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The Crystal Structures of 1,3,5-Trimethylbenzenetricarbonylmolybdenum and Hexamethylbenzenetricarbonylmolybdenum

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The crystal and molecular structures of 1,3,5-trimethylbenzenetricarbonylmolybdenum, $C_{12}H_{12}O_3Mo$ (TMB), and hexamethylbenzenetricarbonylmolybdenum, $C_{15}H_{18}O_3Mo$ (HMB), have been determined from diffractometer data. For both compounds the unit cell is monoclinic, space group $P2_1/c$, with $Z = 4$. For TMB, $a = 8{\cdot}8602\,(6)$, $b = 17{\cdot}090\,(4)$, $c = 9{\cdot}0368\,(7)$ Å, $\beta = 118{\cdot}788\,(5)°$, $R = 0{\cdot}037$ for 1789 observed reflections. For HMB, $a = 8{\cdot}9578\,(6)$, $b = 13{\cdot}688\,(10)$, $c = 14{\cdot}049\,(10)$ Å, $\beta = 121{\cdot}529\,(5)°$, $R = 0{\cdot}041$ for 2186 observed reflections. The molecules have close to C_{3v} symmetry, with methyl carbons displaced out of the benzene ring plane away from the $Mo(CO)_3$ group by 0·035 (5) (TMB) and 0·060 (8) Å (HMB). For TMB the carbonyl groups are eclipsed with respect to the benzene methyl C atoms. For HMB the carbonyl groups are staggered with respect to the benzene ring atoms, and the ring symmetry is reduced to C_{3v} with average short and long C–C bonds in the ring of 1·405 (5) and 1·441 (9) Å. Mo–C(aromatic) average distances are 2·372 (5) (TMB) and 2·392 (5) Å (HMB).

Introduction

Olefin complexes of Cr, Mo and W have been the subject of numerous structural reports, as reviewed, for example, by Quinn & Tsai (1969). Although many structures have been reported for π-cyclopentadienyl and π-cycloheptatrienyl complexes of Mo, structure determinations of π complexes of benzene or benzene derivatives with Mo have been scarce to nonexistent. Distortion of arene geometry by π complexation has also been a structural question. A variety of efforts to decide this issue for dibenzenechromium have been reviewed by Bailey & Dahl (1965*a*) in the context of their study of hexamethylbenzenetricarbonylchromium. This work of Bailey & Dahl showed some indication of displacements of the methyl C atoms away from the Cr atom. However, their values for the ring C–C bond lengths showed appreciable scatter (a sample standard deviation from the mean of 0·036 Å) and were therefore not sufficiently precise to show regular ring distortions of 0·05 Å or less. Bailey & Dahl (1965*b*) also reported a study of benzenetricarbonylchromium in which the averages of the three 'long' and three 'short' bonds in the ring were identical to within the least-squares e.s.d. of 0·01 Å for each bond. The recent careful low-temperature studies by X-ray and neutron diffraction of $(C_6H_6)Cr(CO)_3$ by Rees & Coppens (1973) definitely showed reduction of the benzene ring symmetry to C_{3v}, with a 0·02 Å alternation in bond lengths and the H atoms displaced 0·03 Å from the plane of the ring *towards* the Cr atom.

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We, therefore, are reporting the structures of two π complexes of tricarbonylmolybdenum with substituted benzenes.

Experimental

TMB was prepared, following the procedure of Angelici (1969), by refluxing a mixture of mesitylene and hexacarbonylmolybdenum. Crystals for measurements were grown by evaporation of a chloroform solution.

HMB was similarly prepared by the procedure of Pidock (1967), refluxing a hexane solution of hexamethylbenzene with hexacarbonylmolybdenum. Crystals were obtained from dichloromethane solution with hexane as a precipitating agent. Intensity measurements were made for both compounds at 20 °C with a Picker Nuclear FACS-1 diffractometer in the θ–2θ scan mode, a 1° min^{-1} scan speed, Cu $K\alpha$ radiation, and a graphite crystal monochromator. All reflections were measured for $5° \leq 2\theta \leq 125°$ for two nonequivalent octants of reciprocal space for each compound. Each background was measured for 20 s, and three standard reflections were measured every 50 reflections. For each compound the lattice constants were determined, with the diffractometer, from least-squares treatment of 12 reflections having $2\theta > 46°$.

