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Structure of a Tetracyclic Diketone

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Abstract. Ethyl 3,12-dioxotetracyclo[6.4.0.0^{2,6}.0^{5,9}]dodec-10-ene-11-carboxylate (2), $C_{15}H_{16}O_4$, M_r = 260·29, monoclinic, $A2/n$, a = 11·602 (1), b = 6·922 (1), c = 33·465 (3) Å, β = 106·89 (1)°, V = 2571·3 (4) Å^3, Z = 8, D_x = 1·345 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·91 cm^{-1}, F(000) = 1104, T = 295 K, R = 0·0528 for 1351 reflections. Compound (2) consists of a norbornane moiety with a five-membered ring and a six-membered ring fused along each side. The five-membered ring contains a ketone functionality and is in a half-chair conformation while the cyclohexenone ring exhibits a 1,2-diplanar conformation. The two end bonds of the norbornane moiety, 1·580 (5) and 1·569 (4) Å, are significantly longer than other bonds in the structure. The two ketone groups and attached atoms are each planar (0·004 Å r.m.s.d.) and form an interplanar angle of 46·5 (4)°. The ester side chain is disordered.

Experimental. Studies of Lewis acid-promoted reactions of substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones (PCUD-8,11-diones) with ethyl diazoacetate (EDA) have been reported recently (Marchand, Arney, Gilardi & Flippen-Anderson, 1987; Marchand, Annapurna, Reddy, Watson & Nagl, 1989). In one reaction a substituted tetracyclododecenedione, (2), was isolated in 17% yield (along with several other products) from the reaction of PCUD-8,11-dione (1) with EDA (1·3 equivalents) in the presence of boron trifluoride etherate (Scheme 1). A colorless crystal of (2) with dimensions 0·28 × 0·40 × 0·45 mm was mounted on a Nicolet $R3M/\mu$ update of a $P2_1$ diffractometer; data collected in the ω mode ($3 \le 2\theta \le 45°$), variable scan rate of 4 to 29·3° min^{-1} using graphite monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($25{\cdot}25 \le 2\theta \le 28{\cdot}77°$), systematic extinctions (hkl, $k + l = 2n + 1$; $h0l$, $h + l = 2n + 1$) and statistics consistent with space group $A2/n$ (permutation of $C2/c$, *International Tables for Crystallography*, 1983); monitored reflections ($\bar{1}33$ and $0,0,\overline{18}$) showed variations of less than ±2%; 2405 reflections measured ($h = -12$, 11; k = 0, 7; l = 0, 36), 1687 unique ($R_{\rm int}$ = 0·009) and 1351 $\ge 3\sigma(I)$; Lorentz–polarization corrections and ψ-scan-based empirical absorption correction (transmission factors 0·711–0·990) applied; structure solved by direct-methods, block cascade (Nicolet Instrument Corporation, 1986) least-squares refinement, H atoms located in difference map, the side chain is disordered and two positions can be found for O(4) and C(14) [0·57 (1) and 0·43 (1) occu-

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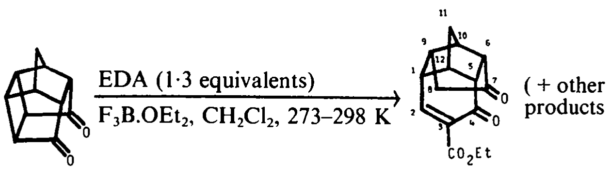
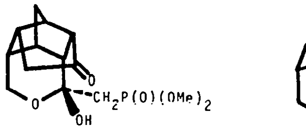
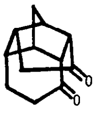
pancy for the two sets] but only one peak refined for C(15), cage H-atom positions refined with isotropic thermal parameters, side-chain H atoms allowed to ride on attached atom at fixed distance with fixed isotropic thermal factors; $R = 0{\cdot}0528$ [$R(\text{all}) = 0{\cdot}0663$], $wR = 0{\cdot}0658$ [$wR(\text{all}) = 0{\cdot}0682$]; for 235 parameters and 1351 reflections, $S = 1{\cdot}687$, $(\Delta/\sigma)_{\max} = 0{\cdot}010$; largest peaks in the final difference map of 0·19 and $-0{\cdot}30\,\text{e}\,\text{Å}^{-3}$; $\sum(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0{\cdot}00078F_o^2]^{-1}$ and $\sigma^2(F_o)$ from counting statistics. All computer programs supplied by Nicolet (Nicolet Instrument Corporation, 1986) for Desktop 30 Microeclipse and Nova 4/C configurations; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Fig. 1 is a drawing of compound (2). Table 1 lists atomic positional parameters and Table 2 gives interatomic distances and valence angles.*



(1) (2)



(3)



(4)

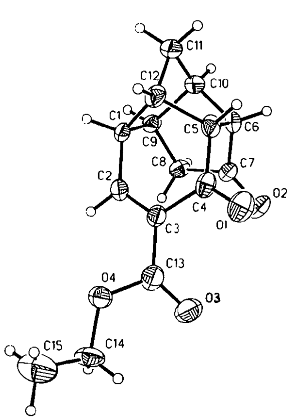


Fig. 1. Drawing of compound (2) with thermal ellipsoids drawn at the 25% probability level. H atoms are represented by spheres of arbitrary size.

