C3—C10	1.373 (5)	1.384 (3)
C4—C5	1.335 (6)	1.350 (4)
C5—C6	1.421 (6)	1.414 (4)
C6—C7	1.356 (6)	1.357 (4)
C7—C8	1.402 (6)	1.410 (3)
C7—C20	—	1.511 (4)
C8—C9	1.408 (5)	1.389 (3)
C9—C10	1.388 (5)	1.394 (3)
C9—C18	1.498 (6)	1.504 (4)
C11—C12	1.490 (5)	1.496 (4)
C12—C13	1.404 (6)	1.391 (4)
C12—C17	1.383 (5)	1.389 (4)
C13—C14	1.373 (6)	1.382 (4)
C14—C15	1.377 (6)	1.383 (4)
C15—C16	1.384 (6)	1.374 (4)
C16—C17	1.380 (6)	1.380 (4)
C18—C19	—	1.539 (4)
C19—C20	—	1.527(4)
C1—O1—C10	104.3 (3)	104.8 (2)
C3—N1—C4	132.2 (4)	132.8 (2)
C3—N1—C8	106.7 (3)	105.9 (2)
C4—N1—C8	121.0 (3)	121.3 (2)
O1—C1—C2	111.6 (3)	111.3 (2)
O1—C1—C11	114.4 (3)	115.0 (2)
C2—C1—C11	133.9 (4)	133.7(2)
C1—C2—C3	104.9 (4)	105.6(2)
N1—C3—C2	144.2 (4)	144.4 (2)
N1—C3—C10	107.1 (3)	107.6 (2)
C2—C3—C10	108.5 (3)	108.0 (2)
N1—C4—C5	120.1 (4)	118.3 (2)
C4—C5—C6	120.6 (4)	121.7 (3)
C5—C6—C7	120.3 (4)	120.6 (2)
C6—C7—C28	121.0 (4)	118.3 (2)
C6—C7—C20	—	127.4 (2)
C8—C7—C20	—	114.2 (2)
N1—C8—C7	116.8 (3)	119.6 (2)
N1—C8—C9	109.5 (4)	111.8 (2)
C7—C8—C9	133.6 (4)	128.6 (2)
C8—C9—C10	103.6 (4)	103.2 (2)
C8—C9—C18	126.4 (4)	118.7 (2)
C10—C9—C18	130.0 (4)	138.1 (2)
O1—C10—C3	110.7 (3)	110.3 (2)
O1—C10—C9	136.2 (4)	138.2 (2)
C3—C10—C9	113.0 (3)	111.5 (2)
O2—C11—C1	120.4 (4)	121.3 (2)
O2—C11—C12	120.4 (4)	120.0 (2)
C1—C11—C12	119.2 (3)	118.6 (2)
C11—C12—C13	117.9 (3)	123.7 (2)
C11—C12—C17	123.6 (4)	117.8 (3)
C13—C12—C17	118.2 (4)	118.5 (3)
C12—C13—C14	120.5 (4)	120.5 (3)
C13—C14—C15	120.4 (4)	119.9 (3)
C14—C15—C16	119.9 (4)	120.2 (3)
C15—C16—C17	119.7 (4)	119.8 (3)
C12—C17—C16	121.2 (4)	121.0 (3)
C9—C18—C19	—	109.1 (2)
C18—C19—C20	—	113.3 (3)
C7—C20—C19	—	111.6 (2)

Table 3. *Comparison of ring planarity in (2a) and (2b) as represented by χ^2 values*

	Pyridine	Pyrrole	Furan	Indolizine	Phenyl
(2a)	159.4	9.9	21.0	425.5	7.3
(2b)	114.1	15.1	20.0	385.4	40.6

Azimuthal scans of several reflections indicated that there was no need to correct for absorption for either compound. In both cases, the H atoms were located from a difference Fourier map and refined isotropically. The structures were solved by direct methods (*MITHRIL*; Gilmore, 1984), utilizing the *TEXSAN* system (Molecular Structure Corporation, 1985).

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Quinine Model Study: Stereospecific Aldol Condensation/Reduction

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Abstract

The racemate *rel*-(1R,2R,αS)-3-acetoxy-2-(α-acetoxy-4-quinolinemethyl)-1-azabicyclo[2.2.2]octane is obtained as the exclusive product in the condensation/reduction reaction sequence. The 1-azabicyclo[2.2.2.]octane moiety is twisted away from the ideal eclipsed geometry.