Crystal data

TMB: $C_{12}H_{12}O_3Mo$, M_r = 300·16, monoclinic, $P2_1/c$, a = 8·8602 (6), b = 17·090 (4), c = 9·0368 (7) Å, β = 118·788 (5)°, Z = 4, D_o = 1·67 (by flotation), D_c = 1·661 g cm^{-3}, $\mu(\text{Cu } K\alpha)$ = 101 cm^{-1}. 1923 unique reflections were measured, 1789 of which were considered as observed with F_o greater than 2·33 standard deviations (counting statistics). Crystal dimensions: 0·15 × 0·15 × 0·15 mm.

HMB: $C_{15}H_{18}O_3Mo$, M_r = 342·23, monoclinic, $P2_1/c$, a = 8·9578 (6), b = 13·688 (10), c = 14·049 (10) Å, β = 121·529 (5)°, Z = 4, D_o = 1·55 (by flotation), D_c = 1·544 g cm^{-3}, $\mu(\text{Cu } K\alpha)$ = 80·5 cm^{-1}. 2341 unique reflections were measured, 2186 of which were considered as observed with F_o greater than 2·33 standard deviations. Crystal dimensions: 0·18 × 0·15 × 0·16 mm.

Standard Lp corrections were made, and spherical-crystal absorption corrections were employed with μR = 0·75 for TMB and 0·70 for HMB. Adequacy of the spherical absorption correction was demonstrated by measurements of all four intensity-equivalent reflections for two sets of indices for TMB and three sets of indices for HMB with 2θ greater than 45°. The maximum intensity deviation from the average in any of these equivalent sets was 3%. H atom scattering factors were those of Stewart, Davidson & Simpson (1965); O atom scattering factors were from *International Tables for X-ray Crystallography* (1968); and the C and Mo atom scattering factors were those of Hanson, Herman, Lea & Skillman (1964). The real and imaginary anomalous-dispersion corrections of Cromer & Liberman (1970) were used for C, O and Mo.

Structure refinement

Both structures were solved by standard heavy-atom Patterson and Fourier procedures, and all non-hydrogen atoms were refined anisotropically to convergence by block-diagonal least squares. Refinement minimized $\Sigma w(|F_o| - |F_c|)^2$ with w chosen to give a uniform $\langle |\Delta F| \rangle$ *vs* $|F|$ distribution. For TMB, $1/w = 4\cdot793 - 0\cdot500\,|F_o| + 0\cdot0152\,|F_o|^2 - 0\cdot00006\,|F_o|^3$; for HMB, $1/w = 3\cdot00 + 0\cdot0000272\,|F_o|^3$.

The three H atoms attached to the ring in TMB were placed, without refinement, in the plane of the ring with C—H bond lengths of 1·06 Å and isotropic B values of 4 Å^2. It was not possible to locate the methyl H atoms unambiguously for either compound, probably because

Table 1. *Positional parameters* ($\times 10^4$) *for the non-hydrogen atoms with their standard deviations*

TMB	x	y	z
C(1)	4218 (5)	1837 (2)	3761 (5)
C(2)	3639 (5)	1166 (2)	4206 (4)
C(3)	2006 (5)	846 (2)	3135 (5)
C(4)	912 (5)	1225 (3)	1601 (5)
C(5)	1460 (5)	1911 (2)	1132 (5)
C(6)	3099 (5)	2219 (2)	2211 (5)
C(7)	5953 (6)	2190 (3)	4930 (6)
C(8)	1402 (6)	122 (3)	3657 (6)
C(9)	287 (6)	2324 (3)	−481 (7)
C(10)	5945 (5)	923 (2)	2085 (5)
C(11)	2868 (6)	938 (2)	−839 (6)
C(12)	3533 (5)	−225 (2)	1473 (4)
O(1)	7370 (4)	967 (2)	2449 (5)
O(2)	2427 (5)	966 (2)	−2272 (4)
O(3)	3489 (4)	−900 (2)	1449 (4)
Mo	3513 (0)	918 (0)	1568 (0)
HMB			
C(1)	−485 (4)	2410 (3)	1194 (3)
C(2)	1067 (5)	2922 (3)	1537 (3)
C(3)	2689 (4)	2413 (3)	1954 (3)
C(4)	2743 (5)	1386 (3)	2016 (3)
C(5)	1146 (5)	849 (3)	1654 (3)
C(6)	−446 (5)	1352 (3)	1243 (3)
C(7)	−2234 (6)	2921 (3)	701 (4)
C(8)	1026 (6)	4018 (3)	1415 (4)
C(9)	4332 (6)	2997 (3)	2294 (4)
C(10)	4423 (5)	844 (3)	2412 (4)
C(11)	1191 (7)	−259 (3)	1668 (4)
C(12)	−2139 (6)	796 (4)	821 (4)
C(13)	−265 (5)	2040 (3)	3468 (4)
C(14)	2834 (5)	2925 (3)	4224 (4)
C(15)	2703 (5)	995 (3)	4279 (3)
O(1)	−1357 (5)	2122 (4)	3660 (4)
O(2)	3633 (4)	3510 (3)	4900 (3)
O(3)	3375 (5)	422 (2)	4982 (3)
Mo	1526 (0)	1949 (0)	3085 (0)

