9)	1·473 (3)	N(3)–C(12)	1·470 (3)
N(3)–C(13)	1·473 (4)	N(3)–C(14)	1·456 (3)
C(1)–C(2)	1·387 (4)	C(1)–C(6)	1·381 (4)
C(2)–C(3)	1·365 (4)	C(3)–C(4)	1·377 (3)
C(4)–C(5)	1·405 (3)	C(4)–C(8)	1·497 (3)
C(5)–C(6)	1·370 (3)	C(9)–C(10)	1·531 (4)
C(9)–C(11)	1·523 (4)	C(9)–C(12)	1·539 (3)
C(14)–C(15)	1·507 (4)	C(15)–C(16)	1·383 (4)
C(15)–C(20)	1·377 (4)	C(16)–C(17)	1·364 (4)
C(17)–C(18)	1·376 (4)	C(18)–C(19)	1·373 (4)
C(19)–C(20)	1·389 (4)		

C(5)–O(1)–C(7)	118·5 (2)	C(18)–O(3)–C(21)	117·8 (2)
C(8)–N(2)–C(9)	126·8 (2)	C(12)–N(3)–C(13)	111·1 (2)
C(12)–N(3)–C(14)	112·7 (2)	C(13)–N(3)–C(14)	110·6 (2)
N(1)–C(1)–C(2)	122·9 (2)	N(1)–C(1)–C(6)	120·0 (2)
C(2)–C(1)–C(6)	117·2 (2)	Cl–C(2)–C(1)	117·9 (2)
Cl–C(2)–C(3)	120·3 (2)	C(1)–C(2)–C(3)	121·7 (3)
C(2)–C(3)–C(4)	122·1 (2)	C(3)–C(4)–C(5)	115·9 (2)
C(3)–C(4)–C(8)	116·5 (2)	C(5)–C(4)–C(8)	127·6 (2)
O(1)–C(5)–C(4)	116·6 (2)	O(1)–C(5)–C(6)	121·2 (2)
C(4)–C(5)–C(6)	122·2 (2)	C(1)–C(6)–C(5)	120·9 (2)
O(2)–C(8)–N(2)	122·4 (2)	O(2)–C(8)–C(4)	119·6 (2)
N(2)–C(8)–C(4)	117·9 (2)	N(2)–C(9)–C(10)	110·9 (2)
N(2)–C(9)–C(11)	110·3 (2)	N(2)–C(9)–C(12)	104·7 (2)
C(10)–C(9)–C(11)	110·8 (2)	C(10)–C(9)–C(12)	107·0 (2)
C(11)–C(9)–C(12)	112·9 (2)	N(3)–C(12)–C(9)	114·5 (2)
N(3)–C(14)–C(15)	112·8 (2)	C(14)–C(15)–C(16)	121·4 (2)
C(14)–C(15)–C(20)	121·3 (2)	C(16)–C(15)–C(20)	117·2 (2)
C(15)–C(16)–C(17)	121·6 (3)	C(16)–C(17)–C(18)	120·6 (3)
O(3)–C(18)–C(17)	116·1 (2)	O(3)–C(18)–C(19)	124·5 (2)
C(17)–C(18)–C(19)	119·4 (2)	C(18)–C(19)–C(20)	119·2 (2)
C(15)–C(20)–C(19)	121·9 (2)		

in the plane. The distance between the tertiary amino nitrogen and the center of the ring, 5·83 Å, is shorter than that in YM-09151-2, 6·26 Å.

An intramolecular hydrogen bond between the amide N(2) and methoxyl O(1) forms a six-membered ring fused with the benzene ring *A*. This type of hydrogen bond is also observed in the benzamide neuroleptics (Furuya *et al.*, 1982; Cesario, Pascard, Moukhtari & Jung, 1981). The N(2)—O(1) distance 2·662 (3) Å is rather shorter than in YM-09151-2, 2·680 (3) Å, and metoclopramide, 2·683 (6) Å. Thus, the benzamide moiety constitutes a rigid part of the molecule by this strong hydrogen bond. The benzene ring *B* is almost planar with maximum atomic deviation 0·014 Å.

It is interesting that the overall structural features of this inactive compound are similar to those of the potent neuroleptic drug YM-09151-2.

