

Fig. 1. Overall views and atomic labelling schemes for (1) and (2) (Johnson, 1976).

Related literature. Some cinnoline derivatives show interesting biological activity and they are used as anti-inflammatory (cinnopentazon, cinnofuradion), analgesic (difalton) and antibacterial (cinoxacin) agents. Cinnoline-type structures have also been used in the search for new non-narcotic analgesic drugs (Stańczak, 1987), which resulted in the preparation of a series of 6,7- or 8-substituted 1,2,3,4-tetrahydrocinnolin-4-ones (Groszkowski & Stańczak, 1989) and their 1,2-dichloroacetyl derivatives (Kwapiszewski, Stańczak & Groszkowski, 1990).

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Structure of a Synthetic Tricyclic Dione* with an Ingenol-Like Ring System

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Abstract. C₁₅H₁₆O₂, *M_r* = 228.29, orthorhombic, *Pbca*, *a* = 7.8945 (5), *b* = 12.652 (2), *c* = 24.118 (5) Å, *V* = 2408.9 (5) Å³, *Z* = 8, *D_x* = 1.259 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 6.17 cm⁻¹, *F*(000) = 976, *T* = 298 (2) K, *R* = 0.046 and *wR* = 0.022 for 940 unique observed reflections. This structure consists of a tricyclic molecule with two exocyclic carbonyl groups and an exocyclic methyl substituent. The two seven-membered rings have three C atoms in

common creating a bicyclo ring system. The unsaturated cycloheptenone ring is in a diplanar conformation with the atoms C7–C10 planar to within 0.003 Å and the remaining three ring atoms (C6, C4, C11) defining a plane at 32.4 (3)°. The cycloheptanone ring is in a distorted twist-chair conformation; the asymmetry parameter for a twofold axis passing through C10 and the midpoint of C3–C15 is ΔC₂ = 4.2°. At the C3–C4 juncture a cyclopentenone ring is fused in an envelope conformation with the C2–C3 double bond at the base of the envelope and C5 on the flap. The dihedral angle between the body and the flap is 11.8°. The exocyclic O1 atom lies

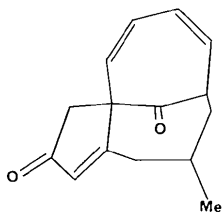
* IUPAC name: 8,9,10,11-tetrahydro-10-methyl-(3α,8α,10α)-3a,8-methano-3aH-cyclopentacyclodecene-2,12(3H)-dione.

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0.08 Å above the plane of the envelope body and the asymmetry parameter for this conformation is $\Delta C_s = 2.1^\circ$. The bond lengths and angles are normal and do not reflect delocalization. The C10—C11—C4 angle in the bicyclo bridge is $118.7(3)^\circ$ and the extant methyl group is *syn* with respect to the bridgehead atoms.

Experimental. This compound was prepared for use as a possible precursor in attempts to reproduce synthetically the complex ring system of the ingenanes, a class of cocarcenogenic diterpenes. X-ray-quality crystals were prepared by recrystallization from 1:1 petroleum ether/ether.

Colorless rods and plates, $0.08 \times 0.16 \times 0.24$ mm; Nicolet P2₁ diffractometer, Ni-filtered Cu K α ; $\theta/2\theta$ scans; $3 \leq 2\theta \leq 100^\circ$; lattice parameters from 25 high angle reflections ($2\theta > 40^\circ$) constrained orthorhombic; no absorption corrections or extinction corrections applied; $0 \leq h \leq 8$, $0 \leq k \leq 13$, $0 \leq l \leq 24$; three standard reflections fluctuated 2%; 1528 total reflections, 1240 unique, 940 observed with $I_o \geq 2.0\sigma(I)$. Direct methods; full-matrix refinement via SHELX76 (Sheldrick, 1976) on F^2 's minimizing $\sum w(|F_o| - |F_c|)^2$; all C and O atoms anisotropic; H atoms were placed in observed positions from a ΔF map and refined positionally and isotropically. Number of parameters varied was 218. For observed reflections $R = 0.046$, $wR = 0.022$, $S = 2.6$, $w = (\sigma_F)^{-2}$. For all (including weak) reflections: $R = 0.066$, $wR = 0.023$. In a final cycle: $(\Delta/\sigma)_{\max} < 0.02$, $(\Delta\rho)_{\max} = 0.21 \text{ e } \text{Å}^{-3}$, $(\Delta\rho)_{\min} = -0.18 \text{ e } \text{Å}^{-3}$. Neutral atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1* gives the atomic coordinates and Table 2 lists bond distances and angles. Fig. 1 illustrates the geometry and labeling scheme. A diagram of the molecule is shown below.



