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A Dimer Ketone Formed *via* Fe(CO)$_5$-Promoted Coupling of 7-Phenoxynorbornadiene to Carbon Monoxide

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Abstract. (*syn,syn*)-1,4,4aα,4bβ,5,8,8aβ,9aα-Octahydro-10,11-diphenoxy-1,4:5,8-dimethanofluoren-9-one (3), $C_{27}H_{24}O_3$, $M_r = 396{\cdot}49$, monoclinic, $P2_1/c$, $a = 14{\cdot}926\,(5)$, $b = 6{\cdot}240\,(2)$, $c = 22{\cdot}082\,(9)$ Å, $\beta = 98{\cdot}09\,(3)°$, $V = 2034\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}29$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}77$ cm^{-1}, $F(000) = 840$, $T = 293$ K, $R = 0{\cdot}046$ for 3023 reflections. The central five-membered ring is almost planar. The norbornene rings are joined in an *anti* fashion to the five-membered ring with the four attached C—C bonds averaging 1·560 (3) Å indicating considerable strain in the molecule. Chemically equivalent bonds are statistically equivalent. The H(1), H(2) and H(8), H(9) atoms are bent away from the methylene bridges and out of the planes defined by C(1)C(2)C(3)C(13) and C(7)C(8)-C(9)C(10) [interplanar angles 4·7 (1) and 8·3 (1)°]. This π-system distortion has been observed in other norbornene systems.

Experimental. The dimer ketone prepared by refluxing 7-phenoxynorbornadiene [(1), 40·7 mmol] with Fe(CO)$_5$ (82·1 mmol) in dry di-*n*-butyl ether (60 ml) under nitrogen for 3 d. The reaction was quenched *via* addition of a solution of FeCl$_3$.7H$_2$O (50 g) in acetone (200 ml) and stirred for 7 d to decompose unreacted Fe(CO)$_5$ and Fe^0 complexes which might be present (Shvo & Hazum, 1974). Column chromatography (Florisil stationary phase, ethyl acetate–hexane mixed solvent gradient elution) yielded two compounds: a cage dimer [(2), 19%] and a dimer ketone [(3), 11%].

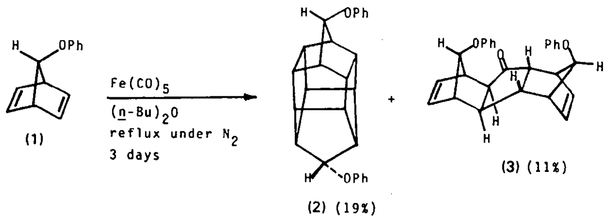

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

	x	y	z	U_{eq}*
C(1)	2472 (1)	9732 (3)	3172 (1)	55 (1)
C(2)	2041 (1)	8251 (3)	3441 (1)	62 (1)
C(3)	1956 (1)	6297 (3)	3037 (1)	53 (1)
C(4)	1270 (1)	6885 (2)	2462 (1)	45 (1)
C(5)	1078 (1)	5114 (2)	1996 (1)	49 (1)
O(5)	712 (1)	3446 (2)	2090 (1)	71 (1)
C(6)	1378 (1)	5730 (2)	1393 (1)	44 (1)
C(7)	582 (1)	6027 (3)	856 (1)	57 (1)
C(8)	−116 (1)	7386 (3)	1094 (1)	64 (1)
C(9)	217 (1)	9328 (3)	1182 (1)	56 (1)
C(10)	1150 (1)	9323 (2)	1001 (1)	44 (1)
C(11)	1779 (1)	7993 (2)	1484 (1)	38 (1)
C(12)	1753 (1)	8676 (2)	2153 (1)	38 (1)
C(13)	2681 (1)	8824 (3)	2574 (1)	43 (1)
C(14)	2854 (1)	6502 (3)	2788 (1)	46 (1)
O(14)	2901 (1)	4918 (2)	2323 (1)	48 (1)
C(15)	993 (1)	7690 (3)	479 (1)	54 (1)
O(15)	1787 (1)	6858 (2)	271 (1)	61 (1)
C(16)	3643 (1)	4856 (2)	2018 (1)	44 (1)
C(17)	3628 (1)	3256 (3)	1585 (1)	53 (1)
C(18)	4338 (1)	3072 (3)	1248 (1)	64 (1)
C(19)	5058 (1)	4460 (4)	1342 (1)	68 (1)
C(20)	5073 (1)	6026 (3)	1778 (1)	64 (1)
C(21)	4368 (1)	6237 (3)	2122 (1)	54 (1)
C(22)	2367 (1)	8258 (3)	49 (1)	58 (1)
C(23)	3244 (1)	7513 (4)	53 (1)	75 (1)
C(24)	3859 (2)	8773 (5)	−191 (1)	99 (1)
C(25)	3614 (2)	10748 (5)	−433 (1)	102 (1)
C(26)	2756 (2)	11488 (4)	−419 (1)	89 (1)
C(27)	2128 (1)	10253 (3)	−185 (1)	69 (1)

