Lemieux, R. U., Fraga, E. & Watanabe, K. A. (1968). *Canad. J. Chem.* **46**, 61–69.
Pravdić, N. & Fletcher, H. G. Jr (1969). *Croat. Chem. Acta*, **41**, 125–133.
Pravdić, N., Židovec, B. & Fletcher, H. G. Jr (1970). *Croat. Chem. Acta*, **32**, 523–533.
Pravdić, N., Židovec, B. & Fletcher, H. G. Jr (1973). *Croat. Chem. Acta*, **45**, 333–342.
Pravdić, N., Židovec, B., Franjić, I. & Fletcher, H. G. Jr (1973). *Croat. Chem. Acta*, **45**, 343–356.
Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972/1973). X-RAY 72/73 system. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Stoddart, J. F. (1971). *Stereochemistry of Carbohydrates*, pp. 50–60. New York: John Wiley.
Sundaralingam, M. (1968). *Biopolymers*, **6**, 189–213.
Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

Acta Cryst. (1976). B**32**, 1838

Dioxygen Tetra(dimethylphenylphosphine)iridium(I) Tetraphenylborate

By Magriet Nolte and Eric Singleton

National Chemical Research Laboratory, CSIR, P.O. Box 395, *Pretoria, Republic of South Africa*

(*Received* 24 *November* 1975; *accepted* 22 *December* 1975)

$[\mathrm{IrO_2\{PC_6H_5(CH_3)_2\}_4}]\mathrm{B(C_6H_5)_4}$, triclinic, $P\bar{1}$, $a=17{\cdot}62$ (2), $b=14{\cdot}30$ (2), $c=11{\cdot}46$ (2) Å, $\alpha=104{\cdot}85$ (5), $\beta=105{\cdot}20$ (5), $\gamma=93{\cdot}18$ (5)°, $Z=2$, $D_c=1{\cdot}37$ g cm^{-3}, $M=1096$. O–O = 1·49; Ir–O = 2·04, 2·05; Ir–P(ax) = 2·39, 2·40; Ir–P(eq) = 2·31, 2·33 Å. The compound is isostructural with the Rh analogue.

Introduction

The cations $[\mathrm{RhO_2L_4}]^+$ $[\mathrm{L=As(CH_3)_2(C_6H_5)}$, $\mathrm{P(CH_3)_2(C_6H_5)}]$ (Nolte & Singleton, 1975, 1976) have similar O–O bond lengths of 1·46 and 1·43 Å respectively, in line with the comparable donor properties of $\mathrm{As(CH_3)_2(C_6H_5)}$ and $\mathrm{P(CH_3)_2(C_6H_5)}$. The close similarity to the length of 1·42 Å found for O–O in $[\mathrm{RhO_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2}]^+$ (McGinnety, Payne & Ibers, 1969) does not fit the trends previously postulated, relating ligand basicity with O–O length in other Rh and Ir dioxygen complexes (McGinnety, Doedens & Ibers, 1967). As a further test of the effects of a change of both metal and ligand on M–O and O–O parameters, the structure of the salt $[\mathrm{IrO_2\{P(CH_3)_2(C_6H_5)\}_4}]\mathrm{B(C_6H_5)_4}$ was undertaken. If ligand effects are more enhanced in Ir than in Rh compounds, then changing from $\mathrm{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2}$ to the more basic $\mathrm{\{P(CH_3)_2(C_6H_5)\}_2}$ would be expected to cause a further elongation of the O–O bond, and this effect should also be coupled with a shortening of the Ir–O bonds if Chatt–Dewar type bonding (Chatt & Duncanson, 1953; Dewar, 1951) is operating.

