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3-Triphenylmethyl-2,4-pentanedione

Richard E. Sykora, Katrina Kalachnikova and Greg T. Spyridis*

Department of Chemistry, University of South Alabama, Mobile, AL 36688-0002, USA
Correspondence e-mail: spyridis@jaguar1.usouthal.edu

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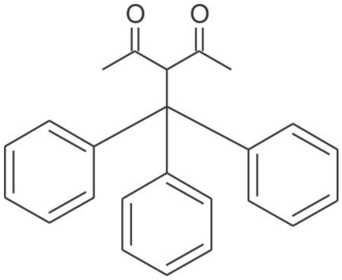
Key indicators: single-crystal X-ray study; *T* = 290 K; mean σ(C–C) = 0.004 Å; *R* factor = 0.047; *wR* factor = 0.148; data-to-parameter ratio = 14.2.

The title compound, $C_{24}H_{22}O_2$, exists exclusively as the keto tautomer in the crystalline state with a dihedral angle of 66.8 (2)° between the carbonyl groups. Furthermore, steric crowding produces an uncommonly long carbon–carbon bond [1.587 (3) Å] linking the triphenylmethyl and diketone moieties.

Related literature

For related literature, see: Emsley (1984); Emsley *et al.* (1986); Lowery *et al.* (1971); Moreno-Manas *et al.* (1991, 1992); Pocker & Spyridis (2002); Wiorkiewicz-Kuczera & Rabczenko (1986); Zaugg & Schaefer (1965).



Experimental

Crystal data

$C_{24}H_{22}O_2$
M_r = 342.42
Monoclinic, $P2_1/n$
a = 9.1906 (11) Å
b = 23.704 (3) Å
c = 9.3251 (13) Å
β = 113.941 (12)°
V = 1856.7 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 290 (2) K
1.00 × 0.48 × 0.17 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.868, T_{max} = 0.991
3594 measured reflections
3378 independent reflections
1775 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.148
S = 0.99
3378 reflections
238 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2043).

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supplementary materials

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3-Triphenylmethyl-2,4-pentanedione

R. E. Sykora, **K. Kalachnikova** and **G. T. Spyridis**

Comment

Acetylacetone (2,4-pentanedione) and other β-diketones are molecules in dynamic equilibrium with both tautomers present in measurable concentrations at equilibrium. The keto-enol ratio in these systems is modulated by solvent polarity, hydrogen bonding capacity, and the concentration of dissolved salts (Pocker & Spyridis, 2002; Emsley, 1984). This ratio is also exquisitely sensitive to the size of the substituents on the carbon between the carbonyls, with the keto concentration increasing as the steric bulk rises (Emsley, 1984). In light of our recent investigations into the keto-enol ratio of acetylacetone in highly concentrated nonaqueous salt solutions (Pocker & Spyridis, 2002), we prepared and crystallized 3-triphenyl-2,4-pentanedione, **1**.

The title compound exists exclusively in the diketo form with steric crowding producing an uncommonly long C3—C6 bond of 1.587 (3) Å. This is close to the adamantyl-diketone bond length of 1.595 (8) Å observed in 3-methyl-3-(1-adamantyl)-2,4-pentanedione, **2** (Moreno-Manas *et al.*, 1992). The C2—C3 and C3—C4 linkages at 1.544 (3) and 1.531 (3) Å, respectively, are also slightly longer than the 1.50 Å typical for sp^2-sp^3 carbon-carbon bonds (Wiorkiewicz-Kuczera & Rabczenko, 1986), as are the phenyl-carbon bonds about C6. Steric congestion also produces bond angles about C3 that are unusually large for a sp^3 hybridized carbon: C2—C3—C6 is 116.5 (2)° while C4—C3—C6 is 117.23 (19)°.

The main factor determining the conformation of the keto tautomer is the strong repulsion of the localized C═O bond dipoles (Emsley *et al.*, 1986). For both **1** and **2** the C2—C3—C4 angle is between 105–107° while for the keto tautomer of acetylaceone (Lowery *et al.*, 1971) the corresponding angle is 114°, possibly in an effort to minimize the interaction between the carbonyl bond dipoles. For β-diketones possessing large groups about C3 semiempirical *MM2* calculations (Moreno-Manas *et al.*, 1991) reveal that the conformations which predominate are those with a dihedral angle between the carbonyls of less than 90°, with their contribution increasing as the bulk of the substituent rises. For **1** only a single conformation is oberved in the crystalline state and it possesses a dihedral angle of 66.8 (2)° between the carbonyls.

