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SYNTHESIS AND CRYSTAL STRUCTURES OF THE α AND β STEREOISOMERS OF TRICARBONYL[(8,9,11,12,13,14-η)-METHYL 12-METHOXYPODOCARPA-8,11,13-TRIEN-19-OATE]CHROMIUM

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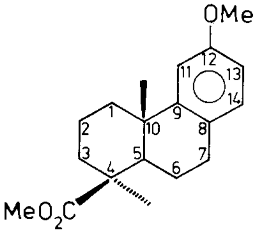
Summary

The η^6-(arene)tricarbonylchromium complexes derived from methyl 12-methoxypodocarpa-8,11,13-trien-19-oate have been synthesised from hexacarbonylchromium using a Strohmeier apparatus. Separation of the stereoisomeric α and β complexes was achieved by manual separation of the crystals formed from hexane/ethyl acetate. X-ray crystallography shows that both isomers crystallise in space group $P2_12_12_1$ with four molecules in unit cells of dimensions α: *a* 7.346(1), *b* 11.535(1), *c* 24.420(2) Å, β: *a* 10.640(1), *b* 13.002(1), *c* 15.121(3) Å. Least-squares refinement returned residuals, *R*, of 0.043 and 0.033 for 1959 and 2916 observed reflections respectively. The $Cr(CO)_3$ fragment is in an eclipsed orientation relative to the η^6 arene ligand in the β isomer, but is midway the eclipsed and staggered orientations in the α isomer.

Introduction

In connection with a project directed at modification of the carbon skeleton of methyl 12-methoxypodocarpa-8,11,13-trien-19-oate via organotransition metal inter-



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mediates, we have synthesised and isolated both diastereomers of the arenetricarbonylchromium complexes derived from this naturally occurring chiral diterpenoid. A crystal structure determination of a monoclinic crystal of the α isomer has been briefly communicated by other workers, but to date the completed structure has not been published [1]. Since our crystallising methods yield an orthorhombic modification of the α isomer, together with the hitherto unreported β isomer, we have determined the crystal structures of both diastereomers.

Experimental

Methyl 12-methoxypodocarpa-8,11,13-triene-19-oate (1.33 g, 4.4 mmol) and hexacarbonylchromium (1.07 g, 4.9 mmol) were placed in a 250 ml flask equipped with a Strohmeier multiple condenser [2], thermometer, magnetic stirrer, and septum cap. The apparatus was evacuated and flushed with argon (3 times) and a slight positive pressure of argon was maintained. Freshly distilled dry dibutyl ether (60 ml) and heptane (30 ml) were then syringed into the flask, and the mixture was heated (oil bath) with stirring. Initially, cold water was run through the upper condenser and the lower condenser was held at 80°C, but when the solvents began to reflux the upper condenser was brought up to 60°C. Heating and stirring were continued for 72 h during which time an intense yellow colour developed. The hot mixture was then filtered under argon through a pad of Celite, and the solvents were removed from the filtrate in vacuo with vigorous stirring and gentle heating. Flash chromatography (silica gel, hexane/ether, 1/9) of the residue under argon afforded a mixture of the α and β stereoisomers (83/17, ^{1}H NMR) of tricarbonyl[(8,9,11,12,13,14-η)-methyl 12-methoxypodocarpa-8,11,13-trien-19-oate]chromium as a yellow solid (1.4 g, 74%). Recrystallisation by vapour diffusion using hexane/ethyl acetate gave a mixture of the α isomer as small yellow needles and the β isomer as larger yellow tablets. The isomers were readily separated manually (attempted separation by careful flash chromatography (hexane/ether, 9/1) afforded fractions enriched in each isomer but clean separation was not achieved).

