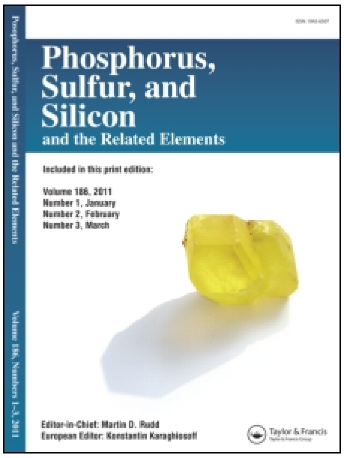

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CRYSTAL AND MOLECULAR STRUCTURE OF BISMUTH TRIS(2,2-DIETHYLTRIMETHYLENE DITHIOPHOSPHATE),$BI[SP(S)OCH_2CEt_2CH_2O]_3$

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CRYSTAL AND MOLECULAR STRUCTURE OF BISMUTH TRIS(2,2-DIETHYLTRIMETHYLENE DITHIOPHOSPHATE),$\mathrm{BI[S\overline{P(S)OCH_2CEt_2CH_2O}]_3}$

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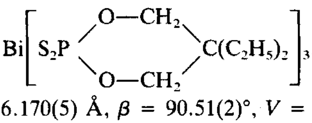
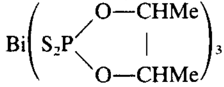
Bismuth tris(2,2-diethyltrimethylene dithiophosphate),  , M = 884.8, monoclinic, $P2_1/c$, a = 9.591(3), b = 10.059(1), c = 36.170(5) Å, β = 90.51(2)°, V = 3489.5 Å^3, Z = 4, Dc = 1.68 g cm^{-3}, (MoKα) = 0.71069 Å, μ = 55.5 cm^{-1}, $F(000)$ = 880, T = 295 K. Final R = 0.122 for 3183 reflections. The coordination geometry around bismuth is slightly distorted octahedral with three short and three long Bi—S bonds (average lengths, 2.74 and 2.85 Å, respectively); 1,3,2-Dioxaphosphorinane rings are present in chair form.

Preliminary data have also been obtained for bismuth tris(2,3-butylene dithiophosphate),  , M = 758.6, monoclinic, $C2/c$, a = 16.684(8), b = 13.682(6), c = 11.930(6) Å, β = 98.45(2), V = 2693.8 Å^3, Z = 4, T = 295 K, Dc = 1.87 g cm^{-3}, μ = 69.1 cm^{-1} and R = 0.052 for 1073 reflections. The chelation is symmetrical in this compound with Bi—S bond lengths of 2.76 and 2.79 Å.

Key words: Bismuth O,O-dialkyldithiophosphates; bismuth O,O-alkylenedithiophosphates; bismuth tris(2,2-diethyltrimethylene dithiophosphate); bismuth tris(2,3-butylene dithiophosphate); crystal and molecular structure.

INTRODUCTION

The versatility of O,O′-dialkyl dithiophosphato ligands[1] in their bonding to metal centres has been demonstrated by the structural determination of a variety of transition[2] as well as main group[3] metal complexes. In recent years, considerable attention has been directed to the synthesis of the corresponding O,O′-alkylene dithiophosphates (which incorporate substituted 5- or 6-membered 1,3,2-dioxaphospholane or -phosphorinane ring in the ligand)[4] with a view to study the effect of the ring size and the nature of substituents on the bonding modes.[5] The crystal structures of only two 5-membered cyclic dithiophosphate complexes, viz., $\mathrm{Ph_3SnS\overline{P(S)OCMe_2CMe_2O}}$ and $\mathrm{Me_2Sn(S\overline{P(S)OCMe_2CMe_2O})_2}$ have been reported as yet.[6,7] In addition to the preliminary data obtained for bismuth tris(butylene dithiophosphate), the present paper deals with the crystal structure of bismuth tris(2,2-diethyltrimethylene dithiophosphate) and is the first report on a metal dithiophosphate incorporating six-membered dioxaphosphorinane rings.

An interesting aspect of the studies on bismuth(III) complexes of dithio ligands containing BiS_6 core is to elucidate the stereochemical activity of the lone pair.