Experimental

The title compound was synthesized as outlined in the literature (Zaugg & Schaefer, 1965) and purified by column chromatography over silica gel using 1:1 *n*-pentane: *n*-hexane as the mobile phase. Crystals suitable for X-ray analysis were grown by slow evaporation from 1:1 *n*-pentane: *n*-hexane at 298 K. The crystals of **1** did not cleave very well and several attempts to break or cut them were unsuccessful. Therefore a larger than standard crystal (1 mm max. dimension) was used for this study. The beam tube that was used was large enough (2 mm i.d.) to ensure that the crystal was completely inside of the X-ray beam during the diffraction experiment.

Refinement

H atoms were placed in calculated positions and allowed to ride during subsequent refinement, with U_{iso}(H) = 1.2U_{eq}(C) and C—H distances of 0.93 Å for H atoms attached to the aromatic rings, U_{iso}(H) = 1.5U_{eq}(C) and C—H distances of 0.96 Å for the methyl H atoms, and U_{iso}(H) = 1.2U_{eq}(C) and a C—H distance of 0.98 Å for the tertiary H atom.

Figures

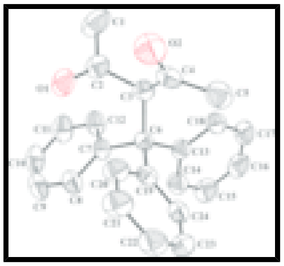


Fig. 1. The molecular structure of **1**, with the atom-numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms are not shown for clarity.

3-Triphenylmethyl-2,4-pentanedione

Crystal data

$C_{24}H_{22}O_2$

M_r = 342.42

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

a = 9.1906 (11) Å

b = 23.704 (3) Å

c = 9.3251 (13) Å

β = 113.941 (12)°

V = 1856.7 (4) Å^3

Z = 4

F_{000} = 728

D_x = 1.225 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 8.1–13.5°

μ = 0.08 mm^{-1}

T = 290 (2) K

Plate, colorless

1.00 × 0.48 × 0.17 mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 290(2) K

$\theta/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

T_{min} = 0.868, T_{max} = 0.991

3594 measured reflections

3378 independent reflections

R_{int} = 0.043

θ_{max} = 25.4°

θ_{min} = 2.5°

$h = 0\rightarrow11$

$k = 0\rightarrow28$

$l = -11\rightarrow10$

3 standard reflections

every 120 min

intensity decay: none

1775 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.148$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.99$	$\Delta\rho_{max} = 0.19$ e Å^{-3}
3378 reflections	$\Delta\rho_{min} = -0.16$ e Å^{-3}
238 parameters	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.014 (2)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.9972 (2)	0.23311 (8)	0.6900 (2)	0.0575 (5)
O2	0.9543 (3)	0.27619 (8)	0.3716 (2)	0.0740 (7)
C1	0.7447 (4)	0.27723 (14)	0.5824 (4)	0.0776 (10)
H1A	0.7873	0.2995	0.6764	0.116*
H1B	0.6527	0.2571	0.5786	0.116*
H1C	0.7152	0.3015	0.4926	0.116*
C2	0.8678 (3)	0.23625 (11)	0.5817 (3)	0.0472 (7)
C3	0.8210 (3)	0.20020 (10)	0.4317 (3)	0.0382 (6)
H3A	0.7051	0.2037	0.3774	0.046*
C4	0.8882 (3)	0.23122 (11)	0.3279 (3)	0.0457 (7)
C5	0.8630 (3)	0.20898 (12)	0.1699 (3)	0.0583 (8)
H5A	0.9423	0.2244	0.1387	0.087*
H5B	0.7591	0.2197	0.0952	0.087*
H5C	0.8714	0.1686	0.1743	0.087*
C6	0.8549 (3)	0.13449 (9)	0.4564 (3)	0.0349 (6)

