Synthesis of Molybdenum(V) and Molybdenum(VI) Derivatives of 5,15-Diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin

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The methoxo-oxomolybdenum(V), diperoxomolybdenum(VI) and *cis*-dioxomolybdenum(VI) derivatives of 5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (**4a, 5c, 6a**) have been prepared and characterized by uv, ir, pmr, mass and esr spectra. The structure of the molybdenum(V) porphyrin was confirmed by X-ray analysis.

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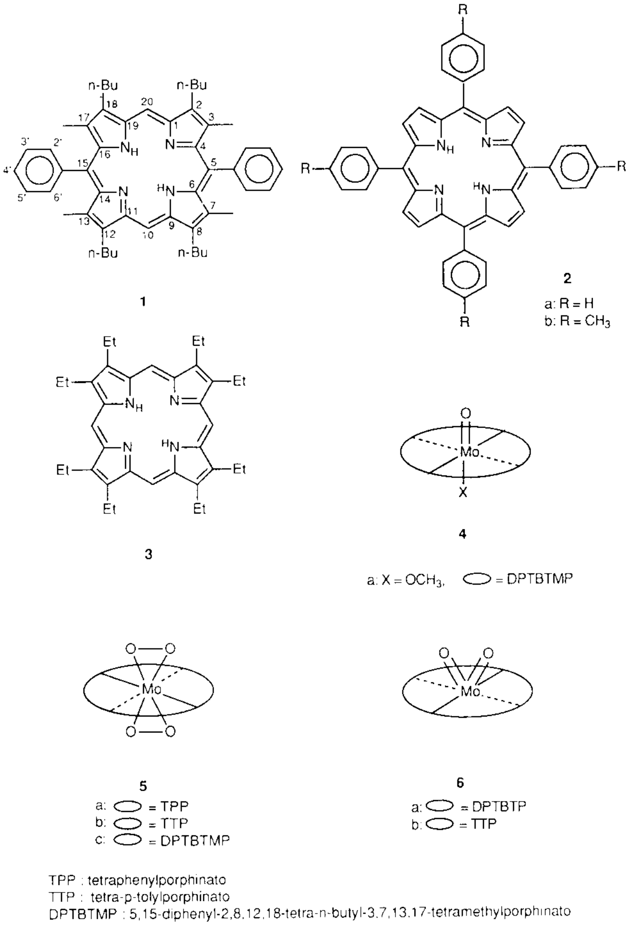
During our investigations on the synthesis and reactivity of artificial enzymes we felt the need to synthesize the molybdenum(V) and molybdenum(VI) derivatives of 5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (**1**). In the literature several methods have been reported for introduction of molybdenum(V) into 5,10,15,20-tetraphenylporphyrin (**2a**), 5,10,15,20-tetra-*p*-tolylporphyrin (**2b**) or 2,3,7,8,12,13,17,18-octaethylporphyrin (**3**), all leading to molybdenum(V) derivatives of the general type **4**, in which the molybdenum atom is ligated by a porphinato group, an oxo group and a ligand X, which is mostly a halogen or alkoxy group. The introduction of molybdenum(V) into the porphyrins was effected by the use of various reagents, such as an excess of molybdenum hexacarbonyl [1,2,3,4], molybdenum pentachloride [5,6], molybdenum dichloride [7], molybdenum dioxo-diacetyl acetonate [7] and molybdenum oxytrichloride [8,9]. Usually the reaction conditions were rather drastic, *e.g.* refluxing for several hours in high boiling solvents such as decalin, mesitylene, or benzonitrile. The yields reported for the metallation step range from 20% to 76%. Ligand exchange reactions have been observed for many compounds. For instance, the chloro ligand in the molybdenum(V) complex of tetraphenylporphyrin is exchanged for the ethoxy group by treatment with chloroform or dichloromethane, containing 1% of ethanol [5b].

The molybdenum(VI) porphyrins were obtained by oxidation of the corresponding molybdenum(V) compounds. It has been reported in the literature that the reaction of the molybdenum(V) derivatives of tetraphenylporphyrin and tetra-*p*-tolylporphyrin with hydrogen peroxide in dichloromethane for 4-6 hours at room temperature leads to the *trans*-diperoxomolybdenum(VI) derivatives **5a** and **5b** [10]. Irradiation of compound **5b** with a 100W Tungsten lamp led to the *cis*-dioxomolybdenum(VI) porphyrin **6b** [11a], of which the structure was proven by X-ray analysis [11b].

