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The Crystal and Molecular Structure of Diphenyl-2-pyridylmethyl Methacrylate

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The molecular structure of diphenyl-2-pyridylmethyl methacrylate has been determined by means of X-ray diffraction. Crystals are monoclinic, space group $P2_1/n$, a=10.334(2), b=22.093(3), c=8.415(1) Å, β=110.92(2)°, and Z=4. The structure was established by the direct method, and refined by the block-diagonal least-squares procedure to R=0.052 (R_w=0.064) for 1702 observed reflections. The molecule has an *antiperiplanar-synperiplanar* conformation. One of the two phenyl groups attached to the C(5) atom is *trans*, and the other phenyl and 2-pyridyl groups are *gauche* to the C(1).

Recently, in a series of studies on the molecular structures of methacrylates and their reactivties in the asymmetric selective polymerization with Grignard reagnt-(−)-sparteine derivatives, molecular structures of (*RS*)-1,2-diphenylethyl methacrylate (1,2-DPEMA),[1] (*RS*)-α-*t*-butylbenzyl methacrylate (*t*-BBMA),[1] (*RS*)-1,2,2,2-tetraphenylethyl methacrylate(TrBzMA),[2] and (1*S*,2*R*)-(+)-1-benzyl-3-dimethylamino-2-methyl-1-phenylpropyl methacrylate (ChMA)[2] have been determined by means of X-ray diffraction. In addition, in order to clarify the role of the α-substituents on the ester group in the sterospecific polymerization of diphenylmethyl methacrylate derivatives with *n*-BuLi, molecular structures of diphenylmethyl methacrylate (DPMMA),[3] 1,1-diphenylethyl methacrylate (1,1-DPEMA),[4] and triphenylmethyl methacrylate (TrMA)[4] have been determined. This paper describes the structural study on diphenyl-2-pyridylmethyl methacrylate (2-PyMA), a new diphenylmethyl methacrylate derivative, which gave a highly isotactic polymer not only by anionic polymerization but also by radical polymerization.[5]

Experimental

Colorless crystals of 2-PyMA were recrystallized from toluene. Unit-cell parameters and reflection intensities were measured on a Rigaku automated, four-circle diffractometer. Nickel-filterd Cu $K\alpha$ radiation was used.

Crystal Data. 2-PyMA, $C_{22}H_{19}O_2N$, M 329.4, monoclinic, space group $P2_1/n$, a=10.334(2), b=22.093(3), c=8.415(1) Å, β=110.92(2)° V=1794.6(4) Å^3, D_c=1.219 g cm^{-3} for Z=4, μ(Cu $K\alpha$)=6.27 cm^{-1}.

Integrated intensities were measured by the θ-2θ scan technique(2θ<110°). The 2θ scan rate and scan width were 4° min^{-1} and $\Delta 2\theta$=(2.0+0.3 tanθ)°, respectively. Backgrounds were counted for 7.5 s before and after each scan. Four standard reflections were measured after every 60 reflections, which showed no intensity decrease during the intensity measurement. The usual Lorentz and polarization corrections were applied but no correction for absorption and extinction was carried out. A total of 1702 reflections was collected($|F_o|>3\sigma(F_o)$).

Structure Solution and Refinement

The structure was solved by the direct method (*MULTAN* 78),[6] and refined by the block-diagonal least-squares procedure (*HBLS* V)[7] minimizing $\Sigma w(\Delta F)^2$. Anisotropic temperature factors were applied for nonhydrogen atoms and isotropic ones for hydrogen atoms. Atomic scattering factors were taken from