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

A good colorless single crystal of (3), m.p. 411 K, was obtained *via* careful fractional crystallization from an ethyl acetate–hexane mixed solvent. Colorless crystal, 0·5 × 0·35 × 0·45 mm; Nicolet $R3m/\mu$ update of $P2_1$ diffractometer; data collected in Wyckoff mode ($4 \leq 2\theta \leq 50°$, 2θ fixed ω varied), scan rate 4 to 29·3° min^{-1}, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($30{\cdot}08 \leq 2\theta \leq 47{\cdot}61°$), angles measured by a centering routine; systematic absences ($h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$) and Laue symmetry $2/m$ consistent with space group $P2_1/c$; monitored reflections $2\bar{3}\bar{5}$ and $4\bar{2}\bar{1}$ showed only statistical variations in

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

C(1)–C(2)	1·315 (3)	C(1)–C(13)	1·509 (2)
C(2)–C(3)	1·505 (2)	C(3)–C(4)	1·560 (2)
C(3)–C(14)	1·523 (2)	C(4)–C(5)	1·510 (2)
C(4)–C(12)	1·540 (2)	C(5)–O(5)	1·208 (2)
C(5)–C(6)	1·511 (2)	C(6)–C(7)	1·566 (2)
C(6)–C(11)	1·536 (2)	C(7)–C(8)	1·495 (3)
C(7)–C(15)	1·515 (3)	C(8)–C(9)	1·314 (3)
C(9)–C(10)	1·503 (2)	C(10)–C(11)	1·557 (2)
C(10)–C(15)	1·532 (2)	C(11)–C(12)	1·544 (2)
C(12)–C(13)	1·559 (2)	C(13)–C(14)	1·534 (2)
C(14)–O(14)	1·434 (2)	O(14)–C(16)	1·375 (2)
C(15)–O(15)	1·427 (2)	O(15)–C(22)	1·368 (2)
C(16)–C(17)	1·380 (2)	C(16)–C(21)	1·378 (2)
C(17)–C(18)	1·383 (3)	C(18)–C(19)	1·373 (3)
C(19)–C(20)	1·370 (3)	C(20)–C(21)	1·388 (3)
C(22)–C(23)	1·388 (3)	C(22)–C(27)	1·375 (3)
C(23)–C(24)	1·375 (4)	C(24)–C(25)	1·372 (4)
C(25)–C(26)	1·366 (4)	C(26)–C(27)	1·370 (3)