Chart 1



TPP : tetraphenylporphinato
TTP : tetra-p-tolylporphinato
DPTBTMP : 5,15-diphenyl-2,8,12,18-tetra-n-butyl-3,7,13,17-tetramethylporphinato

To our knowledge introduction of molybdenum(V) or (VI) into 5,15-diphenylporphyrins has not been reported. We carried out this metallation by refluxing a solution of 5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (**1**) in decalin with a 12 fold excess of molybdenum hexacarbonyl for 6 hours following the directions given in the literature for tetraphenylporphyrin [3]. The purified reaction product was identified as methoxo-oxo-[5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinato] molybdenum(V) (**4a**) by its uv absorption spectrum (maxima at 569, 450 (Soret), 349, 267, and 238 nm in chloroform) and a $Mo=O$ stretching frequency at 901 cm^{-1} in the ir spectrum. The esr spectrum showed 6 weak lines due to ^{95,97}Mo nuclei (I = 5/2); moreover, a strong central line due to the molybdenum nucleus with I = 0 was split into 9 lines because of the interaction with the four nitrogen nuclei (I = 1) of the porphyrin ligand. These data agree with the data given in the literature for paramagnetic molybdenum(V) porphyrin complexes [5b, 13]. Satisfactory elemental analyses were obtained after crystallisation from dichloromethane/methanol 2:1, containing a trace of sodium hydroxide (*cf*, ref [7]). Field desorption (fd) and fast-atom bombardment (fab) mass spectra did not show the molecular ion peaks; instead, the main peak corresponded with a MoO porphinato fragment, resulting from thermal decomposition with loss of the methoxy group. This phenomenon has been reported in the literature for the molybdenum(V) derivative of octaethylporphyrin [7]. The isotopic distribution agreed with the calculated pattern. The pmr spectrum of compound **4a** showed very broad peaks, due to the presence of the paramagnetic molybdenum(V) atom. For further proof of the structure an X-ray analysis was carried out.