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The Polymorphism of 4-Chloro-1,2-dinitrobenzene: Structures of the γ and β Forms

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Abstract. $C_6H_3ClN_2O_4$, $M_r = 202·4$, λ(Mo $K\alpha$) = 0·71069 Å, $F(000) = 408$; γ form: orthorhombic, $P2_12_12_1$, $a = 12·11$ (2), $b = 5·57$ (1), $c = 11·94$ (2) Å, $V = 805·4$ Å^3, $Z = 4$, $D_m = 1·64$, $D_x = 1·67$ Mg m^{-3}, $\mu = 0·395$ mm^{-1}. β form: monoclinic, $P2_1/c$, $a = 7·64$ (1), $b = 7·82$ (1), $c = 14·82$ (1) Å, $\beta = 114·0$ (5)°, $V = 808·9$ Å^3, $D_m = 1·67$, $D_x = 1·66$ Mg m^{-3}, $\mu = 0·394$ mm^{-1}. For γ, $R = 0·033$ for 1053 observed reflexions; for β, $R = 0·065$ for 762 observed reflexions. The molecules in the two polymorphs differ only slightly in shape and dimensions; packing in γ comprises interleaved molecules, in β molecules in layers. Both structures involve close N···O and Cl···O intermolecular contacts. Because of repulsion of O atoms in adjacent rings, the nitro groups rotate relative to the aromatic rings.

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Introduction. The investigation of this compound forms part of a series of studies on nitro compounds which exhibit polymorphism. Groth (1917) has described three polymorphs of the title compound stating that the most stable is the orthorhombic, γ, form with a melting point of 311·5 K. Axial ratios for two monoclinic forms α, β are given by Groth. Elsewhere the melting points of the α, β and γ forms have been given as 309, 310 and 313 K respectively (*Dictionary of Organic Compounds*, 1965).

Experimental. Recrystallization of a commercial sample yielded orthorhombic crystals, elongated parallel to **b** (m.p. 311·5–313 K) showing the forms $\{100\}$ $\{101\}$ $\{110\}$ $\{111\}$; this was the γ form designated by Groth. A single crystal of this form was maintained at 308 K without phase transition. From a hot supersaturated solution in ethanol with rapid stirring while cooling, monoclinic crystals were obtained. Immediate separation from the liquid was necessary to prevent transformation *via* the solution phase to the γ form. These crystals which melted at 310 K were invariably twinned on (001) and showed easy cleavage parallel to (100). This form which was designated β was found to transform slowly in the dry state at room temperature by an overgrowth of tiny randomly oriented crystals of the γ form. These small crystals projected from the faces of the parent crystal like bristles suggesting transition through the vapour phase. Attempts to prepare identifiable samples of the α form were unsuccessful even by rapid cooling of either solutions, molten liquid or the vapour. A possible batch underwent rapid solid-state transformation before examination was possible. Crystals of the β form suitable for X-ray investigation were obtained by careful separation of twinned samples.

Density measured by flotation. Oscillation and Weissenberg photographs with Cu $K\alpha$ ($\lambda = 1{\cdot}542$ Å) gave cell dimensions and space groups of both γ and β polymorphs. Intensity data measured on the STADI-2 two-circle diffractometer with graphite-monochromatized Mo $K\alpha$ for the two polymorphs using crystals sealed in glass capillaries. In both cases separate standards for each layer, recorded every ten measurements, showed variation of no more than 1%. For γ form, 1334 intensities ($2\theta_{\max} = 60°$) measured for layers $k = 0$–8 and, after merging and omission of those for which $I < 3\sigma(I)$, 1053 significant values retained. For β crystal, 1413 measurements ($2\theta_{\max} = 60°$) on layers $k = 0$–8 reduced to 762 significant values by the same rejection criteria; in this case using another crystal, layer $l = 0$ was also measured and used for physical scaling of b layers.

