

Stereochemistry and Stereodynamics of Hexa-*n*-propylbenzene and of its Tricarbonylchromium Complex. Crystal and Molecular Structure of Tricarbonyl(η^6 -hexa-*n*-propylbenzene)chromium(0) †

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Empirical force field calculations indicate that for hexa-*n*-propylbenzene (**1**) the lowest energy 'up-down' stereoisomer is that with D_{3d} symmetry and the barrier to topomerisation of the *n*-propyl group is 57.7 kJ mol⁻¹. The crystal and molecular structure of tricarbonyl(η^6 -hexa-*n*-propylbenzene)-chromium(0) (**3**) shows that in this molecule the ground-state stereoisomer of the uncomplexed arene is retained. A decoalescence phenomenon observed in the 90.56 MHz ¹³C-¹H solution n.m.r. spectrum of (**3**) is attributed to slowed *n*-propyl group rotation and a barrier (ΔG_{300}^\ddagger) of 49.6 kJ mol⁻¹ for this process has been determined from lineshape-fitting studies.

Hexa-*n*-propylbenzene (**1**) is a representative of a class of sterically crowded, homosubstituted hexa-alkylbenzenes C₆R₆, for which the lowest-energy stereoisomer is observed or predicted to have an up-down alternation of the alkyl groups around the ring perimeter.¹ This stereoisomer of D_{3d} symmetry is, however, only one of eight possible arrangements in which the alkyl groups are located on one side or the other of the ring plane. The relative energies of the eight stereoisomers and the barriers to their interconversion by alkyl group rotation are now well understood for hexaethylbenzene (**2**), the prototype of this class of molecule.¹ In (**1**) the extra degree of rotational freedom of each of the *n*-propyl side chains is, at least in principle, an additional source of stereoisomerism.

The preparation of (**1**) was first reported by Hopff and Gati who attributed its non-first-order ¹H n.m.r. spectrum at ambient temperature to the chemical non-equivalence of the α -methylene protons resulting from hindered rotation of the *n*-propyl groups.² However, as recently pointed out by Mislow, the ¹H n.m.r. spectrum of this compound can in fact be fully explained by the chemical equivalence but spin coupling non-equivalence of the α - and β -methylene protons, and therefore there is no requirement to invoke hindered rotation.³

This paper reports: (i) details of empirical force field (EFF) calculations for (**1**) which have given the relative energies of its potentially accessible stereoisomers and the favoured rearrangement pathway and barrier to topomerisation of the *n*-propyl groups; (ii) the crystal and molecular structure of tricarbonyl(η^6 -hexa-*n*-propylbenzene)chromium(0) (**3**); (iii) the barrier to rotation of the propyl groups in (**3**) as determined by dynamic n.m.r. (DNMR) techniques.

Results and Discussion

Empirical Force Field Calculations.—The eight 'up-down' structures were calculated for (**1**) and recalculated for (**2**) by the program BIGSTRN-3⁴ which uses, among others, the MM2 force field.⁵ Calculations based on this force field give both a slightly different ordering and different relative steric energies than those previously reported for the stereoisomers of (**2**).^{1a} It should therefore be noted that the descriptors [(**a**) → (**h**)]

previously adopted for the 'up-down' stereoisomers no longer correctly reflect the relative order of their steric energies. Figure 1 illustrates the eight 'up-down' stereoisomers for (**1**) and (**2**) and their relative steric energies. The relative steric energies of the stereoisomers, all characterised as minima on the hypersurface, are almost equal for (**1**) and (**2**), with corresponding isomers also having the same symmetry. It has previously been shown that the stereoisomers of (**2**) can be partitioned into four sets according to the number of *syn* interactions between ethyl groups in neighbouring (*ortho*) positions whose methyls are located on the same side of the ring, and that the calculated steric energies are qualitatively related to this number.^{1c} An exactly analogous situation applies for (**1**).

The conformation of the alkyl side chain in the D_{3d} ground state, (**a**), structure of (**1**) is characterised by the torsion angle $\phi(C_{\text{aryl}}-C_{\text{alkyl}}-C_{\text{alkyl}}-C_{\text{alkyl}}) = 180^\circ$. In order to search for additional minima these torsion angles were frozen at $\phi = 120^\circ$, while all the other internal parameters were minimised with respect to energy. The resulting S_6 structure is not a minimum structure and lies 57.7 kJ mol⁻¹ above the ground-state structure. Relaxation of the restraint and minimisation gives the original D_{3d} structure. The same procedure was used to search for minimum structures of the highest-energy stereoisomer of (**1**), that with all six propyl groups on the same side of the benzene ring plane. Constraining all six torsion angles to $\phi = 120^\circ$ and minimisation gave a C_6 structure, but with a steric energy 125.5 kJ mol⁻¹ above the original minimum structure which has torsion angles of 168° . It is therefore very unlikely that attractive van der Waals interactions play a significant role in stabilising minimum-energy conformations of (**1**) and, notwithstanding the extra degree of rotational freedom of the *n*-propyl side chains, its static stereochemistry is remarkably similar to that of (**2**).

