Table 3. *Hydrogen bonds*

D—H···*A*	*D*···*A* (Å)	*D*—H (Å)	H···*A* (Å)	∠*D*—H···*A* (°)	Symmetry operation on *A*
O(2)—H(2)···O(1)	2·92 (1)	0·76	2·42	124	x, y, z
O(2)—H(2)···O(5)	2·78 (1)	0·76	2·23	128	$-x, y-\frac{1}{2}, \frac{3}{2}-z$
O(3)—H(3)···O(2)	2·69 (1)	0·74	1·97	169	$1-x, y-\frac{1}{2}, \frac{3}{2}-z$
O(5)—H(5)···O(4)	2·78 (1)	0·77	2·15	140	$x, y+1, z$
O(5)—H(5)···O(6)	2·78 (1)	0·77	2·38	113	x, y, z
O(6)—H···O(1)	3·12 (1)				$\frac{1}{2}+x, \frac{1}{2}-y, 2-z$

in a bifurcated hydrogen bond. The geometrical parameters of this bond (Table 3) were analysed according to the criteria given by Newton, Jeffrey & Takagi (1979). The function of the O(6)—H group is somewhat uncertain because no reliable hydrogen position could be secured. It is quite common that aromatic derivatives with substituents with donor–acceptor properties in the *ortho* position exhibit intramolecular hydrogen bonds (Pimentel & McClellan, 1960; Schuster, Zundel & Sandorfy, 1976). In such a case a bifurcated hydrogen bond can be proposed in which H(5) would be shared between O(4) and O(6) (Table 3). The two-dimensional layers of hydrogen-bonded molecules are linked in the **c** direction *via* the weak interaction O(6)—H···O(1) (Fig. 2).

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The Structure of 5,5-Diphenyl-1,3-oxazolidine-2,4-dione, $C_{15}H_{11}NO_3$

BY PENELOPE W. CODDING

Departments of Chemistry and Pharmacology and Therapeutics, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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Abstract. $M_r = 253{\cdot}26$, monoclinic, $P2_1/c$, $a = 12{\cdot}473\ (8)$, $b = 6{\cdot}025\ (1)$, $c = 16{\cdot}371\ (11)$ Å, $\beta = 90{\cdot}57\ (3)°$, $V = 1230\ (1)$ Å^3, $Z = 4$, $F(000) = 528$, $D_x = 1{\cdot}37$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 1{\cdot}04$ cm^{-1}, $T = 173\ (5)$ K, $R = 0{\cdot}092$, $R_w = 0{\cdot}042$, 1779 observed reflections. The angle between the two phenyl rings is $79{\cdot}7\ (5)°$ and the angles between the oxazolidinedione ring and each of the two phenyl rings

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are 105·7 (5) and 115·2 (5)°; these values are similar to those found in the active anticonvulsant, diphenylhydantoin. The molecules form an intermolecular hydrogen bond between one carbonyl O atom and the amide N atom. Despite the different intermolecular environments of the two carbonyl groups, the C=O bond lengths are the same.

Introduction. Diphenyloxazolidinedione is structurally related to two effective anticonvulsants. It differs from diphenylhydantoin, a commonly prescribed drug useful against the *grand mal* type of seizure, by the replacement of a N atom by an O atom in the heterocyclic ring. It differs from the active form of trimethadione, an anticonvulsant used against absence seizures, by the substitution of phenyl rings for methyl groups on the tetrahedral C atom of the oxazolidine ring. (Trimethadione loses the *N*-methyl group to form the active demethyl derivative *in vivo*.) In contrast to the other two compounds, diphenyloxazolidinedione is not a useful anticonvulsant. The structure of diphenyloxazolidinedione was determined to compare it to the structures of diphenylhydantoin (Camerman & Camerman, 1971; Mastropaolo, Camerman & Camerman, 1983) and trimethadione (Kistenmacher & Stucky, 1970) to ascertain the conformational or electronic differences among the compounds.

Experimental. The title compound was synthesized by Dr Gary L. Jones of the Department of Pharmacology, Texas College of Osteopathic Medecine, Fort Worth, Texas. Colorless needle from carbon tetrachloride/ethyl acetate, 0·10 × 0·19 × 0·31 mm; Enraf–Nonius CAD-4F diffractometer; $\theta_{max} = 27{\cdot}5°$; θ range for 20 reflections that define orientation matrix and cell: 9·7–18·9°; no absorption correction; hkl range: $\pm h$, $+k$, $+l$; standards $27\bar{5}$, $\bar{3}0\bar{4}$ and $0,\bar{1},12$, variation $< 2{\cdot}0\%$; 3275 reflections measured, 2818 unique, 1779 with $I \geq 2{\cdot}0\,\sigma(I)$; direct methods [*MULTAN*78 (Germain, Main & Woolfson, 1971)]; function minimized $\sum w(|F_o| - |F_c|)^2$; weights defined as $w^{-1} = \sigma^2(F_o)$; $S = 1{\cdot}52$; max. shift/error = 0·03; max./min. difference Fourier peaks were $\pm 0{\cdot}4$ e Å^{-3} and were equal to the estimated error; programs: *XRAY*76 (Stewart, 1976); scattering factors from Cromer & Mann (1968).