Comment

The compound (1) was prepared by the aldol condensation of quinoline-4-carboxaldehyde with the lithium enolate of 3-quinuclidinone followed by *in situ* hydride reduction of the ketoalkoxide (Stotter, Friedman & Minter, 1985). The resulting diol, a single diastereomer, was derivatized as the diacetate. As a model for the total synthesis of quinine, this structure verifies the stereoselectivity of the aldol condensation for establishing the required stereochemistry at C(8)—C(9) (Fig. 1).
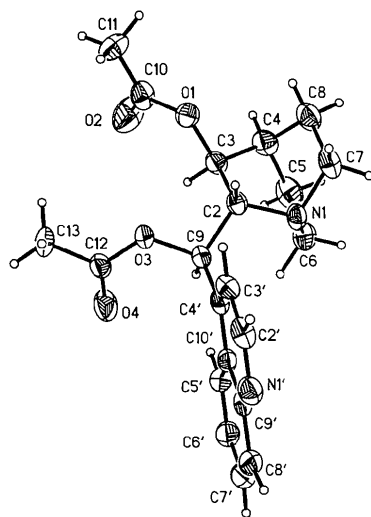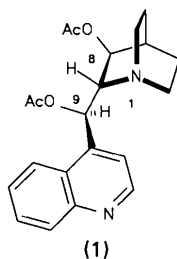

(1)

Fig. 1. Drawing of $C_{21}H_{24}O_4N_2$. Thermal ellipsoids are drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

The aldol condensation followed by reduction produces exclusively the racemate of the *trans*-diastereomer. The 1-azabicyclo[2.2.2.]octane moiety exhibits the usual distortions away from an ideal eclipsed conformation (Baker & Pauling, 1972; Meyerhoffer, 1970; Harlow & Simonsen, 1976*a,b*). The three N(1)—C bonds range from 1.466(5) to 1.477(4) Å, the three C(4)—C bonds range from 1.517(5) to 1.534(6) Å while the torsion angles N(1)—C(2)—C(3)—C(4), N(1)—C(6)—C(5)—C(4) and N(1)—C(7)—C(8)—C(4) are 9.2(4), 4.8(4) and 5.7(3)°, respectively.

Experimental

Crystal data

$C_{21}H_{24}N_2O_4$	$D_x = 1.300$ Mg m^{-3}
$M_r = 368.48$	Mo $K\alpha$ radiation
Monoclinic	$\lambda = 0.71073$ Å
$P2_1/n$	Cell parameters from 25
$a = 8.859$ (3) Å	reflections
$b = 10.075$ (4) Å	$\theta = 19.85$–$25.25°$
$c = 21.189$ (7) Å	$\mu = 0.85$ mm^{-1}
$\beta = 95.62$ (3)°	$T = 298$ K
$V = 1882.0$ (9) Å^3	Prism
$Z = 4$	$0.48 \times 0.25 \times 0.13$ mm
	Colourless

Data collection

Nicolet $R3m/\mu$ diffractometer	1638 observed reflections
	$[I \geq 3\sigma(I)]$
ω scans	$R_{int} = 0.0077$
Absorption correction: ψ	$\theta_{max} = 22.5°$
scan	$h = -9 \rightarrow 1$
$T_{min} = 0.859$, $T_{max} = 0.866$	$k = -10 \rightarrow 10$
	$l = 0 \rightarrow 22$
3585 measured reflections	2 standard reflections
3240 independent reflections	monitored every 100
	reflections
	intensity variation: 2%

Refinement

Refinement on F	$\Delta\rho_{min} = -0.23$ e Å^{-3}
Final $R = 0.0625$	Extinction correction: $F_{corr} =$
$wR = 0.0267$	$F_c/[1+1.6(2)\times10^{-6}$
$S = 1.639$	$\times F_c^2/\sin^2 2\theta]^{0.25}$
1638 reflections	Extinction coefficient:
323 parameters	0.00083
Methyl H atoms not refined,	Atomic scattering factors
all other H atoms refined	from *International Tables*
$w = 1/[\sigma^2(F)+0.0000F^2]$	*for X-ray Crystallography* (1974, Vol. IV, Table
$(\Delta/\sigma)_{max} = 0.013$	*phy* (1974, Vol. IV, Table
$\Delta\rho_{max} = 0.22$ e Å^{-3}	2.3.1)