Table 2. *Coordinates of atoms not refined* ($\times 10^4$)

(i) TMB

$B = 4\cdot0$ Å^2, occupancy factor = 1·0

	x	y	z
H(C6)	3507	2739	1871
H(C2)	4446	889	5375
H(C4)	−329	994	796

$B = 4\cdot5$ Å^2, occupancy factor = 0·5

	x	y	z
H(11)	5915	2804	4746
H(12)	6907	1945	4681
H(13)	6283	2075	6203
H(11*P*)	5830	2605	5739
H(12*P*)	6454	2474	4217
H(13*P*)	6822	1746	5674
H(31)	2003	88	4992
H(32)	1720	−384	3188
H(33)	48	143	3166
H(31*P*)	794	283	4376
H(32*P*)	2466	−245	4398
H(33*P*)	511	−190	2572
H(51)	−1014	2222	−798
H(52)	496	2115	−1471
H(53)	530	2934	−339
H(51*P*)	−488	2732	−268
H(52*P*)	−522	1913	−1400
H(53*P*)	1022	2625	−941

(ii) HMB

$B = 4\cdot5$ Å, occupancy factor = 0·5

	x	y	z
H(11)	−3062	2524	890
H(12)	−2841	2971	−178
H(13)	−2051	3635	1037
H(11*P*)	−2462	3116	1344
H(12*P*)	−3252	2452	129
H(13*P*)	−2240	3563	276
H(21)	35	4317	1526
H(22)	761	4206	609
H(23)	2251	4319	2023
H(21*P*)	1271	4355	2163
H(22*P*)	−220	4243	749
H(23*P*)	1997	4244	1247
H(31)	4258	3689	2606
H(32)	4468	3100	1595
H(33)	5446	2619	2925
H(31*P*)	4981	3172	3155
H(32*P*)	4002	3653	1826
H(33*P*)	5190	2583	2145
H(41)	5496	1266	3015
H(42)	4586	703	1729
H(43)	4401	170	2776
H(41*P*)	5069	723	3284
H(42*P*)	5254	1256	2237
H(43*P*)	4159	160	1999
H(51)	2410	−508	2341
H(52)	1022	−524	909
H(53)	172	−536	1764
H(51*P*)	1381	−521	2434
H(52*P*)	2231	−509	1579
H(53*P*)	−8	−538	1002
H(61)	−1888	132	1269
H(62)	−2716	636	−40
H(63)	−3026	1220	933
H(61*P*)	−2371	689	1481
H(62*P*)	−2061	105	509
H(63*P*)	−3199	1194	173

of rotational disorder for the methyl groups. All refinements were first performed without inclusion of these methyl H atoms in the structure factor calculations. A model for inclusion of these H atoms was then tried in which six H atoms, with occupancy factors of 0·5, were placed around each methyl C atom with C_{6v} local symmetry about the methyl–ring C—C bond. A C—H bond length of 1·06 Å, isotropic B of 4·5 Å^2, and C—C—H angle of 109° were used in the calculations for these methyl H atoms. Their coordinates were recalculated before each cycle of least-squares refinement. The inclusion of these H atoms in F_c reduced R for both compounds by about 0·007, and had the chief effect of improving the precision of resulting bond lengths and angles, *i.e.* the scatter in values for presumably equivalent bonds was reduced. Methyl–ring C—C distances were reduced by 0·005 to 0·010 Å and the averages of the two sets of ring C—C distances in HMB were brought closer together by 0·023 Å. All results reported here are for the calculations including the methyl H atoms in this way.

