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# The Crystal and Molecular Structure of a 1-Oxaspiro[4.4]nonane Derivative: A 1:2 Aldol-type Adduct from the Reaction of 3,3,5,5-Tetramethylcyclopentane-1,2-dione with Acetone

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The crystal and molecular structure of 2-(2-oxo-3,3,5,5-tetramethylcyclopentyl)-1-oxa-7,7,9,9-tetramethylspiro[4.4]nonane-3,6-dione, $C_{21}H_{32}O_4$, has been established by single-crystal X-ray diffraction techniques. The compound is a 1:2 aldol-type adduct from reaction of 3,3,5,5-tetramethylcyclopentane-1,2-dione with acetone. The compound crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with unit cell dimensions $a = 14.910(9)$, $b = 8.495(8)$, $c = 16.394(15)$ Å, $\beta = 92.84(6)°$ and $Z = 4$. The structure was solved by direct methods and refined to $R = 0.086$ for 1880 reflections.

In a previous paper [1] from this Laboratory, we reported the reactions of 3,3,5,5-tetramethylcyclopentane-1,2-dione with some aromatic and aliphatic methyl ketones. The reaction of the diketone with the simplest aromatic methyl ketone, acetophenone, followed the normal aldol reaction sequence yielding a 1:1 adduct, which could be readily characterized by its analytical and spectroscopic data. In sharp contrast, the reactions of the diketone with aliphatic methyl ketones, such as acetone and ethyl methyl ketone, furnished 1:2 aldol-type adducts, and the analytical and spectroscopic data alone were not sufficient for assignment of the structures. It, therefore, became desirable to determine the structures by X-ray diffraction analysis.

In this paper, we describe the crystal and molecular structure of the adduct formed through reaction of 3,3,5,5-tetramethylcyclopentane-1,2-dione with acetone in alkaline medium. A description of the conformation of the molecule is also given. Finally, the 1:2 adduct with a 1-oxaspiro[4.4]nonane structure is discussed by comparison with the products of previously reported aldol reactions of other 1,2-dicarbonyl compounds.

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## EXPERIMENTAL

The preparation and spectral data of the compound have been reported elsewhere.[1] Colourless crystals (m.p. 148.0 – 148.5 °C) were obtained by very slow evaporation of a saturated 1-propanol-water (1:1) solution. Photographic investigations indicated monoclinic symmetry; systematically absent reflections showed the space group to be $P2_1/n$. Lattice parameters were obtained from a least-squares refinement of 15 well-centered diffractometer-measured $\theta$-values.

The specimen selected for intensity data collection was approximately $0.3 \times 0.35 \times 0.4$ mm³. The intensity data were collected on an automatic four-circle Syntex $P2_1$ diffractometer, using $\omega$-scan technique ($5° < 2\theta < 45°$) and monochromatized Mo$K\alpha$-radiation ($\lambda = 0.71069$ Å). The standard reflections showed no systematic variation during the data collection. Of the independent reflections measured, only 1880 had $F > 2\sigma(F)$ and were considered observed. The data were corrected for Lorentz and polarization effects, but no corrections for absorption were made.

## CRYSTAL DATA

$C_{21}H_{32}O_4$, FW = 348.48
Crystal system: Monoclinic
Space group: $P2_1/n$ (No. 14)
$a = 14.910(9)$, $b = 8.495(8)$, $c = 16.394(15)$ Å,
$\beta = 92.84(6)°$, $V = 2074.0$ Å³, $Z = 4$, $F(000) = 760$,
$D_{obs} = 1.11$ g cm$^{-3}$, $D_{calc} = 1.116$ g cm$^{-3}$

## STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by direct methods using the program MULTAN.[3] The phase set with highest combined figure of merit yielded an *E*-map, which revealed the locations of all non-hydrogen atoms among the largest 28 peaks. The refinement of the structure and all subsequent calculations were carried out using the X-RAY 76 program system.[3] The scattering factors for O and C were from Ref. 4 and those for H from Ref. 5. After isotropic and anisotropic refinements the conventional *R* factor was 0.136. At this point all hydrogen atoms were found by calculating a difference Fourier synthesis. Hydrogen atom positions were indicated by peaks of density 0.26 – 0.46 e Å$^{-3}$. In the final refinement, anisotropic temperature coefficients were used for the non-hydrogen atoms and isotropic temperature coefficients for the hydrogen atoms; the *R* value then reduced to 0.086 ($R_w = 0.084$, unit weights) for 1880 reflections. It seems likely that the residual *R*-factor is not low due to the quality of the crystal and the lack of reflections. The final Fourier map showed no residuals greater than 0.27 e Å$^{-3}$.

## DISCUSSION

A schematic drawing and the numbering scheme of the molecule are presented in Fig. 1. A stereoview is shown in Fig. 2. The molecule contains three five-menbered rings with a spiro-carbon atom between rings I and II (Fig. 1). The structure is built-up from discrete molecules, the shortest contact between non-hydrogen atoms of the neighbouring molecules being more than 3.45 Å.

Atomic coordinates and temperature factors are presented in Table 1. Bond lengths, valence angles, dihedral angles and deviations of atoms from some selected least-squares planes are listed in Tables 2, 3, 4 and 5. A list of observed and calculated structure factors is obtainable from the authors.

The C – C bond lengths are in the range 1.51 – 1.56 Å (mean 1.540 Å) and the C=O bond lengths range from 1.19 to 1.22 Å. These values as well as the values of the C – C=O angles (124.2 – 127.4°) and O – C – C angles (103.7 – 111.2°) can be considered to be as expected. Considerable variations were found for C – C – C angles; the spiro-carbon atom C1 shows the greatest distortion from tetrahedral geometry with the valence angles varying from 103.5 to 120.3°. The average standard deviations in the bond distances and angles are 0.009 Å and 0.5°, respectively.

The atom groups of the three five-membered rings O1, C1, C2 and C3; O2, C10, C11 and C12; O4, C13, C14 and C15, each containing a carbonyl group, are planar within experimental errors (Table 5). However, the rings have different conformations. In the ring I the carbon atoms C4 and C5 lie on the same side of the O1, C1, C2, C3 plane, while the rings II and III have half-chair conformations.

The conformation of the molecule found in the solid state by X-ray analysis is nearly identical with that determined in solution by $^1$H NMR spectroscopy. In the crystal the dihedral angle H – C12 – C13 – H was found to

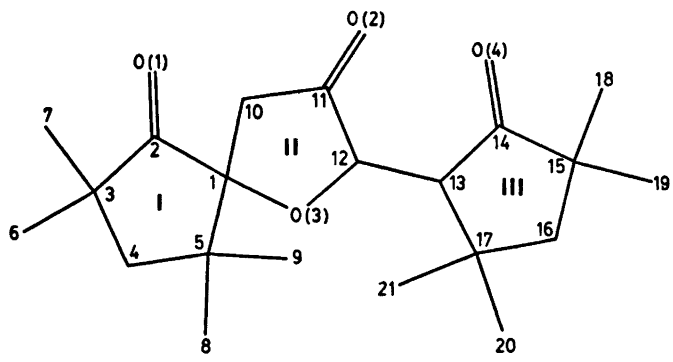


*Fig. 1.* Schematic drawing and numbering system of $C_{21}H_{22}O_4$.