C7	0.8657 (3)	0.11838 (10)	0.6212 (3)	0.0377 (6)
C8	0.9936 (3)	0.09073 (11)	0.7339 (3)	0.0496 (7)
H8A	1.0816	0.0817	0.7132	0.060*
C9	0.9922 (4)	0.07632 (13)	0.8774 (3)	0.0633 (8)
H9A	1.0796	0.0580	0.9522	0.076*
C10	0.8635 (4)	0.08876 (14)	0.9098 (3)	0.0665 (9)
H10A	0.8632	0.0788	1.0062	0.080*
C11	0.7344 (4)	0.11606 (14)	0.7995 (3)	0.0627 (8)
H11A	0.6468	0.1248	0.8212	0.075*
C12	0.7357 (3)	0.13033 (12)	0.6568 (3)	0.0504 (7)
H12A	0.6475	0.1484	0.5824	0.060*
C13	0.7134 (3)	0.09979 (10)	0.3388 (3)	0.0365 (6)
C14	0.6992 (3)	0.04335 (11)	0.3709 (3)	0.0495 (7)
H14A	0.7752	0.0276	0.4617	0.059*
C15	0.5764 (3)	0.00993 (12)	0.2726 (3)	0.0585 (8)
H15A	0.5708	−0.0278	0.2973	0.070*
C16	0.4627 (3)	0.03230 (13)	0.1384 (3)	0.0591 (8)
H16A	0.3789	0.0100	0.0726	0.071*
C17	0.4733 (3)	0.08740 (12)	0.1020 (3)	0.0556 (8)
H17A	0.3975	0.1025	0.0100	0.067*
C18	0.5965 (3)	0.12122 (11)	0.2015 (3)	0.0445 (6)
H18A	0.6009	0.1589	0.1757	0.053*
C19	1.0120 (3)	0.11948 (10)	0.4404 (3)	0.0361 (6)
C20	1.1484 (3)	0.15112 (11)	0.5224 (3)	0.0483 (7)
H20A	1.1444	0.1802	0.5877	0.058*
C21	1.2892 (3)	0.14001 (12)	0.5082 (4)	0.0568 (8)
H21A	1.3793	0.1613	0.5651	0.068*
C22	1.2977 (3)	0.09809 (12)	0.4113 (3)	0.0548 (7)
H22A	1.3920	0.0915	0.3995	0.066*
C23	1.1649 (3)	0.06562 (11)	0.3315 (3)	0.0493 (7)
H23A	1.1701	0.0365	0.2670	0.059*
C24	1.0237 (3)	0.07625 (10)	0.3468 (3)	0.0421 (6)
H24A	0.9352	0.0538	0.2929	0.051*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0433 (11)	0.0637 (12)	0.0543 (12)	−0.0069 (9)	0.0082 (10)	−0.0163 (9)
O2	0.0818 (15)	0.0550 (13)	0.0785 (15)	−0.0209 (11)	0.0257 (12)	0.0060 (11)
C1	0.0573 (19)	0.078 (2)	0.092 (2)	0.0045 (16)	0.0250 (18)	−0.0377 (19)
C2	0.0375 (15)	0.0458 (15)	0.0561 (17)	−0.0059 (12)	0.0168 (14)	−0.0075 (13)
C3	0.0280 (12)	0.0394 (13)	0.0420 (13)	−0.0005 (10)	0.0088 (11)	−0.0024 (11)
C4	0.0377 (14)	0.0385 (14)	0.0538 (17)	0.0031 (12)	0.0113 (12)	0.0090 (12)
C5	0.0631 (19)	0.0624 (17)	0.0569 (17)	0.0063 (15)	0.0321 (15)	0.0117 (15)
C6	0.0282 (12)	0.0387 (13)	0.0339 (13)	0.0014 (10)	0.0085 (10)	0.0008 (10)
C7	0.0301 (13)	0.0447 (14)	0.0322 (13)	−0.0042 (11)	0.0063 (11)	−0.0024 (11)
C8	0.0403 (15)	0.0570 (17)	0.0422 (15)	0.0008 (13)	0.0071 (12)	0.0028 (13)
C9	0.0616 (19)	0.076 (2)	0.0379 (16)	0.0029 (16)	0.0055 (14)	0.0109 (15)

