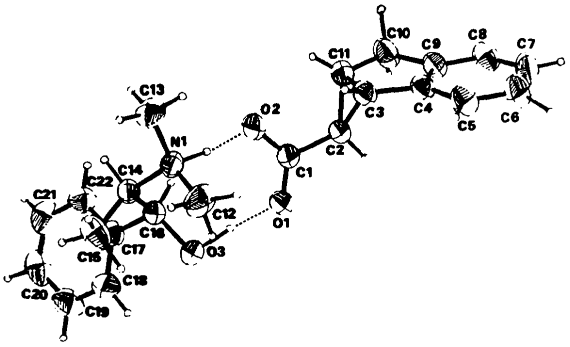

Fig. 1. An *ORTEP* drawing (Johnson, 1976) of the title complex showing the atom numbering. The ellipsoids are drawn at the 50% probability level.

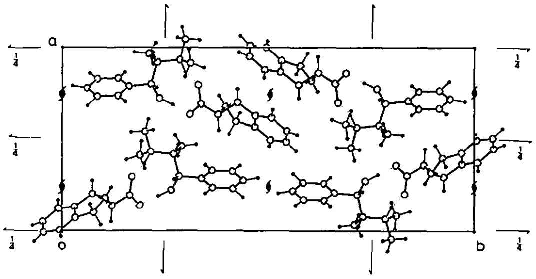

Fig. 2. The crystal structure viewed along the *c* axis.

The conformation of the (+)-*N*-methylephedrine moiety is in its most extended form, the torsion angle N(1)—C(14)—C(16)—C(17) being −174·6 (2)° which is close to those values in other ephedrine derivatives such as (−)-ephedrine hydrochloride, 164·4° (Bergin, 1971), (−)-ephedrine dihydrogen phosphate, 162·8° (Hearn & Bugg, 1972) and *p*-hydroxyephedrine hydrochloride, 178·1° (Dattagupta, Pattanayek & Saha, 1981).

The crystal structure viewed along the *c* axis is shown in Fig. 2. The cation–anion pairs are formed through the two hydrogen bonds, O(3)—H(O3)···O(1) [2·636 (2) Å] and N(1)—H(N1)···O(2) [2·590 (2) Å]. There are bands composed of hydrophilic (near $y = \frac{1}{4}$) and hydrophobic (near $y = \frac{1}{2}$) residues running parallel to the *ac* plane.

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Structure of 1′,3,3′-Trimethyloxazolidine-5-spiro-5′-hydantoin-2,4-dione*

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Abstract. $C_8H_9N_3O_5$, $M_r = 227·18$, hexagonal, $P6_1$, $a = 9·385$ (3), $c = 19·06$ (4) Å, $V = 1453·9$ (7) Å^3, $Z = 6$, $D_x = 1·557$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·87$ cm^{-1}, $F(000) = 708$, $T = 138$ (2) K, $R = 0·031$ for 783 observed reflections. Room-temperature cell constants were also refined: $a = 9·449$ (4), $c = 19·20$ (4) Å, $V = 1484·6$ (9) Å^3. No significant differences were apparent between space groups $P6_1$ and $P6_5$. This unusual compound was formed as a slightly soluble product of electrochemical oxidation of 1,3,7,9-tetramethyluric acid in aqueous solution at pH 2. Both rings of the title compound are planar and are almost perpendicular to each other. The N—C(O)—N—C(O) bond lengths of the hydantoin ring show the characteristic short–long–short pattern. The C—N bond involving the spiro atom is extremely short

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* Hydantoin is 2,4-imidazolidinedione.

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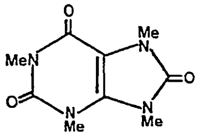
[1·400 (3) Å]. The bond lengths and angles of the oxazolidine ring are normal.

Introduction. The purine 1,3,7,9-tetramethyluric acid (I) gives a single 2 e^- pH-independent voltammetric oxidation peak at a pyrolytic graphic electrode in aqueous buffers between pH 2 and pH 11 (Wrona, Owens & Dryhurst, 1979; Subramanian, Heeg & Dryhurst, 1986). Controlled potential electro-oxidations of (I) at its voltammetric peak potential (0·97 V *vs* the saturated calomel electrode) in phosphate buffers having ionic strengths ranging from 0·1 to 0·5 mol dm^{-3} at pH 2 or in 10^{-2} *M* HCl results in formation of a white crystalline precipitate. A number of other soluble products are also formed which have been described elsewhere (Subramanian, Heeg & Dryhurst, 1986). The slightly soluble product may be separated by filtration and purified by recrystallization from acetonitrile. The structure of this compound is reported herein and is a novel spirohydantoin derivative.