*Table 1.* Fractional atomic coordinates ($\times 10^4$) and thermal parameters [a] ($\times 10^3$) for the non-hydrogen atoms.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| O1 | 2208(3) | 4425(7) | −2492(3) | 72(3) | 109(4) | 59(3) | 3(3) | 28(3) | 16(3) |
| O2 | 4340(3) | 3526(8) | −1053(4) | 40(3) | 174(6) | 133(5) | 2(4) | 14(3) | −89(5) |
| O3 | 2160(2) | 4775(5) | −586(2) | 43(2) | 49(3) | 56(3) | 2(2) | 10(2) | −8(2) |
| O4 | 3357(4) | 3286(6) | 808(3) | 137(5) | 44(3) | 100(4) | 16(3) | −33(4) | −3(3) |
| C1 | 1966(4) | 3432(7) | −1129(4) | 45(4) | 39(4) | 52(4) | 5(3) | 4(3) | −8(3) |
| C2 | 1699(4) | 4201(8) | −1952(4) | 60(4) | 48(4) | 50(4) | 1(3) | 9(3) | 5(3) |
| C3 | 700(4) | 4651(9) | −1967(4) | 53(4) | 76(5) | 53(4) | 11(4) | 7(3) | 19(4) |
| C4 | 357(4) | 3823(9) | −1191(4) | 41(4) | 78(5) | 65(4) | 12(4) | 9(3) | 21(4) |
| C5 | 1087(4) | 2637(8) | −878(4) | 54(4) | 56(4) | 44(4) | −2(3) | 8(3) | −1(3) |
| C6 | 637(5) | 6467(9) | −1897(5) | 87(6) | 74(6) | 87(6) | 32(5) | 19(4) | 29(5) |
| C7 | 238(5) | 4119(11) | −2773(4) | 67(5) | 124(8) | 65(5) | 4(5) | −9(4) | 10(5) |
| C8 | 986(5) | 1042(9) | −1348(4) | 89(5) | 52(5) | 74(5) | −8(4) | −3(4) | 7(4) |
| C9 | 1050(5) | 2350(9) | 38(4) | 69(5) | 72(5) | 64(5) | −9(4) | 10(4) | 14(4) |
| C10 | 2840(4) | 2500(8) | −1114(4) | 45(4) | 62(5) | 62(4) | 15(3) | 3(3) | −19(4) |
| C11 | 3553(4) | 3743(10) | −959(4) | 44(4) | 105(6) | 66(5) | 7(4) | 6(3) | −33(5) |
| C12 | 3090(4) | 5219(8) | −661(4) | 45(4) | 70(5) | 51(4) | −2(4) | 10(3) | −14(4) |
| C13 | 3506(4) | 5825(8) | 153(4) | 45(4) | 57(4) | 51(4) | −3(4) | 9(3) | −9(3) |
| C14 | 3351(4) | 4719(8) | 860(4) | 54(4) | 49(4) | 65(4) | 13(3) | −13(3) | −5(4) |
| C15 | 3229(4) | 5647(8) | 1650(4) | 52(4) | 52(4) | 48(4) | 2(3) | 1(3) | 4(3) |
| C16 | 3422(4) | 7346(8) | 1390(4) | 63(4) | 56(4) | 52(4) | 10(4) | 2(3) | −10(4) |
| C17 | 3249(5) | 7492(8) | 448(4) | 81(5) | 41(4) | 51(4) | −6(4) | 3(3) | −3(4) |
| C18 | 2253(5) | 5366(11) | 1900(5) | 66(5) | 114(7) | 85(6) | −8(5) | 18(4) | 17(5) |
| C19 | 3872(5) | 5050(10) | 2341(5) | 94(6) | 85(6) | 72(5) | −6(5) | −27(4) | 18(5) |
| C20 | 2253(6) | 7897(9) | 236(5) | 118(7) | 64(5) | 74(5) | 39(5) | −24(5) | −12(4) |
| C21 | 3883(7) | 8749(11) | 107(5) | 196(10) | 71(6) | 77(6) | −48(7) | 20(6) | 0(5) |

[a] The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots.+2hka^*b^*U_{12}+\ldots)]$.