α-Isomer: m.p. 142–143°C (Found: C, 60.70; H, 6.24; Cr, 11.78. $C_{22}H_{26}CrO_6$ calcd.: C, 60.3; H, 5.9; Cr, 11.86%). $[\alpha]_D(CHCl_3)$ + 16.4°. $\nu_{max}^{CHCl_3}$ 1958 (antisymmetric stretch $ArCr(CO)_3$) and 1883 cm^{-1} (symmetric stretch $ArCr(CO)_3$). $\lambda_{max}^{CHCl_3}$ 320 nm, ϵ 8678; 239, 11500; 220 (sh), 5607. δ(H) 1.11 s $(H(10))_3$; 1.28, s $(H(15))_3$; 3.65, s $(H(18))_3$ and $(H(19))_3$; 5.20, d × d, J 7 and 1.9 Hz, H(13); 5.35, d, J 1.9 Hz, H(11); 5.50, d, J 7 Hz, H(14). δ(C) 19.7, C(2); 20.1, C(6); 24.9, C(17); 28.6, C(15) and C(7); 37.1, C(3); 37.6, C(1) and C(10); 44.0, C(4); 49.3, C(19); 51.3, C(5); 55.7, C(18); 77.7, C(13); 79.1, C(11); 93.5, C(14); 102.3, C(8); 125.7, C(9); 140.4, C(12); 177.3, C(16); 234.0, $Cr(CO)_3$.

β-Isomer: m.p. 182–184°C (Found: C, 60.0; H, 6.16, Cr, 11.94. $C_{22}H_{26}CrO_6$ calcd.: C, 60.3; H, 5.9; Cr, 11.86%). $[\alpha]_D(CHCl_3)$ + 2.6°. $\nu_{max}^{CHCl_3}$ 1958 and 1883 cm^{-1}. $\lambda_{max}^{CHCl_3}$ 321 nm, ϵ 8506; 240, 10620. δ(H) 1.25, s $(H(15))_3$ and $(H(17))_3$; 3.67, s $(H(18))_3$ and $(H(19))_3$; 5.25, d, J 7 Hz, H(14); 5.45, d × d, J 7 and 2 Hz, H(13); 5.65, d, J 2 Hz, H(11). δ(C) 20.1, C(2); 20.4, C(6); 24.2, C(17); 28.2, C(15); 32.2, C(7); 37.1, C(3); 37.8, C(10); 41.5, C(1); 43.8, C(4); 51.5, C(19); 53.6, C(5); 56.3, C(18); 82.1, C(13); 82.2, C(11); 89.0, C(14); 107.1, C(8); 125.0, C(9); 137.7, C(12); 177.2, C(16); 234.2, $Cr(CO)_3$.

When the above reaction was repeated for 9 h, not only was the yield of the complexes decreased (32%), but also the ratio of the diastereomers had altered to ca. 1/1 (^{1}H NMR) indicating the β-isomer to be the kinetically preferred complex, and the α-isomer to be the thermodynamically preferred complex.

Use of either diglyme/heptane (1/1) or diglyme/heptane/dibutyl ether (4/1/2) as reaction solvents afforded lower yields (20 and 27%, respectively) of the mixture of complexes.

X-ray

Crystals of both isomers belong in the orthorhombic system with systematic absences (h 0 0, $h = 2n + 1$; 0 k 0, $k = 2n + 1$; 0 0 l, $l = 2n + 1$) characteristic of space group $P2_12_12_1$. Crystals suitable for intensity data collection were mounted on fine glass fibres and positioned on a Nonius CAD-4 diffractometer. Unit cell dimensions were derived from least-squares fits to the observed setting angles of twenty-five reflections, using Zr-filtered Mo-K_α radiation.

Intensity data collections employed the $2\theta/\omega$ scan technique with a total background/peak count time ratio of 1/2. The omega scan angle was $0.80 + 0.35\tan\theta$. Reflections were counted for either 60 s or else until $\sigma(I)/I$ was 0.020 [3]. Crystal alignment and possible decomposition were monitored throughout the data collec-

TABLE 1

SUMMARY OF CRYSTAL DATA AND INTENSITY DATA COLLECTIONS FOR THE α AND β ISOMERS OF TRICARBONYL[(8,9,11,12,13,14-η)-METHYL 12-METHOXYPODOCARPA-8,11,13-TRIEN-19-OATE]CHROMIUM