C(2)–C(1)–C(13)	107·8 (1)	C(1)–C(2)–C(3)	108·0 (2)
C(2)–C(3)–C(4)	106·4 (1)	C(2)–C(3)–C(14)	98·1 (1)
C(4)–C(3)–C(14)	101·3 (1)	C(3)–C(4)–C(5)	115·0 (1)
C(3)–C(4)–C(12)	103·7 (1)	C(5)–C(4)–C(12)	106·5 (1)
C(4)–C(5)–O(5)	124·1 (2)	C(4)–C(5)–C(6)	111·3 (1)
O(5)–C(5)–C(6)	124·6 (2)	C(5)–C(6)–C(7)	114·2 (1)
C(5)–C(6)–C(11)	106·1 (1)	C(7)–C(6)–C(11)	103·3 (1)
C(6)–C(7)–C(8)	107·0 (1)	C(6)–C(7)–C(15)	100·1 (1)
C(8)–C(7)–C(15)	99·3 (1)	C(7)–C(8)–C(9)	107·9 (2)
C(8)–C(9)–C(10)	107·7 (2)	C(9)–C(10)–C(11)	108·1 (1)
C(9)–C(10)–C(15)	98·8 (1)	C(11)–C(10)–C(15)	100·0 (1)
C(6)–C(11)–C(10)	102·4 (1)	C(6)–C(11)–C(12)	108·4 (1)
C(10)–C(11)–C(12)	114·5 (1)	C(4)–C(12)–C(11)	107·5 (1)
C(4)–C(12)–C(13)	102·1 (1)	C(11)–C(12)–C(13)	116·6 (1)
C(1)–C(13)–C(12)	105·6 (1)	C(1)–C(13)–C(14)	97·6 (1)
C(12)–C(13)–C(14)	103·0 (1)	C(3)–C(14)–C(13)	94·2 (1)
C(3)–C(14)–O(14)	109·6 (1)	C(13)–C(14)–O(14)	117·0 (1)
C(14)–O(14)–C(16)	119·7 (1)	C(7)–C(15)–C(10)	94·1 (1)
C(7)–C(15)–O(15)	110·3 (1)	C(10)–C(15)–O(15)	116·0 (1)
C(15)–O(15)–C(22)	118·6 (1)	O(14)–C(16)–C(17)	115·2 (1)
O(14)–C(16)–C(21)	124·7 (1)	C(17)–C(16)–C(21)	120·2 (2)
C(16)–C(17)–C(18)	119·7 (2)	C(17)–C(18)–C(19)	120·5 (2)
C(18)–C(19)–C(20)	119·5 (2)	C(19)–C(20)–C(21)	120·9 (2)
C(16)–C(21)–C(20)	119·2 (2)	O(15)–C(22)–C(23)	115·3 (2)
O(15)–C(22)–C(27)	124·6 (2)	C(23)–C(22)–C(27)	120·0 (2)
C(22)–C(23)–C(24)	119·2 (2)	C(23)–C(24)–C(25)	120·6 (2)
C(24)–C(25)–C(26)	119·6 (3)	C(25)–C(26)–C(27)	120·8 (2)
C(22)–C(27)–C(26)	119·7 (2)		

intensities; 3580 independent reflections measured ($0 \leq h \leq 17$, $0 \leq k \leq 7$, $-25 \leq l \leq 25$), $3023 \geq 2{\cdot}5 \times \sigma(I)$; Lorentz–polarization corrections applied, ψ-scan empirical absorption correction (transmission factors 0·888 to 0·936); $R_{\rm int} = 0{\cdot}0164$; structure solved by direct methods, block-cascade least-squares refinement, H atoms found in difference map, 4 H atoms refined isotropically, all other H atoms allowed to ride at fixed distance from C atoms, a single isotropic thermal parameter was refined for the phenyl H atoms while a second isotropic parameter was refined for the remaining H atoms; final $R = 0{\cdot}0468$, $wR = 0{\cdot}0505$ for 289 parameters and 3023 reflections, $S = 1{\cdot}587$, $(\Delta/\sigma)_{\rm max} = 0{\cdot}21$, $(\Delta/\sigma)_{\rm av} = 0{\cdot}040$; largest peaks in the final difference map of $+0{\cdot}20$ and $-0{\cdot}15$ e Å^{-3}; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0{\cdot}00056F_o^2]^{-1}$. All computer programs supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

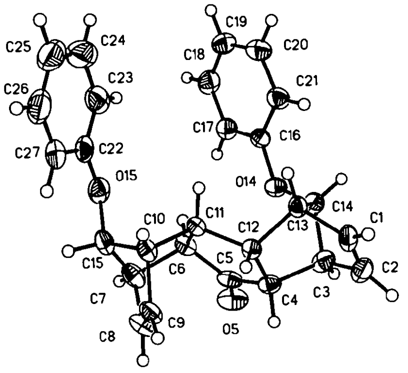

Fig. 1. Drawing of compound (3) with thermal ellipsoids at the 35% probability level and H atoms represented by spheres of arbitrary size.

Table 1 lists atomic positional parameters and Table 2 interatomic distances and valence angles.* A drawing of (3) is given in Fig. 1.

Related literature. The thermal reaction of 7-substituted norbornadienes with $Fe(CO)_5$ has been reported in the literature (Marchand, Goodin, Hossain & van der Helm, 1984; Marchand, Earlywine & Heeg, 1986, and references therein). The crystal structures of several related ketone dimers have been determined (Ealick & van der Helm, 1975; Ealick, van der Helm, Hayes & Marchand, 1978; Marchand, Goodin, Hossain & van der Helm, 1984). The deformation of π-electron systems in molecules such as norbornene and its derivatives is discussed in the proceedings of the symposium on *Stereochemistry and Reactivity in Pi-Systems* (Watson, 1983).