Data collection: $R3m/\mu$ diffractometer control program. Cell refinement: $R3m/\mu$ diffractometer control program. Data reduction: *SHELXTL* (Sheldrick, 1985). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1)	0.1483 (3)	0.7489 (3)	0.5670 (1)	0.055 (1)
C(2)	0.2319 (4)	0.8626 (3)	0.5960 (1)	0.047 (1)
C(3)	0.1488 (4)	0.9274 (4)	0.6482 (2)	0.053 (1)
C(4)	−0.0084 (4)	0.8668 (4)	0.6462 (2)	0.067 (2)
C(5)	0.0116 (5)	0.7193 (5)	0.6629 (2)	0.086 (2)
C(6)	0.1118 (4)	0.6557 (4)	0.6164 (2)	0.073 (2)
C(7)	0.0044 (4)	0.7989 (4)	0.5345 (2)	0.070 (2)
C(8)	−0.0886 (4)	0.8772 (4)	0.5790 (2)	0.075 (2)
C(9)	0.3935 (4)	0.8244 (3)	0.6198 (2)	0.045 (1)
N(1')	0.6566 (3)	0.6513 (3)	0.4784 (1)	0.061 (1)
C(2')	0.5788 (4)	0.7607 (4)	0.4691 (2)	0.060 (2)
C(3')	0.4895 (4)	0.8168 (3)	0.5133 (2)	0.055 (1)

C(4')	0.4820 (3)	0.7579 (4)	0.5711 (2)	0.045 (1)
C(5')	0.5671 (4)	0.5655 (4)	0.6407 (2)	0.057 (2)
C(6')	0.6499 (4)	0.4531 (4)	0.6494 (2)	0.068 (2)
C(7')	0.7325 (5)	0.4056 (5)	0.6014 (2)	0.075 (2)
C(8')	0.7329 (4)	0.4704 (4)	0.5459 (3)	0.066 (2)
C(9')	0.6485 (4)	0.5885 (4)	0.5353 (2)	0.053 (1)
C(10')	0.5631 (4)	0.6390 (4)	0.5835 (2)	0.045 (1)
O(1)	0.1391 (3)	1.0693 (2)	0.6352 (1)	0.062 (1)
C(10)	0.1559 (4)	1.1538 (4)	0.6837 (2)	0.068 (2)
O(2)	0.1723 (4)	1.1165 (3)	0.7375 (1)	0.115 (1)
C(11)	0.1518 (6)	1.2963 (4)	0.6630 (2)	0.083 (2)
O(3)	0.4665 (2)	0.9518 (2)	0.6368 (1)	0.053 (1)
C(12)	0.5811 (4)	0.9531 (4)	0.6825 (2)	0.057 (1)
O(4)	0.6230 (3)	0.8561 (2)	0.7119 (1)	0.088 (1)
C(13)	0.6494 (5)	1.0886 (4)	0.6904 (2)	0.074 (2)