From this point of view, the structures of a number of such complexes show interesting variations. For example, $Bi(S_2CNEt_2)_3$[8,9] and $Bi(S_2PPh_2)_3$[10] are dimeric, $Bi(S_2COPr^i)_3$ is polymeric[11] whereas $Bi[S_2P(OPr^i)_2]_3$[12] and $Bi(S_2PEt_2)_3$[13] are monomeric, with the ligands behaving as bidentate chelating in all the cases in addition to functioning as bridging groups also in dimeric and polymeric species. The chelation is unsymmetrical in all these complexes except in $Bi(S_2PEt_2)_3$.

RESULTS AND DISCUSSION

The structure of the title compound is shown in Figure 1 (ORTEP). Positional parameters of the non—H atoms and the equivalent values of the isotropic and anisotropic temperature factors B(A2) and their estimated standard deviations are given in Table I. The bond lengths and bond angles are shown in Table II.

The molecules consist of neutral well separated monomeric units. The bidentate attachment of each dithiophosphato moiety to bismuth is slightly unsymmetrical with one short (~ 2.73 Å) and one long (~ 2.85 Å) Bi—S bonds. The S—Bi—S bite angle of the cyclic dithiophosphato group is ~ 73° which is almost same as in

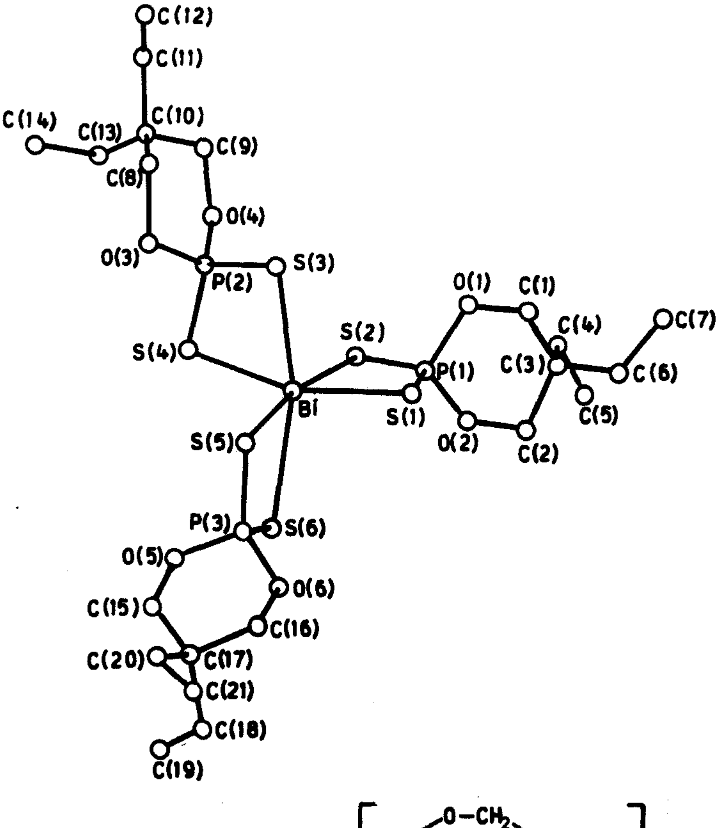
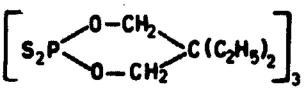


FIGURE 1 Ortep plot of Bi



$$Bi\left[S_2P\begin{matrix}O-CH_2\\ \\O-CH_2\end{matrix}C(C_2H_5)_2\right]_3$$

TABLE I

Fractional atomic coordinates ($\times 10^4$ Bi,S,P; $\times 10^3$ O,C) with estimated standard deviations in parentheses

