# Synthesis and Structural Characterization of Isomeric Coumarino-1,2-Oxaphosphole Derivatives

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The coumarino-[3,4-c]-3H-10-methyl-2-oxo-2-phenyl-1,2-oxaphosphole was prepared by the addition of PhPCl2 to 3-acetylcoumarin in the presence of acetic anhydride. Its conversion to the isomeric coumarino-[3,4-c]-9H-9-methyl-2-oxo-2-phenyl-1,2-oxaphosphole was studied in different reaction conditions. The structures of the two isomers were determined by X-ray crystallography and by *ab initio* molecular orbital calculations.

Introduction.

Oxaphospholes are an important class of organic compounds. They can be prepared by different synthetic pathways [1-5] and some of them show biological properties [6]. Known routes for obtaining oxaphospholes are the addition of phosphorus(III) halides to either 2-hydroxyaldehydes and ketones [7] and the addition-cyclization of electrophilic reagents to 1,2-alkadienephosphonates [8] or acetylenic alcohols [9]. Phosphorylated coumarino derivatives are known to be plant growth regulators and to possess potential biological activities [10,11].

Aimed at finding new synthetic routes for obtaining phosphorylation of coumarin derivatives, we wish to present here a study on the reactivity of dichlorophenylphosphine in a Michael-type addition to 3-acetylcoumarin in the presence of acetic anhydride.

As no crystal data have been previously reported for coumarinooxaphosphole derivatives, the crystal structures of two new compounds have been undertaken for studying structural features of these classes of derivatives. Molecular orbital calculations have been also carried out on these compounds.

Results and Discussion.

Synthetic Approach.

The reaction of dichlorophenylphosphine **1** with 3-acetylcoumarin **2** gave the desired compound coumarino-[3,4-c]-3H-10-methyl-2-oxo-2-phenyl-1,2-oxaphosphole **6** in good yield as large colorless crystals under mild reaction conditions (Scheme 1).

Scheme 1
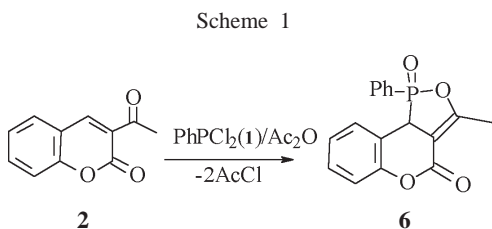


The optimal quantity of acetic anhydride which serves both as reagent and reaction media was found to be in 6:1 molar ratio over the 3-acetylcoumarin. In these conditions, and by using **2** with high purity, the product **6** is formed in pure crystalline form and no further purification was necessary.

The probable mechanism for this reaction includes the 1,4 addition of **1** to **2** followed by two oxo-dehalogenation steps of the phosphonium intermediate, by the acetic anhydride (Scheme 2). According to previous experimental results obtained under heating (50 °C) [12], the interaction between acetic anhydride and **1** could lead to the formation of mixed anhydride of the acetic and chlorophosphonous acids. In a second step, this intermediate could give **5** by 1,4 addition to **2** (Scheme 3).
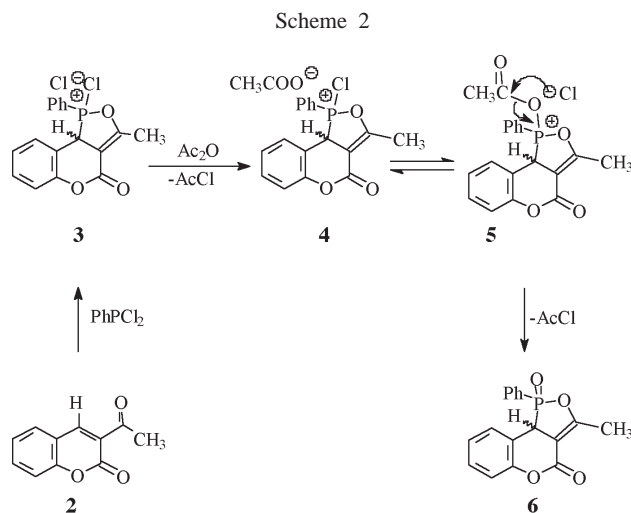
Scheme 2



However, in the conditions applied by us (room temperature), the initial formation of the mixed anhydride, as reported in Scheme 3, seems less favorable than the direct addition of **1** to **2**.