A prismatic crystal, 0·16 × 0·20 × 0·44 mm, was used for data collection. Intensities were collected on a Philips PW1100 four-circle diffractometer over the range $\theta=3$–18° with graphite-monochromated Mo $K\alpha$ radiation. The ω–2θ scan mode was used. Of the 3662 reflexions recorded, 3312 had $I>2\sigma(I)$ and were considered observed. Three standard reflexions were remeasured every hour. They decreased by 8, 5 and 4% during the 68 hour period of data collection; no correction was made for crystal decomposition. Background, Lp and absorption corrections were applied; transmission coefficients varied from 0·51 to 0·74 ($\mu=28{\cdot}2$ cm^{-1}). No corrections were made for extinction. Although the compound appeared to be isostructural with the Rh analogue (Nolte & Singleton, 1976) the structure was solved independently by Patterson and Fourier methods. Least-squares refinement was carried out by the full-matrix technique alternately for different sets of non-hydrogen atoms. Calculations were performed with the *CRYLSQ* program of the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on an IBM 360/65 computer.

All atoms were refined anisotropically with a weighting scheme to reduce the effect of reflexions with large F(obs) and/or small θ values. The final R was 0·054 for the observed intensities. The scattering factors were those of Cromer & Mann (1968), corrected for anomalous dispersion. Final positional and thermal parameters are given in Table 1.* Bond lengths and angles (calculated by the program *BONDLA*, not corrected for thermal motion) are summarized in Tables 2 and 3. Atomic numbering is given in Fig. 1 and a stereo view in Fig. 2, drawn by the program *ORTEP* (Johnson, 1965).

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31576 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and anisotropic temperature factors* ($10^4 \times Å^2$) *with their standard deviations in parentheses*