	x	y	z
Bi	2227.4(15)	2162.4(16)	3691.3(4)
S(1)	5017(12)	2522(11)	3542(3)
S(2)	2486(12)	2489(11)	2916(3)
S(3)	1749(12)	4774(12)	3826(3)
S(4)	-729(12)	2494(10)	3662(3)
S(5)	2431(14)	1625(14)	4434(4)
S(6)	2121(15)	-671(16)	3786(4)
P(1)	4467(10)	2592(9)	3014(3)
P(2)	-297(10)	4388(10)	3738(3)
P(3)	2303(12)	-303(12)	4309(3)
O(1)	505(2)	394(2)	281(1)
O(2)	525(3)	146(3)	277(1)
O(3)	-117(3)	490(3)	406(1)
O(4)	-89(2)	515(2)	338(1)
O(5)	104(3)	-95(3)	455(1)
O(6)	363(3)	-112(3)	444(1)
C(1)	653(4)	404(4)	278(1)
C(2)	677(4)	157(4)	275(1)
C(3)	712(4)	292(4)	255(1)
C(4)	648(4)	293(4)	213(1)
C(5)	701(4)	179(4)	191(1)
C(6)	869(3)	294(3)	253(1)
C(7)	940(4)	407(4)	233(1)
C(8)	-134(4)	645(4)	406(1)
C(9)	-117(4)	660(4)	344(1)
C(10)	-213(4)	686(4)	374(1)
C(11)	-229(4)	841(5)	378(1)
C(12)	-291(5)	909(5)	347(1)
C(13)	-357(5)	623(4)	365(1)
C(14)	-453(5)	641(5)	403(1)
C(15)	120(6)	-161(6)	487(2)
C(16)	385(6)	-149(6)	486(2)

TABLE I (*Cont'd*)

C(17)	244(4)	-226(4)	498(1)	
C(18)	266(7)	-376(7)	486(2)	
C(19)	175(8)	-448(8)	489(2)	
C(20)	255(7)	-200(6)	538(2)	
C(21)	346(13)	-208(11)	556(3)	
C(21)	0.35(1)	-0.21(1)	0.556(3)	24(4)*

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

TABLE II

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

a) Bonds

Bi-S(1)	2.758(12)	Bi-S(2)	2.837(12)
Bi-S(3)	2.712(12)	Bi-S(4)	2.856(11)
Bi-S(5)	2.747(14)	Bi-S(6)	2.87(2)
S(1)-P(1)	1.98(2)	S(2)-P(1)	1.932(15)
S(3)-P(2)	2.02(2)	S(4)-P(2)	1.969(14)
S(5)-P(3)	2.00(2)	S(6)-P(3)	1.93(2)
P(1)-O(1)	1.64(2)	P(1)-O(2)	1.62(3)
P(2)-O(3)	1.54(3)	P(2)-O(4)	1.60(3)
P(3)-O(5)	1.63(3)	P(3)-O(6)	1.58(3)
O(1)-C(1)	1.44(5)	O(2)-C(2)	1.46(5)
O(3)-C(8)	1.57(5)	O(4)-C(9)	1.50(5)
O(5)-C(15)	1.35(7)	O(6)-C(16)	1.57(7)
C(1)-C(3)	1.50(5)	C(2)-C(3)	1.57(5)
C(3)-C(4)	1.63(5)	C(3)-C(6)	1.51(5)
C(4)-C(5)	1.48(6)	C(6)-C(7)	1.50(5)
C(8)-C(10)	1.45(6)	C(9)-C(10)	1.44(6)
C(10)-C(11)	1.58(6)	C(10)-C(13)	1.55(6)

TABLE II (*Cont'd*)