The product **6** remained stable for up to 3 days at room temperature or about 30 days if stored at -18 °C. After this

Scheme 3
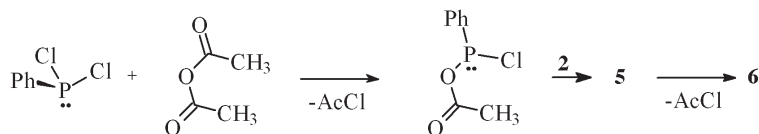


time, it changed to the isomeric coumarino-[3,4-c]-9H-9-methyl-2-oxo-2-phenyl-1,2-oxaphospholes **7a,b** (Scheme 4) and to an unidentified mixture of polymers. On heating, this process occurred in 1 hour. The greater stability of the planar benzopyranone ring system in **7a** and **7b** comparing to **6**, combined with the increased acidity of the H(3) atom in **6** favors this rearrangement. Such an allylic rearrangement was found to occur in similar tricyclic coumarin systems [13].

ture is formed. While the asymmetric unit of **6** is formed by one molecule, two crystallographic independent molecules and a solvation benzene molecule form the asymmetric unit of **7**. Their molecular structures are depicted in Figures 1 and 2, respectively, while selected geometrical parameters are compared in Table 1.

In compound **6** both the hydrogen at position 3 and the exocyclic oxygen bound to P(2) have a *cis* configuration (Figure 1). The distances O(1)-P(2) and P(2)-O(2) are

Scheme 4



**6**                    **7a**                    **7b**
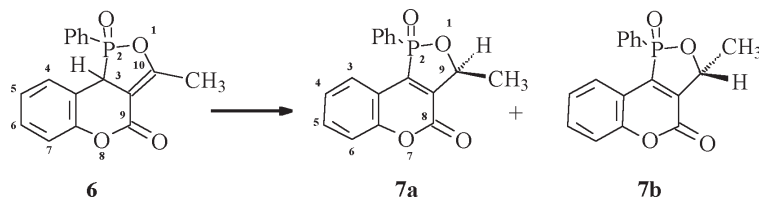
### Crystal and Molecular Structures of 6 and 7.

Single crystals of compounds **6** and **7** have been submitted to X-ray crystallography. Both the compounds crystallize in centric space groups, suggesting that a racemic mix-



Figure 1. X-ray structure of compound **6** Ellipsoids enclose 50% probability.

1.643(2) and 1.465(2) Å, respectively. The distance results O(1)-P(2) are elongated when compared with the average value (1.603(13)Å) of the corresponding distance found in 1,2-oxaphosphole derivatives whose crystal structures are deposited at the Cambridge Crystallographic Data Center. On the other hand, none of these contain a 1,2-oxaphosphol-4-ene moiety.

The coumarino ring system is not planar and it shows the atoms C(3) and O(8) deviating -0.235(3) and -0.115(2) Å, respectively, from the same side of the least squares plane, while C(9) and C(9a) deviate from the opposite side (0.110(3) and 0.175(3) Å, respectively). The pyrane ring presents a boat conformation distorted towards a twist-boat [14]. The total puckering amplitude Q is equal to 0.280(3) Å. The 1,2-oxaphosphole ring shows a twist conformation as it results from $\phi=167.6(8)°$ [14].