With the observed reflections, $R = 0\cdot0372$ and $R_w = 0\cdot0447$ for TMB, and $R = 0\cdot0412$, $R_w = 0\cdot0542$ for HMB. Here $R_w = \Sigma w(\Delta F)^2/\Sigma wF_o^2$.

The positional parameters determined for the two compounds are given in Table 1. Table 2 gives the coordinates of the H atoms used in the structure factor calculations.*

Description and discussion of the structures

Tables 3–6 give the individual bond lengths and bond angles for TMB and HMB. Figs. 1 and 2 show the structures and numbering of the atoms. All bond lengths and angles given in the abstract and discussion are the averages of three to six values (given in Tables 3–6) of quantities which are presumed to be equivalent for each structure, and the uncertainties quoted with these averages are the sample standard deviations for the set of values averaged. Only the e.s.d. values given in the tables are calculated from the least-squares refinements. Table 7 gives the perpendicular distances of atoms from the least-squares ring plane for each compound. Both molecules have close to C_{3v} symmetry, with the carbonyl groups within 2° of eclipsing the methyl carbons in TMB and only 4° from a staggered arrangement with respect to the methyl carbons in HMB.

The projection of the Mo atom onto the ring plane is 0·009 Å from the center of the ring for TMB and

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32367 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

0·012 Å from the ring center for HMB. The general geometry of the HMB molecule is similar to that of the analogous Cr compound (Bailey & Dahl, 1965*a*). Their suggestion that the methyl C atoms were significantly bent out of the ring plane away from the metal atom for the Cr compound is clearly true for the Mo compound, HMB, with an average deviation from the plane of 0·060 (8) Å. The out-of-plane deviation of methyl C atoms in TMB, 0·035 (5) Å, is not as large, but still seems significant. Table 7 gives the deviations from the ring plane for the individual atoms of each compound.

The location of the carbonyl groups over alternate ring C atoms in TMB leads one to predict, by symmetry considerations, the observed result that all six ring C–C bonds are of the same length, averaging 1·408 (10) Å. The distortion of the benzene ring seen in the neutron and X-ray diffraction studies of benzenetricarbonylchromium (Rees & Coppens, 1973) is,

Table 3. *TMB bond lengths* (Å) *and their e.s.d.'s*

Mo–C(1)	2·365 (4)	C(12)–O(3)	1·156 (5)
Mo–C(2)	2·370 (4)	C(1)–C(2)	1·393 (7)
Mo–C(3)	2·371 (6)	C(2)–C(3)	1·408 (5)
Mo–C(4)	2·377 (5)	C(3)–C(4)	1·410 (5)
Mo–C(5)	2·377 (4)	C(4)–C(5)	1·409 (7)
Mo–C(6)	2·371 (4)	C(5)–C(6)	1·404 (5)
Mo–C(10)	1·973 (5)	C(6)–C(1)	1·425 (5)
Mo–C(11)	1·965 (5)	C(1)–C(7)	1·510 (6)
Mo–C(12)	1·955 (4)	C(3)–C(8)	1·510 (7)
C(10)–O(1)	1·144 (6)	C(5)–C(9)	1·498 (6)
C(11)–O(2)	1·160 (6)		

Table 4. *TMB bond angles* (°) *and their e.s.d.'s*

Mo–C(10)–O(1)	175·6 (4)	C(1)–C(2)–C(3)	120·6 (4)
Mo–C(11)–O(2)	177·3 (4)	C(2)–C(3)–C(4)	118·8 (3)
Mo–C(12)–O(3)	176·6 (4)	C(3)–C(4)–C(5)	121·4 (3)
C(10)–Mo–C(11)	88·0 (2)	C(4)–C(5)–C(6)	119·3 (4)
O(1)–Mo–O(2)	89·8 (1)	C(5)–C(6)–C(1)	120·3 (3)
C(11)–Mo–C(12)	88·4 (2)	C(6)–C(1)–C(7)	119·8 (3)
O(2)–Mo–O(3)	89·7 (1)	C(7)–C(1)–C(2)	121·3 (4)
C(10)–Mo–C(12)	89·0 (2)	C(8)–C(3)–C(4)	120·3 (3)
O(1)–Mo–O(3)	91·4 (1)	C(8)–C(3)–C(2)	120·3 (4)
		C(9)–C(5)–C(6)	120·0 (4)
		C(9)–C(5)–C(4)	120·4 (4)

