ω–2θ scans
Absorption correction: empirical *via* ψ scan (*TEXSAN*; Molecular Structure Corporation, 1985)
$T_{\min} = 0.98$, $T_{\max} = 1.00$
1342 measured reflections
1206 independent reflections

$R_{\rm int} = 0.010$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 14$
$l = -11 \rightarrow 10$
3 standard reflections
frequency: 150 min
intensity decay: 3.30%

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.036$
$S = 1.41$
810 reflections
144 parameters
H atoms: see below
$w = 4F_o/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max} = 0.08$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
F(1)	0.3527 (4)	0.1014 (2)	0.5002 (2)	5.66 (9)
F(2)	−0.0836 (4)	0.0894 (2)	0.3889 (2)	5.68 (8)
F(3)	0.6672 (3)	0.1583 (2)	0.0566 (2)	5.17 (7)
F(4)	0.2411 (4)	0.1479 (2)	−0.0702 (2)	4.92 (7)
O(1)	0.2350 (5)	−0.0901 (2)	0.3333 (2)	5.5 (1)
N(1)	0.3196 (6)	0.3444 (2)	0.1012 (3)	5.1 (1)
C(2)	0.2372 (8)	0.4329 (3)	0.1742 (4)	6.1 (2)
C(3)	0.1342 (9)	0.4242 (3)	0.3094 (4)	6.5 (2)
C(4)	0.1194 (7)	0.3186 (3)	0.3716 (3)	5.6 (2)
C(5)	0.1865 (6)	0.1068 (3)	0.3598 (3)	4.3 (1)
C(6)	0.2674 (6)	0.0108 (3)	0.2663 (3)	4.1 (1)
C(7)	0.3579 (6)	0.0281 (3)	0.1364 (3)	4.1 (1)
C(8)	0.3886 (6)	0.1429 (3)	0.0751 (3)	3.8 (1)
C(9)	0.3019 (6)	0.2419 (3)	0.1629 (3)	3.9 (1)
C(10)	0.2030 (6)	0.2242 (3)	0.2970 (3)	3.9 (1)
C(11)	0.307 (1)	−0.1896 (3)	0.2560 (4)	7.0 (2)

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

N(1)—C(2)	1.323 (4)	C(8)—C(9)	1.501 (4)
N(1)—C(9)	1.332 (4)	C(9)—C(10)	1.382 (4)
C(2)—C(3)	1.389 (5)	C(6)—O(1)	1.348 (4)
C(3)—C(4)	1.366 (5)	O(1)—C(11)	1.430 (4)
C(4)—C(10)	1.387 (4)	C(5)—F(1)	1.375 (3)
C(5)—C(10)	1.495 (4)	C(5)—F(2)	1.372 (3)
C(5)—C(6)	1.494 (4)	C(8)—F(3)	1.378 (3)
C(6)—C(7)	1.327 (4)	C(8)—F(4)	1.378 (3)
C(7)—C(8)	1.471 (4)		
C(2)—N(1)—C(9)	117.1 (3)	C(8)—C(9)—C(10)	120.5 (3)
N(1)—C(2)—C(3)	123.7 (3)	C(5)—C(10)—C(9)	121.0 (2)
C(2)—C(3)—C(4)	118.4 (3)	C(6)—C(5)—C(10)	116.5 (2)
C(3)—C(4)—C(10)	119.1 (3)	C(5)—C(6)—O(1)	110.5 (2)
C(4)—C(10)—C(9)	118.0 (2)	C(7)—C(6)—O(1)	127.3 (3)
N(1)—C(9)—C(10)	123.6 (2)	C(6)—O(1)—C(11)	116.4 (2)
C(5)—C(6)—C(7)	122.2 (3)	F(1)—C(5)—F(2)	103.5 (2)
C(6)—C(7)—C(8)	122.5 (3)	F(3)—C(8)—F(4)	103.3 (2)
C(7)—C(8)—C(9)	117.2 (2)		

The title structure was solved by direct methods. One of the H atoms of the CH_3 group was found in a difference Fourier map, while the others were assigned based on the expected bonding geometry. All of the H atoms were included in the final cycle of the refinement. Calculations were performed on a VAXstation 3200.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Highly Strained Tertiary Acetate: 2,2′-Spirobiadamant-1-yl Acetate

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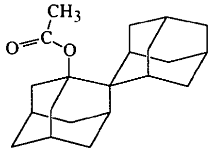
Abstract

The four C—C bonds to the spiro-C atom in the title compound, 2,2′-spirobitricyclo[3.3.1.1^{3,7}]dec-1-yl acetate, $C_{21}H_{30}O_2$, are all unusually long and the corresponding bond angles are either substantially smaller (intracyclic) or larger (exocyclic) than usual.