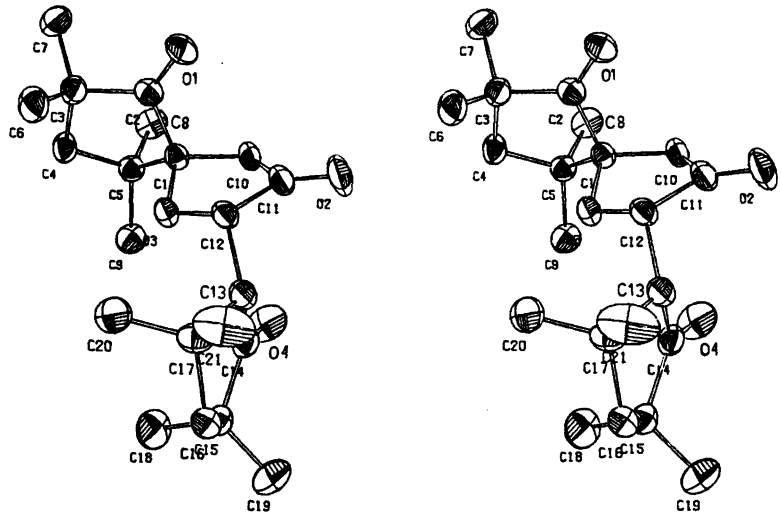


*Fig. 2.* A stereoview of the $C_{21}H_{32}O_4$ molecule. Hydrogen atoms have been omitted for clarity. The thermal ellipsoids have been drawn as 30 % probability ellipsoids.

*Table 2.* Bond lengths (Å).

| | | | | | |
|---|---|---|---|---|---|
| O1–C2 | 1.210(8) | C3–C4 | 1.562(10) | C13–C14 | 1.518(9) |
| O2–C11 | 1.196(8) | C3–C6 | 1.551(11) | C13–C17 | 1.550(9) |
| O3–C1 | 1.467(7) | C3–C7 | 1.528(10) | C14–C15 | 1.536(9) |
| O3–C12 | 1.448(7) | C4–C5 | 1.551(9) | C15–C16 | 1.536(9) |
| O4–C14 | 1.220(8) | C5–C8 | 1.563(10) | C15–C18 | 1.551(10) |
| C1–C2 | 1.534(9) | C5–C9 | 1.524(9) | C15–C19 | 1.534(10) |
| C1–C5 | 1.548(9) | C10–C11 | 1.511(10) | C16–C17 | 1.558(9) |
| C1–C10 | 1.524(9) | C11–C12 | 1.523(11) | C17–C20 | 1.547(11) |
| C2–C3 | 1.537(9) | C12–C13 | 1.533(9) | C17–C21 | 1.550(12) |

*Table 3.* Bond angles (°).

| | | | | | |
|---|---|---|---|---|---|
| C1–O3–C12 | 108.2(4) | C1–C5–C4 | 102.6(5) | O4–C14–C13 | 124.2(6) |
| O3–C1–C2 | 103.7(5) | C1–C5–C8 | 108.0(5) | O4–C14–C15 | 124.9(6) |
| O3–C1–C5 | 108.8(5) | C1–C5–C9 | 113.9(5) | C13–C14–C15 | 110.8(5) |
| O3–C1–C10 | 104.6(4) | C4–C5–C8 | 110.5(5) | C14–C15–C16 | 102.5(5) |
| C2–C1–C5 | 103.5(5) | C4–C5–C9 | 111.8(5) | C14–C15–C18 | 107.2(5) |
| C2–C1–C10 | 114.8(5) | C8–C5–C9 | 109.8(6) | C14–C15–C19 | 111.0(6) |
| C5–C1–C10 | 120.3(5) | C1–C10–C11 | 103.5(6) | C16–C15–C18 | 114.1(6) |
| O1–C2–C1 | 124.5(6) | O2–C11–C10 | 127.4(8) | C16–C15–C19 | 113.4(5) |
| O1–C2–C3 | 126.3(6) | O2–C11–C12 | 124.9(7) | C18–C15–C19 | 108.4(6) |
| C1–C2–C3 | 109.2(5) | C10–C11–C12 | 107.6(5) | C15–C16–C17 | 109.0(5) |
| C2–C3–C4 | 103.4(5) | O3–C12–C11 | 105.3(5) | C13–C17–C16 | 101.9(5) |
| C2–C3–C6 | 108.0(6) | O3–C12–C13 | 111.2(5) | C13–C17–C20 | 112.5(5) |
| C2–C3–C7 | 109.6(6) | C11–C12–C13 | 112.7(5) | C13–C17–C21 | 110.6(6) |
| C4–C3–C6 | 111.3(6) | C12–C13–C14 | 112.7(5) | C16–C17–C20 | 110.5(6) |
| C4–C3–C7 | 114.8(6) | C12–C13–C17 | 118.9(5) | C16–C17–C21 | 109.8(6) |
| C6–C3–C7 | 109.4(6) | C14–C13–C17 | 106.1(5) | C20–C17–C21 | 111.1(6) |
| C3–C4–C5 | 108.0(5) | | | | |