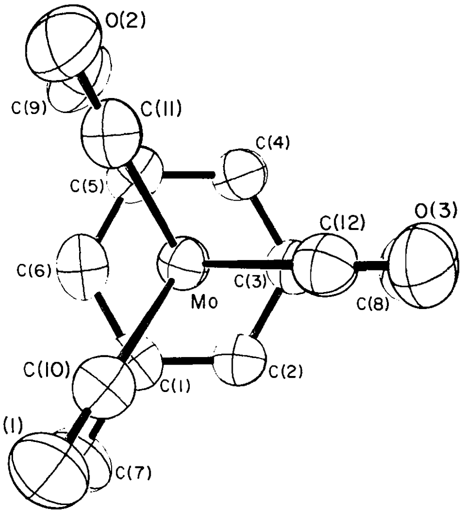

Fig. 1. Structural formula and numbering of atoms for 1,3,5-trimethylbenzenetricarbonylmolybdenum (TMB).

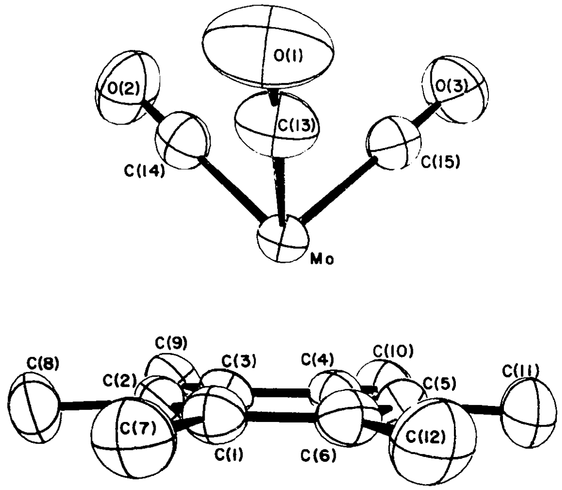

Fig. 2. Structural formula and numbering of atoms for hexamethylbenzenetricarbonylmolybdenum (HMB).

Table 5. *HMB bond lengths* (Å) *and their e.s.d.'s*

Mo–C(1)	2·386 (3)	C(1)–C(2)	1·399 (6)
Mo–C(2)	2·395 (4)	C(2)–C(3)	1·431 (6)
Mo–C(3)	2·397 (5)	C(3)–C(4)	1·408 (5)
Mo–C(4)	2·397 (5)	C(4)–C(5)	1·444 (6)
Mo–C(5)	2·388 (4)	C(5)–C(6)	1·407 (6)
Mo–C(6)	2·389 (3)	C(6)–C(1)	1·448 (6)
Mo–C(13)	1·945 (6)	C(1)–C(7)	1·513 (6)
Mo–C(14)	1·939 (4)	C(2)–C(8)	1·509 (5)
Mo–C(15)	1·944 (4)	C(3)–C(9)	1·516 (6)
C(13)–O(1)	1·147 (8)	C(4)–C(10)	1·500 (6)
C(14)–O(2)	1·159 (5)	C(5)–C(11)	1·517 (5)
C(15)–O(3)	1·154 (5)	C(6)–C(12)	1·514 (6)

Table 6. *HMB bond angles* (°) *and their e.s.d.'s*

Mo–C(13)–O(1)	177·2 (4)	C(6)–C(1)–C(2)	119·3 (3)
Mo–C(14)–O(2)	179·0 (5)	C(7)–C(1)–C(2)	122·0 (3)
Mo–C(15)–O(3)	178·9 (4)	C(7)–C(1)–C(6)	118·5 (3)
C(13)–Mo–C(14)	87·5 (2)	C(8)–C(2)–C(3)	119·3 (4)
O(1)–Mo–O(2)	88·0 (1)	C(8)–C(2)–C(1)	119·9 (4)
C(14)–Mo–C(15)	86·0 (2)	C(9)–C(3)–C(4)	120·7 (3)
O(2)–Mo–O(3)	86·3 (1)	C(9)–C(3)–C(2)	118·9 (3)
C(13)–Mo–C(15)	87·6 (2)	C(10)–C(4)–C(5)	119·7 (3)
O(1)–Mo–O(3)	88·3 (1)	C(10)–C(4)–C(3)	120·9 (4)
C(1)–C(2)–C(3)	120·7 (3)	C(11)–C(5)–C(6)	120·6 (4)
C(2)–C(3)–C(4)	120·4 (3)	C(11)–C(5)–C(4)	119·3 (4)
C(4)–C(5)–C(6)	120·0 (3)	C(12)–C(6)–C(1)	119·4 (3)
C(5)–C(6)–C(1)	120·2 (3)	C(12)–C(6)–C(5)	120·5 (4)