(I)

Experimental. Colorless, multifaceted, nearly spherical crystals, 0·20 × 0·20 × 0·20 mm; Nonius CAD-4 diffractometer, monochromated Mo *K*α, $\theta/2\theta$ scans; $3 \leq 2\theta \leq 50°$; lattice parameters from 48 high-angle reflections measured at both positive and negative 2θ values; no correction for absorption or secondary extinction; 0 to 11 *h*, 0 to 11 *k*, 0 to 22 *l*; 3 intensity monitors varied 1%; 1072 total reflections, 841 unique, 783 with $I \geq 2\sigma(I)$, $R_{\rm int} = 0·026$; calculation of *I*: $I = S - rB$, where S = scan counts, r = scan time/background ratio, B = sum of the background counts; calculation of $\sigma(I)$: $\sigma^2 = S + r^2B + (pI)^2$ where $p = 0·04$. Direct methods, hydrogen atoms placed in observed positions with *U*(H) refined; full-matrix anisotropic refinement on nonhydrogen atoms yielded $R = 0·031$, $wR = 0·039$, $S = 1·6$, $w = (\sigma_F)^{-2}$; max. shift/e.s.d. in final LS cycle $<0·02\sigma$; max. and min. electron density in final ΔF map +0·17 and −0·18 e Å^{-3}; neutral-atom scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974); calculations performed with local modifications of *SHELX*76 (Sheldrick, 1976) and *MULTAN*80 (Main *et al.*, 1980) crystallographic programs.

An attempt to establish the chirality of the compound proceeded as follows. The structure was refined to convergence in space group $P6_1$ as described above. Concurrently, the atomic coordinates were recast at $-x$, $-y$, $-z$ and refined in the enantiomeric space group $P6_5$. At convergence this model yielded $R = 0·031$ and $wR = 0·039$, equivalent to the refinement in space group $P6_1$. No specific configuration can be assigned on this basis.

Discussion. The atomic coordinates are given in Table 1, and bond lengths and angles are shown in Table 2.* Figs. 1 and 2 illustrate the geometry, labeling and packing of the molecule. The molecule consists of two

Table 1. *Atom parameters and their e.s.d.'s*

The *z* coordinate of C(1) was not varied during refinement.

	x	*y*	*z*	$U_{\rm eq}$*(Å^2)
C(1)	0·3856 (3)	−0·0390 (4)	0·2331	0·019 (1)
O(1)	0·4917 (3)	0·0765 (2)	0·2861 (2)	0·0229 (8)
C(2)	0·6514 (4)	0·1256 (3)	0·2710 (2)	0·021 (1)
O(2)	0·7628 (3)	0·2111 (3)	0·3087 (2)	0·0308 (9)
N(1)	0·6591 (3)	0·0592 (3)	0·2077 (2)	0·0195 (9)
C(3)	0·8140 (4)	0·0952 (4)	0·1740 (2)	0·032 (1)
C(4)	0·5073 (4)	−0·0336 (4)	0·1780 (2)	0·019 (1)
O(3)	0·4730 (3)	−0·0993 (3)	0·1221 (2)	0·0270 (9)
C(5)	0·2861 (4)	−0·2105 (4)	0·2680 (2)	0·018 (1)
O(4)	0·3462 (3)	−0·2828 (2)	0·2967 (2)	0·0273 (9)
N(2)	0·1274 (3)	−0·2540 (3)	0·2599 (2)	0·0176 (9)
C(6)	−0·0113 (4)	−0·4081 (4)	0·2854 (2)	0·029 (1)
C(7)	0·1088 (4)	−0·1344 (4)	0·2231 (2)	0·018 (1)
O(5)	−0·0207 (2)	−0·1453 (3)	0·2072 (2)	0·0264 (9
N(3)	0·2632 (3)	−0·0075 (3)	0·2089 (2)	0·0210 (9
C(8)	0·2969 (4)	0·1394 (4)	0·1688 (3)	0·027 (1)