	α-Isomer	β-Isomer
Formula	$C_{22}H_{26}O_6Cr$	$C_{22}H_{26}O_6Cr$
Molecular weight	438.22	438.22
Crystal habit and colour	multifaceted needles, yellow	multifaceted tablets, yellow
a (Å)	7.346(1)	10.640(1)
b (Å)	11.535(1)	13.002(1)
c (Å)	24.420(2)	15.121(3)
V (Å^3)	2069.26	2091.84
Temperature (K)	291 ± 1	292 ± 1
Z	4	4
Space group	$P2_12_12_1$	$P2_12_12_1$
ρ_c (g cm^{-3})	1.406	1.391
ρ_o (g cm^{-3})		1.394(5) (aq. KCl/KI)
F(0 0 0)	230	230
Crystal size (mm)	0.24 × 0.22 × 0.17	0.76 × 0.68 × 0.46
μ(Mo-K_α) (cm^{-1})	6.15	6.09
Transmission coefficients	max. 0.998	0.999
	min. 0. 987	0.976
θ(maximum) (°)	30	33
Total reflections	2914	4018
Observed data	1959 $I > 3\sigma(I)$	2916 $I > 2.5\sigma(I)$

tions by remeasuring three selected standard reflections after every 100 measurements, however no non-statistical variations were recorded. The crystals diffracted strongly, and an aluminium foil attenuator was inserted into the path of the diffracted beam whenever the observed count rate exceeded 10000 c s^{-1}. The data were corrected for Lorentz, polarisation, and absorption effects, and equivalent measurements were averaged together [4]. Details of crystal data and intensity data collection procedures are summarised in Table 1.

Structure determinations and refinements

Both structures were solved independently using conventional heavy-atom Patterson and electron density maps. The structure determination of the α form was rendered more difficult because of false symmetry in the early electron density maps (arising from the y coordinate of 0.0 for the Cr atom). Once the false symmetry was broken, refinement proceeded smoothly.

Refinement was by full-matrix least-squares procedures, minimising the function

TABLE 2

ATOMIC POSITIONS ($\times 10^4$) FOR THE α AND β ISOMERS OF TRICARBONYL[(8,9,11,12,13,14-η)-METHYL 12-METHOXYPODOCARPA-8,11,13-TRIEN-19-OATE]CHROMIUM

Atom	α-Isomer			β-Isomer		
	x	y	z	x	y	z
Cr	475(1)	−39(1)	529(0)	1723(0)	2042(0)	3910(0)
O(1)	5032(6)	3213(4)	2346(1)	2467(2)	−2517(2)	3502(2)
O(2)	3142(6)	4660(4)	2553(2)	4264(3)	−2765(2)	2801(2)
O(3)	−1654(7)	−1904(3)	1335(2)	4009(2)	3784(1)	3940(2)
O(4)	2707(7)	289(4)	−477(2)	−450(3)	590(2)	3850(2)
O(5)	−1322(10)	2167(5)	205(2)	1749(3)	1927(3)	1941(1)
O(6)	−2578(9)	−1121(6)	−94(2)	−49(3)	3803(2)	3701(3)
C(1)	−404(7)	2345(5)	1668(2)	5401(2)	152(2)	3759(2)
C(2)	−351(8)	3583(5)	1905(3)	6031(3)	−846(2)	3463(2)
C(3)	1028(8)	4310(5)	1621(2)	5724(2)	−1739(2)	4069(2)
C(4)	2955(8)	3812(4)	1652(2)	4306(2)	−1911(2)	4225(2)
C(5)	2904(7)	2537(4)	1418(2)	3704(2)	−860(2)	4501(2)
C(6)	4753(7)	1922(5)	1368(2)	2323(2)	−872(2)	4783(2)
C(7)	4600(8)	903(5)	978(2)	2091(3)	49(2)	5366(2)
C(8)	2925(7)	183(5)	1072(2)	2574(2)	1033(2)	4968(2)
C(9)	1394(7)	584(4)	1371(2)	3414(2)	1026(2)	4243(2)
C(10)	1459(7)	1752(4)	1680(2)	3962(2)	26(2)	3847(2)
C(11)	−123(7)	−138(4)	1427(2)	3810(2)	1987(2)	3893(2)
C(12)	−158(9)	−128(4)	1222(2)	3478(3)	2920(2)	4292(2)
C(13)	1354(10)	−1685(5)	920(2)	2619(3)	2925(2)	5009(2)
C(14)	2844(8)	−956(5)	846(2)	2186(3)	1985(2)	5335(2)
C(15)	4240(10)	4566(5)	1301(2)	4180(3)	−2695(2)	4981(2)
C(16)	3669(8)	3931(5)	2234(2)	3710(3)	−2423(2)	3423(2)
C(17)	1861(8)	1414(5)	2279(2)	3402(3)	−142(2)	2917(2)
C(18)	−1903(12)	−3003(5)	1070(3)	3354(4)	4725(2)	4025(3)
C(19)	5811(9)	3277(7)	2886(2)	1819(4)	−2973(4)	2777(3)
C(20)	1808(7)	164(5)	−94(2)	392(3)	1156(2)	3881(2)
C(21)	−643(10)	1328(5)	355(2)	1748(3)	1976(3)	2706(2)
C(22)	−1366(11)	−710(6)	136(2)	622(3)	3119(3)	3792(2)