As the experimental conditions for introduction of

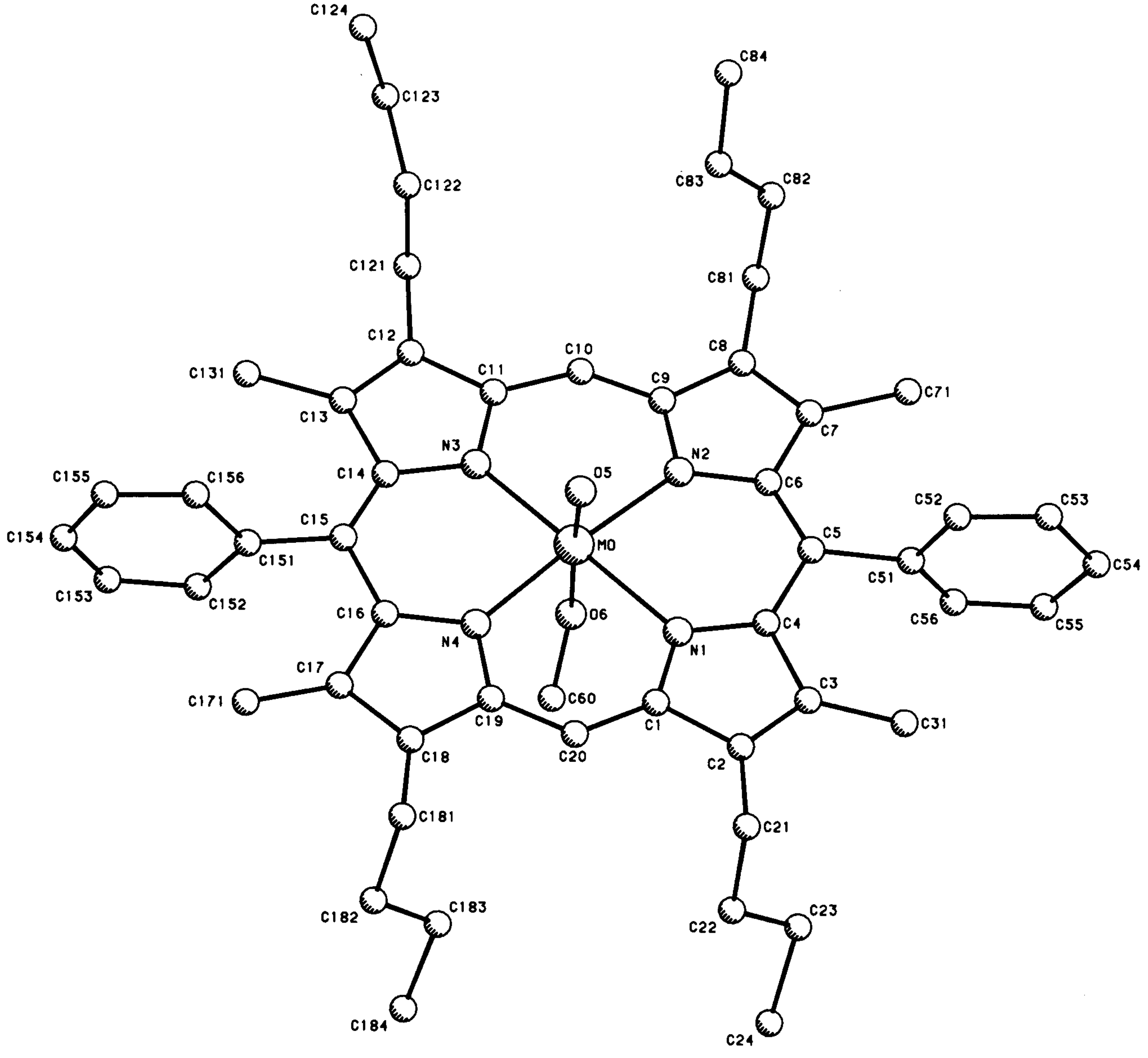


Figure 1

molybdenum(V) were rather drastic, requiring high temperatures, we looked for milder methods. We found that **4a** could also be prepared conveniently by refluxing the diphenylporphyrin **1** together with a tenfold excess of molybdenum hexacarbonyl in toluene instead of decalin for 17 hours. The yield obtained in this way was 60%.

X-ray Analysis of Methoxo-oxo[5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinatol] Molybdenum(V) (**4a**).

Crystals of $C_{53}H_{63}N_4O_2Mo$ are monoclinic with space group Pa and 2 molecules in a unit cell of dimensions a = 22.880(9), b = 7.802(3), c = 12.856(6) Å and β = 97.92(6)°. A crystal of dimensions 0.05 x 0.18 x 0.35 mm was used to collect 3650 intensities ($2.5 < 0 < 60°$) on a NONIUS CAD4 diffractometer employing graphite-monochromated CuKα radiation (λ = 1.5418 Å), 582 of which were below the $2.5\sigma(I)$ level and were treated as unobserved. The crystal structure was determined by means of the heavy-atom method. Refinement proceeded by anisotropic block-diagonal least-squares calculations. The H atoms were introduced at their calculated positions and were not refined. An empirical absorption correction (DIFABS [12]) was applied ($\mu(CuK\alpha) = 27.4\ cm^{-1}$). Unit weights were employed and the anomalous dispersion was taken into account. The final R value was 0.095. The final coördinates are listed in Table I. The molecule is depicted in the PLUTO drawing of Figure 1, which also gives the atomic numbering used in the crystallographic analysis.

The bond distances and angles are listed in Tables II and III. The butyl chains have rather poor distances and angles and abnormally large thermal parameters. This is probably due to conformational disorder.

The porphyrin system C1-C20, N1-N4 is planar within 0.074 Å with Mo at 0.092 Å from the best plane. The configuration of the four N atoms is planar within 0.012 Å with Mo at 0.094 Å from the best plane. The phenyl rings are nearly perpendicular to the porphyrin moiety (89.4 and 88.9°). The butyl groups are more or less planar with maximum deviations of 0.018 Å for C21-C24, 0.055 Å for C81-C84, 0.109 Å for C121-C124, and 0.012 Å for C181-C184. Their best planes make angles of 71, 70, 84, and 75° respectively with the plane of the porphyrin system. The line 05-06 is nearly perpendicular to the porphyrin plane (87.5°).

Oxydation of Mo(V) to Mo(VI) Derivatives.

The oxidation of the methoxo-oxomolybdenum(V) complex **4a** was carried out with hydrogen peroxide, in a similar way as described in the literature for tetraphenylporphyrin [10]. The reaction product was purified by chromatography and identified as diperoxo-[5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinato]-

Table I

Fractional Co-ordinates of the Non-hydrogen Atoms and Equivalent Isotropic Thermal Parameters