Thermal parameters are in the form $T = \exp[-2\pi^2(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	1833 (1)	2202 (1)	4450 (1)	469 (4)	353 (4)	603 (5)	22 (3)	204 (3)	138 (3)
P(1)	2169 (2)	578 (3)	4135 (4)	585 (26)	412 (24)	777 (29)	83 (20)	280 (22)	175 (21)
P(2)	1069 (2)	3539 (3)	4456 (4)	650 (26)	309 (22)	692 (27)	39 (19)	225 (22)	156 (19)
P(3)	2840 (2)	2798 (3)	3760 (4)	531 (25)	433 (23)	667 (28)	3 (19)	216 (21)	109 (20)
P(4)	2554 (2)	2769 (3)	6551 (4)	577 (26)	430 (23)	685 (28)	60 (19)	273 (22)	163 (20)
O(1)	755 (6)	1420 (7)	4150 (9)	758 (71)	605 (64)	762 (73)	70 (53)	231 (57)	243 (55)
O(2)	855 (6)	1592 (7)	2972 (10)	748 (73)	778 (74)	898 (81)	154 (58)	285 (62)	348 (63)
C(11)	2027 (8)	−32 (9)	5312 (13)	566 (104)	310 (82)	771 (107)	−6 (73)	300 (85)	94 (75)
C(111)	2646 (9)	−424 (10)	5986 (14)	754 (112)	386 (88)	686 (105)	130 (80)	219 (89)	109 (81)
C(112)	2491 (10)	−937 (10)	6817 (14)	904 (126)	369 (89)	719 (110)	61 (84)	287 (96)	57 (80)
C(113)	1737 (10)	−1034 (11)	6957 (16)	860 (132)	522 (103)	954 (131)	25 (93)	460 (109)	141 (91)
C(114)	1114 (10)	−650 (11)	6283 (17)	755 (119)	486 (100)	1164 (144)	−22 (87)	399 (108)	271 (100)
C(115)	1265 (9)	−145 (10)	5440 (16)	746 (118)	380 (91)	1069 (132)	−59 (80)	465 (101)	196 (88)
C(12)	3145 (9)	319 (10)	3971 (16)	695 (105)	515 (94)	1011 (125)	246 (80)	441 (95)	205 (87)
C(13)	1520 (10)	−234 (10)	2702 (15)	933 (124)	449 (96)	838 (119)	57 (86)	226 (98)	−2 (85)
C(21)	1403 (9)	4711 (10)	5643 (14)	661 (101)	466 (94)	733 (111)	102 (78)	250 (87)	202 (83)
C(211)	1791 (9)	5494 (10)	5391 (16)	686 (106)	363 (95)	1070 (133)	149 (83)	319 (97)	132 (93)
C(212)	2097 (10)	6345 (12)	6327 (19)	874 (127)	558 (113)	1245 (163)	182 (94)	445 (120)	207 (116)
C(213)	2038 (12)	6452 (12)	7540 (20)	1147 (156)	568 (117)	1201 (165)	153 (105)	361 (134)	99 (118)
C(214)	1632 (13)	5711 (12)	7805 (17)	1507 (183)	619 (126)	932 (140)	431 (126)	450 (131)	165 (112)
C(215)	1294 (10)	4821 (11)	6822 (16)	987 (131)	609 (111)	840 (128)	340 (96)	305 (106)	268 (101)
C(22)	81 (9)	3212 (11)	4615 (18)	615 (105)	621 (104)	1301 (151)	66 (84)	365 (103)	200 (101)
C(23)	796 (11)	3835 (13)	2940 (17)	1036 (136)	817 (120)	873 (126)	115 (102)	149 (104)	435 (101)
C(31)	2773 (8)	2124 (10)	2144 (13)	481 (97)	472 (92)	710 (109)	35 (76)	143 (86)	180 (81)
C(311)	2095 (9)	1578 (11)	1376 (14)	846 (122)	587 (103)	710 (122)	88 (90)	274 (99)	287 (94)
C(312)	2034 (12)	1052 (12)	120 (16)	1414 (177)	774 (125)	719 (132)	35 (117)	414 (124)	391 (106)
C(313)	2685 (13)	1088 (13)	−313 (16)	1530 (200)	746 (127)	725 (133)	166 (126)	465 (130)	325 (103)
C(314)	3390 (12)	1667 (15)	455 (18)	1053 (155)	1259 (169)	857 (152)	371 (128)	467 (123)	378 (132)
C(315)	3435 (10)	2179 (13)	1703 (15)	836 (129)	1111 (144)	641 (119)	212 (106)	337 (101)	231 (104)
C(32)	2917 (11)	4068 (10)	3690 (18)	1128 (141)	402 (94)	1303 (154)	76 (90)	744 (123)	253 (97)
C(33)	3869 (9)	2755 (12)	4603 (16)	577 (103)	818 (117)	884 (123)	−38 (87)	179 (90)	134 (96)
C(41)	1925 (9)	2783 (10)	7591 (14)	694 (109)	431 (91)	723 (113)	116 (81)	295 (91)	250 (84)
C(411)	2213 (10)	3321 (11)	8873 (15)	1018 (132)	670 (111)	742 (125)	182 (96)	401 (109)	304 (97)
C(412)	1719 (12)	3308 (12)	9667 (16)	1217 (160)	757 (123)	759 (126)	217 (112)	381 (121)	311 (100)
C(413)	960 (12)	2766 (13)	9187 (18)	1063 (150)	918 (140)	915 (141)	343 (118)	463 (127)	370 (119)
C(414)	689 (10)	2245 (13)	7939 (17)	958 (134)	892 (133)	959 (139)	214 (105)	471 (120)	523 (114)
C(415)	1179 (9)	2254 (10)	7128 (15)	825 (121)	491 (97)	990 (127)	174 (87)	539 (108)	370 (90)
C(42)	3341 (9)	2094 (12)	7198 (16)	619 (104)	751 (112)	949 (125)	147 (86)	127 (91)	387 (97)
C(43)	3109 (9)	4024 (10)	7119 (14)	681 (103)	398 (87)	718 (104)	−189 (75)	131 (84)	−64 (76)
B	3594 (10)	6941 (12)	2841 (16)	544 (120)	477 (107)	638 (126)	122 (91)	217 (96)	240 (98)
C(51)	3701 (8)	7637 (10)	1916 (13)	561 (103)	543 (95)	712 (106)	67 (78)	221 (83)	273 (83)
C(52)	4432 (11)	7822 (16)	1709 (21)	812 (137)	1375 (175)	1601 (195)	210 (120)	594 (134)	1001 (161)
C(53)	4558 (13)	8473 (16)	1010 (23)	1073 (165)	1236 (173)	1625 (206)	115 (132)	772 (154)	775 (163)
C(54)	3938 (12)	8901 (13)	458 (19)	1162 (169)	867 (136)	1120 (156)	111 (120)	512 (134)	471 (116)
C(55)	3208 (11)	8734 (12)	630 (16)	1102 (150)	710 (116)	879 (129)	90 (107)	280 (114)	312 (104)
C(56)	3084 (9)	8083 (10)	1357 (14)	873 (122)	502 (95)	674 (105)	121 (86)	196 (91)	267 (86)
C(61)	3988 (8)	7556 (10)	4317 (14)	403 (86)	559 (101)	786 (119)	179 (77)	223 (82)	218 (91)
C(62)	3873 (8)	7163 (10)	5292 (14)	587 (98)	622 (101)	657 (111)	180 (78)	242 (85)	263 (88)
C(63)	4184 (9)	7663 (12)	6562 (16)	640 (109)	839 (127)	860 (128)	298 (98)	304 (98)	253 (106)
C(64)	4631 (9)	8588 (12)	6948 (17)	599 (110)	735 (127)	1046 (148)	184 (96)	227 (102)	118 (107)
C(65)	4747 (8)	8998 (11)	6025 (18)	445 (97)	525 (107)	1196 (160)	163 (80)	197 (101)	28 (102)
C(66)	4441 (8)	8493 (10)	4728 (16)	461 (93)	399 (99)	1070 (136)	92 (80)	166 (92)	172 (95)
C(71)	4039 (7)	5959 (10)	2444 (13)	415 (87)	525 (97)	757 (114)	−53 (74)	177 (79)	319 (86)
C(72)	3969 (9)	5487 (12)	1156 (14)	762 (113)	932 (128)	592 (112)	133 (97)	247 (90)	81 (97)
C(73)	4365 (10)	4682 (12)	814 (16)	677 (114)	824 (125)	871 (131)	97 (99)	285 (100)	9 (102)
C(74)	4828 (9)	4299 (11)	1731 (16)	673 (112)	665 (111)	898 (133)	68 (87)	249 (101)	231 (99)
C(75)	4902 (9)	4757 (11)	3006 (15)	586 (101)	622 (109)	941 (128)	−92 (85)	237 (94)	385 (98)
C(76)	4503 (7)	5588 (9)	3363 (14)	411 (86)	360 (85)	953 (119)	77 (71)	234 (82)	318 (82)
C(81)	2640 (8)	6631 (9)	2600 (14)	481 (99)	397 (88)	861 (112)	123 (76)	283 (86)	303 (85)
C(82)	2222 (8)	7192 (11)	3319 (15)	481 (104)	656 (105)	983 (124)	151 (82)	296 (90)	429 (93)
C(83)	1401 (9)	7004 (11)	3096 (16)	721 (125)	606 (109)	1013 (132)	142 (93)	324 (102)	368 (98)
C(84)	962 (9)	6228 (11)	2113 (17)	654 (111)	509 (104)	1151 (142)	90 (86)	370 (103)	361 (101)
C(85)	1352 (9)	5645 (11)	1337 (18)	665 (127)	645 (115)	1228 (152)	34 (95)	263 (109)	357 (106)
C(86)	2189 (9)	5832 (11)	1589 (16)	577 (112)	595 (106)	980 (127)	−36 (87)	202 (94)	318 (97)

