Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical
T_{min} = 0.6763, T_{max} = 0.9749
4777 measured reflections
2625 independent reflections
2350 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.020
θ_{max} = 75° (full sphere of data to 65°, hemisphere for 65 < θ < 75°)
h = $-9 \rightarrow 10$
k = $-10 \rightarrow 10$
l = $-12 \rightarrow 12$
3 standard reflections frequency: 167 min intensity variation: 1%

Refinement

Refinement on F
R = 0.037
wR = 0.059
S = 2.642
2350 reflections
212 parameters
All H-atom parameters refined
$w = 4F^2[\sigma^2(I) + (0.02F^2)^2]^{-1}$
$(\Delta/\sigma)_{max}$ = 0.02

$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = -0.32 e Å^{-3}
Extinction correction: $(I + gI_c)^{-1}$ applied to F_c
Extinction coefficient: 2.7 (7) × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	0.08659 (4)	0.33167 (5)	0.71043 (4)	4.426 (8)
O1	0.0951 (2)	0.1814 (2)	0.7978 (1)	5.84 (3)
O2	-0.0705 (1)	0.4233 (2)	0.6391 (1)	5.45 (3)
N	0.2298 (2)	0.2928 (2)	0.5868 (1)	4.34 (3)
C1	0.4032 (2)	0.1948 (2)	0.6157 (2)	4.22 (3)
C2	0.4375 (3)	0.0322 (2)	0.6728 (2)	5.62 (4)
C3	0.6049 (3)	-0.0648 (3)	0.6956 (2)	6.71 (5)
C4	0.7389 (3)	-0.0026 (3)	0.6582 (2)	6.90 (5)
C5	0.7075 (2)	0.1574 (2)	0.5998 (2)	5.99 (4)
C6	0.5394 (2)	0.2613 (2)	0.5796 (2)	4.40 (3)
C7	0.5100 (2)	0.4299 (2)	0.5229 (2)	4.51 (3)
C8	0.1478 (2)	0.4602 (2)	0.8091 (2)	4.18 (3)
C9	0.1188 (2)	0.6232 (2)	0.7534 (2)	5.58 (4)
C10	0.1650 (2)	0.7267 (2)	0.8282 (2)	5.83 (4)
C11	0.2409 (2)	0.6710 (2)	0.9579 (2)	5.22 (4)
C12	0.2691 (3)	0.5085 (3)	1.0112 (2)	6.16 (5)
C13	0.2222 (2)	0.4012 (2)	0.9385 (2)	5.36 (4)
C14	0.2897 (3)	0.7873 (3)	1.0375 (2)	7.34 (5)

Table 2. *Geometric parameters (Å, °)*

S—O1	1.421 (1)	C5—C6	1.398 (2)
S—O2	1.431 (1)	C6—C7	1.428 (2)
S—N	1.633 (1)	C7—C7′	1.189 (2)
S—C8	1.759 (2)	C8—C9	1.382 (2)
N—C1	1.428 (2)	C8—C13	1.373 (2)
C1—C2	1.377 (2)	C9—C10	1.376 (3)
C1—C6	1.401 (2)	C10—C11	1.378 (3)
C2—C3	1.378 (3)	C11—C12	1.373 (3)
C3—C4	1.364 (3)	C11—C14	1.506 (3)
C4—C5	1.363 (3)	C12—C13	1.393 (3)
O1—S—O2	119.49 (8)	C1—C6—C5	118.1 (1)
O1—S—N	107.95 (7)	C1—C6—C7	121.7 (1)
O1—S—C8	108.50 (8)	C5—C6—C7	120.2 (2)
O2—S—N	104.95 (7)	C6—C7—C7′	178.2 (2)
O2—S—C8	108.42 (7)	S—C8—C9	118.4 (1)
N—S—C8	106.85 (7)	S—C8—C13	121.3 (1)
S—N—C1	122.1 (1)	C9—C8—C13	120.4 (2)
N—C1—C2	120.1 (2)	C8—C9—C10	119.7 (2)
N—C1—C6	. 120.1 (1)	C9—C10—C11	121.3 (2)
C2—C1—C6	119.8 (1)	C10—C11—C12	118.2 (2)
C1—C2—C3	120.4 (2)	C10—C11—C14	120.1 (2)
C2—C3—C4	120.5 (2)	C12—C11—C14	121.7 (2)
C3—C4—C5	119.9 (2)	C11—C12—C13	121.8 (2)
C4—C5—C6	121.3 (2)	C8—C13—C12	118.7 (2)