	X	Y	Z	Ueq
Mo	0.00000(0)	0.18078(20)	0.00000(0)	0.0600(7)
C1	0.0774(7)	-0.1323(21)	0.0615(13)	0.043(9)
C2	0.1177(7)	-0.2139(22)	0.1482(13)	0.049(10)
C3	0.1232(7)	-0.1081(24)	0.2321(13)	0.054(11)
C4	0.0850(6)	0.0465(22)	0.2003(12)	0.041(9)
C5	0.0734(8)	0.1961(26)	0.2650(13)	0.059(12)
C6	0.0394(8)	0.3358(22)	0.2287(13)	0.049(10)
C7	0.0297(9)	0.4839(25)	0.2877(14)	0.059(11)
C8	-0.0057(7)	0.5880(24)	0.2207(16)	0.057(11)
C9	-0.0173(8)	0.5039(24)	0.1238(12)	0.051(10)
C10	-0.0523(7)	0.5505(28)	0.0385(16)	0.068(13)
C11	-0.0710(7)	0.5018(21)	-0.0631(13)	0.044(9)
C12	-0.1073(6)	0.5849(24)	-0.1494(14)	0.051(10)
C13	-0.1134(7)	0.4718(24)	-0.2334(13)	0.049(10)
C14	-0.0766(8)	0.3235(27)	-0.1999(14)	0.060(11)
C15	-0.0703(7)	0.1798(22)	-0.2577(13)	0.052(10)
C16	-0.0299(7)	0.0423(26)	-0.2274(13)	0.052(11)
C17	-0.0202(6)	-0.1122(22)	-0.2917(13)	0.045(10)
C18	0.0168(7)	-0.2279(22)	-0.2217(12)	0.045(10)
C19	0.0269(6)	-0.1384(17)	-0.1232(12)	0.034(8)
C20	0.0620(7)	-0.2125(17)	-0.0349(13)	0.041(9)
C21	0.1442(7)	-0.3848(24)	0.1405(13)	0.049(10)
C22	0.2002(10)	-0.3796(33)	0.0883(20)	0.091(19)
C23	0.2470(14)	-0.2916(44)	0.1463(28)	0.137(26)
C24	0.3033(21)	-0.3105(59)	0.0758(47)	0.228(37)
C31	0.1612(10)	-0.1370(29)	0.3349(15)	0.074(14)
C51	0.1070(7)	0.1848(23)	0.3744(13)	0.049(10)
C52	0.0771(8)	0.1179(27)	0.4526(14)	0.061(12)
C53	0.1030(11)	0.1217(34)	0.5553(16)	0.085(16)
C54	0.1631(12)	0.1950(43)	0.5809(22)	0.124(23)
C55	0.1888(11)	0.2499(40)	0.4980(18)	0.098(18)
C56	0.1618(9)	0.2584(27)	0.3971(17)	0.073(14)
C60	0.1108(14)	0.2271(45)	-0.0950(35)	0.187(36)
C71	0.0504(9)	0.5293(29)	0.4028(15)	0.071(14)
C81	-0.0296(8)	0.7662(22)	0.2523(12)	0.050(10)
C82	-0.0838(15)	0.7627(32)	0.3047(31)	0.146(26)
C83	-0.1352(14)	0.6843(54)	0.2672(32)	0.163(36)
C84	-0.1929(16)	0.7054(69)	0.3140(38)	0.218(40)
C121	-0.1383(9)	0.7563(25)	-0.1359(17)	0.067(13)
C122	-0.1986(10)	0.7388(36)	-0.1000(29)	0.130(25)
C123	-0.2359(12)	0.9110(51)	-0.1064(37)	0.178(30)
C124	-0.2998(24)	0.8621(74)	-0.0976(60)	0.322(45)
C131	-0.1515(9)	0.5127(28)	-0.3354(15)	0.066(13)
C151	-0.0933(7)	0.1799(26)	-0.3682(13)	0.054(11)
C152	-0.0649(8)	0.2427(28)	-0.4503(13)	0.062(12)
C153	-0.0942(12)	0.2496(36)	-0.5509(16)	0.092(17)
C154	-0.1486(10)	0.1819(34)	-0.5757(14)	0.084(15)
C155	-0.1800(9)	0.1126(35)	-0.5028(19)	0.088(17)
C156	-0.1534(8)	0.1162(32)	-0.3996(14)	0.071(13)
C171	-0.0428(9)	-0.1565(26)	-0.4000(14)	0.064(12)
C181	0.0384(8)	-0.3928(24)	-0.2447(14)	0.054(11)
C182	0.0919(11)	-0.3826(41)	-0.3137(20)	0.106(20)
C183	0.1414(15)	-0.3018(52)	-0.2600(34)	0.170(35)
C184	0.1910(13)	-0.3049(50)	-0.3341(28)	0.142(31)
N1	0.0617(5)	0.0218(20)	0.0991(10)	0.046(8)
N2	0.0106(5)	0.3561(16)	0.1299(10)	0.044(8)
N3	-0.0537(6)	0.3475(18)	-0.0957(11)	0.050(8)
N4	-0.0012(6)	0.0198(20)	-0.1264(10)	0.048(8)
05	-0.0583(5)	0.0566(16)	0.0438(10)	0.059(8)
06	0.0671(4)	0.2847(15)	-0.0442(10)	0.052(7)

Table II

Bond Distances of the Non-Hydrogen Atoms (Å) with Standard Deviations in Parentheses