The dihedral angle between the least squares plane defined by the oxaphosphole ring and that defined by the ten-membered coumarine system is 23.83(11)°. The phenyl ring bound to P(2) is close to perpendicularity to the oxaphosphole ring and its orientation is almost parallel to a line joining P(2) and C(10) as it results from the pseudo-torsion angle C(2')-C(1')-P(2)…C(10) equal to –2.4(3)°.
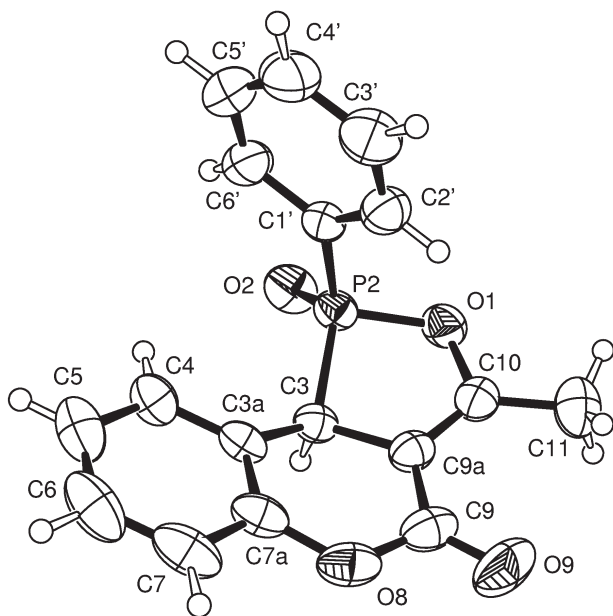
The crystal structure of **6** is stabilized by Van der Waals interactions and non classical intermolecular hydrogen
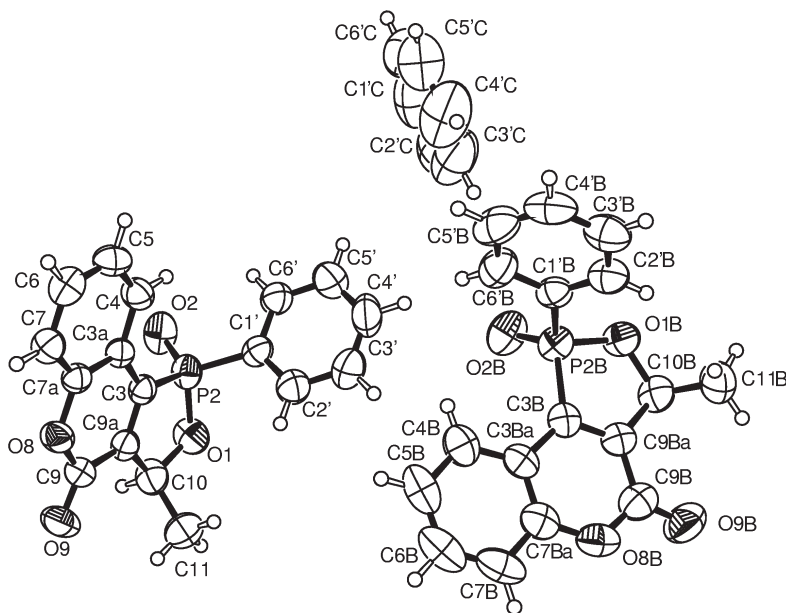
Figure 2. X-ray structure of **7** solvated with a molecule of benzene Ellipsoids enclose 50% probability.

Table 1

Selected geometrical parameters (Å, °) for **6** and **7** obtained by X-ray crystallography and by theoretical calculations.