be *ca.* 70° [observed 71(5)°, idealized 69° calculated with the aid of atoms C11, C12, C13 and C14]. The small value of the vicinal coupling constant (1.6 Hz) of the corresponding protons observed in the $^1$H NMR spectrum indicates that the free rotation around the C12–C13 bond is hindered in solution, and the molecule exists in the form of an equilibrium mixture of two or more conformers, the dihedral angle H–C12–C13–H being between 60 and 120° according to the Karplus equation.[6] From the stereoview (Fig. 2) and molecular models of the compound it can be seen that the bulky methyl groups C8, C9, C20 and C21 offer considerable hindrance to rotation around the C12–C13 bond.

The 1-oxaspiro[4.4]nonane structure is unusual among aldol-type adducts reported to be formed through reactions of enolizable [7] or non-enolizable [8] 1,2-dicarbonyl compounds with various carbonyl compounds. Enolizable ali-

*Table 4.* Dihedral angles (°).

| | |
|---|---|
| O3–C12–C11–C10 | 4.6(7) |
| O3–C12–C13–C14 | 50.4(7) |
| C1–C10–C11–C12 | 15.2(7) |
| C2–C1–C5–C4 | −36.2(6) |
| C2–C3–C4–C5 | −12.9(7) |
| C11–C12–C13–C14 | −67.5(7) |
| C14–C15–C16–C17 | 23.6(6) |
| C15–C14–C13–C17 | −13.8(7) |

*Table 5.* Deviations (Å) of atoms from the least-squares planes containing carbonyl groups.

| | | | | | | |
|---|---|---|---|---|---|---|
| I. | Plane through O1, C1, C2 and C3 | | | | | |
| | O1 | C1 | C2 | C3 | C4 | C5 |
| | 0.00 | 0.00 | 0.00 | 0.00 | −0.27 | −0.74 |
| II. | Plane through O2, C10, C11 and C12 | | | | | |
| | O2 | C10 | C11 | C12 | O3 | C1 |
| | 0.00 | 0.00 | 0.00 | 0.00 | 0.10 | −0.40 |
| III. | Plane through O4, C13, C14 and C15 | | | | | |
| | O4 | C13 | C14 | C15 | C16 | C17 |
| | 0.01 | 0.00 | −0.01 | 0.00 | 0.19 | −0.32 |

phatic and alicyclic 1,2-dicarbonyl compounds have been known to furnish 1:2 adducts with a monoketone but, in contrast to the present case, only one molecule of the α-diketone is required for formation of the adduct.[7] Rather than 1:2 adducts, reactions of non-enolizable 1,2-dicarbonyl compounds with monoketones generally afford 1:1 adducts, such as carbinols or cyclopentadienones,[8] which are "expected" products of a "normal" aldol reaction sequence.

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