Solutions of crystal structures obtained by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) which gave positions of all atoms other than H. *SHELX*76 (Sheldrick, 1976) used for data reduction and also for full-matrix least-squares refinement of structures (on F) including positions and anisotropic U_{ij} for non-H atoms. $(F_o - F_c)$ maps used to locate H atoms which were included, but not refined, at calculated positions (C—H fixed at 1·08 Å and individual isotropic U values). Finally for γ form, interlayer scale factors for data-collection layers refined. Refinements terminated when parameter shifts $\leq 0{\cdot}01$ e.s.d. $R = 0{\cdot}033$ (γ), 0·065 (β); for both refinements unit weights used. On final $(F_o - F_c)$ map largest features $< 0{\cdot}3$ e Å^{-3} (β) and $< 0{\cdot}2$ e Å^{-3} (γ). Atomic scattering factors from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates are listed in Table 1.*

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^4$)

	x	y	z	U_{eq}
(a) γ Form				
Cl	2700 (1)	4127 (2)	5766 (1)	615
C(1)	757 (2)	−1899 (5)	4276 (2)	380
C(2)	539 (2)	−1107 (6)	5357 (2)	370
C(3)	1131 (2)	733 (6)	5825 (2)	418
C(4)	1957 (2)	1786 (6)	5190 (2)	437
C(5)	2191 (2)	1025 (7)	4112 (2)	484
C(6)	1586 (2)	−837 (7)	3653 (2)	463
N(1)	76 (2)	−3736 (5)	3725 (2)	463
N(2)	−269 (2)	−2341 (6)	6089 (2)	486
O(1)	540 (2)	−5100 (5)	3079 (2)	667
O(2)	−921 (2)	−3710 (5)	3922 (2)	601
O(3)	−245 (2)	−4512 (5)	6127 (2)	691
O(4)	−883 (2)	−1079 (6)	6653 (2)	696
H(1)	960 (2)	1339 (6)	6667 (2)	
H(2)	1757 (2)	−1459 (7)	2814 (2)	
H(3)	2843 (2)	1878 (7)	3640 (2)	

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
(b) β Form				
Cl	2530 (4)	2077 (4)	7249 (2)	839
C(1)	2538 (11)	−2586 (11)	8994 (6)	536
C(2)	2425 (10)	−962 (11)	9347 (5)	447
C(3)	2403 (11)	480 (11)	8835 (5)	502
C(4)	2512 (12)	287 (11)	7929 (6)	552
C(5)	2604 (12)	−1282 (12)	7552 (6)	620
C(6)	2626 (12)	−2768 (12)	8081 (6)	564
N(1)	2709 (11)	−4148 (11)	9586 (6)	684
N(2)	2189 (10)	−777 (10)	10290 (5)	578
O(1)	1795 (11)	−5368 (10)	9157 (6)	998
O(2)	3808 (10)	−4053 (9)	10464 (5)	770
O(3)	1024 (9)	−1683 (9)	10413 (4)	795
O(4)	3135 (9)	334 (10)	10851 (4)	844
H(1)	2313 (11)	1731 (11)	9122 (5)	
H(2)	2714 (12)	−4018 (12)	7793 (6)	
H(3)	2657 (12)	−1370 (12)	6837 (6)	

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

Discussion. Bond distances and angles in the two polymorphs are illustrated in Fig. 1, values for the γ form having appreciably higher accuracy than those for the β form. Only in one instance does the difference between corresponding distances or angles exceed twice the combined e.s.d.'s.

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* Lists of structure factors and anisotropic U_{ij} have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42339 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Considerable deviations from planarity occur in the molecules of both polymorphs, rotations of the nitro groups relative to the aromatic rings arising from the repulsion of O atoms in adjacent groups. In the β form the two nitro-group rotations have similar values but one of those, N(1)O(1)O(2) (Table 2), in the γ form is significantly smaller. In addition, adjacent C—N bonds in both polymorphs are bent relative to the plane of the nucleus away from each other (Table 3). The intramolecular contacts O(2)···O(3) are similar in the two forms [γ, 2·793 (3); β, 2·798 (10) Å] and are in good agreement with twice the van der Waals radius of oxygen, 1·40 Å (Bondi, 1964). No other structure involving adjacent nitro groups on a benzene nucleus has been reported, therefore direct comparison of the nitro-group rotations is not possible but numerous examples of nitro-group rotations greater than those observed here have been reported.

