

Two new polymorphs of diphenyl-(4-pyridyl)methyl methacrylate

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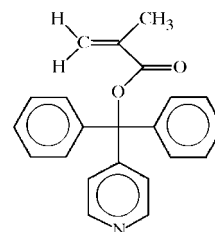
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The title compound (D4PyMA), C₂₂H₁₉NO₂, exhibits polymorphism after crystallization by slow evaporation from a binary mixture of chloroform and hexane. Long needle-like crystals have an orthorhombic structure (space group *Fdd2*), with one molecule in the asymmetric unit, while small tablet-like crystals exhibit a monoclinic crystal structure (space group *P2₁/n*), in which two independent but chemically identical molecules comprise the asymmetric unit. The bond lengths and angles are normal, while the torsion angles around the –C–O– bond linking the diphenyl(4-pyridyl)methyl and methacrylate groups show the flexibility of the molecule by way of packing effects. The two polymorphs both contain weak C–H··· π and C–H···O/N contacts but have different conformations.

Comment

Methacrylate monomers with large bulky ester groups have been synthesized in order to study stereospecific and asymmetric polymerization, in which the ester group plays an important role. Okamoto *et al.* (1983, 1994) reported on a series of bulky methacrylates and found that many of these types of monomer yield highly isotactic optically active polymers with one-handed helical conformations by asymmetric anionic polymerization. The bulky side groups of the monomers containing pyridyl groups are especially interesting, because of their ability to form complexes with acidic low-molecular-weight molecules. Poly(4-vinylpyridine) complexed with, for example, nona- or pentadecylphenol self-assembles in lamellar structures with a periodicity of the order of 30–50 Å (Ruokolainen *et al.*, 1996). Block co-polymers containing 4-vinylpyridine blocks complexed with nona- or pentadecylphenol resulted in supramolecular polymeric materials with hierarchical structure-within-structure morphologies (Ruokolainen *et al.*, 1998, 1999). As a result of its helical conformation, poly[diphenyl(4-pyridyl)methyl methacrylate], (D4PyMA) complexed with similar amphiphiles, may give rise

to self-assembled structures that are even more interesting. After thorough purification of the synthesized monomer of D4PyMA, two types of crystals were found and two polymorphs, (I) (orthorhombic) and (II) (monoclinic), were detected, as described below. An extensive literature search revealed no reports of the crystal structure of D4PyMA. The crystal and molecular structures of diphenyl(2-pyridyl)methyl methacrylate (D2PyMA) have, however, been reported (Kageyama *et al.*, 1986). The crystal structures of related methacrylates with a large bulky ester substituent, such as 1,1-diphenylethyl, triphenylmethyl (Kageyama *et al.*, 1985) and diphenylmethyl (Kageyama *et al.*, 1982), all have monoclinic space groups (*P2₁/a*, *P2₁/a* and *C2/c*, respectively).



D4PyMA

The molecular geometries of polymorphs (I) and (II), with the atomic numberings, are shown in Figs. 1 and 2. The structure of D2PyMA, which differs only in the position of the N atom in the pyridyl ring, is reported (Kageyama *et al.*, 1986) to be monoclinic, with the same space group (*P2₁/n*) as (II). In D2PyMA there is only one molecule in the asymmetric unit, whereas polymorph (II) contains two. Furthermore, the structure of D2PyMA was determined at ambient temperature, whilst that of (II) was determined at 100 K.

The distance between two adjacent double bonds is of importance in allowing polymerization in the crystalline state (below the melting temperature); a distance of 3.76 Å is short enough to form linear polymers using γ -radiation (Enkelmann *et al.*, 1978). However, it is not only the distance that is important; the crystal geometry also has to be taken into account. Hence, methyl acrylate does not react under γ -radiation, although the distance between the double bonds is 3.711 Å (Brown *et al.*, 1971).