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

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

C(1)—O(1)	1·451 (4)	C(4)—O(3)	1·192 (5)
C(1)—C(4)	1·534 (4)	C(5)—O(4)	1·208 (3)
C(1)—C(5)	1·550 (3)	C(5)—N(2)	1·342 (4)
C(1)—N(3)	1·400 (3)	N(2)—C(6)	1·463 (4)
O(1)—C(2)	1·360 (4)	N(2)—C(7)	1·406 (4)
C(2)—O(2)	1·190 (4)	C(7)—O(5)	1·206 (4)
C(2)—N(1)	1·377 (5)	C(7)—N(3)	1·366 (4)
N(1)—C(3)	1·466 (4)	N(3)—C(8)	1·466 (4)
N(1)—C(4)	1·367 (4)		
C(1)—O(1)—C(2)	109·5 (3)	O(2)—C(2)—N(1)	127·4 (3)
C(1)—C(4)—N(1)	105·0 (3)	N(1)—C(4)—O(3)	128·7 (3)
C(1)—C(4)—O(3)	126·3 (3)	C(3)—N(1)—C(4)	124·3 (4)
C(1)—C(5)—O(4)	124·7 (3)	C(4)—C(1)—C(5)	112·4 (2)
C(1)—C(5)—N(2)	105·5 (2)	C(4)—C(1)—N(3)	116·4 (2)
C(1)—N(3)—C(7)	112·1 (2)	C(5)—C(1)—N(3)	103·2 (2)
C(1)—N(3)—C(8)	123·8 (2)	C(5)—N(2)—C(6)	124·5 (2)
O(1)—C(1)—C(4)	103·3 (2)	C(5)—N(2)—C(7)	112·2 (2)
O(1)—C(1)—C(5)	108·0 (2)	O(4)—C(5)—N(2)	129·8 (3)
O(1)—C(1)—N(3)	113·6 (2)	N(2)—C(7)—O(5)	125·4 (3)
O(1)—C(2)—O(2)	123·3 (4)	N(2)—C(7)—N(3)	107·0 (2)
O(1)—C(2)—N(1)	109·3 (3)	C(6)—N(2)—C(7)	123·4 (2)
C(2)—N(1)—C(3)	123·4 (3)	C(7)—N(3)—C(8)	124·0 (2)
C(2)—N(1)—C(4)	112·1 (3)	O(5)—C(7)—N(3)	127·5 (3)

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* Lists of structure factor amplitudes, anisotropic thermal parameters, H-atom parameters, torsion angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. 42762 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

substituted heterocyclic rings that are fused through a single carbon atom and nearly perpendicularly oriented. The oxazolidine ring [C(1), O(1), C(2), N(1), C(4)] is practically planar; the maximum deviation of a ring atom from the best plane is C(1) at −0·05 Å, and the carbonyl oxygen substituents are displaced −0·06 and 0·13 Å [O(2) and O(3) respectively] from the best plane while the methyl carbon lies in the plane. The hydantoin ring atoms [C(1), C(5), N(2), C(7), N(3)] form a plane within experimental error with their substituents very close to it. The dihedral angle between the two ring planes is 91·5 (1)°.

The C—N bond lengths in the five examples of C(O)—N type linkages vary from 1·342 to 1·406 Å; four of them are longer than the C—N bond length for urea [1·356 (7) Å; Caron & Donohue, 1964]. Although this length ranges from 1·30 to 1·45 Å in a series of closely related hydantoins (Camerman & Camerman, 1971; Florencio, Smith-Verdier & García-Blanco, 1978; van Koningsveld, 1976; Lisgarten & Palmer, 1980; Mootz, 1965; Pascard-Billy, 1970; Vilches, Florencio, Smith-Verdier & García-Blanco, 1981), the short–long–short pattern of N(*R*)—C(O)—N(*R*)—C(O) distances prevails, and is characteristic in most hydantoin ring systems. The lengths of the two C—C(O) bonds involving the tetrahedral carbon atom C(1) are 1·534 (4) and 1·550 (3) Å, slightly longer than expected for a carbon–carbon single bond shortened by the presence of a carbonyl [1·516 (5) Å; *International Tables for X-ray Crystallography,* 1962]. The C—N bond involving the central carbon atom C(1) is anomalously short [1·400 (3) Å] on the basis of an expected three-coordinate nitrogen single bond [1·472 (5) Å; *International Tables for X-ray Crystallography,* 1962] and in comparison to the list of related hydantoins above (range 1·44–1·47 Å). The tetrahedral carbon to ether oxygen length is normal. The four C=O bonds and three N—CH$_3$ bonds are in good agreement with their respective averages 1·20 (1) and 1·465 (2) Å.

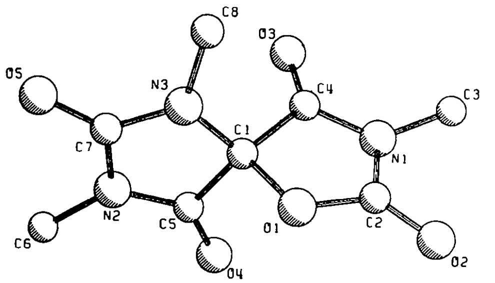
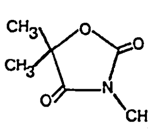


Fig. 1. *PLUTO* (Motherwell, 1978) drawing of 1′,3,3′-trimethyloxazolidine-5-spiro-5′-hydantoin-2,4-dione illustrating atomic labeling. The view bisects the best planes of the ring atoms.