$\Sigma w(|F_o|-|F_c|)^2$. Atomic scattering factors and dispersion corrections were for neutral atoms. After initial isotropic refinement, anisotropic thermal parameters were refined for all non-hydrogen atoms. Difference electron density maps revealed positions for all hydrogen atoms, and these were subsequently included in fixed positions with isotropic temperature factors set at $U = 0.06$ for aromatic and methylene hydrogens and $U = 0.08$ for methyl hydrogens. It was observed that the most intense reflections appeared to be suffering from the effects of secondary extinction, and accordingly 5 reflections for the α form and 8 reflections for the β form were assigned zero weights. After three further least-squares cycles the refinements converged with R and R_w $(\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{\frac{1}{2}})$ being 0.043 and 0.045 for the α isomer, and 0.033 and 0.037 for the β isomer, respectively. Reflection weights were $w \propto 1/(\sigma^2(F)+gF^2)$, with final values for g being 4.29×10^{-4} and 2.16×10^{-3}.

Final atomic coordinates are listed in Table 2. Hydrogen atom positions, bond angles, thermal parameters, and tables of observed and calculated structure factor amplitudes are available on request from the authors (G.R.C.).

Description of the crystal structures

Crystals of both isomers contain one monomer per asymmetric unit. Each chromium coordinates to three carbonyl groups and bonds in the η^6 mode to the aromatic ring of the podocarpate moiety. In the α isomer the $Cr(CO)_3$ lies below the aromatic ring (i.e. below relative to the methyl group on C(10)) whereas it lies above the aromatic ring in the β isomer. The geometries are readily visualised as being variants of the "piano stool" arrangement adopted by benzenechromium tricarbonyl [5,6], and are shown in Figs. 1 and 2.

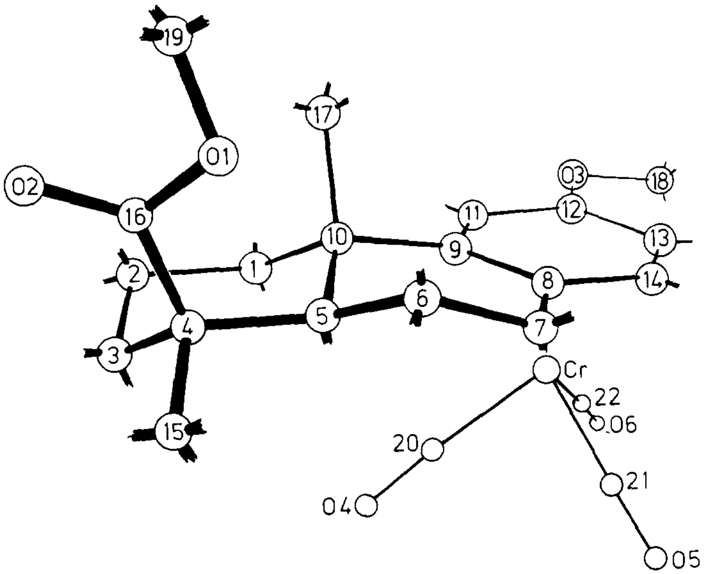

Fig. 1. Molecular geometry and atomic numbering for the α-isomer of tricarbonyl[(8,9,11,12,13,14-η)-methyl 12-methoxypodocarpa-8,11,13-trien-19-oate]chromium.

