Table 3. *Densities for* (I)–(VI)

	Experimental ($g\ cm^{-3}$)	Space group (Z)	Calculated** ($g\ cm^{-3}$)	Δ(%)‡
(I)	1·58*	$P\bar{1}$ (2)†	1·582	−0·13
(II)	1·62*	$P\bar{1}$ (2)†	1·567	3·27
(III)	1·547§††	$C2/c$(12)¶	1·574	−1·75
		$P\bar{1}$ (2)†	1·587	−2·58
(IV)	1·75*	$P\bar{1}$ (2)†	1·697	3·03
(V)	1·694‡‡	$P2_1/c$(4)¶	1·692	0·12
		$P\bar{1}$ (2)†	1·680	0·88
(VI)	1·739‡‡	$P\bar{1}$ (4)¶	1·745	−0·35
		$P\bar{1}$ (2)†	1·696	2·47
		$P2_1/c$ (4)†	1·724	0·87

* Determined by neutral buoyancy solvent methods (Paquette *et al.*, 1986).

† Space group (Z) used for *MOLPAK* search.

‡ $\Delta = [(\rho_{exp} - \rho_{calc})/\rho_{exp}] \times 100$.

§ X-ray density calculated from unit-cell colume.

¶ Actual crystal space group; *MOLPAK* performed prior to *WMIN* calculations.

** Density obtained from a *WMIN* refinement of the structure in the indicated space group.

†† 1·75 g cm^{-3} reported previously, see * above.

‡‡ X-ray density calculated from unit-cell volume (Paquette *et al.*, 1986). The solvent-derived density of (VI) is 1·76 g cm^{-3}, see * above.

groups apparently do not increase packing efficiency by tucking the substituents under the basket rim as was previously suggested. That the calculated densities for the dinitro isomers (I)–(III) are within about 0·02 g cm^{-3} of each other indicates the crystal packing efficiencies are likely to be very similar and, therefore, are not influenced by the placement of the nitro-group substituents on the basket rim.

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Structure of 1-(4-Chlorobenzoyloxy)-4,5-dimethyl-1,2,3-triazole (CBODT)

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Abstract. 4,5-Dimethyl-1,2,3-triazolyl *p*-chlorobenzoate, $C_{11}H_{10}ClN_3O_2$, $M_r = 251·67$, orthorhombic, $P2_12_12_1$, $a = 13·675$ (2), $b = 11·018$ (2), $c = 7·990$ (1) Å, $V = 1203·86$ Å^3, $Z = 4$, $D_m = 1·398$, $D_x = 1·388$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 3·17$ cm^{-1}, $F(000) = 520$, $T = 298$ K, final $R = 0·057$ for 1176 unique reflections. The mean plane of the chlorophenyl ring is almost perpendicular [95·6 (2)°] to that of the triazole ring but is almost coplanar [7·3 (2)°] with that of the ester group. The latter forms an angle of 89·8 (2)° with the least-squares plane of the dimethyltriazole group.

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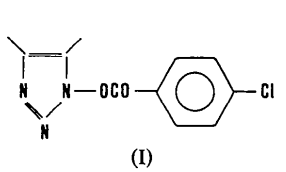
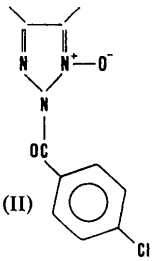
Introduction. The title compound (I) (hereafter CBODT) was prepared by lead tetraacetate oxidation of the corresponding hydroxyiminoaroylhydrazone of biacetyl within the framework of a systematic investigation of a series of compounds with different substituents (H, CH_3, Cl, CH_3O, NO_2). Structure assignment from ^1H and ^{13}C NMR data was difficult since all three possible structures (I), (II) and (III) could coexist (Nagarajan, Wilson & Rinehart, 1985; Horiki, 1977). In order to identify the real structure in the solid state an X-ray analysis was undertaken. The interest in the 1-aroyloxy-4,5-dimethyl-1,2,3-triazoles results from their use as aroyl transfer agents (Takeda, Tsuboyama, Hoshino, Kishino & Ogura, 1987; MacCarthy, Hegarthy & Hathaway, 1977).