Discussion

The structure consists of discrete cations and anions separated by more than 3·0 Å between non-hydrogen atoms and is isostructural with the Rh analogue. Coordination around the Ir atom is trigonal bipyramidal, with the dioxygen ligand occupying one position in the equatorial plane. As expected (Gillespie, 1963) the lengths of the axial Ir–P bonds (2·39 and 2·40 Å) are greater than those of the equatorial bonds (2·31 and 2·33 Å). Very similar values were obtained in the structure of $[RhO_2\{P(CH_3)_2C_6H_5\}_4]B(C_6H_5)_4$ [mean values 2·39(ax) and 2·32 Å (eq)], despite the difference in the central metal atom. The O–O length is 1·49 Å, longer than the 1·43 Å found in the Rh analogue but shorter than the 1·52 Å observed in the $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ compound (Nolte, Singleton & Laing, 1975), but the differences are not significant. The Ir–O values of 2·04 and 2·05 Å are identical with the Rh–O distances observed in the $[RhO_2\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2]^+$ and $[RhO_2\{As(CH_3)_2C_6H_5\}_4]^+$ cations. P–C lengths are the same for methyl and phenyl groups: average value 1·83 (3) Å. The mean phenyl C–C distance is 1·40 Å; B–C lengths vary between 1·63 and 1·67 Å, with a mean of 1·65 Å.