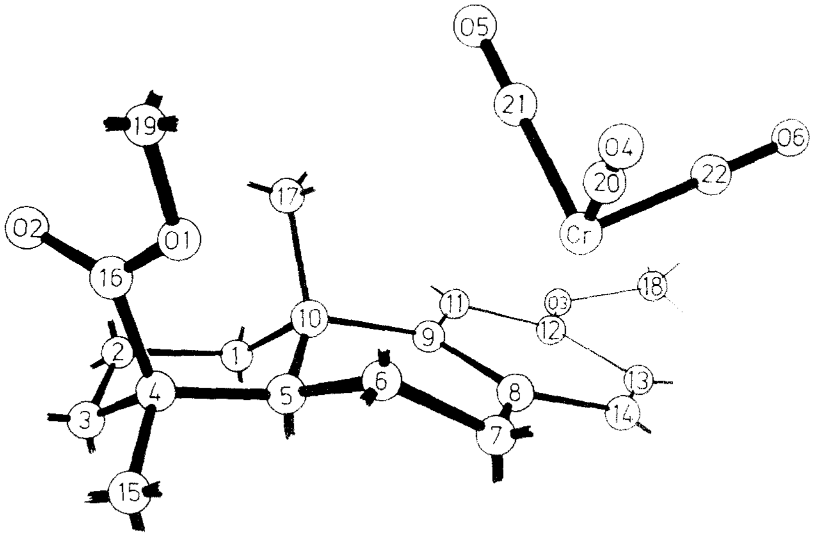

Fig. 2. Molecular geometry and atomic numbering for the β-isomer of tricarbonyl[(8,9,11,12,13,14-η)-methyl 12-methoxypodocarpa-8,11,13-trien-19-oate]chromium.

Bond lengths are listed in Table 3. All bonds are normal, and there is no evidence for alternating short and long bonds around the aromatic ring as was found in the low temperature X-ray and neutron diffraction studies of benzenechromium tricarbonyl [6]. The average Cr–C (aromatic) distances of 2.240 and 2.246 Å respectively are typical values. The displacements of the chromium atom from the least-squares planes of the C_6 rings are 1.740 and 1.748 Å respectively.

TABLE 3

BOND DISTANCES (Å) FOR THE α AND β ISOMERS OF TRICARBONYL[(8,9,11,12,13,14-η)-METHYL 12-METHOXYPODOCARPA-8,11,13-TRIEN-19-OATE]CHROMIUM

Atoms	α	β	Atoms	α	β
Cr–C(8)	2.250(4)	2.258(2)	C(1)–C(10)	1.530(7)	1.545(3)
Cr–C(9)	2.281(4)	2.288(2)	C(2)–C(3)	1.486(8)	1.514(4)
Cr–C(11)	2.241(4)	2.222(2)	C(3)–C(4)	1.530(8)	1.543(3)
Cr–C(12)	2.265(5)	2.264(3)	C(4)–C(5)	1.578(7)	1.567(3)
Cr–C(13)	2.222(6)	2.234(3)	C(4)–C(15)	1.543(8)	1.538(4)
Cr–C(14)	2.179(5)	2.211(3)	C(4)–C(16)	1.521(7)	1.521(4)
Cr–C(20)	1.824(5)	1.826(3)	C(5)–C(6)	1.538(7)	1.530(3)
Cr–C(21)	1.828(6)	1.824(3)	C(5)–C(10)	1.534(7)	1.542(3)
Cr–C(22)	1.829(7)	1.835(3)	C(6)–C(7)	1.518(7)	1.508(4)
O(1)–C(16)	1.328(7)	1.334(4)	C(7)–C(8)	1.502(7)	1.504(4)
O(1)–C(19)	1.438(6)	1.426(4)	C(8)–C(9)	1.419(7)	1.415(3)
O(2)–C(16)	1.211(6)	1.196(3)	C(8)–C(14)	1.426(7)	1.417(4)
O(3)–C(12)	1.342(7)	1.365(3)	C(9)–C(10)	1.546(6)	1.545(3)
O(3)–C(18)	1.435(7)	1.414(4)	C(9)–C(11)	1.398(7)	1.421(3)
O(4)–C(20)	1.155(6)	1.160(4)	C(10)–C(17)	1.543(7)	1.543(4)
O(5)–C(21)	1.149(7)	1.158(4)	C(11)–C(12)	1.410(7)	1.401(3)
O(6)–C(22)	1.156(8)	1.148(4)	C(12)–C(13)	1.412(8)	1.418(4)
C(1)–C(2)	1.541(7)	1.527(4)	C(13)–C(14)	1.392(9)	1.396(4)