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

N(1)—C(2)	1.466 (4)	C(2')—C(3')	1.402 (5)
N(1)—C(6)	1.466 (5)	C(3')—C(4')	1.368 (5)
N(1)—C(7)	1.477 (4)	C(4')—C(10')	1.408 (5)
C(2)—C(3)	1.532 (4)	C(5')—C(6')	1.352 (5)
C(2)—C(9)	1.520 (4)	C(5')—C(10')	1.416 (5)
C(3)—C(4)	1.517 (5)	C(6')—C(7')	1.394 (6)
C(3)—O(1)	1.457 (5)	C(7')—C(8')	1.345 (7)
C(4)—C(5)	1.534 (6)	C(8')—C(9')	1.412 (6)
C(4)—C(8)	1.530 (5)	C(9')—C(10')	1.424 (5)
C(5)—C(6)	1.529 (6)	O(1)—C(10)	1.331 (4)
C(7)—C(8)	1.530 (5)	C(10)—O(2)	1.195 (4)
C(9)—C(4')	1.512 (5)	C(10)—C(11)	1.500 (5)
C(9)—O(3)	1.466 (4)	O(3)—C(12)	1.333 (4)
N(1')—C(2')	1.305 (5)	C(12)—O(4)	1.199 (4)
N(1')—C(9')	1.372 (5)	C(12)—C(13)	1.495 (5)
C(2)—N(1)—C(6)	109.8 (2)	C(2')—C(3')—C(4')	120.2 (3)
C(2)—N(1)—C(7)	107.8 (2)	C(9)—C(4')—C(10')	122.6 (3)
C(6)—N(1)—C(7)	108.1 (3)	C(3')—C(4')—C(10')	117.9 (3)
N(1)—C(2)—C(3)	112.1 (3)	C(6')—C(5')—C(10')	121.5 (3)
N(1)—C(2)—C(9)	111.2 (3)	C(5')—C(6')—C(7')	120.2 (4)
C(3)—C(2)—C(9)	111.9 (3)	C(6')—C(7')—C(8')	121.2 (4)
C(2)—C(3)—C(4)	108.2 (3)	C(7')—C(8')—C(9')	120.0 (4)
C(2)—C(3)—O(1)	107.8 (3)	N(1')—C(9')—C(8')	117.1 (3)
C(4)—C(3)—O(1)	110.7 (3)	N(1')—C(9')—C(10')	123.0 (3)
C(3)—C(4)—C(5)	107.4 (3)	C(8')—C(9')—C(10')	119.9 (3)
C(3)—C(4)—C(8)	109.8 (3)	C(4')—C(10')—C(5')	125.1 (3)
C(5)—C(4)—C(8)	108.3 (3)	C(4')—C(10')—C(9')	117.9 (3)
C(4)—C(5)—C(6)	108.5 (3)	C(5')—C(10')—C(9')	117.1 (3)
N(1)—C(6)—C(5)	112.0 (3)	C(3)—O(1)—C(10)	118.9 (3)
N(1)—C(7)—C(8	112.4 (3)	O(1)—C(10)—O(2)	121.9 (3)
C(4)—C(8)—C(7)	108.0 (3)	O(1)—C(10)—C(11)	112.9 (3)
C(2)—C(9)—C(4')	114.9 (3)	O(2)—C(10)—C(11)	125.2 (3)
C(2)—C(9)—O(3)	103.8 (2)	C(9)—O(3)—C(12)	118.3 (2)
C(4')—C(9)—O(3)	108.1 (3)	C(3)—C(12)—O(4)	123.0 (3)
C(2')—N(1')—C(9')	116.7 (3)	O(3)—C(12)—C(13)	111.1 (3)
N(1')—C(2')—C(3')	124.4 (4)	O(4)—C(12)—C(13)	125.8 (3)

N(1)—C(2)—C(3)—C(4)	−9.2 (4)	C(3)—C(2)—N(1)—C(6)	−52.9 (3)
N(1)—C(6)—C(5)—C(4)	−4.8 (4)	C(3)—C(2)—N(1)—C(7)	64.6 (3)
N(1)—C(7)—C(8)—C(4)	−5.7 (4)	C(5)—C(6)—N(1)—C(2)	60.9 (3)
C(2)—C(3)—C(4)—C(5)	64.4 (4)	C(5)—C(6)—N(1)—C(7)	−56.4 (4)
C(2)—C(3)—C(4)—C(8)	−53.2 (4)	C(8)—C(7)—N(1)—C(2)	−55.5 (3)
C(6)—C(5)—C(4)—C(3)	−56.7 (4)	C(8)—C(7)—N(1)—C(6)	63.1 (4)
C(6)—C(5)—C(4)—C(8)	61.8 (4)	O(1)—C(3)—C(2)—C(9)	105.3 (3)
C(7)—C(8)—C(4)—C(3)	61.4 (4)	C(3)—C(2)—C(9)—C(4')	179.1 (3)
C(7)—C(8)—C(4)—C(5)	−55.5 (4)	C(3)—C(2—C(9)—O(3)	−63.1 (3)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55750 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1035]

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Hexanitrodiphenylmethane

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Abstract

An X-ray diffraction study of a crystal of 2,2',-4,4',6,6'-hexanitrodiphenylmethane showed that the two phenyl rings are essentially planar and are nearly perpendicular to each other, confirming previous conclusions drawn from ^{13}C NMR measurements.

Comment

In the course of our studies into the effect of structure upon the intrinsic reactivity of carbon acids, we have examined a number of nitro-substituted diphenylmethanes (1a)–(1g) (Fig. 1). Both kinetic data for proton abstraction/carbanion reprotonation and spectroscopic measurements (^1H and ^{13}C NMR,