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Damnacanthal

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Abstract

The structure of a natural product isolated from the plant *Morinda citrifolia* L. was determined by X-ray diffraction; the compound is shown to be 9,10-dihydro-3-hydroxy-1-methoxy-9,10-dioxo-2-anthracenecarboxaldehyde, $C_{16}H_{10}O_5$. An intramolecular hydrogen bond exists between the hydroxyl and formyl groups with the O···O distance being 2.591 (4) Å.

Comment

A natural product isolated from the plant *Morinda citrifolia* L. was found to inhibit ras oncogene functions (Hiramatsu, Imoto, Koyano & Umezawa, 1993). The X-ray crystal structure analysis revealed

that the molecule is damnacanthal, which had been isolated previously from *Damnacanthus indicus* (Konoshima, Kozuka, Koyama, Okatani, Tagahara & Tokuda, 1989). In 2-hydroxy-1-napthaldehyde, similar intramolecular hydrogen bonding is observed with an O···O distance of 2.567 (3) Å (Maniukiewicz & Bukowska-Strzyżewska, 1992).
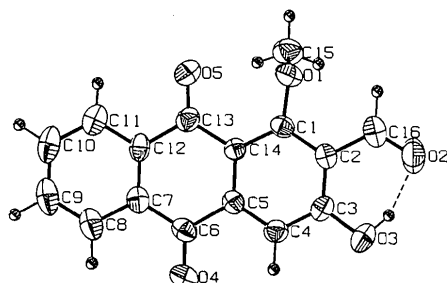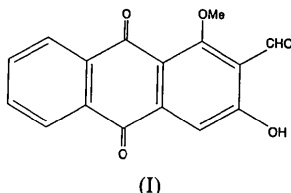

(I)

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule with 50% probability ellipsoids. H atoms are represented by circles of radii 0.15 Å.

Experimental

Crystal data

$C_{16}H_{10}O_5$
$M_r = 282.25$
Monoclinic
$P2_1/n$
$a = 15.834 (2)$ Å
$b = 9.558 (2)$ Å
$c = 8.216 (1)$ Å
$\beta = 95.77 (1)°$
$V = 1237.1 (3)$ Å^3
$Z = 4$
$D_x = 1.51$ Mg m^{-3}
$D_m = 1.52$ Mg m^{-3}
Density measured by flotation in aq. KI solution

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10-15°$
$\mu = 0.106$ mm^{-1}
$T = 298$ K
Prism
$0.60 \times 0.30 \times 0.20$ mm
Yellow
Crystal source: isolated from *Morinda citrifolia* L.

Data collection

Rigaku AFC-5 diffractometer
θ-2θ scans
Absorption correction: none
2954 measured reflections
2847 independent reflections
1010 observed reflections
$[F_o > 3\sigma(F_o)]$

$R_{int} = 0.03$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 20$
$k = -12 \rightarrow 0$
$l = -10 \rightarrow 10$
5 standard reflections monitored every 100 reflections
intensity variation: 4%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.046$
$S = 1.82$
1010 reflections
189 parameters
H-atom parameters not refined
$w = 1/[\sigma^2 F_o + (0.015|F_o|)^2]^{-1/2}$

$(\Delta/\sigma)_{max} = 0.25$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Calculations were performed using *CRYSTAN-GM* software (MAC Science, 1992) on a SUN SPARC-2 workstation. All of the H atoms were located in difference syntheses.