C(11)-C(12)	1.42(7)	C(13)-C(14)	1.69(7)
C(15)-C(17)	1.41(7)	C(16)-C(17)	1.63(7)
C(17)-C(18)	1.59(8)	C(17)-C(20)	1.48(8)
C(18)-C(19)	1.13(11)	C(20)-C(21)	1.08(14)
b) Angles			
S(1)-Bi-S(2)	72.4(3)	S(1)-Bi-S(3)	94.2(3)
S(1)-Bi-S(4)	160.4(3)	S(1)-Bi-S(5)	99.0(4)
S(1)-Bi-S(6)	100.9(4)	S(2)-Bi-S(3)	94.7(3)
S(2)-Bi-S(4)	92.6(3)	S(2)-Bi-S(5)	169.8(4)
S(2)-Bi-S(6)	103.7(4)	S(3)-Bi-S(4)	74.0(3)
S(3)-Bi-S(5)	91.4(4)	S(3)-Bi-S(6)	159.0(4)
S(4)-Bi-S(5)	97.0(4)	S(4)-Bi-S(6)	94.8(4)
S(5)-Bi-S(6)	71.9(4)	Bi-S(1)-P(1)	86.7(5)
Bi-S(2)-P(1)	85.4(5)	Bi-S(3)-P(2)	87.2(5)
Bi-S(4)-P(2)	84.3(5)	Bi-S(5)-P(3)	88.0(6)
Bi-S(6)-P(3)	85.7(6)	S(1)-P(1)-S(2)	115.3(7)
S(1)-P(1)-O(1)	112(1)	S(1)-P(1)-O(2)	112(1)
S(2)-P(1)-O(1)	108(1)	S(2)-P(1)-O(2)	109(1)
O(1)-P(1)-O(2)	101(1)	S(3)-P(2)-S(4)	114.2(7)
S(3)-P(2)-O(3)	110(1)	S(3)-P(2)-O(4)	112(1)
S(4)-P(2)-O(3)	108(1)	S(4)-P(2)-O(4)	106(1)
O(3)-P(2)-O(4)	106(1)	S(5)-P(3)-S(6)	114.4(8)
S(5)-P(3)-O(5)	108(1)	S(5)-P(3)-O(6)	113(1)
S(6)-P(3)-O(5)	112(1)	S(6)-P(3)-O(6)	105(1)
O(5)-P(3)-O(6)	104(2)	P(1)-O(1)-C(1)	116(2)
P(1)-O(2)-C(2)	117(2)	P(2)-O(3)-C(8)	112(2)
P(2)-O(4)-C(9)	114(2)	P(3)-O(5)-C(15)	125(3)
P(3)-O(6)-C(16)	121(3)	O(1)-C(1)-C(3)	112(3)
O(2)-C(2)-C(3)	108(3)	C(1)-C(3)-C(2)	109(3)
C(1)-C(3)-C(4)	111(3)	C(1)-C(3)-C(6)	113(3)
C(2)-C(3)-C(4)	110(3)	C(2)-C(3)-C(6)	105(3)
C(4)-C(3)-C(6)	108(3)	C(3)-C(4)-C(5)	111(3)
C(3)-C(6)-C(7)	120(3)	O(3)-C(8)-C(10)	110(3)

TABLE II (*Cont'd*)

O(4)-C(9)-C(10)	114(3)	C(8)-C(10)-C(9)	102(3)
C(8)-C(10)-C(11)	105(3)	C(8)-C(10)-C(13)	121(3)
C(9)-C(10)-C(11)	108(3)	C(9)-C(10)-C(13)	111(3)
C(11)-C(10)-C(13)	110(3)	C(10)-C(11)-C(12)	116(4)
C(10)-C(13)-C(14)	106(3)	O(5)-C(15)-C(17)	125(5)
O(6)-C(16)-C(17)	106(4)	C(15)-C(17)-C(16)	114(4)
C(15)-C(17)-C(18)	119(4)	C(15)-C(17)-C(20)	105(4)
C(16)-C(17)-C(18)	105(4)	C(16)-C(17)-C(20)	98(4)
C(18)-C(17)-C(20)	114(4)	C(17)-C(18)-C(19)	119(7)
C(17)-C(20)-C(21)	129(9)		

open chain dithiophosphate[12] and dithiophosphinate[10] but it is greater than the corresponding bite angle in $Bi(S_2CNEt_2)_3$ (63.5°).[9] With three short and three long Bi—S bonds, the configuration of $:BiS_6$ core is approximately C_{3v}. However, the distortion from the regular octahedron appears to be less pronounced in comparison to the complexes of other dithio ligands, except dialkyl dithiophosphinate; this is indicated by the ratio of the two types of bonds in various dithio complexes of bismuth (Table III).

Similar to other dithio complexes, the BiS_2P chelate ring in the title compound is planar with the angle at phosphorus of 115° and those at the two sulphurs being in the range of 85–88°. The average difference in the two sulphur angles in the three BiS_2P chelate rings is 2.3° which is smaller than the average difference in $Bi[S_2P(OPr^i)_2]_3$ (4.0°). In related compounds with more unsymmetrical coordination, this difference may be ~ 10°. The two P—S bonds in the 4-membered rings are almost same (1.93–2.07 Å), the average difference being 0.07 Å.