Mo	–	N1	2.16(1)	C15	–	C151	1.45(2)
Mo	–	N2	2.15(1)	C16	–	C17	1.50(3)
Mo	–	N3	2.07(1)	C16	–	N4	1.38(2)
Mo	–	N4	2.05(1)	C17	–	C18	1.46(2)
Mo	–	O5	1.80(1)	C17	–	C171	1.46(2)
Mo	–	O6	1.89(1)	C18	–	C19	1.44(2)
C1	–	C2	1.49(2)	C18	–	C181	1.42(3)
C1	–	C20	1.39(2)	C19	–	C20	1.42(2)
C1	–	N1	1.36(2)	C19	–	N4	1.39(2)
C2	–	C3	1.35(2)	C21	–	C22	1.53(3)
C2	–	C21	1.47(3)	C22	–	C23	1.40(4)
C3	–	C4	1.51(2)	C23	–	C24	1.68(7)
C3	–	C31	1.50(3)	C51	–	C52	1.39(3)
C4	–	C5	1.48(3)	C51	–	C56	1.37(3)
C4	–	N1	1.35(2)	C52	–	C53	1.37(3)
C5	–	C6	1.38(3)	C53	–	C54	1.48(4)
C5	–	C51	1.51(2)	C54	–	C55	1.36(4)
C6	–	C7	1.42(3)	C55	–	C56	1.36(3)
C6	–	N2	1.36(2)	C60	–	O6	1.34(4)
C7	–	C8	1.37(3)	C81	–	C82	1.49(4)
C7	–	C71	1.53(3)	C82	–	C83	1.35(5)
C8	–	C9	1.40(3)	C83	–	C84	1.53(6)
C8	–	C81	1.57(3)	C121	–	C122	1.52(3)
C9	–	C10	1.32(2)	C122	–	C123	1.59(5)
C9	–	N2	1.32(2)	C123	–	C124	1.53(6)
C10	–	C11	1.37(3)	C151	–	C152	1.40(3)
C11	–	C12	1.44(2)	C151	–	C156	1.47(2)
C11	–	N3	1.35(2)	C152	–	C153	1.37(3)
C12	–	C13	1.39(3)	C153	–	C154	1.35(3)
C12	–	C121	1.53(3)	C154	–	C155	1.37(3)
C13	–	C14	1.46(3)	C155	–	C156	1.38(3)
C13	–	C131	1.51(2)	C181	–	C182	1.61(3)
C14	–	C15	1.36(3)	C182	–	C183	1.39(4)
C14	–	N3	1.38(2)	C183	–	C184	1.58(5)
C15	–	C16	1.43(2)				

Table III

Bond Angles of the Non-hydrogen Atoms with Standard Deviations in Parentheses

N1	–	Mo	–	N2	85.0(5)
N1	–	Mo	–	N3	175.3(5)
N1	–	Mo	–	N4	93.0(5)
N1	–	Mo	–	O5	87.6(5)
N1	–	Mo	–	O6	86.1(5)
N2	–	Mo	–	N3	93.2(5)
N2	–	Mo	–	N4	174.0(5)
N2	–	Mo	–	O5	96.2(5)
N2	–	Mo	–	O6	87.2(5)
N3	–	Mo	–	N4	88.4(5)
N3	–	Mo	–	O5	96.8(5)
N3	–	Mo	–	O6	89.5(5)
N4	–	Mo	–	O5	89.3(6)
N4	–	Mo	–	O6	87.0(5)
O5	–	Mo	–	O6	172.5(5)
C2	–	C1	–	C20	122(1)
C2	–	C1	–	N1	106(1)
C20	–	C1	–	N1	132(1)
C1	–	C2	–	C3	108(1)
C1	–	C2	–	C21	124(1)
C3	–	C2	–	C21	128(1)
C2	–	C3	–	C4	107(1)
C2	–	C3	–	C31	126(2)
C4	–	C3	–	C31	127(2)
C3	–	C4	–	C5	128(1)
C3	–	C4	–	N1	106(1)
C5	–	C4	–	N1	125(1)
C4	–	C5	–	C6	125(1)
C4	–	C5	–	C51	112(2)
C6	–	C5	–	C51	123(2)
C5	–	C6	–	C7	126(2)
C5	–	C6	–	N2	126(2)
C7	–	C6	–	N2	108(1)
C6	–	C7	–	C8	106(2)
C6	–	C7	–	C71	131(2)
C8	–	C7	–	C71	123(2)
C7	–	C8	–	C9	108(2)
C7	–	C8	–	C81	124(2)
C9	–	C8	–	C81	128(2)
C8	–	C9	–	C10	129(2)
C8	–	C9	–	N2	109(1)
C10	–	C9	–	N2	122(2)
C9	–	C10	–	C11	142(2)
C10	–	C11	–	C12	133(2)
C10	–	C11	–	N3	118(2)
C12	–	C11	–	N3	109(1)
C11	–	C12	–	C13	107(2)
C11	–	C12	–	C121	122(2)
C13	–	C12	–	C121	130(2)
C12	–	C13	–	C14	106(1)
C12	–	C13	–	C131	122(2)
C14	–	C13	–	C131	132(2)
C13	–	C14	–	C15	126(2)
C13	–	C14	–	N3	108(2)
C15	–	C14	–	N3	126(2)
C14	–	C15	–	C16	125(2)
C14	–	C15	–	C151	119(2)
C16	–	C15	–	C151	114(2)