Comment

The 1-substituted tertiary derivatives of 2,2′-spirobiadamantane (Boelema, Strating & Wynberg, 1972;

Graham & Schleyer, 1972), usually referred to as [1]diadamantane (Graham, Schleyer, Hageman & Wenkert, 1973), are atypical in that they are thermodynamically less stable than the corresponding 4-substituted secondary derivatives (Lomas, Cordier & Briand, 1996; Lomas, Cordier, Briand & Vaissermann, 1996). The abnormally high solvolysis rate of 1-chloro[1]diadamantane is attributed to steric strain between the substituent and the closest methylene H atoms of the non-substituted adamantyl unit. 1-Halo[1]diadamantanes are too reactive for X-ray study but the acetate, (I), is expected to show much the same structural features.



(I)

The torsion angle which positions atom C(20) relative to C(2) is nearly 180° [177.1 (2)°], while that for O(2) relative to C(1) is not far from 0° [−1.4 (2)°]. This means that the carbonyl O(2) atom is close to and approximately equidistant from atoms C(8) and C(9), while the methyl group is oriented away from the rest of the molecule. The distances between the O(2) atom and the nearest H atoms at these atoms are short but quite different [2.36 (3) and 2.51 (3) Å] because of the slight twist in the acetoxy group and deformation of the methylene groups. The other O atom, O(1), is, as expected, at a very short distance from the closest H atoms at C(16) and C(18) [2.26 (3) and 2.29 (3) Å], despite the marked elongation of the C(1)—C(2) bond [1.580 (3) Å].

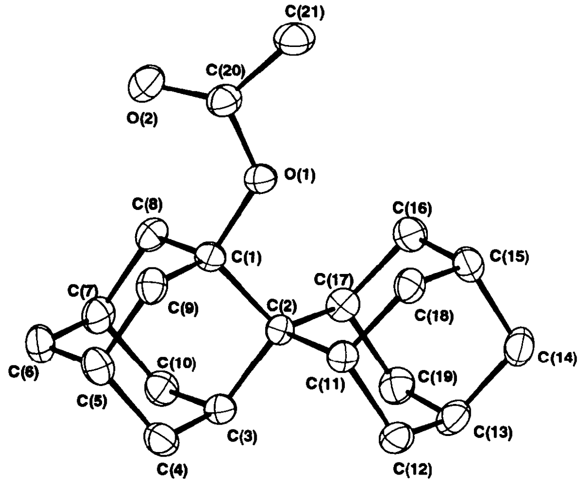


Fig. 1. *CAMERON* (Pearce, Watkin & Prout, 1992) diagram of the molecular structure of the title compound showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

As in the previously studied *anti*-4-bromo[1]diadamantane (Lomas, Cordier, Briand & Vaissermann, 1996), there is considerable distortion about the spiro-C(2) atom. The intracyclic C—C—C angles at C(2) are small, that for the substituted adamantyl unit being smaller than that for the non-substituted unit. The exocyclic bond angles at C(2) are large for the carbon which bears the substituent, C(1) [114.4 (2)°], but almost normal for C(3). All C—C bonds to C(2) are substantially longer than usual (average 1.571 Å), with those for the substituted adamantyl unit significantly longer than the others.

The X-ray crystal structure of only one other [1]diadamantane derivative, 5,5′,7,7′-tetrabromo[1]diadamantane, has been determined (Sosnowski, Rheingold & Murray, 1985), but no details of the geometry were published.

Experimental

The title acetate was prepared by refluxing 1-hydroxy[1]diadamantane with acetic anhydride in acetic acid (Lomas, Cordier & Briand, 1996). Recrystallization was from hexane (m.p. 400 K).