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for compound* (2)

	x	*y*	*z*	*U**
C(1)	9472 (2)	−1427 (4)	6384 (1)	54 (1)
C(2)	8603 (2)	−71 (4)	6106 (1)	55 (1)
C(3)	8883 (3)	1715 (4)	6018 (1)	53 (1)
C(4)	10122 (3)	2455 (4)	6194 (1)	56 (1)
O(1)	10441 (2)	3997 (3)	6087 (1)	85 (1)
C(5)	10971 (3)	1170 (4)	6505 (1)	55 (1)
C(6)	10847 (2)	1255 (4)	6959 (1)	53 (1)
C(7)	9659 (3)	2048 (4)	6984 (1)	51 (1)
O(2)	9419 (2)	3733 (3)	7013 (1)	71 (1)
C(8)	8835 (3)	373 (4)	6973 (1)	56 (1)
C(9)	9497 (2)	−1315 (4)	6858 (1)	53 (1)
C(10)	10827 (3)	−873 (4)	7074 (1)	59 (1)
C(11)	11481 (3)	−1919 (4)	6810 (1)	76 (1)
C(12)	10770 (3)	−989 (4)	6404 (1)	61 (1)
C(13)	7950 (3)	3032 (5)	5756 (1)	69 (1)
O(3)	7740 (2)	4625 (4)	5854 (1)	89 (1)
O(4)†	7194 (13)	2181 (28)	5422 (5)	65 (3)
O(4*A*)†	7551 (12)	2222 (25)	5379 (5)	133 (6)
C(14)†	6197 (10)	3227 (19)	5170 (3)	87 (4)
C(14*A*)†	6762 (21)	3232 (27)	5039 (7)	180 (11)
C(15)	5756 (5)	2300 (8)	4808 (2)	158 (3)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

† Disordered positions O(4) and C(14) 0·57 (1) occupancy factors, and O(4*A*) and C(14*A*) 0·43 (1) occupancy factors.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for compound* (2)

C(1)—C(2)	1·490 (4)	C(1)—C(9)	1·580 (5)
C(1)—C(12)	1·519 (4)	C(2)—C(3)	1·332 (4)
C(3)—C(4)	1·478 (4)	C(3)—C(13)	1·489 (4)
C(4)—O(1)	1·217 (4)	C(4)—C(5)	1·500 (4)
C(5)—C(6)	1·569 (4)	C(5)—C(12)	1·534 (4)
C(6)—C(7)	1·508 (4)	C(6)—C(10)	1·524 (4)
C(7)—O(2)	1·209 (3)	C(7)—C(8)	1·496 (4)
C(8)—C(9)	1·508 (4)	C(9)—C(10)	1·533 (4)
C(10)—C(11)	1·507 (5)	C(11)—C(12)	1·514 (4)
C(13)—O(3)	1·196 (4)	C(13)—O(4)	1·340 (16)
C(13)—O(4*A*)	1·334 (16)	O(4)—C(14)	1·416 (19)
O(4*A*)—C(14*A*)	1·422 (24)	C(14)—C(15)	1·335 (12)
C(14*A*)—C(15)	1·360 (21)		

C(2)—C(1)—C(9)	114·0 (2)	C(2)—C(1)—C(12)	112·6 (2)
C(9)—C(1)—C(12)	102·5 (2)	C(1)—C(2)—C(3)	123·9 (2)
C(2)—C(3)—C(4)	120·3 (2)	C(2)—C(3)—C(13)	121·1 (3)
C(4)—C(3)—C(13)	118·6 (2)	C(3)—C(4)—O(1)	122·0 (2)
C(3)—C(4)—C(5)	115·9 (2)	O(1)—C(4)—C(5)	122·0 (3)
C(4)—C(5)—C(6)	115·1 (2)	C(4)—C(5)—C(12)	113·4 (2)
C(6)—C(5)—C(12)	101·5 (2)	C(5)—C(6)—C(7)	114·1 (2)
C(5)—C(6)—C(10)	102·7 (2)	C(7)—C(6)—C(10)	104·9 (2)
C(6)—C(7)—O(2)	126·2 (3)	C(6)—C(7)—C(8)	107·7 (2)
O(2)—C(7)—C(8)	126·1 (3)	C(7)—C(8)—C(9)	103·8 (2)
C(1)—C(9)—C(8)	115·6 (2)	C(1)—C(9)—C(10)	101·9 (2)
C(8)—C(9)—C(10)	104·0 (2)	C(6)—C(10)—C(9)	99·2 (2)
C(6)—C(10)—C(11)	105·6 (3)	C(9)—C(10)—C(11)	103·7 (2)
C(10)—C(11)—C(12)	94·9 (2)	C(1)—C(12)—C(5)	106·8 (2)
C(1)—C(12)—C(11)	103·3 (3)	C(5)—C(12)—C(11)	102·0 (2)
C(3)—C(13)—O(3)	125·1 (3)	C(3)—C(13)—O(4)	114·2 (8)
O(3)—C(13)—O(4)	119·8 (8)	C(3)—C(13)—O(4*A*)	107·0 (7)
O(3)—C(13)—O(4*A*)	127·2 (7)	C(13)—O(4)—C(14)	119·7 (15)
O(4*A*)—C(14)—C(15)	104·2 (10)	O(4)—C(14*A*)—C(15)	106·7 (16)
O(4*A*)—C(14*A*)—C(15)	117·9 (16)		