Table 1. *Positional parameters and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	0.0866 (2)	−0.2956 (2)	0.3052 (3)	4.0 (1)
O2	−0.1148 (2)	−0.3989 (3)	0.0020 (4)	5.8 (1)
O3	−0.1639 (2)	−0.1399 (3)	−0.0097 (3)	5.1 (1)
O4	−0.0406 (2)	0.2961 (3)	0.2262 (3)	5.3 (1)
O5	0.1744 (2)	−0.0978 (3)	0.4872 (3)	6.0 (1)
C1	0.0354 (2)	−0.1862 (4)	0.2532 (4)	2.9 (1)
C2	−0.0372 (2)	−0.2200 (4)	0.1483 (4)	3.1 (1)
C3	−0.0931 (2)	−0.1136 (4)	0.0924 (4)	3.3 (1)
C4	−0.0768 (2)	0.0244 (4)	0.1383 (4)	3.3 (1)
C5	−0.0061 (2)	0.0556 (4)	0.2433 (4)	2.9 (1)
C6	0.0074 (2)	0.2071 (4)	0.2885 (4)	3.5 (1)
C7	0.0800 (2)	0.2430 (4)	0.4083 (4)	3.4 (1)
C8	0.0929 (3)	0.3820 (4)	0.4563 (5)	4.5 (1)
C9	0.1589 (3)	0.4162 (4)	0.5715 (5)	5.4 (1)
C10	0.2134 (3)	0.3137 (5)	0.6395 (5)	5.0 (1)
C11	0.2021 (2)	0.1756 (4)	0.5896 (4)	4.2 (1)
C12	0.1350 (2)	0.1393 (4)	0.4743 (4)	3.3 (1)
C13	0.1244 (2)	−0.0103 (4)	0.4253 (4)	3.4 (1)
C14	0.0520 (2)	−0.0485 (4)	0.3051 (4)	2.8 (1)
C15	0.1629 (2)	−0.3090 (4)	0.2223 (5)	4.9 (1)
C16	−0.0533 (2)	−0.3650 (4)	0.0956 (5)	4.3 (1)

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

O1—C1	1.365 (4)	C5—C14	1.414 (5)
O1—C15	1.452 (5)	C5—C6	1.505 (5)
O2—C16	1.222 (5)	C6—C7	1.476 (5)
O3—C3	1.354 (4)	C7—C12	1.392 (5)
O4—C6	1.219 (4)	C7—C8	1.395 (5)
O5—C13	1.226 (5)	C8—C9	1.377 (6)
C1—C14	1.400 (5)	C9—C10	1.384 (6)
C1—C2	1.403 (5)	C10—C11	1.388 (6)
C2—C3	1.396 (5)	C11—C12	1.395 (5)
C2—C16	1.467 (5)	C12—C13	1.490 (5)
C3—C4	1.388 (5)	C13—C14	1.482 (5)
C4—C5	1.376 (4)	O2···O3	2.591 (4)
C1—O1—C15	114.6 (3)	C12—C7—C8	120.0 (3)
O1—C1—C14	122.5 (3)	C12—C7—C6	120.6 (3)
O1—C1—C2	116.1 (3)	C8—C7—C6	119.4 (3)
C14—C1—C2	121.3 (3)	C9—C8—C7	120.0 (4)
C3—C2—C1	119.2 (3)	C8—C9—C10	120.6 (4)
C3—C2—C16	120.3 (3)	C9—C10—C11	119.8 (4)
C1—C2—C16	120.4 (3)	C10—C11—C12	120.3 (3)
O3—C3—C4	117.7 (3)	C7—C12—C11	119.4 (3)
O3—C3—C2	121.8 (3)	C7—C12—C13	122.0 (3)
C4—C3—C2	120.5 (3)	C11—C12—C13	118.6 (3)
C5—C4—C3	119.6 (3)	O5—C13—C14	122.2 (3)
C4—C5—C14	122.1 (3)	O5—C13—C12	119.5 (3)
C4—C5—C6	116.8 (3)	C14—C13—C12	118.3 (3)
C14—C5—C6	121.1 (3)	C1—C14—C5	117.2 (3)