A comparison of the bond lengths and angles associated with the M, P and O atoms (Tables 2 and 3) shows that there are no particular trends in the M–P, O–O and M–O lengths. The only major differences between the coordination geometries are the P(ax)–M–P(ax) and P(ax)–M–P(eq) bond angles, and these are due to the differences in the geometry of the ligands (Nolte, Singleton & Laing, 1976). The results confidently predicted from the π-bonding theory (McGinnety, Payne & Ibers, 1969) have not materialized.

We thank Dr Michael Laing, Chemistry Department, University of Natal, for his critical evaluation of the manuscript and for improvements he suggested.

References

Chatt, J. & Duncanson, L. A. (1953). *J. Chem. Soc.* pp. 2939–2947.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Dewar, M. J. S. (1951). *Bull. Soc. Chim. Fr.* **18**, C71–C77.

Gillespie, R. G. (1963). *J. Chem. Soc.* pp. 4679–4685.

Johnson, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report *ORNL*-3794.

McGinnety, J. A., Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 2243–2250.

McGinnety, J. A., Payne, N. C. & Ibers, J. A. (1969). *J. Amer. Chem. Soc.* **91**, 6301–6310.

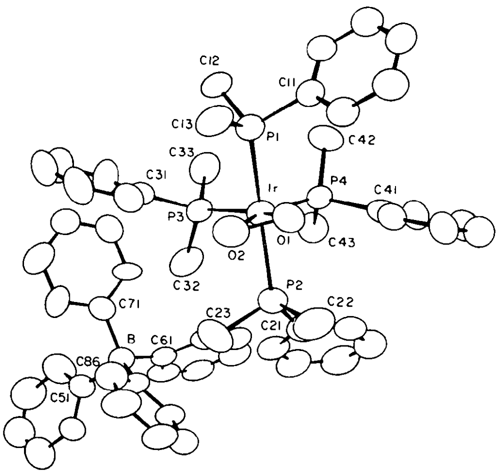


Fig. 1. Molecular geometry of $[IrO_2\{P(CH_3)_2C_6H_5\}_4]$ $[B(C_6H_5)_4]$ with atomic numbering.

Table 2. *Bond lengths* (Å)

	$IrO_2[P(CH_3)_2C_6H_5]_4^+$	$RhO_2[P(CH_3)_2C_6H_5]_4^{+(a)}$	$IrO_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]^{+(b)}$
M—P(1) (ax)	2·389 (5)	2·389	2·366
M—P(2) (ax)	2·398 (5)	2·388	2·353
M—P(3) (eq)	2·327 (5)	2·326	2·308
M—P(4) (eq)	2·312 (5)	2·316	2·342
M—O(1)	2·050 (10)	2·038	2·052
M—O(2)	2·037 (9)	2·033	2·062
O(1)–O(2)	1·485 (17)	1·429	1·522

(*a*) Nolte & Singleton (1976); (*b*) Nolte, Singleton & Laing (1975).

Table 3. *Bond angles* (°)

	$IrO_2[P(CH_3)_2C_6H_5]_4^+$	$RhO_2[P(CH_3)_2C_6H_5]_4^{+(a)}$	$IrO_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]^{+(b)}$
P(ax)–M—P(ax)	161·1 (2)	161·3	175·3
P(eq)–M—P(eq)	93·4 (2)	93·8	97·0
P(ax)–M—P(eq)	95·7 (2)	96·3	83·4, 99·4$^{(c)}$
O(1) –M—O(2)	42·6 (5)	41·1	43·4
M—O(1)–O(2)	68·2 (6)	69·3	68·6
M—O(2)–O(1)	69·2 (5)	69·6	67·9

(*a*) Nolte & Singleton (1976); (*b*) Nolte, Singleton & Laing (1975); (*c*) the two values refer to angles internal and external to the chelate rings.