molybdenum(VI) (**5c**). The uv spectrum showed absorption maxima at 732, 591, 557, 515, 437 (Soret), 353, and 238 nm. The absorption maximum of the Soret band was found at a wavelength 13 nm lower than the corresponding absorption maximum of the molybdenum(V) porphyrin **4a**. A comparable difference of 10 nm was observed between the Soret bands of the methoxo-oxomolybdenum(V) derivative of tetraphenylporphyrin and the diperoxomolybdenum(VI) derivative of tetra-*p*-tolylporphyrin [10,4b]. In the ir spectrum the Mo=O stretching frequency of the molybdenum(V) porphyrins had disappeared and a new peak due to the O-O vibration was found at 955 cm^{-1} (964 cm^{-1} in the literature for the tetra-*p*-tolyl derivative [10]).

The pmr spectrum was in agreement with the structure proposed; all protons absorbed at slightly lower field than in the corresponding free base (about 0.1 ppm difference) and the NH absorbances were absent. The fd mass spec-

Table III (continued)

C15	–	C16	–	C17	126(1)
C15	–	C16	–	N4	124(2)
C17	–	C16	–	N4	109(1)
C16	–	C17	–	C18	106(1)
C16	–	C17	–	C171	131(2)
C18	–	C17	–	C171	123(2)
C17	–	C18	–	C19	105(1)
C17	–	C18	–	C181	128(1)
C19	–	C18	–	C181	127(1)
C18	–	C19	–	C20	121(1)
C18	–	C19	–	N4	113(1)
C20	–	C19	–	N4	126(1)
C1	–	C20	–	C19	125(1)
C2	–	C21	–	C22	113(2)
C21	–	C22	–	C23	114(2)
C22	–	C23	–	C24	105(3)
C5	–	C51	–	C52	117(2)
C5	–	C51	–	C56	120(2)
C52	–	C51	–	C56	122(2)
C51	–	C52	–	C53	120(2)
C52	–	C53	–	C54	119(2)
C53	–	C54	–	C55	116(2)
C54	–	C55	–	C56	125(2)
C51	–	C56	–	C55	118(2)
C8	–	C81	–	C82	116(2)
C81	–	C82	–	C83	126(3)
C82	–	C83	–	C84	124(4)
C12	–	C121	–	C122	114(2)
C121	–	C122	–	C123	114(2)
C122	–	C123	–	C124	107(3)
C15	–	C151	–	C152	127(2)
C15	–	C151	–	C156	118(2)
C152	–	C151	–	C156	115(1)
C151	–	C152	–	C153	120(2)
C152	–	C153	–	C154	121(2)
C153	–	C154	–	C155	123(2)
C154	–	C155	–	C156	117(2)
C151	–	C156	–	C155	123(2)
C18	–	C181	–	C182	112(2)
C181	–	C182	–	C183	112(3)
C182	–	C183	–	C184	107(3)
Mo	–	N1	–	C1	119(1)
Mo	–	N1	–	C4	129(1)
C1	–	N1	–	C4	112(1)
Mo	–	N2	–	C6	130(1)
Mo	–	N2	–	C9	121(1)
C6	–	N2	–	C9	109(1)
Mo	–	N3	–	C11	123(1)
Mo	–	N3	–	C14	127(1)
C11	–	N3	–	C14	109(1)
Mo	–	N4	–	C16	128(1)
Mo	–	N4	–	C19	124(1)
C16	–	N4	–	C19	107(1)
Mo	–	O6	–	C60	134(2)

trum showed a weak set of parent peaks together with much stronger peaks corresponding with the 5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinato MoO fragment, again indicating thermal decomposition. The fab mass spectrum only showed a set of peaks for the latter fragment. The isotopic distribution agreed with the pattern calculated. Conversion of the diperoxo- into the *cis*-dioxomolybdenum(VI) porphyrin by irradiation as described in the literature [11a] proved extremely slow for our porphyrin derivative. Thus, we had to irradiate a solution of 50 mg of the diperoxo compound **5c** in 100 ml of dichloromethane for one week with a 100W Tungsten lamp in order to obtain complete conversion into *cis*-dioxo-[5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinato]molybdenum(VI) **(6a)**. However, the synthesis could be improved by irradiating the diperoxo compound **5c** in tetrahydrofuran with a 25 W uv lamp; irradiation for 15 minutes resulted in complete conversion.