O4—C6—C7	122.0 (3)	C1—C14—C13	122.9 (3)
O4—C6—C5	120.0 (3)	C5—C14—C13	119.8 (3)
C7—C6—C5	118.0 (3)	O2—C16—C2	122.7 (4)

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Two Diastereoisomers of 1-(10-Trifluoromethyl-11,12-dioxatetracyclo-[6.2.1.1³,⁶.0²,⁷]dodeca-4,9-dien-9-yl)ethyl Phenylacetate, C₂₁H₁₉F₃O₄: Members of a Series of Adducts Generated by Repeated Diels–Alder Cycloaddition of Furan to 5,5,5-Trifluoropent-3-yn-2-yl Phenylacetate

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Abstract

Both the title bis adducts are *anti* joined, differing only in the enantiomeric form of the (phenylacetoxy)ethyl substituent relative to the main ring system. In each case, a CF₃ fluorine nearly eclipses the double bond [F—C—C=C; isomer (1), 5.9 (7); isomer (2), 10 (2)°], thereby

permitting the adjacent substituent to stagger and the bulky phenylacetoxy group to project away [C=C—C—O; isomer (1), −161.6 (4); isomer (2), 157 (1)°]. Changes in steric congestion introduced by the structural differences are relatively minor, allowing similar quantities of both compounds to be produced [isomer (1), 10; isomer (2), 8%].

Comment

This structural determination was undertaken to identify the two title diastereoisomers (I) and relate their stereochemistry to the 1:1 adducts (see reaction scheme below), which had been separated (Barlow, Tajammal & Tipping, 1993; Tajammal, 1991) but for which X-ray structure determination was not possible because they were liquids.
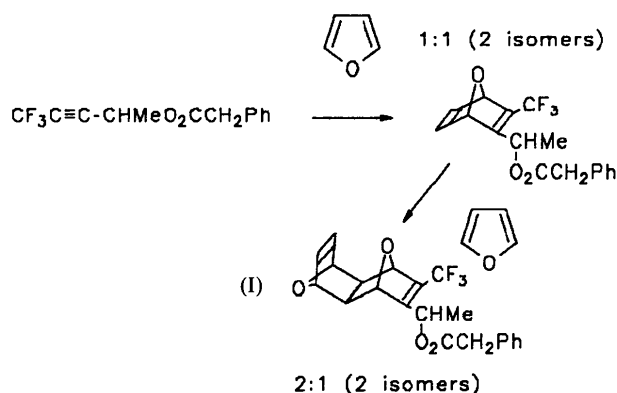
The exclusive production of *anti*-joined products indicates that the reaction pathway from 1:1 to 1:2 adducts is stereoselective. The absence of *syn*-joined bis adducts was also noted by Hall, Harkema, den Hertog, van Hummel & Reinhoudt (1981) when they reacted 2-butynedinitrile with 2,3,4,5-tetramethylfuran. They con-
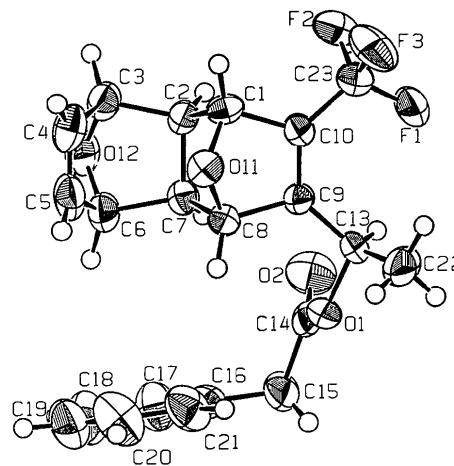

Fig. 1. Isomer (1) (1*R*,2*S*,3*R*,6*S*,7*R*,8*S*,13*R*) including atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976).