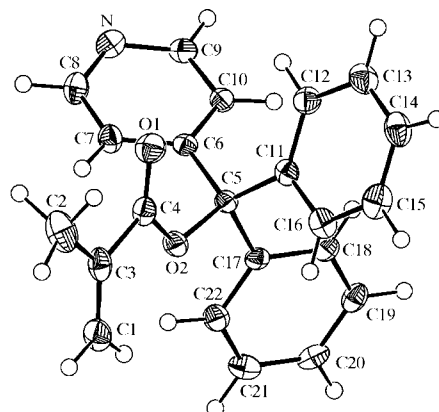


Figure 1

A perspective drawing of (I), showing the atomic labelling scheme for non-H atoms, which are represented by displacement ellipsoids drawn at the 50% probability level.

Polymerization in the crystalline phase is very unlikely for either polymorph, since the shortest intermolecular distance between the mid-points of the double bonds is 5.455 (5) Å in (I) [C1=C3; the two closest equivalent mid-points are at $(\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z)$ and $(-\frac{1}{4}+x, \frac{1}{4}-y, -\frac{1}{4}+z)$], and 4.117 (6) Å (C11=C13; symmetry code of closest mid-point: $-x, 1-y, 1-z$) and 4.914 (6) Å (C21=C23; symmetry code of closest mid-point: $-x, 1-y, -z$) in the two residues of (II). In (I), the observed C—H... π contacts shorter than 3.0 Å are C13—H13...Cg1 (2.71 Å; Cg1 is the centroid of the N/C6—C10 ring; symmetry code: $\frac{1}{2}-x, -y, \frac{1}{2}+z$), C8—H8...Cg2 (2.85 Å; Cg2 is the centroid of the C11—C16 ring; symmetry code: $x, y, -1+z$) and C10—H10...Cg3 (2.94 Å; Cg3 is the centroid of the C17—C22 ring; symmetry code: $-x, -y, z$). In (II), the contacts are C29—H29...Cg4 (2.94 Å; Cg4 is the centroid of the N11/C16—C110 ring; symmetry code: $-x, 1-y, 1-z$) and

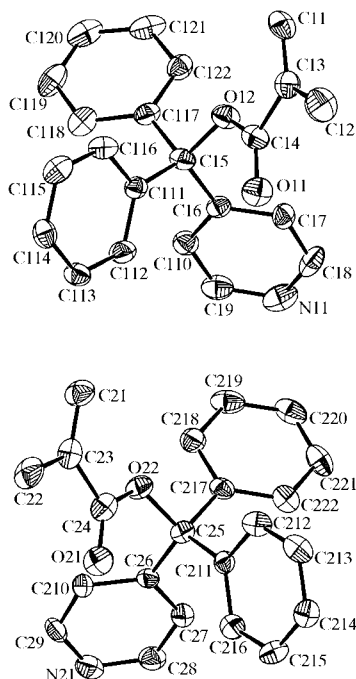


Figure 2

A perspective drawing of the two unique molecules of polymorph (II), showing the atomic labelling scheme. Non-H atoms are represented by displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

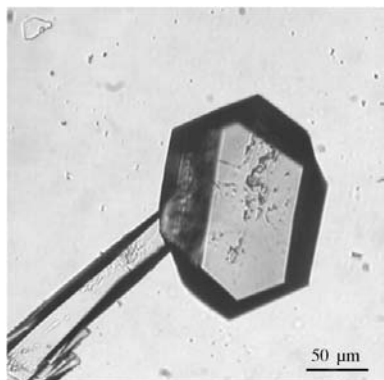


Figure 3

A microscopic picture of a crystal of the monoclinic compound, (II), on top of a crystal of the orthorhombic compound, (I).

C114—H114...Cg5 (2.60 Å; Cg5 is the centroid of the N21/C26—C210 ring; symmetry code: $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$). [For a general discussion of C—H... π contacts, see Malone *et al.* (1997), Nishio *et al.* (1998) and Desiraju & Steiner (1999).]