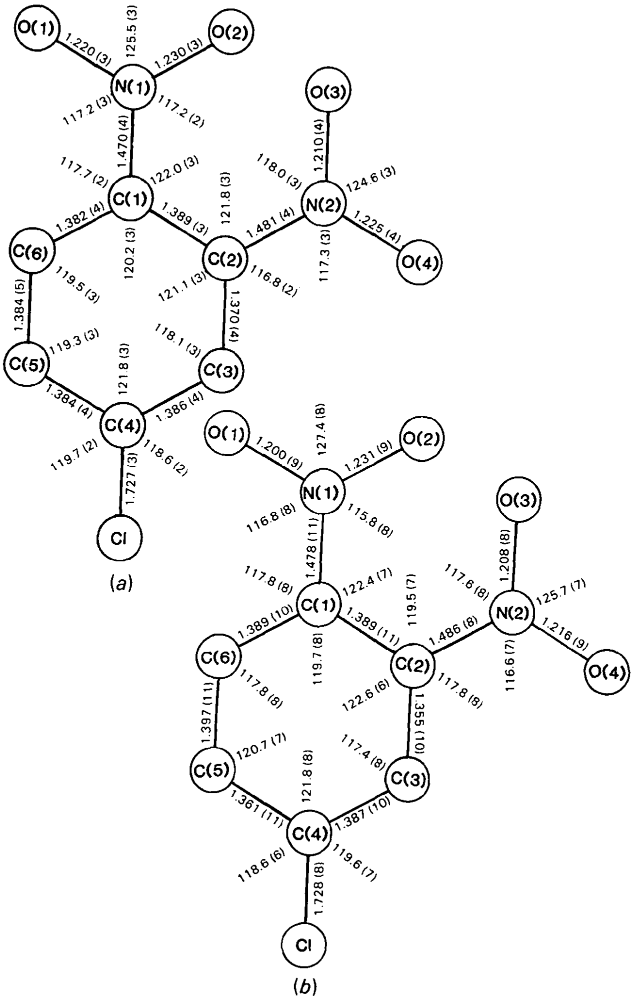

Fig. 1. Bond distances and angles in (*a*) γ-4-chloro-1,2-dinitrobenzene and (*b*) β-4-chloro-1,2-dinitrobenzene.

Table 2. *Torsional angles* (°) *in* γ *and* β *forms*

	γ Form	β Form
C(6)C(1)N(1)O(1)	37·5 (5)	44·5 (5)
C(6)C(1)N(1)O(2)	−136·7 (5)	−133·9 (5)
C(2)C(1)N(1)O(1)	−146·6 (5)	−139·7 (5)
C(2)C(1)N(1)O(2)	36·2 (5)	41·9 (5)
C(1)C(2)N(2)O(3)	44·6 (5)	44·5 (5)
C(3)C(2)N(2)O(3)	−130·1 (5)	−131·3 (5)
C(1)C(2)N(2)O(4)	−138·5 (5)	−138·1 (5)
C(3)C(2)N(2)O(4)	46·9 (5)	45·6 (5)

Table 3. *Distances of atoms* (Å) *from the least-squares plane through* C(1)C(2)C(3)C(4)C(5)C(6) (*average e.s.d.* γ 0·004, β 0·01 Å)

	γ Form	β Form
Cl	−0·024	0·029
C(1)	−0·003	0·004
C(2)	0·002	−0·003
C(3)	0·000	−0·002
C(4)	−0·002	0·007
C(5)	0·001	−0·006
C(6)	0·001	0·001
N(1)	−0·104	0·108
N(2)	0·134	−0·101
O(1)	0·437	0·917
O(2)	−0·821	−0·569
O(3)	0·968	0·611
O(4)	−0·577	−0·918

It has long been recognized that the presence of an electron-withdrawing substituent on the benzene ring has the effect of increasing the endocyclic angle at the C atom involved and of shortening adjacent ring bonds. The effect, which has been explained by Carter, McPhail & Sim (1966), is shown in the present structures although the presence of three electronegative groups introduces competing effects. The angles at C(1), C(2) and C(4) are all greater than 120°; there is, however, no obvious explanation of the shortening of the C(2)–C(3) bond.

The two polymorphs have quite different molecular packing arrangements (Fig. 2). The β form has a layer structure, with molecular planes parallel to (100). The closest approaches are between molecules related by centres of symmetry at 0,0,0 and $\frac{1}{2},\frac{1}{2}$,0. The distances involved are N(2)···O(3), 2·95 (1) Å and N(1)···O(2), 3·04 (1) Å. The contacts are approximately normal to the π systems of the nitro groups involved and are shorter than the combined van der Waals distances, 3·25 Å (Bondi, 1964). In the γ polymorph the molecules are interleaved with close contacts, 3·049 (3) Å, between N(1)···O(1) of molecules related by the 2_1 axis parallel to **b**. Both polymorphs have short Cl···O contacts; 3·06 (1) Å in β between Cl···O(4) of molecules related by the *c*-glide plane and 3·073 (3) Å in the γ form between Cl···O(2) of molecules related by 2_1 parallel to **a**. Similar short Cl···O contacts have been reported in picryl chloride (Willis, Stewart, Ammon & Preston, 1971) and 1,3-dichloro-2,4,6-trinitrobenzene (Holden & Dickinson, 1967).