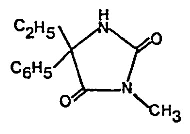
The oxazolidinedione portion of the title compound is similar to the dimethyl substituted molecule, 3,5,5-trimethyl-2,4-oxazolidinedione, (II) (Kistenmacher & Stucky, 1970). Bond distances and bond angles compare well in the two compounds; the largest differences are in the bond lengths adjacent to the tetrahedral carbon atom and are on the order of 4σ: C—C(O) = 1·534 (4), 1·510 (3) Å and C—O = 1·451 (4), 1·462 (2) Å for the title compound and 3,5,5-trimethyl-2,4-oxazolidinedione, respectively.

In this structure, and in all the heterocyclic compounds referenced herein, the ring nitrogen atoms assume a trigonal planar geometry with associated bond angles averaging 120 (1)° and their substituents lying close to or in the best plane defined by the ring atoms. This indicates some degree of sp^2 hybridization and π-electron delocalization within the ring.

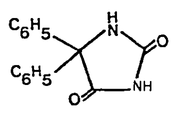
The most widely used anticonvulsant and antiepileptic drugs are either oxazolidine or hydantoin derivatives. The structures of trimethadione [3,5,5-trimethyl-2,4-oxazolidinedione, (II)] and the hydantoin-derived drugs methoin [5-ethyl-3-methyl-5-phenylhydantoin, (III)] and phenytoin [5,5-diphenylhydantoin, (IV)] are shown below.



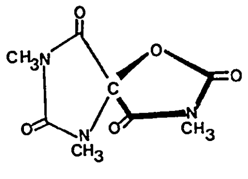
(II)



(III)



(IV)



(V)

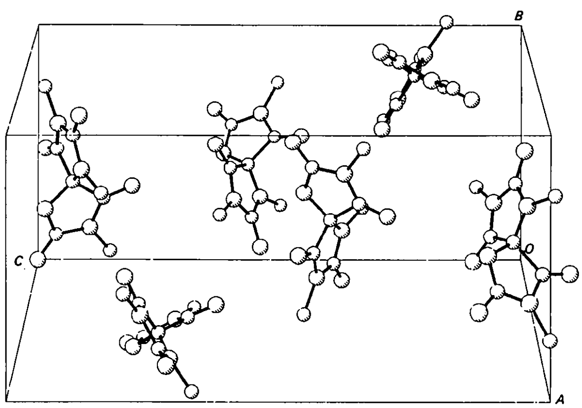


Fig. 2. Packing diagram viewed along the *a* crystallographic axis.

The novel spiro compound described in this report (V) clearly has structural features which are found in both the oxazolidine and hydantoin drugs. Furthermore, it has been suggested (Camerman & Camerman, 1971) that the spatial properties of the C(5) substituents of compounds such as (II)–(IV) relative to the rest of the molecule may be an important factor in determining the site of action of these drugs. The spatial properties of the oxazolidine residue relative to the hydantoin residue of the spiro compound (V) are very similar to those of the C(5) phenyl substituents of (IV) relative to the hydantoin ring (Camerman & Camerman, 1971). The presence of both oxazolidine and hydantoin ring structures in (V) along with the spatial relationships between these two rings suggests that this spiro compound may have important anticonvulsant and/or antiepileptic properties.

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Structure of 2-Chloro-10-phenylphenothiazine

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Abstract. $C_{18}H_{12}ClNS$, $M_r = 309{\cdot}82$, monoclinic, $P2_1/c$, $a = 19{\cdot}689\ (4)$, $b = 7{\cdot}240\ (1)$, $c = 23{\cdot}582\ (4)$ Å, $\beta = 116{\cdot}90\ (1)°$, $V = 2997{\cdot}8\ (9)$ Å^3, $Z = 8$, $D_x = 1{\cdot}373$, $D_m = 1{\cdot}37$ g cm^{-3} (by flotation), λ(Mo $K\alpha$) $= 0{\cdot}7107$ Å, $\mu = 3{\cdot}78$ cm^{-1}, $F(000) = 1280$, $T = 295$ K. Final $R = 0{\cdot}036$ for 2929 observed reflections. The central ring of the phenothiazine ring system is in a boat conformation. The folding angle between the least-squares planes of the benzo and the chlorobenzo rings is 153·0 (1) and 153·3 (1)° for the two crystallographically independent molecules in the unit cell. The 10-phenyl substituent is in an equatorial position with respect to the central ring of the phenothiazine ring system.

Introduction. This paper reports the structure of 2-chloro-10-phenylphenothiazine and is a continuation of the structural studies of substituted phenothiazines (Jovanovic, Biehl, de Meester & Chu, 1984). The main objective of these studies is to determine the effect of the substituents on the conformation and configuration of the phenothiazine ring system and to compare the conformation in the solid state with that deduced in solution.

The ^{13}C chemical shifts have been assigned on the basis of model compounds and substituent chemical-shift constants (Jovanovic & Biehl, 1984). The lack of influence of the 2-chloro substituent on the chemical shifts of the C atoms in the unsubstituted benzo ring indicates that the title compound exists in solution in the butterfly conformation.

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