Table 1. Final Atomic Coordinates of Non-hydrogen Atoms and the Equivalent Isotropic Temperature Factors[9] with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2
O (1)	0.2219 (3)	0.18044 (10)	−0.2049 (3)	4.08
O (2)	0.4432 (3)	0.15879 (12)	−0.1719 (4)	5.78
N	0.1749 (3)	0.01633 (12)	−0.2427 (4)	4.04
C (1)	0.3492 (4)	0.19408 (16)	−0.2043 (5)	4.29
C (2)	0.3569 (4)	0.25932 (16)	−0.2484 (5)	5.02
C (3)	0.2447 (5)	0.29643 (18)	−0.2813 (7)	7.07
C (4)	0.4873 (5)	0.2777 (3)	−0.2574 (7)	7.70
C (5)	0.1953 (4)	0.12056 (13)	−0.1496 (4)	3.42
C (6)	0.2993 (4)	0.10999 (15)	0.0320 (4)	3.80
C (7)	0.3089 (4)	0.15542 (18)	0.1511 (5)	5.29
C (8)	0.4030 (5)	0.1492 (3)	0.3178 (6)	6.83
C (9)	0.4841 (5)	0.0984 (3)	0.3646 (6)	7.43
C (10)	0.4732 (5)	0.0533 (3)	0.2489 (6)	6.58
C (11)	0.3826 (4)	0.05925 (18)	0.0823 (5)	4.95
C (12)	0.0473 (4)	0.12515 (14)	−0.1502 (4)	3.33
C (13)	−0.0472 (4)	0.16640 (15)	−0.2534 (5)	4.64
C (14)	−0.1824 (4)	0.16648 (16)	−0.2577 (6)	5.29
C (15)	−0.2269 (4)	0.12622 (17)	−0.1640 (5)	4.89
C (16)	−0.1339 (4)	0.08434 (16)	−0.0633 (5)	4.38
C (17)	0.0017 (4)	0.08428 (15)	−0.0564 (4)	3.84
C (18)	0.1945 (3)	0.07344 (14)	−0.2826 (4)	3.30
C (19)	0.2001 (4)	0.08826 (17)	−0.4399 (5)	4.58
C (20)	0.1897 (4)	0.0426 (2)	−0.5566 (5)	5.58
C (21)	0.1721 (4)	−0.01570 (18)	−0.5149 (5)	5.14
C (22)	0.1648 (4)	−0.02717 (15)	−0.3579 (5)	4.66

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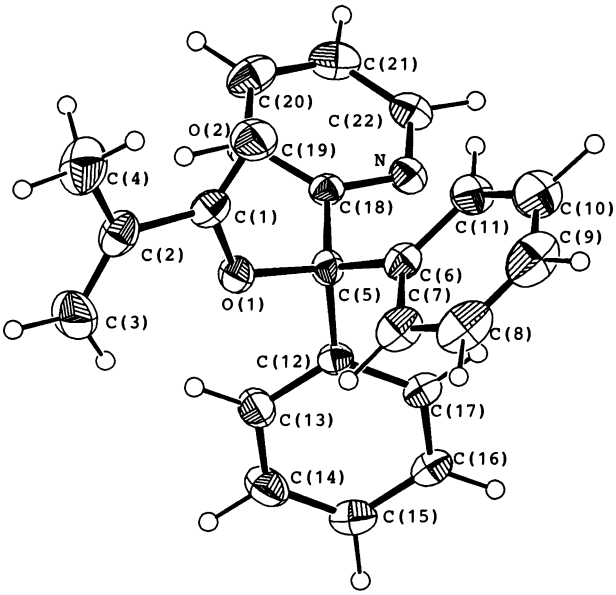
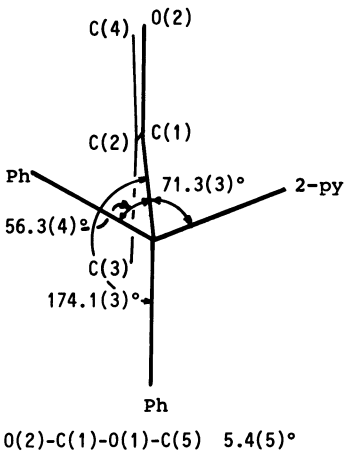


Fig. 1. A perspective view[10] of the 2-PyMA molecule with the atom labelling.
Non-hydrogen atoms are represented as thermal ellipsoids with 30% probability level, hydrogen atoms as spheres with $B=1.0$ Å^2.