however, readily apparent in the alternating lengths of the ring C–C bonds found in HMB. The long and short bonds of the former compound, averaging 1·420 and 1·403 Å, are to be compared with the comparable averages for the three long and three short bonds of 1·441 (9) and 1·405 (5) Å in HMB. The bond-alternation effect seems to be enhanced on substitution of Mo for Cr in combination with the methyl substitution. Bailey & Dahl (1965*a*) reported for the Cr analog of HMB the values for ring C–C distances (taken consecutively around the ring) of 1·448, 1·379, 1·424, 1·461, 1·419 and 1·370 Å. It seems difficult to discuss reduction of ring symmetry with regular bond-length changes of 0·05 Å or less with these results. They suggested a possible twofold distortion of the benzene ring and proposed that the experimental evidence in the literature for a sixfold symmetry axis in the uncoordinated hexamethylbenzene molecule involved some ambiguities. We do not believe that the precision of their bond-length values justifies further consideration of such a twofold distortion in the aromatic ligand. Our results show no such twofold ring distortion.

Table 7. *Deviations* (Å) *of atoms from the least-squares plane determined by the benzene-ring atoms*

(*a*) TMB

C(1)	0·008	C(9)	–0·033
C(2)	–0·009	C(10)	3·052
C(3)	0·005	C(11)	3·101
C(4)	–0·001	C(12)	3·064
C(5)	0·001	O(1)	3·644
C(6)	–0·004	O(2)	3·761
C(7)	–0·040	O(3)	3·691
C(8)	–0·031	Mo	1·908

(*b*) HMB

C(1)	0·007	C(11)	–0·065
C(2)	–0·004	C(12)	–0·059
C(3)	–0·001	C(13)	3·057
C(4)	0·003	C(14)	3·124
C(5)	0·001	C(15)	3·121
C(6)	–0·006	O(1)	3·691
C(7)	–0·059	O(2)	3·830
C(8)	–0·090	O(3)	3·835
C(9)	–0·042	Mo	1·923
C(10)	–0·046		

We believe the most significant argument for the 0·036 Å bond-length alternation which we claim to observe in HMB is the precision we find in the sets of chemically equivalent bonds and the agreement of this precision with the bond-length uncertainties calculated from the least-squares e.s.d. values. The average of the six methyl–ring C–C bond lengths reported by Bailey & Dahl (1965*a*) for hexamethylbenzenetricarbonylchromium, 1·52 (3) Å, and the corresponding average of 1·512 (6) Å found here for HMB are in satisfactory agreement. Carbonyl bond lengths do not seem to be very sensitive to the nature of other ligands on Cr and Mo. The average C–O bond length for TMB and HMB, 1·153 (6) Å, is to be compared with 1·158 Å for benzenetricarbonylchromium (Rees & Coppens, 1973), 1·16 Å for hexamethyltricarbonylchromium,