The H atoms were located in difference Fourier syntheses. They were included in the model with fixed isotropic thermal parameters and their coordinates were refined. In the final cycles the coordinates of all the atoms and the anisotropic thermal parameters of the non-hydrogen atoms were refined. The 2442 reflections used for refinement were the observed reflections plus those unobserved with $|F_c| > 2{\cdot}0\,\sigma(F_o)$.

Discussion. The molecular conformation and atomic labeling scheme are shown in Fig. 1. The atomic coordinates are in Table 1 and the bond distances and angles are in Table 2.* The structure of diphenyloxazolidinedione is similar to that of the active anticonvulsant, diphenylhydantoin (DPH), in conformation and in overall dimensions. The relative orientations of the three rings in each structure are similar (values in *Abstract*). The distances between hydrophobic groups and hydrogen-bonding groups in anticonvulsants have been used to develop a model for active drugs. The phenyl-ring centroid to O-atom distances in diphenyloxazolidinedione are the same as the average values found for diphenylhydantoin, within two standard deviations of the average. These distances are the same for the two molecular types even though diphenyloxazolidinedione is not an active anticonvulsant. In these molecules the two different heterocyclic rings are planar; the standard deviation for the oxazolidine ring is 0·009 Å. The planarity of these rings is probably due to a delocalization of π electrons in the heterocycle; this delocalization may be enhanced by the aromatic substituents.

Diphenyloxazolidinedione exhibits different bond lengths and conformation in the oxazolidine ring from those found in trimethadione (Kistenmacher & Stucky, 1970). A comparison of the dimensions of the phenyl- and methyl-substituted compounds shows that the largest changes occur in the two bonds between the site of the substituent and the N atom. The diphenyl compound shows longer bonds: C(4)–C(5) is 1·537 (7) Å compared to 1·510 (3) Å, C(5)–N(1) is

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, hydrogen-atom parameters and bond lengths involving hydrogens have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39676 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

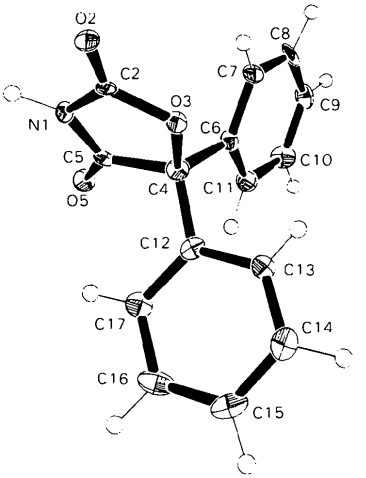

Fig. 1. The molecular conformation of 5,5-diphenyl-1,3-oxazolidine-2,4-dione. The thermal ellipsoids were drawn at the 50% probability level using *ORTEP* (Johnson, 1976).

1·384 (6) Å *vs* 1·357 (3) Å; a smaller difference is found between C(2)–O(3), 1·354 (5) Å *vs* 1·337 (3) Å. In contrast to the oxazolidine ring in the diphenyl compound, the ring in trimethadione is nonplanar; the N atom deviates by 0·083 (2) Å from the best plane of the other four atoms of the ring.

The two C—N bond distances in diphenyloxazolidinedione are equal (see Fig. 1), which is different from the observation of C—N lengths in diphenylhydantoin (Camerman & Camerman, 1971). In the active compound (DPH), the shorter C—N distance is more directly connected to the site of phenyl substitution. This short distance is similar to the values observed in three other active compounds (Codding, Lee & Richardson, 1984). The phenyl substituents in diphenyloxazolidinedione appear to have little electronic interaction with the heterocyclic ring.

CNDO/2 calculations (Pople & Segal, 1966) on the three molecules, trimethadione, diphenyloxazolidinedione and diphenylhydantoin show that the overlap populations (bond orders) are different in these molecules. The overlap populations in the bonds in the hydantoin ring are greater in each case than the comparable bond in the oxazolidine ring of the diphenyl compound. Trimethadione also has higher overlap populations than diphenyloxazolidinedione in all the bonds of the oxazolidine ring except N(1)—C(2) where the values are approximately equal. The lowest overlap population in DPO is that between C(4) and O(3) and has a value of 1·013; the comparable overlap is 1·261 in DPH and 1·030 in trimethadione. Thus the calculations predict weak bonding in the heterocycle especially in the aforementioned bond. One possible explanation for the inactivity of diphenyloxazolidinedione is that the weak bonding in the heterocyclic ring causes the molecule to be labile in the biological environment.