O(2)-C(1)-O(1)-C(5) 5.4(5)°

Fig. 2. Conformation about the C(5)–O(1) bond.

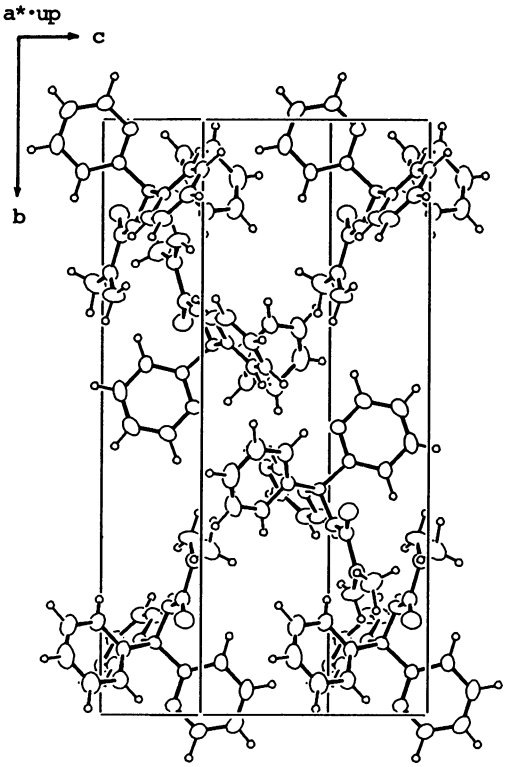


Fig. 3. Crystal structure projected along the a* axis.[10]

International Tables for X-Ray Crystallography.[8] Finally, the R value converged to 0.053 (R_w=0.064). The weighting scheme used at the final stage was $w=\{\sigma^2(F_o)-0.00438\,|F_o|+0.00170|F_o|^2\}^{-1}$ for $|F_o|>0$. σ is the standard deviation obtained by the counting statistics.

The final atomic parameters and equivalent temperature factors are given in Table 1.††† All computations were done on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

Molecular Structure. Figure 1 shows a perspective view[10] of 2-PyMA molecule with the atom labelling. Selected bond lengths and bond angles are given in Table 2, and some least-squares planes and dihedral angles in Table 3.

This molecule has an *antiperiplanar-synperiplanar (ap-sp)* structure: the conformation of the C(2)=C(3) [1.366(7) Å] and C(1)=O(2) [1.199(5) Å] double bonds about the C(1)–C(2) [1.498(5) Å] is *ap* and that of the C(1)=O(2) and the C(5)–O(1) ester bond [1.461(4) Å] about the C(1)–O(1) is *sp*, which is different from those of α-substituted diphenylmethyl methacrylates, 1,1-DPEMA and TrMA but similar to DPMMA. However, TrMA and 2-PyMA act similarly in the stereospecific polymerization; both monomers afford almost 100% isotactic polymers in the anionic polymerization, and even radical polymerization produce the isotactic polymers.[5,11] Therefore, the conformation of the C(2)=C(3) and C(1)=O(2) of the methacrylates in the solid state may not be important for the stereospecific polymerization. In solution both monomers likely take the same conformation considering from the results by ^{1}H NMR study with a shift reagent.[12]

The methacryloyl residue is planar within 0.04 Å (Plane 1), and the dihedral angle between the plane defined by the C(1), C(2), C(3), and C(4) atoms (Plane 2) and that made by the C(1), C(2), O(1), and O(2) (Plane 3) is only 1.7(2)°. Two benzene and a pyridine

††† Tables of anisotropic temperature factors, coordinates of hydrogen atoms, and the observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8641.