(I)



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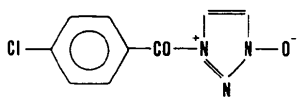

(III)

Experimental. Pure colourless crystals, size 0·5 × 0·5 × 0·8 mm. D_m measured by flotation in KBr solution, computer-controlled Philips PW 1100 four-circle single-crystal diffractometer, graphite-monochromated Mo $K\alpha$, $\theta/2\theta$ scan mode; scan width 1·3°, scan speed 0·08° s^{-1}; lattice parameters and standard deviations were calculated by least-squares analysis with *LATCON* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) of the θ angles of 92 strong reflections in the θ range 9–18°. Absorption correction not applied; 4931 reflections (1239 independent) were measured in the range $\theta = 3$–25°, index range $h = -16 \rightarrow 16$, $k = -13 \rightarrow 13$, $l = 0 \rightarrow 9$; no significant variation of intensity in the three standard reflections ($00\bar{2}$, $02\bar{1}$, 020) measured every 120 min; correction for Lorentz and polarization factors calculated with *DATRED* (Main, 1970). $R_{int} = 0{\cdot}057$ from 4018 equivalent reflections, 1176 reflections were recognized as observed and 63 as unobserved with $F_o < 4\sigma(F_o)$ [$\sigma(F_o)$ from counting statistics]. The structure was solved by direct phase determination with the *MULTAN* system (Main, Lessinger, Woolfson, Germain & Declercq, 1977); refinement based on F magnitudes by blocked full-matrix least-squares calculation with *SHELX*76 (Sheldrick, 1976). H atoms fixed in calculated positions (C—H = 0·96 Å) with fixed isotropic temperature factors derived from those of the C atoms to which they are bonded. All non-H atoms were anisotropically refined; 154 parameters; weighting scheme $w = 1/[\sigma^2(F_o) + gF_o^2]$ with $g = 0{\cdot}0208$; final $R = 0{\cdot}057$, $wR = 0{\cdot}076$, $S = 0{\cdot}414$, $(\Delta/\sigma)_{max} = 0{\cdot}032$, residual $\Delta\rho$ peaks from −0·31 to +0·25 e Å^{-3}; the correct enantiomer was chosen on the basis of the smaller value of the quantity $RG = (\sum w\Delta F^2/\sum wF_o^2)^{1/2}$ which was 0·0994 for the proposed structure while for the second enantiomer it was 0·1013; no secondary extinction, atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The best-plane parameters given in the deposited data were calculated with the program *BP*70 (Ito & Sugawara, 1983).

Discussion. The final positional and equivalent isotropic temperature coefficients are given in Table 1.* Interatomic distances and angles are given in Table 2. A clinographic projection of the molecule with the atomic numbering is shown in Fig. 1, while a clinographic projection of the unit cell showing the molecular packing is given in Fig. 2. The predominant feature of the molecular configuration is the distribution of all atoms on two almost perpendicular planes. The mean plane of the dimethyltriazole group forms an angle of 85·4 (1)° with that of the remaining part of the molecule. The plane of the ester group is inclined at 7·1 (2)° to the mean plane of the phenyl ring and is perpendicular [89·4 (2)°] to that of the triazole group. The chlorophenyl ring is planar to within 0·020 (3) Å, while the dimethyltriazole ring is planar to within 0·012 (4) Å. In the triazole ring system, N(1) is trigonal coplanar with the O(2), N(2) and C(8) atoms. Also the distances N(1)—O(1) = 1·385 (5) and O(1)—C(3) = 1·409 (6) Å are almost identical to the corresponding values of 1·383 (11) and 1·418 (13) Å found in 1-(benzoyloxy)benzotriazole (MacCarthy *et al.*, 1977). This remarkably long O(1)—C(3) distance explains the facile breaking of this bond in hydrolysis and aminolysis reactions of 1-amino-1,2,3-triazoles (Theocharis, 1987). The perpendicular arrangement of the planes of the triazole ring and the ester group leads to an N(2)—C(3) separation of 3·12 (1) Å, which agrees very well with the corresponding value of 3·02 Å in 1-(benzoyloxy)benzotriazole (MacCarthy *et al.*, 1977). This distance does not permit any interaction between the nucleophilic N(2) and the carbonyl group; hence (I) is the only structure existing in the solid state. The same structural assignment was also reported by MacCarthy