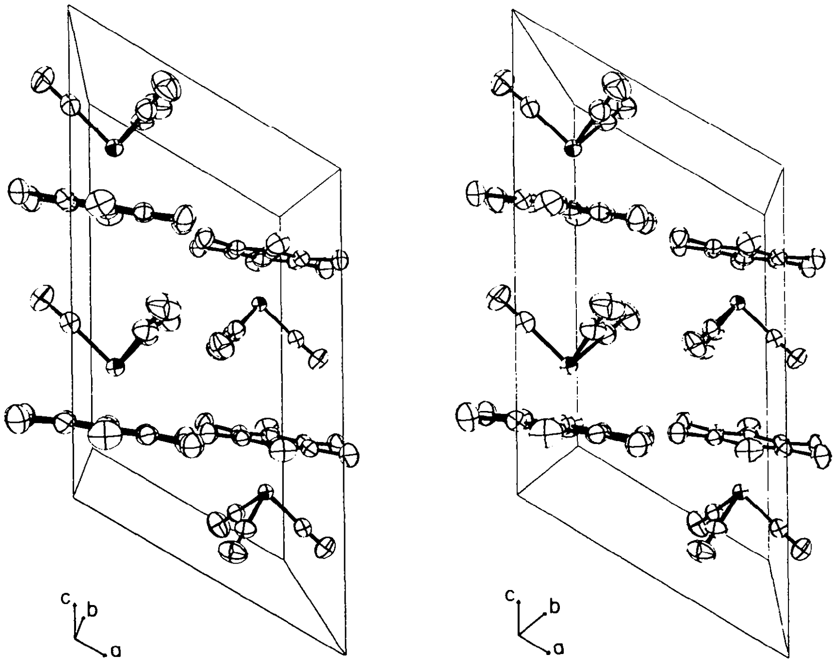

Fig. 3. Packing in the unit cell for hexamethylbenzenetricarbonylmolybdenum (HMB).

and the range of 1·15 to 1·20 Å for a series of cyclopentadienyl Mo carbonyls cited by Rajaram & Ibers (1973). The angles between the carbonyl groups, 89·9 (1) for TMB and 87 (1)° for HMB, are also within the cited standard deviation of the value of 87·5 (15)° in benzenetricarbonylchromium (Rees & Coppens, 1973) and 89·5 (7)° in hexamethylbenzenetricarbonylchromium (Bailey & Dahl, 1965*a*). The Mo–C–O bond angles, 176·5 (8) for TMB and 178·4 (10)° for HMB, may be significantly non-linear, as has been discussed from a theoretical standpoint by Kettle (1965), who also cited a number of examples with an average deviation of 5° from linearity. The molecular-orbital arguments of Kettle predict that the carbonyl groups should be bent *away* from the threefold axis; the torsion angle defined by the sequence O–C–Mo–(ring center) should be near zero. The computed values for this angle for TMB are 13, 14 and 13°. The corresponding values for the three carbonyl groups for HMB are 43, 35 and 93°. The qualitative prediction is verified for TMB, but the agreement is not good for HMB. However, the actual distortions from linearity of the O–C–Mo triads are small and the errors in these calculated torsion angles are therefore relatively large. The Mo–C(carbonyl) distance of 1·964 (10) Å in TMB is probably significantly longer than the value of 1·943 (3) Å seen in HMB. Both values are at the short end of the range of 1·96 to 2·02 Å reported and cited by Churchill & O'Brien (1969) and Rajaram & Ibers (1973) for substituted Mo carbonyls. The Mo–C(ring) distances of 2·372 (5) for TMB and 2·392 (5) Å for HMB are both significantly longer than the value of 2·316 Å for the π-cycloheptatrienyl Mo complex reported by them and is at the high end of the 2·33–2·38 Å range of values for Mo–C(ring) distances in a series of cyclopentadienyl examples cited by them and by Rajaram & Ibers (1973). Churchill & O'Brien (1969) have noted that for arene metal complexes, the metal–C(ring) distance seems to be approximately constant, as ring size varies from C_8 to C_4, so that the metal–ring plane distance is determined by the geometry of this bonded distance and the number of metal–C(ring) contacts possible.

The combination of longer Mo–C(ring) and shorter Mo–C(carbonyl) distances found for both TMB and HMB suggests, in comparison with the values for cyclopentadienyl Mo carbonyls, weaker bonding to the benzene ring with a concomitant increase in the Mo–C(carbonyl) bond order.