Table 2. Selected Bond Lengths and Bond Angles with Estimated Standard Deviations in Parentheses

Bond lengths[l/Å]			
O (1) - C (1)	1.348 (4)	O (1) - C (5)	1.461 (4)
O (2) - C (1)	1.199 (5)	C (1) - C (2)	1.498 (5)
C (2) - C (3)	1.366 (7)	C (2) - C (4)	1.435 (7)
C (5) - C (6)	1.540 (5)	C (5) - C (12)	1.531 (4)
C (6) - C (7)	1.397 (5)	C (12) - C (13)	1.391 (5)
C (6) - C (11)	1.384 (5)	C (12) - C (17)	1.388 (5)
C (7) - C (8)	1.400 (6)	C (13) - C (14)	1.385 (6)
C (8) - C (9)	1.372 (7)	C (14) - C (15)	1.373 (6)
C (9) - C (10)	1.368 (7)	C (15) - C (16)	1.384 (6)
C (10) - C (11)	1.386 (6)	C (16) - C (17)	1.381 (5)
C (5) - C (18)	1.527 (4)	C (18) - C (19)	1.385 (5)
C (18) - N	1.339 (4)	C (19) - C (20)	1.385 (6)
C (22) - N	1.343 (5)	C (20) - C (21)	1.364 (6)
		C (21) - C (22)	1.373 (5)
Bond angles [ϕ/°]			
C (1) - O (1) - C (5)	119.7 (3)	O (1) - C (1) - O (2)	124.5 (4)
O (1) - C (1) - C (2)	110.7 (3)	O (2) - C (1) - C (2)	124.9 (4)
C (1) - C (2) - C (3)	120.8 (4)	C (1) - C (2) - C (4)	114.8 (4)
C (3) - C (2) - C (4)	124.4 (5)	O (1) - C (5) - C (6)	108.0 (3)
O (1) - C (5) - C (12)	103.9 (3)	O (1) - C (5) - C (18)	109.7 (3)
C (6) - C (5) - C (12)	110.9 (3)	C (6) - C (5) - C (18)	116.3 (3)
C (12) - C (5) - C (18)	107.4 (3)	C (5) - C (6) - C (7)	116.6 (3)
C (5) - C (6) - C (11)	124.3 (3)	C (7) - C (6) - C (11)	119.0 (4)
C (6) - C (7) - C (8)	119.7 (4)	C (7) - C (8) - C (9)	120.2 (5)
C (8) - C (9) - C (10)	120.3 (5)	C (9) - C (10) - C (11)	120.3 (5)
C (6) - C (11) - C (10)	120.5 (4)	C (5) - C (12) - C (13)	121.6 (3)
C (5) - C (12) - C (17)	119.8 (3)	C (13) - C (12) - C (17)	118.4 (4)
C (12) - C (13) - C (14)	119.6 (4)	C (13) - C (14) - C (15)	121.8 (4)
C (14) - C (15) - C (16)	118.9 (4)	C (15) - C (16) - C (17)	119.9 (4)
C (12) - C (17) - C (16)	121.4 (4)	C (5) - C (18) - C (19)	123.3 (3)
C (5) - C (18) - N	114.8 (3)	C (19) - C (18) - N	121.6 (3)
C (18) - C (19) - C (20)	119.1 (4)	C (19) - C (20) - C (21)	119.3 (4)
C (20) - C (21) - C (22)	118.7 (4)	C (21) - C (22) - N	123.1 (4)
C (18) - N - C (22)	118.2 (3)		

rings attached to the C(5) atom are all planar within 0.01 Å. Bond lengths [av. 1.385 and 1.384 Å] and bond angles [both 120.0°] in phenyl rings are normal. The nitrogen atoms of the 2-pyridyl group is located far from the methacryl residue. The N-C(18) [1.339(4) Å] and N-C(22) [1.343(5) Å] bond lengths are respectively equal to the corresponding lengths in the pyridine molecule at 153 K [1.336 Å].[13] The C(19)-C(20) bond length [1.385(6) Å] is slightly longer than the corresponding C-C length in pyridine [1.378 Å]. The C(18)-N-C(22) angle [118.2(3)°] is slightly larger and the N-C(18)-C(19) [121.6(3)°] smaller than the C-N-C [116.6°] and N-C-C [123.7°] angle in pyridine, respectively. Among the bond angles around the C(5) atom, the C(6)-C(5)-C(18) angle [116.3(3)°] is much larger, whereas the O(1)-C(5)-C(12) [103.9(3)°] is much smaller than the tetrahedral angle.