| | 6 | 7 | |
| --- | --- | --- | --- |
| | X-ray | X-ray | |
| | | Mol. 1 | Mol. 2 |
| O(1)-C(10) | 1.388(3) | 1.458(5) | 1.463(4) |
| O(1)-P(2) | 1.643(2) | 1.593(3) | 1.585(3) |
| P(2)-O(2) | 1.465(2) | 1.459(3) | 1.465(3) |
| P(2)-C(1') | 1.784(3) | 1.786(4) | 1.779(4) |
| P(2)-C(3) | 1.817(3) | 1.812(3) | 1.788(4) |
| C(3)-C(9A) | 1.508(4) | 1.345(5) | 1.334(5) |
| C(7A)-O(8) | 1.403(4) | 1.382(4) | 1.384(5) |
| O(8)-C(9) | 1.376(4) | 1.368(4) | 1.382(5) |
| C(9)-O(9) | 1.193(4) | 1.203(4) | 1.194(5) |
| C(9A)-C(10) | 1.337(4) | 1.501(5) | 1.509(5) |

| | 6 | 7 | |
| --- | --- | --- | --- |
| | X-ray | X-ray | |
| | | Mol. 1 | Mol. 2 |
| C(10)-O(1)-P(2) | 111.9(2) | 116.1(2) | 116.2(2) |
| O(1)-P(2)-O(2) | 113.9(1) | 116.5(2) | 117.4(2) |
| O(1)-P(2)-C(1') | 105.8(1) | 105.9(2) | 105.3(2) |
| O(2)-P(2)-C(3) | 117.0(1) | 114.6(1) | 115.4(2) |
| O(1)-P(2)-C(3) | 93.9(1) | 93.4(1) | 94.1(2) |
| C(1')-P(2)-C(3) | 111.1(1) | 110.9(2) | 110.8(2) |
| C(3A)-C(3)-P(2) | 121.2(2) | 130.8(3) | 130.1(3) |
| C(9A)-C(3)-P(2) | 101.4(2) | 107.2(3) | 108.8(3) |
| C(4)-C(3A)-C(3) | 124.5(2) | 125.6(3) | 124.5(4) |
| C(3)-C(9A)-C(9) | 121.2(3) | 121.2(3) | 121.8(4) |
| O(1)-C(10)-C(9A) | 114.3(2) | 104.7(3) | 104.7(3) |
| C(9A)-C(10)-C(11) | 131.4(3) | 114.3(3) | 115.0(3) |
| O(1)-C(10)-C(11) | 114.3(3) | 109.6(3) | 109.1(3) |

Table 1 (continued)

Dihedral angles (°) [a]

| Planes | 6 | 6 | 7 | | 7 |
| --- | --- | --- | --- | --- | --- |
| | X-ray | B3LYP [b] | X-ray | | B3LYP [b] |
| | | | Mol. 1 | Mol. 2 | |
| 1 ^ 2 | 21.96(13) | 25.8 | 5.4(2) | 0.8(2) | 2.9 |
| 1 ^ 3 | 24.34(15) | 33.9 | 6.3(2) | 2.5(2) | 2.2 |
| 2 ^ 3 | 6.49(15) | 9.2 | 0.9(2) | 2.1(2) | 0.9 |
| 1 ^ 4 | 84.58(15) | 95.7 | 84.7(2) | 74.8(2) | 96.5 |
| 1 ^ 5 | 23.83(11) | 30.8 | 5.9(2) | 1.7(2) | 2.5 |

[a] Planes defined as: 1: O(1) P(2) C(3) C(9A) C(10); 2: C(3) C(3A) C(7A) O(8) C(9) C(9A); 3: C(3A) C(4) C(5) C(6) C(7) C(7A); 4: C(1') C(2') C(3') C(4') C(5') C(6'); 5: C(3) C(3A) C(4) C(5) C(6) C(7) C(7A) O(8) C(9) C(9A); [b] Calculated at the B3LYP 6-31G(d,p) level of theory.

bonds involving the exocyclic oxygen atoms: C(2')-H(2')···O(2) $(x, 1/2-y, -1/2+z)$ (d H···O=2.51 Å) and C(7)-H(7)···O(9) $(-x, 1/2+y, -1/2-z)$ (d H···O=2.39 Å).