Two very weak hydrogen-bond-like contacts were also observed, *viz.* a C19—H19...N($-x, -y, 1+z$) contact (2.54 Å) in (I) and a C110—H110...O11($\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$) contact (2.44 Å) in (II).

The density of the orthorhombic structure is greater than that of the monoclinic structure. This result suggests that the orthorhombic form may be thermodynamically more stable (Burger & Ramberger, 1979).

The main differences in the conformations appear around the Cn5—On2 bond. The C4—O2—C5—C11 torsion angle in (I) is 55.9 (3)°, and the corresponding angles in (II) are 50.3 (4) and -52.4 (4)°. The C4—O2—C5—C6 torsion angle in (I) is -72.2 (2)°, and the corresponding angles in (II) are -77.7 (4) and 75.5 (4)°. The C4—O2—C5—C17 angle in (I) is 173.0 (2)°, and the corresponding angles in (II) are 166.5 (3) and -169.5 (3)°.

Several examples of concomitant polymorphism have been reported previously, for example, benzanilide from ethanol in a triclinic form (Bowes *et al.*, 2003) and a monoclinic form (Kashino *et al.*, 1979). Yet another example is the crystallization of 2-iodo-4-nitroaniline from ethanol, which yields a mixture of triclinic and orthorhombic crystals (McWilliam *et al.*, 2001). Fig. 3 shows the two crystal types, *viz.* the monoclinic crystal, (II), grown on top of an orthorhombic needle-like crystal of (I).

Experimental

D4PyMA was synthesized according to the following procedure. To a suspension (60 wt% in mineral oil from Fluka) of NaH (13.9 g, 0.35 mol) in a 1000 ml three-necked flask, flushed with dry N₂ gas and equipped with a reflux condenser, hexane (35 ml) was added and the mixture stirred for 1 h. The supernatant hexane/mineral oil mixture was removed with a syringe. To the remaining NaH (30.5 g, 0.117 mol), α -(4-pyridyl)benzhydrol suspended in tetrahydrofuran (THF, 300 ml) was added stepwise (H₂) with stirring. After adding all the α -(4-pyridyl)benzhydrol suspension, the reaction mixture was refluxed for 20 h. The mixture was then cooled to 273 K, and freshly distilled methacryloyl chloride (12.2 g, 0.117 mol) was added dropwise with stirring. After the addition was complete, the mixture was stirred for an additional 20 h at room temperature. Subsequently, THF was removed by evaporation. The reaction product was added stepwise to a solution of Na₂CO₃ (5.5 g, 51.9 mmol) in a 350 ml water/ice mixture. Extraction was carried out with diethyl ether (300 ml). The diethyl ether layer contained the product, and the water layer contained the excess methacryloyl chloride and NaCl. The remaining undissolved products were filtered off if necessary and the layers were separated. The remaining water layer was extracted another two times. The diethyl ether fractions were combined and the solvent was removed by evaporation. The crude product (dark-red oil) was purified by column chromatography over neutral Al₂O₃ activity type 1 using a chloroform–hexane mixture (2:1 v/v) and was recrystallized twice, first from a hexane–diethyl ether mixture (1:1 v/v) and secondly from chloroform (yield 12.1 g, 36.7 mmol, 35.5% of pure monomer). ¹H NMR (Varian VXR, 300 MHz, CDCl₃): δ 1.93 (s, 3H, CH₃), 5.60

(s, 1H, vinyl H), 6.19 (s, 1H, vinyl H), 7.1–7.4 (m, 12H, aromatic), 8.48–8.51 (d, 2H, aromatic next to N). MS (Jeol JMS 600H 70 eV EI): $m/z = 329$ (calculated: 329.4). Single crystals of (I) and (II) suitable for analysis were grown by slow evaporation from a chloroform–hexane (5:95 v/v) solution at room temperature in air.