The molecular conformation about the O(5)-C(1) bond is shown in Fig. 2. Similar to 1,1-DPEMA,[4] one of the two phenyl groups attached to the C(5) atom is trans to the C(1), and the other and the 2-pyridyl group gauche. This conformation is also similar to those of TrMA[4] and ChMA,[2] each of which has no hydrogen atom on the C(5).

Crystal Structure. The packing mode of molecules in the crystal is shown in Fig. 3[10] Close intermolecular contacts between non-hydrogen atoms of pyridine rings in adjacent molecules are observed: C(21)(x, y, z)···C(22)($-x$, $-y$, $-1-z$)=3.392(6), N(x, y, z)···C(21)($-x$, $-y$, $-1-z$)=3.435(5), and C(20)(x, y, z)···C(22)($-x$, $-y$, $-1-x$)=3.489(6) Å. The C(15)(x, y, z)···O(2) ($-1+x$, y, z) distance is also short [3.461(5) Å].

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Table 3. Least-Squares Planes, Deviations of Atoms from the Planes [l/Å], Dihedral Angles between the Planes [ϕ/°], and Angles between the Vector and Plane [ϕ/°] (The planes are defined in terms of Cartesian coordinates by AX+BY+CZ=D, where the X and Y axes are parallel to the a and b axes, respectively, and the Z axis parallel to the c* axis.) Estimated Standard Deviations in Parentheses

Plane 1: O(1), O(2), C(1), C(2), C(3), and C(4)
A, B, C, and D in Å=0.0546, −0.2470, −0.9675, −0.7258

O(1)	O(2)	C(1)	C(2)	C(3)	C(4)
0.006(9)	−0.007(9)	−0.001(9)	−0.010(10)	−0.020(10)	0.034(10)

Plane 2: C(1), C(2), C(3), and C(4)
A, B, C, and D in Å=−0.0326, 0.2455, 0.9689, 0.6387

C(1)	C(2)	C(3)	C(4)
−0.002(19)	0.009(19)	−0.006(19)	−0.005(19)

Plane 3: O(1), O(2), C(1), and C(2)
A, B, C, and D in Å=0.0613, −0.2441, −0.9678, −0.7640

O(1)	O(2)	C(1)	C(2)
−0.000(12)	−0.001(12)	0.002(12)	−0.001(12)

Plane 4: O(1), O(2), and C(5)
A, B, C, and D in Å=0.0802, −0.3352, −0.9387, −0.4089

Plane 5: C(6), C(7), C(8), C(9), C(10), and C(11)
A, B, C, and D in Å=−0.8570, −0.4492, 0.2524, 3.5959

C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
−0.001(5)	0.006(6)	−0.005(7)	−0.005(7)	−0.011(7)	−0.005(6)

Plane 6: C(12), C(13), C(14), C(15), C(16), and C(17)
A, B, C, and D in Å=−0.0246, 0.6470, 0.7621, −0.8115

C(12)	C(13)	C(14)	C(15)	C(16)	C(17)
0.004(6)	−0.008(7)	0.002(7)	0.006(7)	−0.006(6)	0.001(6)

Plane 7: C(18), C(19), C(20), C(21), C(22), and N
A, B, C, and D in Å=−0.9178, 0.1284, −0.3756, 1.5709

C(18)	C(19)	C(20)	C(21)	C(22)	N
−0.010(7)	0.010(8)	0.001(8)	−0.006(7)	0.000(7)	0.005(7)

Dihedral angles:
between planes 2 and 3: 178.4(2)
between planes 3 and 4: 5.6(3)
between planes 1 and 5: 100.4(2)
between planes 1 and 6: 154.0(2)
between planes 1 and 7: 73.6(2)

Angles between the vector and plane:
between the C(5)-O(1) vector and the plane 5: 47.8(2)
between the C(5)-O(1) vector and the plane 6: 20.6(2)
between the C(5)-O(1) vector and the plane 7: 2.8(2)

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