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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 44661 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of an Imidazoline Ribonucleoside

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Abstract. 1-(β-D-Ribofuranosyl)-2-oxo-4-imidazoline-4-carboxylic acid dihydrate, $C_9H_{12}N_2O_7.2H_2O$, $M_r = 296{\cdot}23$, monoclinic, $P2_1$, $a = 9{\cdot}3754\,(10)$, $b = 5{\cdot}0542\,(4)$, $c = 13{\cdot}3075\,(10)$ Å, $\beta = 103{\cdot}155\,(9)°$, $V = 614{\cdot}03\,(10)$ Å^3, $Z = 2$, $D_x = 1{\cdot}602$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 12{\cdot}175$ cm^{-1}, $F(000) = 312$, $T = 295$ K, $R = 0{\cdot}0311$ for 2458 reflections ($F \geq 4\sigma_F$). The sugar bond lengths and bond angles are normal. The sugar ring is C_3, *endo* (conformation $^3T_4$) with angle of pseudorotation 26·9° and $\tau_m = 32{\cdot}0°$. The conformation around C4′—C5′ is *gt* [torsion angles: O4′, 67·1 (2); C3′, −175·94 (13)°]. The glycosidic torsion angle, $\chi =$ O4′—C1′—N1—C2, is −122·68 (14)°. Nine hydrogen bonds with $d(\mathrm{H}\cdots A)$ ranging from 1·64 (3) to 2·20 (3) Å exist in the crystal structure. The imidazoline ring is planar [r.m.s.d. 0·003 (3) Å]. The carboxylic acid function is twisted 1·14 (8)° out of the plane of the imidazoline ring.

Experimental. The title compound, 1-(β-D-ribofuranosyl)-2-oxo-4-imidazoline-4-carboxylic acid dihydrate (1) was synthesized by the base-induced ring contraction of uridine previously reported by Otter, Falco & Fox (1969). Transparent crystals were grown from an acetone/water solution. The data collection and refinement are summarized in Table 1.

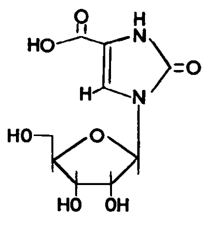
Table 1. *Summary of data collection and refinement for* (1)

(*A*) Data collection (295 K)*†	
Mode	ω–2θ scan
Scan range (°)	$0{\cdot}80 + 0{\cdot}15\tan\theta$
Background	Scan 0·25 times scan range before and after scan
Scan rate (° min^{-1})	1·5–8·3
Exposure time (h)	17·1
Stability correction range on *I*	1·000–1·003
2θ range (°)	3·0–152·0
Range in *hkl*, min.	0, −6, −16
max.	11, 6, 16
Total reflections measured, unique	2722, 2482
R_{int}	0·0093
Crystal dimensions (mm)	0·36 × 0·20 × 0·13
Crystal volume (mm^3)	0·00912
Crystal faces	$\{001\}$; $\{100\}$; $(0\bar{1}0)$; (011); $(01\bar{1})$
Transmission-factor range	0·672–0·866
(*B*) Structure refinement‡	
Reflections used ($F \geq 4\sigma_F$)	2458
Number of variables	245
Extinction parameter	1·86 (5) × 10^{-5}
Goodness of fit, *S*	1·878
R, *wR*	0·0311, 0·0441
R for all data	0·0315
Max., av. Δ/σ	0·0033, 0·0006
Max., min. density in $\Delta\rho$ map (e Å^{-3})	0·49, −0·27

* Unit-cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with $54{\cdot}9 < 2\theta < 59{\cdot}5°$.

† Enraf–Nonius CAD-4 diffractometer with a graphite monochromator was used. Crystal and instrument stability was monitored by re-measurement of 3 check reflections every hour. A linear fit of the intensities of these reflections was used to correct the data.

‡ Function minimized was $\sum w(F_o - F_c)^2$, where $w^{-1} = (\sigma_F^2 + 0{\cdot}0004F^2)$. $\sigma_F = F\sigma_I/2I$; $\sigma_I = [N_{\mathrm{pk}} + N_{\mathrm{bg1}} + N_{\mathrm{bg2}}]^{1/2}$.



(1)

The positions of the 20 non-H atoms were obtained by direct methods (*SHELXS*86; Sheldrick, 1986); the 16 H atoms were located in a difference map as peaks of 0·45–0·89 e Å^{-3} at $R = 0{\cdot}053$. All atomic positions were varied as well as all anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. Refinement by full-matrix least squares was carried out with *SHELX*76 (Sheldrick, 1976). Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray*

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