The two molecules of the asymmetric unit of **7** show close metrical and conformational parameters. The distances O(1)-P(2) and P(2)-O(2) are 1.593(3) and 1.459(3)Å in molecule 1, while they are 1.585(3) and 1.465(3) Å in molecule 2. These values are in agreement with those found in the two crystallographic structures of 2-phenyl-1,2-oxaphosphol-3-ene 2-oxide derivatives deposited at Crystallographic Data Center [15, 16]. In these compounds the P-O and P=O bond lengths average 1.606(15) and 1.466(6) Å, respectively.

The exocyclic oxygen bound to P(2) and the hydrogen at C(10) have a *cis* configuration. The coumarino system is planar. For all the ten atoms, the deviations from the least

squares plane are less than 0.02 Å. The distance C(3)-C(9a) is equal to 1.345(5) and 1.334(5) Å in the two molecules, thus reflecting its double bond nature. This distance is much longer in **6** (1.508(4) Å) as in this latter compound it involves one $sp^3$ and one $sp^2$ carbon atoms. Accordingly, the bond length C(9a)-C(10) is much shorter in **6** (1.337(4) Å) than in the two molecules of **7** (1.501(5) and 1.509(5) Å, respectively).

The oxaphosphole ring shows an envelope conformation in one molecule of the asymmetric unit of **7**, while it is close to the planarity in the other. This ring is almost coplanar with the coumarino system as a result of the dihedral angle between the two least squares planes, that is equal to 5.91(16)° and 1.73(16)° in the two molecules of the asymmetric unit of **7**. As observed for **6**, also in **7** the pendant phenyl ring is almost perpendicular to the oxaphosphole ring as shown by the pseudo-torsion angle C(2')-C(1')-P(2)···C(10) equal to –14.8(4) and 5.6(4)°, respectively, in the two molecules of **7**.

The conformations of the coumarino oxaphosphole systems in the energy minimized structures of **6** and **7** are quite close to those determined by X-ray crystallography (see below). This suggests that packing and reticular forces play only a minor role in driving the conformational features of the heterocyclic moieties in the two compounds. On the other hand, these forces play a role in determining the orientation of the phenyl ring where the largest differences (about 10°) are found between the energy-minimized and the crystal structures (Table 2).

The crystal structure of **7** is stabilized by Van der Waals interactions and non classical hydrogen bonds both intramolecular (C(4')-H(4') ···O(2B), d H···O=2.54 Å) and intermolecular (C(10B)-H(10B)···O(2B) (*1-x,1-y,1-z*), d H···O=2.55 Å).

Theoretical Calculations.

Both compounds **6** and **7** were studied by *ab initio* calculations (Table 2) [17]. The theoretical data showed the higher stability of **7** in comparison with **6** (ΔE=8.12 kcal mol⁻¹). In both compounds, the phosphorus atom P(2) and the carbon atoms linked to the oxygen atoms (*i.e.* C(7a), C(9), C(10)) have a positive charge, ranging from +0.59 (C(9) (**7**)) to +0.29 (C(10) (**7**)), while for the phosphorus atom the atomic

### Table 2

Energy values for the species **6** and **7** carried out at the B3LYP 6-31G(d,p) level of theory.

| | SCF [a] | ZPVE [b] | SCF + ZPVE [a] | ΔE [c] | μ [d] |
|---|---|---|---|---|---|
| **6** | -1297.951475 | 0.235414 | -1297.716062 | 8.12 | 4.80 |
| **7** | -1297.965179 | 0.236170 | -1297.729009 | 0 | 5.19 |

[a] units of hartree; [b] Zero point vibrational energies corrected by 0.893; units of hartree; [c] kcal mol⁻¹; [d] Dipole moment; Debye.

charges are +1.02 in **6** and +0.99 in **7**. The oxygen atoms carry negative charges decreasing in the order O(1) > O(2) > O(8) > O(9). Also the endocyclic atom C(3), linked to the phosphorus atom, has a negative charge equal to -0.43 (**6**) and -0.17 (**7**). All the other atoms have charges less than ±0.1. The calculations have shown that **7** has the highest dipole moment (5.19 Debye) while for **6** it is 4.80 Debye.