Polymorph (I)

Crystal data

$C_{22}H_{19}NO_2$	Mo $K\alpha$ radiation
$M_r = 329.40$	Cell parameters from 4817 reflections
Orthorhombic, $Fdd2$	$\theta = 2.3$ – 27.4°
$a = 19.170$ (1) Å	$\mu = 0.08$ mm $^{-1}$
$b = 42.244$ (3) Å	$T = 100$ (1) K
$c = 8.4475$ (6) Å	Needle, colorless
$V = 6840.9$ (8) Å 3	$0.38 \times 0.10 \times 0.06$ mm
$Z = 16$	
$D_x = 1.279$ Mg m $^{-3}$	

Data collection

Bruker SMART APEX area-detector diffractometer	1944 independent reflections
φ and ω scans	1750 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS, Bruker, 2000)	$R_{int} = 0.052$
$T_{min} = 0.910$, $T_{max} = 0.994$	$\theta_{max} = 26.7^\circ$
13 883 measured reflections	$h = -24 \rightarrow 24$
	$k = -53 \rightarrow 53$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0124P)^2 + 8.7015P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.24$ e Å $^{-3}$
1944 reflections	$\Delta\rho_{min} = -0.20$ e Å $^{-3}$
291 parameters	
H-atom parameters constrained	

Polymorph (II)

Crystal data

$C_{22}H_{19}NO_2$	$D_x = 1.266$ Mg m $^{-3}$
$M_r = 329.40$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2934 reflections
$a = 16.712$ (2) Å	$\theta = 2.5$ – 26.8°
$b = 11.891$ (1) Å	$\mu = 0.08$ mm $^{-1}$
$c = 17.724$ (2) Å	$T = 100$ (1) K
$\beta = 101.045$ (2) $^\circ$	Platelet, colorless
$V = 3456.9$ (6) Å 3	$0.20 \times 0.18 \times 0.06$ mm
$Z = 8$	

Data collection

Bruker SMART APEX area-detector diffractometer	6100 independent reflections
φ and ω scans	3615 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS, Bruker, 2000)	$R_{int} = 0.077$
$T_{min} = 0.973$, $T_{max} = 0.995$	$\theta_{max} = 25.0^\circ$
24 310 measured reflections	$h = -19 \rightarrow 19$
	$k = -14 \rightarrow 14$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.105$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$wR(F^2) = 0.265$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.46$	$(\Delta/\sigma)_{max} = 0.032$
6100 reflections	$\Delta\rho_{max} = 0.98$ e Å $^{-3}$
453 parameters	$\Delta\rho_{min} = -0.30$ e Å $^{-3}$

Crystals of the monoclinic phase, (II), were grown together; consequently, a single crystal had to be cleaved from an aggregate, resulting in plate-shaped fragments. Most crystals of (II) showed broad profiles

with anisotropic mosaicity. At ambient temperature, only very weak low-order reflections of (II) were observed, from which the unit cell was determined [$a = 16.974$ (5) Å, $b = 11.967$ (4) Å, $c = 17.968$ (6) Å, $\beta = 100.795$ (6) $^\circ$ and $V = 3585$ (2) Å 3]. The volume of (II) is comparable to two times the reported value of the unit cell of D2PyMA (3589 Å 3 ; Kageyama *et al.*, 1986), the latter with $Z = 4$. The absolute configuration of the orthorhombic phase, (I), could not be determined reliably; therefore Friedel pairs were merged. The N-atom positions were discriminated from the other possible positions by comparing the geometric and displacement parameters after isotropic refinement. All H atoms in (I) and (II) were placed in idealized positions and constrained to ride on their parent atoms. The final difference Fourier map for (II) contained a relatively large residual electron density. No satisfactory discrete disorder model could be fitted to this density.

For both compounds, data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2000); data reduction: XPREP (Bruker, 2000); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLUTO (Meetsma, 2004) and PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1099). Services for accessing these data are described at the back of the journal.

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