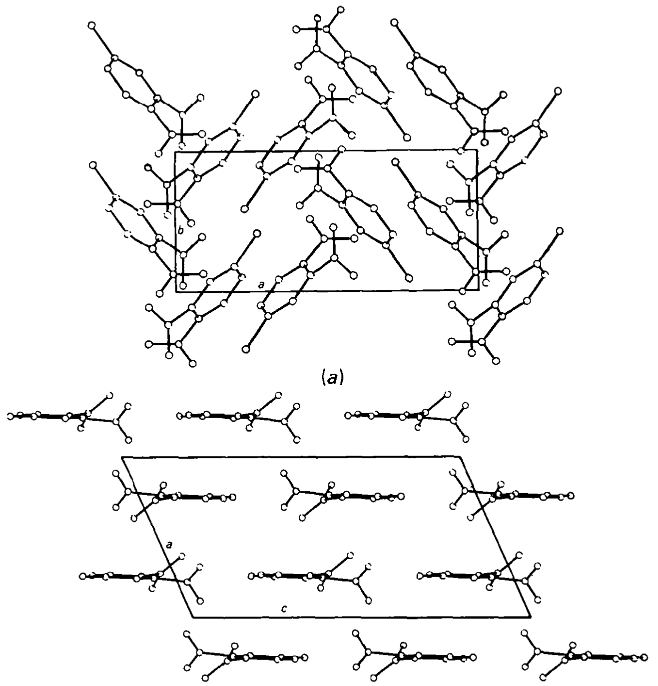

Fig. 2. Packing of molecules in (a) γ-4-chloro-1,2-dinitrobenzene and (b) β-4-chloro-1,2-dinitrobenzene.

The polymorphs appear to contain alternative and quite different modes of packing of almost identical molecules. Similar intermolecular interactions are involved in the two structures giving rise to closely similar unit-cell volumes.

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Benzyl (±)-1α-Hydroxy-7β-phenoxyacetamido-1-carbacephalosporanate*

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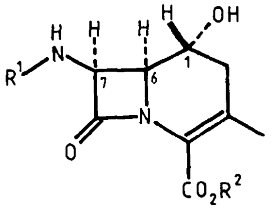
Abstract. $C_{24}H_{24}N_2O_6$, $M_r = 436{\cdot}47$, monoclinic, $I2/c$, $a = 20{\cdot}900\,(3)$, $b = 10{\cdot}340\,(2)$, $c = 24{\cdot}226\,(5)$ Å, $\beta = 120{\cdot}82\,(2)°$, $V = 4496\,(1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}29$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}10$ mm^{-1}, $F(000) = 1840$, $T = 293$ K, $R = 0{\cdot}045$ for 2466 reflections. The β-lactam N atom is displaced by 0·20 (1) Å from the plane of the three atoms to which it is bonded; despite this, the compound lacks antibiotic activity. The N—C and C—O bond lengths show that there is less $p\pi$ overlap in the β-lactam than in the side-chain amide. There are two intermolecular hydrogen bonds.

Introduction. 1-Carbacephem derivatives have high levels of antibacterial activity (Doyle *et al.*, 1980). The 1α-hydroxy-1-carbacephem system (1) was prepared in the hope that it would display enhanced activity by analogy with cephen *R*-sulfoxides (de Koning, Marx, Poot, Smid & Vermeij, 1977) but, in the event, proved to be inactive (Bremner, Colvin, Gallacher & MacLeod, 1983). An X-ray study of the title compound [(1): $R^1 = \mathrm{PhOCH_2CO}$ and $R^2 = \mathrm{PhCH_2}$] was undertaken to confirm the structure and relative stereochemistry and to obtain geometrical details of the β-lactam system.



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[*] Benzyl (±)-5α-hydroxy-3-methyl-8-oxo-7β-phenoxyacetamido-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylate.

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