### EXPERIMENTAL

All solvents were distilled before use. 3-acetylcoumarin [18] and dichlorophenylphosphine [19] were prepared by standard procedures. 3-acetylcoumarin was submitted to double recrystallization from tetrachloromethane, m.p. 123.5-124 °C.

Acetic anhydride (Merck) was used as received. Silicagel Merck 60, 43-60 Mesh ASTM was used for flash-chromatographic separation. Melting points were determined in open capillaries on a Gallenkamp apparatus and are uncorrected. Microanalyses were carried out by means of a Perkin-Elmer 240C or a Perkin-Elmer Series II CHNS/O Analyzer 2400. NMR spectra were recorded on a Bruker AC 200 spectrometer for CDCl₃ solutions at 200.13 MHz for ¹H and at 50.33 MHz for the ¹³C nucleus (TMS as internal standard). The values of chemical shifts are expressed in ppm and coupling constants (*J*) in Hz.

Preparation of Coumarino-[3,4-*c*]-3*H*-10-methyl-2-oxo-2-phenyl-1,2-oxaphosphole (**6**).

To a mixture of 1 g (5.3 mmol) of **2** and 3 mL (3.2 mmol) of acetic anhydride, 1.08 g (6 mmol) of dichlorophenylphosphine was added at once under inert gas. The mixture was then slightly warmed until the coumarin was dissolved. The reaction mixture was allowed to react at room temperature. After 10-15 hours, large, colorless crystals of **6** formed and were collected by filtration, washed with dry toluene and dried in vacuum. The compound showed two melting points: at 72-73°C, with formation of a liquid and solid phases, while the solid melted at 200°C; ¹H NMR: δ 2.54 (dd, 3H) CH₃ ($^3J_{HH}$=1.23, $^3J_{PH}$=2.94); 4.81 (dm, 1H) P-C*H* ($^1J_{PH}$=29.7); ¹³C NMR (only characteristic signals given): δ 19.92, 19.99 (d) C¹⁰-CH₃ ($^3J_{CP}$=1.96); 39.71, 41.00 (d) C³ ($J_{CP}$=22.01); 102.88, 102.95 (d) C¹⁰ ($^3J_{CP}$=3.7); 115.88, 115.94 (d) C⁹-*C*=C¹⁰ ($^2J_{CP}$=4.5); 167.18, 133.20 (d, $^3J_{CP}$=2.74).

*Anal.* Calcd. for C₁₇H₁₃O₄P: C, 65.3; H, 4.2. Found: C, 65.4; H, 4.1.

Preparation of Coumarino-[3,4-*c*]-9*H*-9-methyl-2-oxo-2-phenyl-1,2-oxaphosphole (**7**).

Compound **6** (1 g, 3.2 mmol) was boiled in benzene (30 mL) for 1 hour. The solvent was removed under reduced pressure and the residue was extracted with two 10 mL portions of methylene chloride. The combined extracts were evaporated and the residue was submitted to flash-chromatography, eluent: methylene chloride/ethyl acetate. Yield: 30-35%. ¹H NMR: δ 1.88 (d, 3H) C*H*-CH₃ ($^3J_{HH}$=6.7); 5.83 (q, 1H) CH-C*H₃* ($^3J_{HH}$=6.7); 7.19-7.64 (m, 7H) Ar,Ph; 7.89 (dd, 1H) Ph ($^3J_{HH}$=1.46, $^4J_{HP}$=13.93); ¹³C NMR (only characteristic signals given): δ 19.95 (d) C⁹-CH₃ ($^4J_{CP}$=4.57); 80.46 (d) C⁹ ($^3J_{CP}$=1.83); 115.1 (d, $^2J_{CP}$=10.96); 127.16, 129.47 (d) C⁹-C-*C*-P ($^1J_{CP}$=145.2).