The six-membered 1,3,2-dioxaphosphorinane rings are present in chair form with the phosphorus and the middle carbon being equi-distant from the plane of the ring in opposite directions. Interestingly, the sulphur atoms forming the shorter bonds with bismuth are in the axial positions of the phosphorinane rings. In spite of the very small difference in the two P—S bonds of each ligand, it is obvious

TABLE III

Average Bi—S bond lengths in bismuth *tris*-derivatives with 1,1-dithio ligands

Compound	Average Bi—S bond lengths (Å)		Ratio	Reference
$Bi(S_2POCH_2CEt_2CH_2O)_3$	2.73	2.85	0.958	this work
$Bi[S_2P(OPr^i)_2]_3$	2.70	2.87	0.941	12
$Bi(S_2CNEt_2)_3$	2.70	2.94	0.918	9
$Bi(S_2COPr^i)_3$	2.68	2.93	0.914	11
$Bi(S_2PPh_2)_3$	2.71	2.98	0.909	10
$Bi(S_2PEt_2)_3$	2.78	2.79	0.995	13
$Bi(S_2POCHMeCHMeO)_3$	2.76	2.79	0.989	this work

from the data that the axial sulphurs are forming longer bonds with phosphorus. This gives an indication that in the free dithiophosphoric acids, the thiolato and thiono sulphurs are present in the axial and equitorial positions, respectively.

The correlation of stereochemical activity of the lone pair on bismuth in the dithio complexes with the distortion from the regular octahedral structure needs a closer look. The earlier view[12] that the lone pair is present above the triangular face of the less strongly bonded sulphur atoms should be revised in view of (a) the dimerisation of $Bi(S_2CNEt_2)_3$ and $Bi(S_2PPh_2)_3$ with the intermolecular Bi—S bond present at the same position where the lone pair is expected,[9,10] and (b) the symmetrical chelation of diethyldithiophosphinato groups in $Bi(S_2PEt_2)_3$ which would indicate stereochemical inactivity of the lone pair on the same argument.[13] In the title cyclic dithiophosphato derivatives, there is very little distortion although the ligand moieties are sterically less crowded than diisopropyl dithiophosphato groups.

Preliminary crystal structure data have also been obtained for the cyclic tris(butylene dithiophosphate), $Bi(S_2POCHMeCHMeO)_3$. The ORTEP plot is shown in Figure 2 along with the relevant bond angles and bond lengths. It is interesting that in this case, the chelation of the dithio ligand is symmetrical (Bi—S bond lengths are 2.76 and 2.79 Å). Consequently, the two P—S bonds are also same (1.98 and 1.97

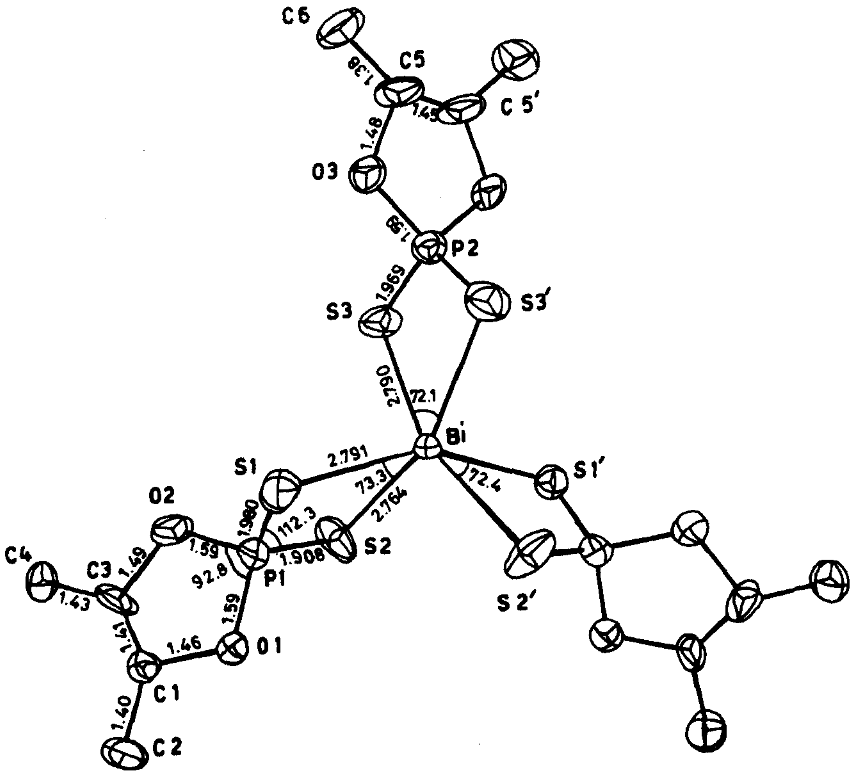
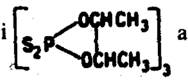
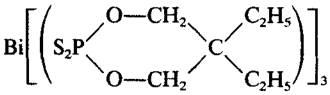