* Lists of structure amplitudes, anisotropic thermal parameters of the non-H atoms, coordinates and isotropic temperature factors for H atoms and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44697 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å²) *for the non-*H *atoms in CBODT*

	x	y	z	B_{eq}*
Cl	−0·2717 (1)	0·0276 (1)	0·6942 (2)	5·8
O(1)	0·2104 (2)	0·0419 (3)	0·7603 (5)	4·3
O(2)	0·1939 (3)	0·2005 (4)	0·5794 (6)	6·4
N(1)	0·3082 (3)	0·0751 (3)	0·7677 (5)	3·8
N(2)	0·3713 (3)	0·0263 (4)	0·6594 (6)	5·0
N(3)	0·4553 (3)	0·0753 (4)	0·6981 (6)	4·8
C(1)	0·4435 (3)	0·1536 (4)	0·8302 (5)	3·9
C(2)	0·3468 (3)	0·1544 (3)	0·8764 (5)	3·6
C(3)	0·1563 (3)	0·1207 (4)	0·6576 (6)	4·2
C(4)	0·0514 (3)	0·0896 (4)	0·6659 (5)	3·6
C(5)	−0·0110 (4)	0·1560 (4)	0·5623 (6)	4·6
C(6)	−0·1115 (4)	0·1350 (5)	0·5681 (6)	4·7
C(7)	−0·1465 (3)	0·0496 (4)	0·6805 (6)	4·1
C(8)	−0·0857 (3)	−0·0150 (4)	0·7840 (6)	4·4
C(9)	0·0150 (3)	0·0051 (4)	0·7779 (6)	4·1
C(10)	0·5279 (4)	0·2219 (5)	0·8994 (8)	5·5
C(11)	0·2912 (5)	0·2174 (5)	1·0090 (8)	5·2

* $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in CBODT*

Cl–C(7)	1·733 (5)	O(1)–C(3)	1·409 (6)
N(1)–N(2)	1·337 (6)	C(3)–O(2)	1·196 (6)
N(2)–N(3)	1·307 (6)	C(3)–C(4)	1·476 (6)
N(3)–C(1)	1·371 (6)	C(4)–C(5)	1·398 (6)
C(1)–C(2)	1·372 (6)	C(5)–C(6)	1·388 (7)
C(1)–C(10)	1·475 (7)	C(6)–C(7)	1·384 (7)
C(2)–C(11)	1·476 (7)	C(7)–C(8)	1·370 (7)
C(2)–N(1)	1·339 (5)	C(8)–C(9)	1·390 (6)
N(1)–O(1)	1·385 (5)	C(9)–C(4)	1·381 (6)

O(1)–N(1)–N(2)	119·1 (3)	C(4)–C(3)–O(2)	127·9 (4)
O(1)–N(1)–C(2)	125·4 (4)	O(2)–C(3)–O(1)	122·1 (4)
N(2)–N(1)–C(2)	115·4 (4)	C(3)–C(4)–C(5)	116·5 (4)
N(1)–N(2)–N(3)	104·1 (4)	C(3)–C(4)–C(9)	122·5 (4)
N(2)–N(3)–C(1)	110·4 (4)	C(9)–C(4)–C(5)	120·9 (4)
C(2)–C(1)–N(3)	108·7 (4)	C(4)–C(5)–C(6)	119·8 (4)
C(2)–C(1)–C(10)	130·3 (4)	C(5)–C(6)–C(7)	118·4 (5)
N(3)–C(1)–C(10)	121·0 (4)	C(6)–C(7)–C(8)	122·0 (4)
C(1)–C(2)–C(11)	133·6 (4)	C(6)–C(7)–Cl	118·6 (4)
N(1)–C(2)–C(1)	101·7 (4)	C(8)–C(7)–Cl	119·4 (4)
N(1)–C(2)–C(11)	124·7 (4)	C(7)–C(8)–C(9)	119·9 (4)
N(1)–O(1)–C(3)	111·6 (3)	C(8)–C(9)–C(4)	119·0 (4)
C(4)–C(3)–O(1)	110·0 (4)		

et al. (1977), while the possible structure (II), found in analogous benzotriazoles (Nagarajan *et al.*, 1985), could not be identified, at least in the solid state. The overall geometry of the triazole ring agrees well with average values for 1,2,3-triazoles (Wamhoff, 1984). The bond orders in the triazole ring have been evaluated using a bond-length *vs* bond-order plot (Burke-Laing & Laing, 1976) and assuming all atoms to have sp^2 hybridization (Fig. 3). The bond orders thus obtained are in very good agreement with those found in 1-hydroxybenzotriazole (Bosch, Jung & Winter, 1983). From the bond-order values it is concluded that there is significant electron delocalization in the ring. The tri-coordinate N(1) has its p electron delocalized into the π cloud, thus causing the increased double-bond character of the N(1)–C(2) and N(1)–N(2) bonds (Burke-Laing & Laing, 1976). The bond-order values show that no simple valence-bond structure can be drawn and the 1-aroyloxy-1,2,3-triazole structure determined cannot be described uniquely by formula (I).