Related literature. The structures of two closely related substituted tetracyclododecanes (3) (Watson, Nagl, Marchand, Reddy, Reddy & Dave, 1989) and

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52158 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(4) (Marchand, Rajapaksa, Reddy, Watson & Nagl, 1989) have been reported. The synthesis and chemistry of compound (2) and related materials have been reported (Marchand, Arney, Gilardi & Flippen-Anderson, 1987; Marchand, Annapurna, Reddy, Watson & Nagl, 1989).

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N-(Diméthyl-4,6 pyridyl-2) (Nitro-4 phényl)-2 Propionamide

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(*Reçu le* 18 *juin* 1989; *accepté le* 14 *août* 1989)

Abstract. $C_{16}H_{17}N_3O_3$, $M_r = 299{\cdot}3$, monoclinic, $P2_1/n$, $a = 10{\cdot}015$ (3), $b = 11{\cdot}531$ (3), $c = 13{\cdot}681$ (2) Å, $\beta = 107{\cdot}14$ (2)°, $V = 1510$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}317$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}087$ mm^{-1}, $F(000) = 632$, $T = 294$ (1) K, $R = 0{\cdot}045$ for 930 independent reflections. There is a delocalized orbital along the amide group. The least-squares planes of the two rings make an angle of 81·2 (2)°. The atoms of the nitro group are very near to the phenyl-ring plane and those of the amide group are near to the pyridyl ring plane. The molecules form layers which spread out along the $z = 0$ and $z = \frac{1}{2}$ planes. Two molecules in two neighbouring layers are linked by an N—H···O hydrogen bond. The title compound belongs to a group of drugs with anti-inflammatory properties. It has been synthetized and studied in order to adjust the pharmacological activity of *N*-(4,6-dimethyl-2-pyridyl)benzamide, which is the typical compound of the group.

Partie expérimentale. Cristal approximativement parallélépipédique: 0,08 × 0,15 × 0,35 mm. Dimensions de la maille déterminées avec 25 réflexions telles que $5{,}24 \le \theta \le 17{,}90°$. Diffractomètre Enraf–Nonius CAD-4. $0{,}049 \le (\sin\theta)/\lambda \le 0{,}527$ Å^{-1}, $0 \le h \le 13$, $0 \le k \le 12$ et $-14 \le l \le 13$. Réflexions de contrôle de l'intensité: 211, $\bar{3}1\bar{4}$ et $22\bar{2}$. Pas de variation significative des intensités au cours des mesures. $\sigma(I)/I$ (contrôle) = 0,0018. 1853 réflexions indépendantes. 923 réflexions inobservées [$I < 1{,}5\sigma(I)$]. Pas de correction d'absorption. Méthodes directes, programme *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Affinement sur F, programme à matrice complète. Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974). H liés à N(7), C(16), C(17) et C(19): série de Fourier des ΔF. Autres H: positions calculées. Paramètres affinés: x, y, z et β_{ij} de C, N et O. Paramètres de position et d'agitation des H non affinés (nombre insuffisant de réflexions observées). $B(\mathrm{H}) = B_{\text{éq}}$ de l'atome lié à H + 1 Å^2. $R = 0{,}045$, $wR = 0{,}041$, $w = 1/\sigma^2(F)$, $S = 1{,}13$, $(\Delta/\sigma)_{\max} < 0{,}01$, $|\Delta\rho|_{\max} = 0{,}17$ (4) e Å^{-3}. Coefficient d'extinction secondaire isotrope $g = 3{,}5\ (8) \times 10^{-7}$. Programmes de calcul du système *SDP* (B. A. Frenz & Associates Inc., 1982). Angles des plans moyens: programme

0108-2701/90/010154-03$03.00