A close contact between O(5) and O(2) at $(x, y-1, z)$ of 3·220 (5) Å pushes the O(5) atom out of the least-squares plane of the oxazolidine ring by 0·07 (1) Å. An intermolecular hydrogen bond between O(2) and N(1) at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ prevents the movement of O(2) from the plane. The hydrogen bond is strong as judged by the distances: O(2)···N(1), 2·789 (5); O(2)···H(1), 1·75 (3) Å and the angle: O(2)···H(1)—N(1), 171 (3)°. The two C=O distances are equal even though only one carbonyl O atom participates in a hydrogen bond.

The similarity of the conformations of diphenyloxazolidinedione to diphenylhydantoin demonstrates that shape alone does not determine anticonvulsant activity. Subtle electronic effects as evidenced by bond lengths must also play a role in the action of anti-seizure drugs.

Table 1. *Positional parameters* (×10⁴) *and equivalent isotropic thermal parameters* (×10) *for diphenyloxazolidinedione*

B_{eq} is defined as $\frac{1}{3}$ the trace of the B_{ij} matrix.

	x	*y*	*z*	B_{eq}(Å²)
N(1)	5949 (3)	2420 (7)	3013 (2)	11
C(2)	5840 (3)	4365 (9)	3450 (3)	12
O(2)	5202 (2)	5847 (6)	3337 (2)	13
O(3)	6574 (2)	4426 (5)	4065 (2)	11
C(4)	7228 (3)	2402 (9)	4064 (3)	12
C(5)	6777 (4)	1132 (9)	3322 (3)	14
O(5)	7090 (2)	−602 (6)	3039 (2)	16
C(6)	8395 (3)	2991 (8)	3895 (3)	12
C(7)	8686 (4)	5016 (8)	3534 (3)	13
C(8)	9755 (4)	5403 (9)	3337 (3)	18
C(9)	10527 (3)	3841 (9)	3513 (3)	18
C(10)	10236 (4)	1838 (9)	3876 (3)	19
C(11)	9176 (4)	1428 (9)	4065 (3)	16
C(12)	7066 (3)	1259 (8)	4873 (3)	11
C(13)	7461 (3)	2252 (9)	5570 (3)	13
C(14)	7335 (4)	1297 (9)	6325 (3)	18
C(15)	6821 (4)	−758 (10)	6394 (3)	20
C(16)	6420 (4)	−1761 (9)	5687 (3)	21
C(17)	6531 (3)	−768 (9)	4926 (3)	16

Table 2. *Bond distances* (Å) *and angles* (°) *in diphenyloxazolidinedione*

N(1)–C(2)	1·380 (7)	C(2)–N(1)–C(5)	111·3 (4)
C(2)–O(2)	1·209 (6)	N(1)–C(2)–O(3)	109·9 (4)
		N(1)–C(2)–O(2)	127·9 (4)
C(2)–O(3)	1·354 (5)	O(2)–C(2)–O(3)	122·2 (4)
O(3)–C(4)	1·467 (6)	C(2)–O(3)–C(4)	110·4 (3)
C(4)–C(5)	1·537 (7)	O(3)–C(4)–C(5)	102·4 (3)
C(4)–C(6)	1·525 (6)	O(3)–C(4)–C(6)	109·8 (4)
C(4)–C(12)	1·508 (7)	O(3)–C(4)–C(12)	107·4 (4)
C(5)–O(5)	1·209 (6)	C(5)–C(4)–C(12)	114·5 (4)
		C(5)–C(4)–C(6)	108·4 (4)
C(5)–N(1)	1·384 (6)	C(6)–C(4)–C(12)	113·6 (4)
		C(4)–C(5)–O(5)	128·0 (4)
C(6)–C(7)	1·404 (7)	C(4)–C(5)–N(1)	106·0 (4)
C(6)–C(11)	1·381 (7)	O(5)–C(5)–N(1)	125·9 (4)
		C(4)–C(6)–C(7)	121·9 (4)
C(7)–C(8)	1·395 (6)	C(4)–C(6)–C(11)	118·5 (4)
C(8)–C(9)	1·374 (7)	C(7)–C(6)–C(11)	119·6 (4)
C(9)–C(10)	1·395 (8)	C(6)–C(7)–C(8)	119·6 (4)
C(10)–C(11)	1·382 (7)	C(7)–C(8)–C(9)	120·4 (5)
		C(8)–C(9)–C(10)	119·8 (4)
C(12)–C(13)	1·376 (7)	C(9)–C(10)–C(11)	120·2 (4)
C(12)–C(17)	1·395 (7)	C(10)–C(11)–C(6)	120·4 (5)
		C(4)–C(12)–C(13)	118·7 (4)
C(13)–C(14)	1·373 (7)	C(4)–C(12)–C(17)	121·5 (4)
C(14)–C(15)	1·400 (8)	C(13)–C(12)–C(17)	119·8 (4)
C(15)–C(16)	1·395 (7)	C(12)–C(13)–C(14)	121·4 (5)
C(16)–C(17)	1·390 (7)	C(13)–C(14)–C(15)	119·9 (5)
		C(14)–C(15)–C(16)	118·5 (5)
		C(15)–C(16)–C(17)	121·3 (5)
		C(16)–C(17)–C(12)	119·0 (4)