Related literature. A description of the synthesis of the reported structure has been published (Rigby,

* Lists of anisotropic thermal parameters, H-atom parameters, structure factors and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53290 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{Å}^2)$
O1	0.5104 (4)	-0.1421 (2)	0.4755 (1)	0.067 (1)
O2	0.3005 (3)	-0.1064 (2)	0.3169 (1)	0.056 (1)
C1	0.3810 (6)	-0.1080 (3)	0.4554 (2)	0.047 (2)
C2	0.2073 (6)	-0.1469 (3)	0.4641 (2)	0.043 (2)
C3	0.0988 (5)	-0.0955 (3)	0.4323 (2)	0.036 (2)
C4	0.1848 (4)	-0.0139 (3)	0.3944 (2)	0.033 (2)
C5	0.3686 (6)	-0.0138 (4)	0.4167 (2)	0.050 (2)
C6	0.1068 (5)	0.0944 (3)	0.3999 (2)	0.042 (2)
C7	0.0608 (5)	0.1620 (4)	0.3606 (2)	0.049 (2)
C8	0.0520 (6)	0.1484 (4)	0.3011 (2)	0.054 (2)
C9	0.0325 (6)	0.0576 (4)	0.2744 (2)	0.054 (2)
C10	0.0183 (6)	-0.0495 (3)	0.3018 (2)	0.042 (2)
C11	0.1794 (5)	-0.0615 (3)	0.3358 (2)	0.038 (2)
C12	-0.1529 (6)	-0.0617 (4)	0.3316 (2)	0.047 (2)
C13	-0.1639 (6)	-0.1465 (4)	0.3764 (2)	0.047 (2)
C14	-0.1012 (8)	-0.2556 (4)	0.3580 (3)	0.060 (2)
C15	-0.0896 (6)	-0.1124 (4)	0.4322 (2)	0.043 (2)

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

O1—C1	1.210 (5)	C6—C7	1.327 (6)
O2—C11	1.202 (5)	C7—C8	1.446 (6)
C1—C2	1.472 (6)	C8—C9	1.326 (7)
C1—C5	1.516 (7)	C9—C10	1.511 (7)
C2—C3	1.320 (6)	C10—C11	1.521 (6)
C3—C4	1.538 (5)	C10—C12	1.539 (6)
C3—C15	1.503 (6)	C12—C13	1.525 (7)
C4—C5	1.548 (6)	C13—C14	1.532 (7)
C4—C6	1.508 (5)	C13—C15	1.531 (6)
C4—C11	1.537 (5)		
O1—C1—C2	127.6 (4)	C4—C11—C10	118.7 (3)
O1—C1—C5	125.5 (4)	C5—C4—C6	110.6 (3)
O2—C11—C4	120.8 (3)	C5—C4—C11	110.2 (3)
O2—C11—C10	120.5 (3)	C6—C4—C11	115.2 (3)
C1—C2—C3	110.9 (4)	C6—C7—C8	130.2 (4)
C1—C5—C4	105.9 (4)	C7—C8—C9	126.1 (4)
C2—C1—C5	106.9 (4)	C8—C9—C10	125.0 (4)
C2—C3—C4	112.9 (4)	C9—C10—C11	105.3 (3)
C2—C3—C15	125.0 (4)	C9—C10—C12	111.1 (4)
C3—C4—C5	101.9 (3)	C10—C12—C13	116.9 (4)
C3—C4—C6	112.2 (3)	C11—C10—C12	118.2 (3)
C3—C4—C11	105.8 (3)	C12—C13—C14	114.2 (4)
C3—C15—C13	114.9 (4)	C12—C13—C15	113.7 (4)
C4—C3—C15	122.1 (3)	C14—C13—C15	112.7 (4)
C4—C6—C7	129.3 (4)		