Fig. 3 shows that in HMB the aromatic ligands pack

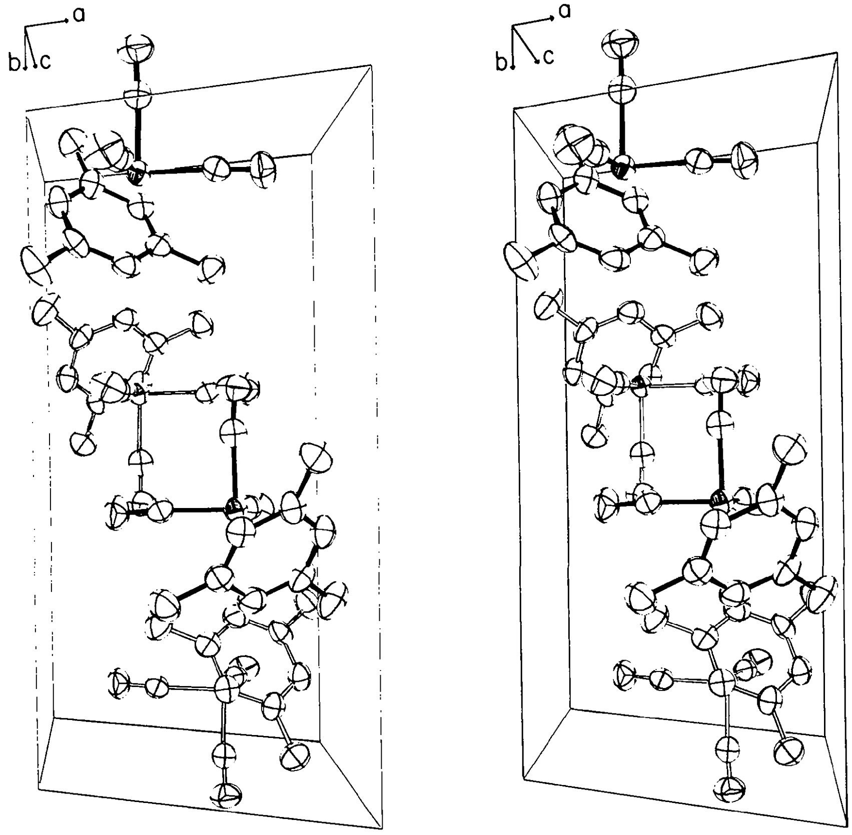

Fig. 4. Packing in the unit cell for 1,3,5-trimethylbenzenetricarbonylmolybdenum (TMB).

in layers parallel to the *b* cell axis, with interleaved $Mo(CO)_3$ groups. The shortest non-bonded interatomic distance between atoms of different $Mo(CO)_3$ groups is the value of 3·109 Å found for one O—O distance. Other such distances are greater than 3·7 Å. The spacing between the layers is then apparently determined by the intermolecular O(carbonyl)—C(methyl) distances, which have minimum values for the three O atoms of 3·347, 3·335 and 3·570 Å. Intramolecular O(carbonyl)—C(methyl) distances are longer. The near-neighbor intramolecular C(carbonyl)—C(ring) distances range from 3·137 to 3·242 Å (average 3·20 Å) and the corresponding values for the C(carbonyl)—C(methyl) distances range from 3·537 to 3·70 Å (average 3·62 Å). The layer structure shows no obvious intermolecular contacts which would prevent intramolecular energetics from dominating the rotational orientation of the $Mo(CO)_3$ group with respect to the hexamethylbenzene ring.

Fig. 4 shows the packing in the unit cell for TMB. Pairs of molecules are oriented so that the tricarbonyl groups intermesh with near-neighbor O—O distances ranging from 3·228 to 3·327 Å (average 3·290 Å). The shortest intermolecular O(carbonyl)—C(methyl) distances for each of the three O atoms are 3·504, 3·414 and 3·611 Å (average 3·548 Å). The shortest intramolecular C(carbonyl)—C(methyl) distances are 3·358, 3·414 and 3·377 Å (average 3·383 Å). These intramolecular distances are 0·1 to 0·2 Å shorter than the corresponding distances in HMB. Rotation of the $Mo(CO)_3$ group in TMB to give the staggered arrangement seen in HMB would presumably reduce the intramolecular non-bonded repulsions between the carbonyl groups and the trimethylbenzene ligand at the cost of less efficient packing between the carbonyl groups and the trimethylbenzene ligands of adjacent molecules.

Extended Hückel calculations for frontier molecular orbitals have recently been reported by Elian, Chen, Mingos & Hoffman (1976) for the molecular fragments $M(CO)_3$ and $M(CH)_n$, where n varied from 3 to 8 and M was Cr, Mn or Fe. The deformation of aromatic ring substituents was considered in the $M(CH)_n$ work. The bending of H atoms out of the plane of the aromatic ring towards the metal was explained as an electronic effect. However, deformation of substituent methyl groups away from the metal atom was thought likely to be because of steric effects. Deformations of aromatic-ring geometry were not discussed, and more complete calculations with a complete complex species such as HMB are needed to provide a further theoretical basis for consideration of ring-deformation effects and magnitudes of barriers expected for the rotation of the $Mo(CO)_3$ group about its axis normal to the ring of an aromatic ligand.

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