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Acide *tert*-Butyl-2 Cyclohexène-3 Carboxylique-1-*trans*, $C_{11}H_{18}O_2$

PAR ROBERT VIANI

Département de Physique, Faculté des Sciences, Université Nationale de Côte d'Ivoire, 04 *BP* 322, *Abidjan* 04, *Côte d'Ivoire*

JACQUES LAPASSET

Laboratoire de Minéralogie – Cristallographie, associé au CNRS (*LA*233), *Université de Montpellier* II, *Place E. Bataillon,* 34060 *Montpellier CEDEX, France*

ET JEAN-PIERRE AYCARD

Laboratoire de Chimie Organique Structurale, Université de Provence, Centre de Saint-Jérôme, 13397 *Marseille CEDEX, France*

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Abstract. $M_r = 182{\cdot}26$, monoclinic, $P2_1/c$, $a = 6{\cdot}478$ (5), $b = 13{\cdot}534$ (8), $c = 12{\cdot}457$ (8) Å, $\beta = 92{\cdot}58$ (5)°, $V = 1091$ (2) Å^3, $Z = 4$, $D_m = 1{\cdot}10$ (2), $D_x = 1{\cdot}110$ Mg m^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}599$ mm^{-1}, $F(000) = 400$, $T = 292$ K, final $R = 0{\cdot}058$ for 1612 observed reflexions. The molecular structure shows that the ring conformation is intermediate between half-chair and sofa. The conformation of the carboxy group is governed by intramolecular non-bonded interactions. The eight heavy atoms are coplanar and the molecules associate in pairs which are centrosymmetric.

Introduction. Une série de molécules dérivées du cyclohexène disubstitué (Viani, Lapasset, Aycard, Lafrance & Bodot, 1978; Viani & Lapasset, 1978, 1981; Cossu, Viani & Lapasset, 1981; Viani, Cossu & Lapasset, 1981) présentent une forte interaction *gauche* entre un groupement *tert*-butyle et un substituant cyano vicinal. Une étude par résonance magnétique nucléaire (Aycard & Bodot, 1975; Lafrance, Aycard & Bodot, 1977) a montré l'influence de ces interactions sur les équilibres conformationnels. Des mises en équilibre chimique ont précisé les différences d'enthalpie libre entre diastéréoisomères (Aycard & Bodot, 1973).

Lorsque le groupement cyano est remplacé par un groupement méthoxycarbonyle, comme pour la molécule du présent manuscrit, il apparaît des variations significatives des différences d'enthalpie libre associées à ces divers équilibres. Ces variations résultent, vraisemblablement, des contraintes stériques accrues qui se manifestent lorsque le groupement carboxylate est situé en position axiale.

L'étude cristallographique de molécules comportant ce groupement présente donc un intérêt certain en vue d'une comparaison des données structurales ainsi acquises.

Partie expérimentale. Préparation donnée par Monnier (1977), par saponification de l'ester correspondant (Aycard & Bodot, 1973). Densité mesurée par flottation, monocristal de dimensions 0,30 × 0,22 × 0,20 mm, diffractomètre Nonius CAD-4. 15 réflexions ont servi à déterminer les paramètres de la maille. 1862 réflexions indépendantes enregistrées en balayage θ–2θ ($\theta < 65°$); 1613 réflexions conservées [$I > 3\sigma(I)$]; 2 réflexions de référence mesurées toutes les 48 mesures; décroissance des intensités de l'ordre de 24% sur la durée totale de l'enregistrement; correction des intensités par interpolation linéaire. Intensités corrigées des facteurs de Lorentz et de polarisation, pas d'absorption. h 0–7, k 0–15, l −14–14. Structure résolue par méthodes directes (*MULTAN*; Main, Woolfson, Lessinger, Germain & Declercq, 1974). Affinement par moindres carrés avec matrice complète (*ORFLS*; Busing, Martin & Levy, 1962) ($\sum w|\,|F_o| - |F_c|\,|^2$ minimisé). Hydrogènes localisés par Fourier différence sauf H(121) lié à O(12). Agitation thermique anisotrope

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