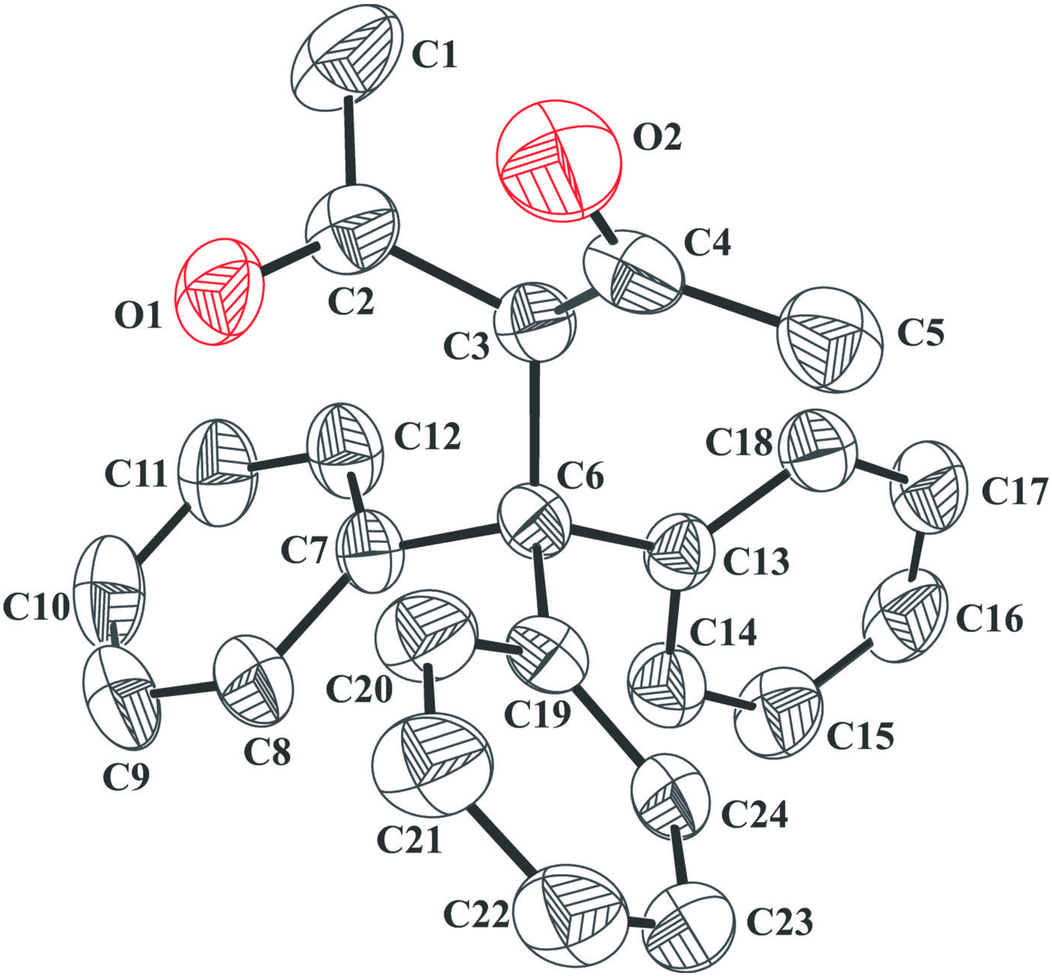
C10	0.078 (2)	0.085 (2)	0.0332 (16)	−0.0149 (18)	0.0195 (16)	−0.0009 (15)
C11	0.0549 (18)	0.087 (2)	0.0472 (17)	−0.0075 (16)	0.0221 (15)	−0.0045 (16)
C12	0.0375 (14)	0.0686 (19)	0.0419 (16)	−0.0021 (13)	0.0129 (12)	−0.0005 (13)
C13	0.0333 (13)	0.0408 (14)	0.0344 (13)	−0.0011 (10)	0.0126 (11)	−0.0032 (11)
C14	0.0499 (16)	0.0475 (16)	0.0437 (15)	−0.0022 (13)	0.0112 (13)	−0.0008 (13)
C15	0.0632 (19)	0.0460 (16)	0.0615 (18)	−0.0150 (14)	0.0202 (16)	−0.0102 (14)
C16	0.0455 (17)	0.0642 (19)	0.0583 (19)	−0.0119 (14)	0.0114 (15)	−0.0238 (15)
C17	0.0399 (15)	0.0672 (19)	0.0432 (16)	−0.0009 (14)	0.0000 (13)	−0.0110 (14)
C18	0.0380 (14)	0.0473 (15)	0.0418 (14)	0.0004 (11)	0.0096 (12)	−0.0014 (12)
C19	0.0303 (13)	0.0383 (13)	0.0374 (13)	0.0041 (10)	0.0112 (10)	0.0051 (11)
C20	0.0358 (14)	0.0486 (15)	0.0583 (17)	0.0003 (12)	0.0167 (13)	−0.0069 (13)
C21	0.0324 (15)	0.0601 (18)	0.074 (2)	−0.0009 (13)	0.0181 (14)	−0.0084 (16)
C22	0.0381 (15)	0.0669 (19)	0.0624 (19)	0.0089 (13)	0.0235 (14)	0.0030 (15)
C23	0.0503 (17)	0.0562 (17)	0.0440 (15)	0.0122 (13)	0.0219 (13)	−0.0011 (13)
C24	0.0378 (14)	0.0478 (15)	0.0344 (13)	0.0046 (11)	0.0082 (11)	0.0015 (11)

Geometric parameters (Å, °)