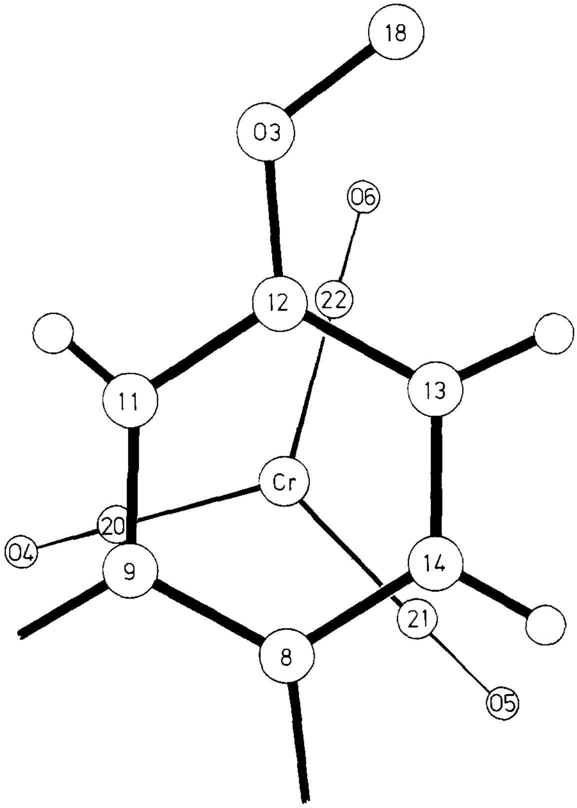

Fig. 3. Relative orientation of carbonyl groups in the α-isomer of tricarbonyl[(8,9,11,12,13,14-η)-methyl 12-methoxypodocarpa-8,11,13-trien-19-oate]chromium.

The orientation of the carbonyl groups relative to the atoms of the aromatic ring are shown in Figs. 3 and 4. In the β isomer the bonds are eclipsed, whereas in the α isomer they lie approximately midway between the eclipsed and staggered orientations. It is interesting to note that in most other (π-arene) $Cr(CO)_3$ complexes the CO and ring atoms are either fully eclipsed or fully staggered. In seeking a possible explanation for the intermediate alignment adopted in the present α isomer it was noticed from a calculation of the intermolecular distances that O(4) made three particularly short contacts with atoms in different neighbouring molecules. The particular contacts are O(4)–O(5) at $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$ 3.09 Å, O(4)–C(15) at $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$ 3.25 Å, and O(4)–C(18) at $\frac{1}{2}+x$, $-\frac{1}{2}-y$, $-z$ 3.02 Å. The logical explanation is that O(4) is required by crystal packing forces to occupy a small pocket between neighbouring molecules, and it is this factor which has forced the intermediate orientation. The carbonyl atoms of the β isomer are not thus constrained, and a nearly eclipsed configuration is adopted.

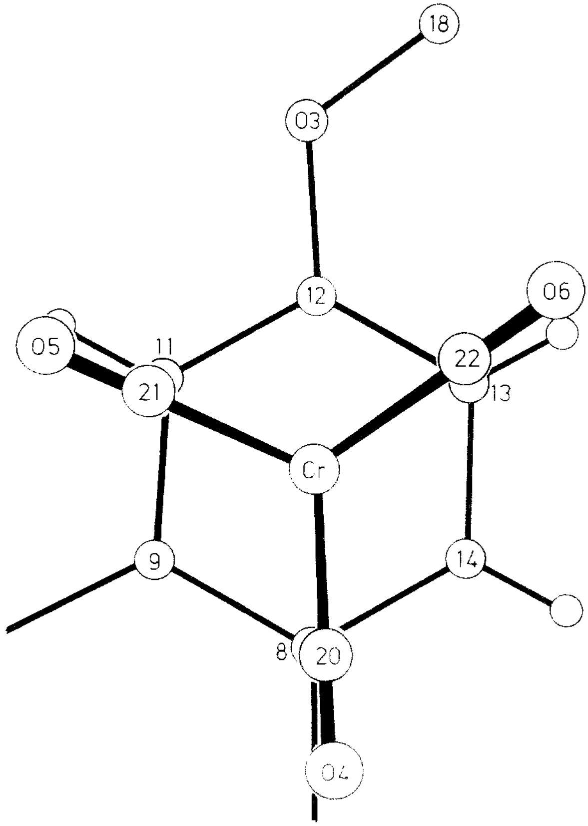

Fig. 4. Relative orientation of carbonyl groups in the β-isomer of tricarbonyl[(8,9,11,12,13,14-η)-methyl 12-methoxypodocarpa-8,11,13-trien-19-oate]chromium.

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