Crystal data

$C_{21}H_{30}O_2$
M_r = 314.47
Monoclinic
$P2_1/c$
a = 7.267 (2) Å
b = 17.837 (7) Å
c = 12.975 (7) Å
β = 98.78 (3)°
V = 1662.1 (1.2) Å^3
Z = 4
D_x = 1.26 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71076 Å
Cell parameters from 25 reflections
θ = 11.0–11.5°
μ = 0.073 mm^{-1}
T = 293 K
Prism
0.65 × 0.32 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3290 measured reflections
2931 independent reflections
1972 observed reflections [$F^2>3\sigma(F)^2$]

$R_{\rm int}$ = 0.0314
$\theta_{\rm max}$ = 25°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 21$
$l = -15 \rightarrow 15$
2 standard reflections frequency: 60 min intensity decay: <1%

Refinement

Refinement on F
R = 0.0422
wR = 0.0405
S = 3.55
1972 reflections
300 parameters

$\Delta\rho_{\rm max}$ = 0.80 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.61 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 167 (10)

Only coordinates of H atoms refined and one overall U_{iso} parameter
Unit weights applied
$(\Delta/\sigma)_{max} = 0.41$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
O(1)	0.0921 (2)	0.6358 (1)	0.8014 (1)	0.0383
O(2)	0.3032 (3)	0.7306 (1)	0.8220 (2)	0.0598
C(1)	−0.0274 (3)	0.6624 (1)	0.7066 (2)	0.0344
C(2)	−0.1791 (3)	0.5997 (1)	0.6753 (2)	0.0301
C(3)	−0.2996 (4)	0.6335 (2)	0.5748 (2)	0.0386
C(4)	−0.3905 (4)	0.7077 (2)	0.5971 (2)	0.0455
C(5)	−0.2397 (4)	0.7658 (2)	0.6322 (2)	0.0475
C(6)	−0.1220 (4)	0.7775 (2)	0.5459 (2)	0.0483
C(7)	−0.0329 (4)	0.7034 (2)	0.5216 (2)	0.0439
C(8)	0.0893 (4)	0.6748 (2)	0.6194 (2)	0.0393
C(9)	−0.1173 (4)	0.7366 (1)	0.7301 (2)	0.0399
C(10)	−0.1845 (4)	0.6459 (2)	0.4870 (2)	0.0427
C(11)	−0.3057 (3)	0.5833 (1)	0.7600 (2)	0.0359
C(12)	−0.4675 (4)	0.5317 (2)	0.7140 (2)	0.0434
C(13)	−0.3919 (4)	0.4572 (2)	0.6814 (2)	0.0474
C(14)	−0.2886 (4)	0.4181 (2)	0.7778 (3)	0.0492
C(15)	−0.1273 (4)	0.4682 (2)	0.8270 (2)	0.0445
C(16)	0.0034 (4)	0.4813 (2)	0.7464 (2)	0.0416
C(17)	−0.0982 (4)	0.5217 (1)	0.6502 (2)	0.0381
C(18)	−0.2033 (4)	0.5434 (2)	0.8569 (2)	0.0381
C(19)	−0.2580 (4)	0.4691 (2)	0.6026 (2)	0.0456
C(20)	0.2436 (4)	0.6725 (2)	0.8500 (2)	0.0426
C(21)	0.3257 (5)	0.6300 (2)	0.9430 (2)	0.0520

Table 2. *Selected geometric parameters (Å, °)*

C(1)—C(2)	1.580 (3)	C(2)—C(11)	1.565 (3)
C(2)—C(3)	1.575 (3)	C(2)—C(17)	1.564 (3)
C(1)—C(2)—C(3)	102.7 (2)	C(1)—C(2)—C(17)	114.4 (2)
C(1)—C(2)—C(11)	114.4 (2)	C(3)—C(2)—C(17)	110.3 (2)
C(3)—C(2)—C(11)	109.9 (2)	C(11)—C(2)—C(17)	105.1 (2)

C(2)—C(1)—O(1)—C(20)	177.1 (2)
C(1)—O(1)—C(20)—O(2)	−1.4 (2)
C(1)—O(1)—C(20)—C(21)	178.9 (2)

Table 3. *Contact distances (Å)*

O(1)···H(161)	2.26 (3)	O(2)···H(82)	2.36 (3)
O(1)···H(182)	2.29 (3)	O(2)···H(92)	2.51 (3)

H atoms were located by means of a Fourier difference map.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *CAMERON* (Pearce, Watkin & Prout, 1992). Software used to prepare material for publication: *CRYSTALS*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1240). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,6-Dibenzoylhydroquinone

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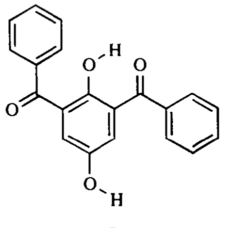
Abstract

The title compound, $C_{20}H_{14}O_4$, forms an infinite network of O—H···O and C—H···O hydrogen bonds. The phenyl rings of the benzoyl groups are non-coplanar with the hydroquinone moiety.

Comment

In the crystal structure of the title compound, (I), O—H···O and C—H···O hydrogen bonds (Desiraju, 1991) are found to be important.



(I)