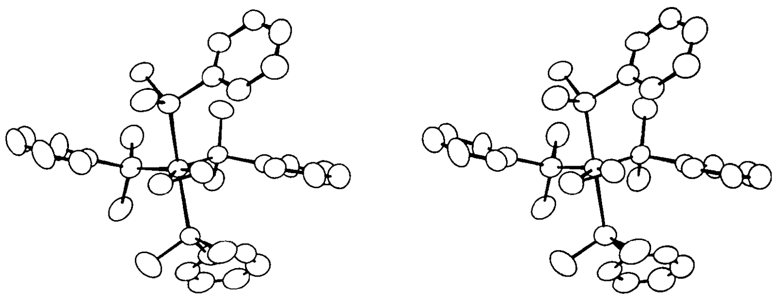


Fig. 2. Stereoscopic view of the cation $[IrO_2\{P(CH_3)_2C_6H_5\}_4]^+$.

Nolte, M. J. & Singleton, E. (1975). *Acta Cryst.* B**31**, 2223–2227.
Nolte, M. J. & Singleton, E. (1976). *Acta Cryst.* B**32**, 1410-1413.
Nolte, M. J., Singleton, E. & Laing, M. (1975). *J. Amer. Chem. Soc.*, **97**, 6396–6400.
Nolte, M. J., Singleton, E. & Laing, M. (1976). *J. Chem. Soc. Dalton.* In the press.
Stewart, J. M., Kruger, G. J., Ammon, H., Dickinson, C. H. & Hall, S. R. (1972). The X-RAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ of Maryland, College Park, Maryland.

Acta Cryst. (1976). B**32**, 1841

Crystal and Molecular Structure of the *p*-Bromobenzenesulphonate Derivative of the Complex Tetranortriterpenoid Prieurianin, $C_{44}H_{53}O_{18}SBr$

By A. Forbes Cameron and Fergus D. Duncanson

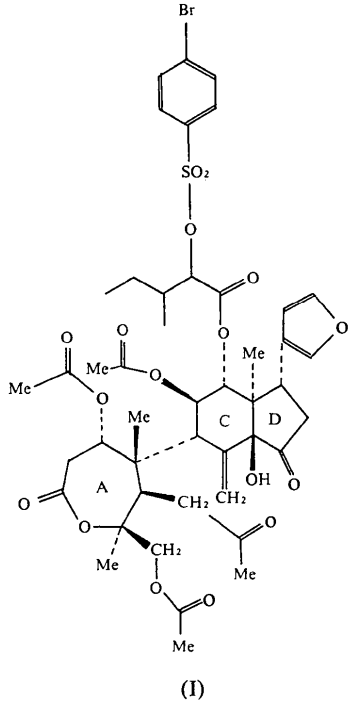
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

(*Received* 3 *December* 1975; *accepted* 31 *December* 1975)

The structure of the title compound has been determined from 1926 independent reflexions collected on a diffractometer. The crystals are orthorhombic, space group $P2_12_12_1$, with $Z=4$, $a=11{\cdot}339$, $b=16{\cdot}371$, $c=27{\cdot}737$ Å. The structure was solved by a combination of the heavy-atom and direct-phasing techniques, and has been refined by least squares to a final R of 0·096.

Introduction

Prieurianin, a complex tetranortriterpenoid, was first isolated in 1965 by light petroleum extraction of the timber of *Trichilia prieuriana* (Meliaceae) (Bevan, Ekong & Taylor, 1965). However, until recently the structure has remained obscure since conventional spectroscopic studies, although indicating the presence of several of the functional groups, gave little information about the overall chemical constitution. Accordingly, we undertook an X-ray analysis of the *p*-bromobenzenesulphonate derivative of prieurianin (I) concurrently with a thorough spectroscopic analysis, which included ^{13}C NMR studies at elevated temperature with the more advanced techniques of proton-noise and continuous-wave decoupling, and ^1H NMR studies at a range of elevated and sub-ambient temperatures. Both the spectroscopic and crystallographic approaches independently led to correct elucidations of the molecular structure, and in addition the latter study also resolved several stereochemical ambiguities which remained from the spectroscopic studies (Gullo *et al.*, 1975). We describe here the details of the X-ray analysis; full accounts of the spectroscopic and chemical studies will be published elsewhere.



(I)