O1—C2	1.211 (3)	C11—C12	1.378 (4)
O2—C4	1.212 (3)	C11—H11A	0.9300
C1—C2	1.493 (4)	C12—H12A	0.9300
C1—H1A	0.9600	C13—C14	1.388 (3)
C1—H1B	0.9600	C13—C18	1.391 (3)
C1—H1C	0.9600	C14—C15	1.379 (3)
C2—C3	1.544 (3)	C14—H14A	0.9300
C3—C4	1.531 (3)	C15—C16	1.370 (4)
C3—C6	1.587 (3)	C15—H15A	0.9300
C3—H3A	0.9800	C16—C17	1.363 (4)
C4—C5	1.492 (4)	C16—H16A	0.9300
C5—H5A	0.9600	C17—C18	1.390 (3)
C5—H5B	0.9600	C17—H17A	0.9300
C5—H5C	0.9600	C18—H18A	0.9300
C6—C7	1.547 (3)	C19—C24	1.379 (3)
C6—C19	1.551 (3)	C19—C20	1.393 (3)
C6—C13	1.554 (3)	C20—C21	1.379 (3)
C7—C8	1.383 (3)	C20—H20A	0.9300
C7—C12	1.393 (3)	C21—C22	1.366 (4)
C8—C9	1.386 (4)	C21—H21A	0.9300
C8—H8A	0.9300	C22—C23	1.378 (4)
C9—C10	1.366 (4)	C22—H22A	0.9300
C9—H9A	0.9300	C23—C24	1.385 (3)
C10—C11	1.376 (4)	C23—H23A	0.9300
C10—H10A	0.9300	C24—H24A	0.9300
C2—C1—H1A	109.5	C10—C11—C12	119.7 (3)
C2—C1—H1B	109.5	C10—C11—H11A	120.2
H1A—C1—H1B	109.5	C12—C11—H11A	120.2
C2—C1—H1C	109.5	C11—C12—C7	121.6 (3)
H1A—C1—H1C	109.5	C11—C12—H12A	119.2
H1B—C1—H1C	109.5	C7—C12—H12A	119.2

O1—C2—C1	121.7 (2)	C14—C13—C18	116.5 (2)
O1—C2—C3	122.7 (2)	C14—C13—C6	118.9 (2)
C1—C2—C3	115.6 (2)	C18—C13—C6	124.7 (2)
C4—C3—C2	105.75 (19)	C15—C14—C13	122.2 (3)
C4—C3—C6	117.23 (19)	C15—C14—H14A	118.9
C2—C3—C6	116.5 (2)	C13—C14—H14A	118.9
C4—C3—H3A	105.4	C16—C15—C14	120.0 (3)
C2—C3—H3A	105.4	C16—C15—H15A	120.0
C6—C3—H3A	105.4	C14—C15—H15A	120.0
O2—C4—C5	119.9 (3)	C17—C16—C15	119.5 (3)
O2—C4—C3	119.1 (2)	C17—C16—H16A	120.2
C5—C4—C3	120.9 (2)	C15—C16—H16A	120.2
C4—C5—H5A	109.5	C16—C17—C18	120.5 (3)
C4—C5—H5B	109.5	C16—C17—H17A	119.7
H5A—C5—H5B	109.5	C18—C17—H17A	119.7
C4—C5—H5C	109.5	C17—C18—C13	121.3 (2)
H5A—C5—H5C	109.5	C17—C18—H18A	119.4
H5B—C5—H5C	109.5	C13—C18—H18A	119.4
C7—C6—C19	110.60 (18)	C24—C19—C20	117.6 (2)
C7—C6—C13	105.55 (18)	C24—C19—C6	123.1 (2)
C19—C6—C13	110.85 (18)	C20—C19—C6	119.3 (2)
C7—C6—C3	108.44 (18)	C21—C20—C19	121.0 (3)
C19—C6—C3	110.29 (18)	C21—C20—H20A	119.5
C13—C6—C3	111.00 (17)	C19—C20—H20A	119.5
C8—C7—C12	117.5 (2)	C22—C21—C20	120.7 (3)
C8—C7—C6	124.3 (2)	C22—C21—H21A	119.7
C12—C7—C6	118.1 (2)	C20—C21—H21A	119.7
C7—C8—C9	120.8 (3)	C21—C22—C23	119.2 (3)
C7—C8—H8A	119.6	C21—C22—H22A	120.4
C9—C8—H8A	119.6	C23—C22—H22A	120.4
C10—C9—C8	120.5 (3)	C22—C23—C24	120.3 (3)
C10—C9—H9A	119.7	C22—C23—H23A	119.9
C8—C9—H9A	119.7	C24—C23—H23A	119.9
C9—C10—C11	119.8 (3)	C19—C24—C23	121.2 (2)
C9—C10—H10A	120.1	C19—C24—H24A	119.4
C11—C10—H10A	120.1	C23—C24—H24A	119.4

Fig. 1


C1
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