The reaction product **6a** was identified by its uv spectrum which showed maxima at 345, 416 (Soret), 536, and 567 nm. The wavelength of the Soret absorption maximum in the *cis*-dioxo product is 21 nm lower than in the diperoxo complex; in the literature almost the same difference (20 nm) was reported for the *p*-tolylporphyrin derivatives [11a]. In the ir spectrum of the *cis*-dioxo product strong absorptions were observed at 900 and 860 cm^{-1}. These corresponded with the two peaks at 900 and 866 cm^{-1} which were found for the *cis*-dioxomolybdenum(VI) complex of tetra-*p*-tolylporphyrin **(6b)** and assigned to the $Mo=O$ stretching frequency [11a]. The fd mass spectrum showed a peak corresponding with the 5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinato MoO fragment, due to loss of oxygen. In the pmr spectrum of **6a** the two α-CH_2 protons of the *n*-butyl groups were not equivalent, contrary to those in the pmr specrtrum of the free base porphyrin **1**. This is due to the presence of the *cis* dioxo group at one face of the porphyrin [*cf.* 11a]. For the same reason the two *ortho* protons of the *meso* phenyl substituents gave different δ values. Evidently, rotation around the C-C bond between the porphyrin and the *meso* phenyl group is slow on the nmr time scale due to steric hindrance. Upon raising the temperature to 333K we observed broadening of the signals of the phenyl protons but the coalescence temperature was not reached. This implies that the barrier for rotation around the C-C bond between the porphyrin and the phenyl group is higher than the value reported in the literature for the *cis*-dioxomolybdenum(VI) derivative of tetra-*p*-tolylporphyrin **(6b)** where for $\Delta G_c\ddagger$ a value of 13.8 ± 1 kcal mol^{-1} was calculated [11b]. Evidently, the height of the rotation barrier is increased by the presence of the methyl and butyl groups in the porphyrin.

EXPERIMENTAL

The ir spectra were measured on a Philips PU 9706 spectrometer as potassium bromide pellets. The uv absorption spectra were recorded on a Beckman DU-7 and a Varian DMS 100 spectrophotometer. The compounds were dissolved in chloroform which was dried on basic alumina. The pmr spectra were measured on a 200 MHz Bruker AC-200 E spectrometer in deuteriochloroform solution. Field desorption (fd) mass spectra were obtained on a MS 902 mass spectrometer equipped with a VG ZAB console. Fast-atom bombardment (fab) ionisation mass spectra were recorded on a VG-ZABHFQ mass spectrometer. The porphyrin samples were dissolved in a 3-nitrobenzylalcohol matrix. The esr spectra were determined on a Varian E-6 X-band spectrometer. Tetrahydrofuran was purified by filtration over basic alumina. All compounds gave satisfactory elemental analyses; however, for the *cis*-dioxo compound **6a** the presence of 0.2 mol of dichloromethane had to be assumed. The tendency of diphenylporphyrins to occlude solvent molecules has been reported before [14].

5,15-Diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (**1**).

This compound was prepared in the way, described previously [15].

Methoxo-oxo-[5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinato]molybdenum(V) (**4a**).

A solution of 300 mg (0.4 mmole) of 5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin (**1**) and 1.05 g (4 mmoles) of molybdenum hexacarbonyl in 100 ml of dry toluene was refluxed in a nitrogen atmosphere for 17 hours. The solvent was evaporated *in vacuo* and the residual crude product was chromatographed on alumina, eluent chloroform. The first fraction was discarded, the second green fraction was collected. After evaporation of the solvent the solid residue was refluxed in 50 ml of a 1:2 mixture of chloroform and methanol. Evaporation of the solvent and chromatography of the residue over alumina, eluent chloroform, gave 214 mg (60%) of pure porphyrin **4a**; uv: λ max 569 nm (ϵ 15900), 450 nm (ϵ 74800) (Soret), 349 nm (ϵ 60900), 267 nm (ϵ 19500), 238 nm (ϵ 37500); ir: ν (Mo = O) 901 cm^{-1}; esr: 6 weak lines (A = 44G); central line split into 9 lines (A = 2.4G); ms: (fab) (m/e) 849-859 (MH-OCH$_3$)$^+$.

Anal. Calcd. for $C_{53}H_{63}N_4O_2Mo$: C, 72.00; H, 7.18; N, 6.34. Found: C, 71.88; H, 7.14; N, 6.20.

Diperoxo[5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinato]molybdenum(VI) (**5c**).

To a solution of 100 mg (0.1 mmole) of the methoxo-oxoporphyrin **4a** in 20 ml of dichloromethane an excess of hydrogen peroxide (10 ml of a 30% solution in water) was added. The mixture was stirred for 5 hours at 20°. The dichloromethane layer was separated and washed with water; the dichloromethane was removed under reduced pressure. The residue was purified by chromatography over neutral alumina, act. III, eluent dichloromethane/petroleum ether 40-60 1:1. The first, red fraction was collected. After concentration 72 mg (72%) of pure product was obtained; uv: λ max 732 nm (ϵ 2740), 591 nm (ϵ 3610), 557 nm (ϵ 22400), 515 nm (ϵ 2890), 437 nm (ϵ 231000) (Soret), 353 nm (ϵ 33500), 238 nm (ϵ 29600); ir: ν (0-0) 957 cm^{-1}; pmr: δ 1.16 (t, 12H, δ-butyl), 1.82 (m, 8H, γ-butyl), 2.25 (m, 8H, β-butyl), 2.52 (s, 12H, CH_3), 4.01 (m, 8H, α-butyl), 7.78 (m, 4H, H-3′,5′), 7.83 (m, 2H, H-4′), 8.16 (dd, 4H, H-2′,6′), 10.30 (s, 2H, H-5,15); ms: (fab) (m/e) 849-859 (MH-O$_3$)$^+$.