The geometrical features of the benzene ring are in good agreement with the usually accepted values with mean bond length of 1·385 Å and mean angle of 120·0°. The Cl atom has a deviation of 0·06 (1) Å from the benzene ring and the Cl–C(7) bond length of 1·735 (5) Å is identical to that found in 3-(*p*-chlorophenyl)-3a-methyl-4-oxo-5,6,6a-triphenyl-3a,4-dihydrocyclopenta[2,3-*d*]isoxazoline (Bozopoulos, Kokkou & Rentzeperis, 1980).

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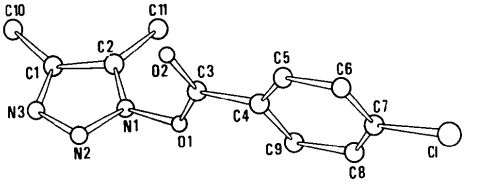

Fig. 1. Clinographic projection of the CBODT molecule.

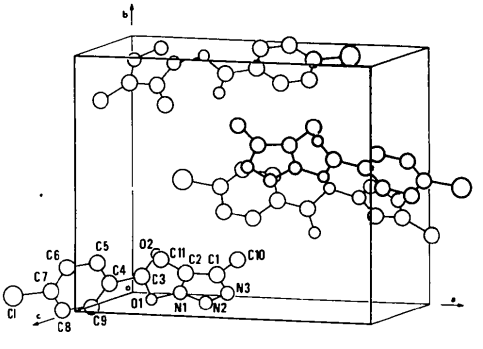

Fig. 2. Clinographic projection of the unit cell showing the molecular packing in CBODT.

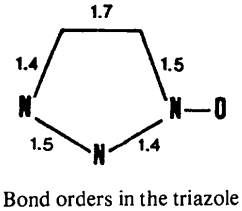

Fig. 3. Bond orders in the triazole ring.

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Structure of a 3α-(D-Methylglycoside) of 7,8β-Epoxysinogenin – a Cardioactive Steroid

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Abstract. $C_{30}H_{42}O_{10}$, $M_r = 562{\cdot}66$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}125$ (1), $b = 15{\cdot}632$ (2), $c = 36{\cdot}115$ (4) Å, $V = 5716$ (1) Å^3, $Z = 8$, $D_m = 1{\cdot}312$ (2) (flotation), $D_x = 1{\cdot}308$ g cm^{-3}, Cu $K\alpha(\lambda = 1{\cdot}5418$ Å), $\mu = 7{\cdot}18$ cm^{-1}, $F(000) = 2416$, $T = 295$ K. Final $R(F) = 0{\cdot}07$ for 3348 significant reflections with $I \geq 2{\cdot}5\sigma(I)$. The *A, B, C, D* rings of the aglycone ring are found to be in *cis–trans–cis* fashion forming a buckled structure. The lactone is in C17β conformation. The molecules are stabilized by intermolecular hydrogen bonds. The longest direction of the steroid molecule is nearly parallel to the *a* axis. The conformational features exhibited by the molecule support proposals on activity.

Introduction. The title compound (Fig. 1), which is a cardiac glycoside, is extracted from the plant *Cryptolepsis buchanani* (local name Krishna Sariva) and belongs to the class of digitalis. The active components of digitalis are glycosides of digitoxigenins, digoxigenin and gitoxigenin. Digitalis compounds have been categorized as cardiotonic steroids because of their profound effect on the heart. They increase the force of contraction of heart muscle, which makes them a drug of choice in the treatment of congestive heart failure. The activity of a cardiac steroid depends upon the presence of a five- or a six-membered unsaturated lactone ring in the β-configuration at the C(17) position; a hydroxyl group at C(14) and *cis* fusion of rings *C* and *D* are also essential. The C(17) substituent containing a conjugated system, normally a lactone ring, is supposed to enhance the basicity of the carbonyl O and thus act as a proton receptor (Repke & Portius, 1966; Repke & Dittrich, 1982). The sugar residue attached at C(3) does not contribute to the inhibition of the ATPase by these compounds (Bowman & Rand, 1980; Stryer, 1975) but they have been reported to modify the activity of cardiac glycosides. The present study was undertaken to establish the chemical structure of the title compound and to correlate the activity with the observed conformational features.

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† DCB contribution No. 713.

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