*Anal.* Calcd. for C₁₇H₁₃O₄P×0.5C₆H₆: C, 68.3; H, 4.6. Found: C, 68.4; H, 4.7.

Theoretical Calculations.

*Ab initio* molecular orbital calculations were performed on compounds **6** and **7** by using the Gaussian 98 package [17] implemented on a IBM SP4 supercomputer at Cineca in Bologna (Italy). All geometries were fully optimized without any constraints at the Becke 3LYP (B3LYP) [20] with the 6-31G(d,p) level of theory. The final lowest energy geometries were confirmed as a minimum on the molecular potential energy surface by normal-mode vibrational frequency calculations that produced all real frequences. Zero-point energies and statistical thermodynamic properties at 298.15 K and 1 atm were calculated at the B3LYP 6-31G(d,p) level of theory.

X-ray Crystallography.

Single crystals of **6** and **7** were submitted to X-ray data collection on a Siemens P4 four-circle diffractometer with graphite monochromated Mo-$K\alpha$ radiation ($\lambda =0.71069$ Å). Lattice parameters were determined by least-squares refinements on 52 (**6**) and 38 (**7**) randomly selected and automatically centered reflections. The $\omega/2\theta$ scan technique was used in the data collections. Empirical absorption correction (psi scan) was applied for **6**. The structures were solved by direct methods implemented in the SHELXS-97 program [21]. The refinements were carried out by full-matrix anisotropic least-squares on $F^2$ for all reflections for non-H atoms by using the SHELXL-97 program [22]. Crystal data are reported in Table 3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 214496 (**6**) 214497 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail. deposit@ccdc.cam.ac.uk].

Table 3

Crystal data for **6** and **7**.

| | **6** | **7** |
|---|---|---|
| Formula | $C_{17}H_{13}O_4P$ | $C_{17}H_{13}O_4P \times$ 0.5 $C_6H_6$ |
| M | 312.24 | 351.30 |
| Crystal size/(mm) | 0.10×0.25×0.20 | 0.20×0.25×0.40 |
| Crystal System | Monoclinic | Triclinic |
| Space Group | $P2_1$/c (no. 14) | P-1 (no. 2) |
| $a$/Å | 13.3524(16) | 9.9120(10) |
| $b$/Å | 10.4335(9) | 13.449(3) |
| $c$/Å | 10.7084(8) | 14.146(2) |
| $\alpha$/° | | 68.681(10) |
| $\beta$/° | 102.962(7) | 84.492(6) |
| $\gamma$/° | | 89.402(10) |
| U/Å$^3$ | 1453.8(2) | 1748.0(5) |
| Temperature /K | 293 | 293 |
| Z | 4 | 4 |
| F(000) | 648 | 732 |
| $D_c$/g cm$^{-3}$ | 1.43 | 1.33 |
| $\mu$(Mo-$K_\_$)/mm$^{-1}$ | 0.205 | 0.178 |
| Scan mode | $\omega$ | $\omega$ |
| Scan range/° | $2 \leq \theta \leq 25$ | $2 \leq \theta \leq 25$ |
| Scan width/° | 1.14 | 0.86 |
| Scan speed/° min$^{-1}$ | 3.0 | 3.0 |
| Collected reflections | 3346 | 6373 |
| Independent reflections | 2563 ($R_{int}$=0.03) | 5999 ($R_{int}$=0.02) |
| Absorption correction | psi scan | none |
| Transmission min/max | 0.2936 / 0.3094 | – |
| Obs. reflections ($I > 2\sigma(I)$) | 1853 | 3591 |
| N. parameters refined | 210 | 479 |
| $R_1$ ($I > 2\sigma(I)$) | 0.05 | 0.06 |
| $wR_2$ ($I > 2\sigma(I)$) | 0.10 | 0.13 |

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