Anal. Calcd. for $C_{52}H_{60}N_4O_4Mo$: C, 69.31; H, 6.71; N, 6.21. Found: C, 69.45; H, 6.73; N, 5.96.

Cis-dioxo[5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphinato]molybdenum(VI) (**6a**).

A solution of 30 mg (0.03 mmole) of the diperoxomolybdenum(VI) porphyrin **5c** in 350 ml of purified tetrahydrofuran was irradiated for 15 minutes with a high pressure uv-lamp (Hanau, Q150, 25W). The solvent was evaporated and the residue was purified by chromatography over neutral alumina, act. III, eluent dichloromethane/petroleum ether 40-60 1:1, yield 23 mg (79%); uv: λ max 567 nm (ϵ 16400), 536 nm (ϵ 6830), 416 nm (ϵ 82300) (Soret), 345 nm (ϵ 35300); ir : ν (Mo = O) 860 cm^{-1}, 900 cm^{-1}; pmr: δ 1.02 (t, 12H, δ-butyl), 1.68 (m, 8H, γ-butyl), 2.03 (m, 8H, β-butyl), 2.35 (s, 12H, methyl), 3.84 (m, 4H, α-butyl), 4.00 (m, 4H, α-butyl), 7.78 (m, 8H, H-3′,4′,5′,6′), 8.03 (dd, 2H, H-2′), 10.54 (s, 2H, H-5, 15); ms: (FD) (m/e) 848-858 (M-O)$^+$.

Anal. Calcd. for $C_{52}H_{60}N_4O_2Mo \cdot 0.2CH_2Cl_2$: C, 70.76; H, 6.87; N, 6.32. Found: C, 70.65; H, 6.95; N, 6.04.

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REFERENCE AND NOTES

[1] H. Ledon, *C. R. Seances Acad. Sci., Ser. C.*, **287**, 59 (1978).

[2] T. S. Srivastava and E. B. Fleischer, *J. Am. Chem. Soc.*, **92**, 5518 (1970).

[3] E. B. Fleischer and T. S. Srivastava, *Inorg. Chim. Acta*, **5**, 151 (1971).

[4a] H. Ledon and B. Mentzen, *Inorg. Chim. Acta*, **31**, L393 (1978); [b] H. J. Ledon, M. C. Bonnet, Y. Brigandat and F. Varescon, *Inorg. Chem.*, **19**, 3488 (1980).

[5a] T. Imamura, K. Hasegawa, T. Tanaka, W. Nahajima and M. Fujimoto, *Bull. Chem. Soc. Japan*, **57**, 194 (1984); [b] T. Imamura, T. Numatatsu, M. Terui and M. Fujimoto, *Bull. Chem. Soc. Japan*, **54**, 170 (1981).

[6] Y. Matsuda, F. Kubota and Y. Murakami, *Chem. Letters*, 1281 (1977).

[7] J. W. Buchler, L. Puppe, K. Rohbock and H. H. Schneeberger, *Chem. Ber.*, **106**, 2710 (1973).

[8] T. Diebold, B. Chevrier and R. Weiss, *Inorg. Chem.*, **18**, 1193 (1979).

[9] M. S. Bains and D. G. Davis, *Inorg. Chim. Acta*, **37**, 53 (1979).

[10] B. Chevrier, Th. Diebold and R. Weiss, *Inorg. Chim. Acta*, **19**, L57 (1976).

[11a] H. Ledon, M. C. Bonnet and J. Y. Lallemand, *J. Chem. Soc., Chem. Commun.*, 702 (1979); [b] B. F. Mentzen, M. C. Bonnet and H. J. Ledon, *Inorg. Chem.*, **19**, 2061 (1980).

[12] N. Walker and D. Stuart, *Acta Cryst.*, **A39**, 158 (1983).

[13] T. Imamura, N. Terui, Y. Takahashi, T. Numatatsu and M. Fujimoto, *Chem. Letters*, 89 (1980).

[14] G. M. Sanders, M. van Dijk, A. van Veldhuizen, H. C. van der Plas, U. Hofstra and T. J. Schaafsma, *J. Org. Chem.*, **53**, 5272 (1988).

[15] G. M. Sanders, M. van Dijk, B. M. Machiels and A. van Veldhuizen, *J. Org. Chem.*, **56**, 1301 (1991).