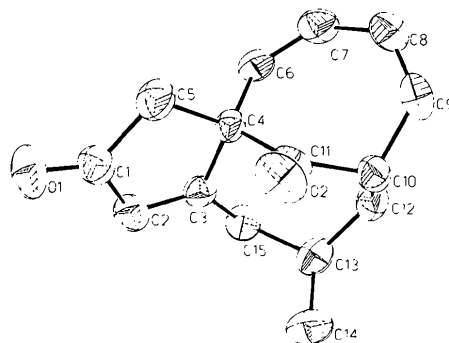


Fig. 1. ORTEP drawing (at 50% probability) of 8,9,10,11-tetrahydro-10-methyl-(3 α ,8 α ,10 α)-3a,8-methano-3aH-cyclopentacyclodecene-2,12(3H)-dione showing the adopted labeling.

Moore & Rege, 1986). The structure of ingenol triacetate, a modified derivative of the natural product ingenol-3-hexadecanoate, has been examined (Zechmeister, Brandl & Hoppe, 1970; Paquette, Nitz, Ross & Springer, 1984). There are many examples in the literature of cycloheptane-cyclopentene fused rings (e.g. McPhail & Sim, 1973), especially as sesquiterpenoids with an additional lactone ring. Ring conformations have been discussed by Toromanoff (1980) and asymmetry parameters are described by Ladd & Palmer (1985).

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Structure of *N,N*-Dimethyl-9-anthrylacamide*

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Abstract. $C_{18}H_{17}NO$, $M_r = 263.33$, monoclinic, $P2_1/n$, $a = 13.124$ (6), $b = 9.636$ (3), $c = 12.203$ (5) Å, $\beta = 113.84$ (2)°, $V = 1412$ (1) Å³, $Z = 4$, $D_x = 1.24$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.083$ mm⁻¹, $F(000) = 263$, $T = 295$ K, $R = 0.055$ for 1200 reflections [$|F_o| > 3\sigma(F_o)$]. The structure consists of two planes of an anthracene π system and an *N,N*-dimethylacetamido moiety. The planes are nearly perpendicular because of steric repulsion between the H atoms at C(1) and C(8) and the *N,N*-dimethylcarbamoylmethyl group, the dihedral angle being 82.1 (1)°. More steric repulsion between the 9-anthryl and dimethylamino groups might give the conformer, with these groups on the opposite sides of the CH₂—CO bond axis.

Experimental. The dehydration coupling of 9-anthrylacetic acid with dimethylamine gave the title compound, which will be reported in detail elsewhere. Single crystals of the compound were prepared by slow evaporation of a dichloromethane–hexane solution. A pale-yellow plate crystal with dimensions 0.44 × 0.52 × 0.26 mm was used for the X-ray diffractometry. Enraf–Nonius CAD-4 diffractometer operating at 50 kV/26 mA, graphite-monochromated

Mo $K\alpha$ radiation. Accurate cell parameters by least-squares fit for 25 reflections with $15 < 2\theta < 25^\circ$. Intensity data collected by θ – 2θ scan, scan rates varied 1.2–4.1° min⁻¹, scan range (°) 1.0 + 0.5tan θ , $2\theta_{\text{max}} = 60^\circ$, $h = -18$ to 18, $k = 0$ to 13, $l = 0$ to 17. Three standard reflections monitored every 7200 s showed no crystal movement or decay. Intensities corrected for absorption effects by numerical Gaussian integration method, transmission factor range = 0.980–0.963; 4625 reflections measured, 1200 reflections with $|F_o| > 3\sigma(F_o)$ observed.

The structure was solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and refined on F by the full-matrix least-squares technique (*RADIEL*; Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). All non-H atoms refined anisotropically. H atoms were located by difference synthesis and refined isotropically. Weighting scheme $w = [\sigma(F_o)^2 + (0.040|F_o|)^2]^{-1}$; extinction correction applied yielding a secondary-extinction coefficient g of 3.1 (3) × 10⁻⁴ (Zachariasen, 1967), $R(F) = 0.055$, $wR(F) = 0.073$, GOF = 1.35 for 1200 independent reflections, 250 parameters refined. Maximum and minimum peak heights in difference Fourier map were 0.19 and -0.13 e Å⁻³, max. shift/e.s.d. = 0.51. Atomic scattering factors and anomalous-scattering corrections from *International Tables for X-ray Crys-*

* 2-(9-Anthryl)-*N,N*-dimethylacetamide.

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