FIGURE 2 Ortep plot of Bi  $Bi\left[S_2P\left\langle\begin{matrix}OCHCH_3\\ \vert\\ OCHCH_3\end{matrix}\right.\right]_3$ along with intramolecular distances (Å) and angles (°).

Å). All the four angles of the 4-membered PS_2Bi rings are almost identical to the corresponding angles of these rings in 2,2-diethyltrimethylene dithiophosphate.

EXPERIMENTAL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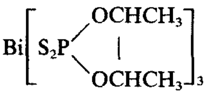
were obtained by the reaction of $BiCl_3$ with ammonium 2,2-diethyltrimethylene dithiophosphate and ammonium butylene dithiophosphate, respectively.[14]

Crystal Data. (i) $C_{21}H_{42}BiO_6P_3S_6$, $M = 884.8$, monoclinic, space group $P2_1/c$, $a = 9.591(3)$, $b = 10.059(1)$, $c = 36.170(5)$ Å, $\beta = 90.51(2)°$, $V = 3489.5$ Å^3, $Z = 4$, $Dc = 1.68$ g cm^{-3}, monochromated Mo—Kα radiation, $\lambda = 0.71069$ Å, $T = 295$ K, $F(000) = 880$ and $\mu = 55.5$ cm^{-1}. Data were collected using a crystal *ca* 0.20 × 0.30 × 0.12 mm, on an Enraf-Nonius CAD 4 diffractometer in the θ-2θ mode with $\Delta\theta = (0.8 + 0.35 \tan\theta)°$ and maximum scan time of 1 minute. Cell parameters were refined from 25 reflections with $16 < \theta < 18$. Intensity of two standard reflections ($7\overline{3}\overline{2}$ and $\overline{3}\overline{7}\overline{5}$) remained unchanged after 1800 seconds. Out of 6682 unique reflections, measured for $2 < \theta < 25°$ and $\pm$ h(11) + k(11) + l(43), and 3183 with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/LP$. There was no crystal decay. An absorption correction was made using DIFABS[15] after isotropic refinement, with maximum and minimum corrections of 1.273 and 0.693.

The structure was solved by routine heavy atom methods and refined by full matrix least square with Bi anisotropic and all other atoms isotropic. The ethyl groups attached to C(17) have high temperature factors which may possibly be due to disorder. Hydrogen atoms were omitted. The weighting scheme was $W = 1/\sigma(F^2)$ and the final residuals were $R = 0.122$, $R^1 = 0.177$. A final difference map had peaks of up to 5.0e Å^3 close to Bi. Programs from the Enraf-Nonius SDP-Plus peckage were run on a PDP 11/34 computer. (ii) $C_{12}H_{24}BiO_6P_3S_3$, $M = 758.6$, monoclinic, space group C_2/c, $a = 16.684(8)$, $b = 13.682(6)$, $c = 11.930(6)$ Å, $\beta = 98.45(2)°$, $V = 2693.8$ Å^3, $Z = 4$, $Dc = 1.87$ and $\mu = 69.1$ cm^{-1} and $R = 0.052$ for 1073 reflections.

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