Rotation of the ethyl groups of (**2**) has been found to be completely uncorrelated, *i.e.* only one ethyl group may move at a time from an up to a down position.¹ Topomerisation of the *n*-propyl groups of (**1**) may be described by a similar rearrangement graph to that already proposed for (**2**).^{1a} However, as shown in Figure 2, it is probably preferable to double some edges to indicate that interconversion of two stereoisomers can occur *via* diastereoisomeric pathways.⁶ For example, stereoisomer (**c**) can interconvert by rotation of a single propyl group to give stereoisomers (**a**), (**d**), (**e**), or (**f**). Assuming ideal C_s symmetry for stereoisomer (**c**) (Figure 3), rotation of the propyl group C(51), C(52), and C(53) leads to the

† Supplementary data available: thermal parameters and H-atom coordinates. See Instructions for Authors, *J. Chem. Soc., Perkin Trans 2*, Issue 1, 1987.

Number of non-bonded <i>syn</i> -alkyl interactions	Stereoisomer symmetry descriptors	Relative steric energies (kJ mol ⁻¹)		
		(1)	(2)	
		$C_6(C_{6v})$	38.5	38.9
		$C_1(C_s)$	36.8	36.6
		$C_i(C_{2h})$	37.1	37.5
		$C_2^1(C_s)$	31.4	31.4
		$C_2(C_2)$	22.4	22.1
		$C_1(C_s)$	18.6	18.9
		$C_{2v}(C_{2v})$	21.7	21.5
		$D_{3d}(D_{3d})$	0.0	0.0

Figure 1. The eight stereoisomers of hexa-*n*-propylbenzene (**1**) and hexaethylbenzene (**2**), their descriptors, actual and highest (in parentheses) symmetries, and relative EFF-calculated steric energies (kJ mol⁻¹). The stereoisomers are schematically represented by Figures with filled and open circles that represent alkyl groups pointing towards and away from the observer

ground-state stereoisomer (**a**), whereas rotation of propyl group C(21), C(22), and C(23) gives stereoisomer (**f**). As sighted from C(5) to the bond C(2)–C(21) it makes no difference if C(22) rotates clockwise or counterclockwise, the pathways are enantiomeric and equal in energy. However, rotation of C(42), which leads to stereoisomer (**d**), or C(32), which gives (**e**), can occur on diastereoisomeric pathways depending on the sense of rotation. Thus six pathways lead from (**c**) to four different stereoisomers.

Rearrangement pathways were calculated using the incremental driving technique whereby a torsion angle, ϕ [C(3)–C(2)–C(21)–C(22)], was frozen at decreasing values, while all other internal parameters were minimised with respect to energy. The favoured rearrangement pathway for (**1**), like that for (**2**), was found to be (**1a**) \rightarrow (**1c**) \rightarrow (**1d**) \rightarrow (**1b**) \rightarrow (**1d**) \rightarrow (**1c**) \rightarrow (**1a**). However, for (**1**) the rate-limiting step is (**c**) \rightarrow (**d**), rather than (**a**) \rightarrow (**c**), with the transition state 57.7 kJ mol⁻¹ above the ground state, slightly higher than that for (**2**) (49.4 kJ mol⁻¹).

The centre of symmetry and C_2 axes in the ground-state D_{3d} stereoisomer of (**1**) may be removed upon complexation of the arene with Cr(CO)₃. As a result, the two faces of the benzene

ring become non-equivalent and differentiable, and site-exchange phenomena resulting from rotation of the *n*-propyl side chains can be monitored by DNMR techniques. The X-ray crystal structure of tricarbonyl(η^6 -hexa-*n*-propylbenzene)-chromium(0) (**3**) shows that in this molecule the ground state stereoisomer (**a**) of the free arene is retained and three propyl groups are proximal and three distal, in contrast to dicarbonyl-(η^6 -hexa-*n*-propylbenzene)(triphenylphosphine)chromium(0) where all the propyls are forced onto the distal face of the benzene ring.⁷ The molecular structure of (**3**) is shown in Figure 4. Although the molecule lacks crystallographically imposed symmetry it still possesses effective C_{3v} symmetry. The carbonyls efficiently eclipse the three arene carbon atoms to which the distal propyl groups are attached and there is some evidence of steric strain imposed by the Cr(CO)₃ moiety, with the $C_{\text{arene}}-C_{\text{alkyl}}-C_{\text{alkyl}}$ angles of the proximal propyl groups averaging 115.7° compared with 111.4° for the corresponding angle of the distal propyl groups.

The 90.56 MHz ¹³C-¹H} n.m.r. spectrum in [²H₈]toluene displays five signals at ambient temperatures, corresponding to the Me (14.2), β -CH₂ (25.6), α -CH₂ (30.0), C_{arene} (109.6), and CO (233.5 p.p.m.) carbons. As the solution is cooled the α -CH₂

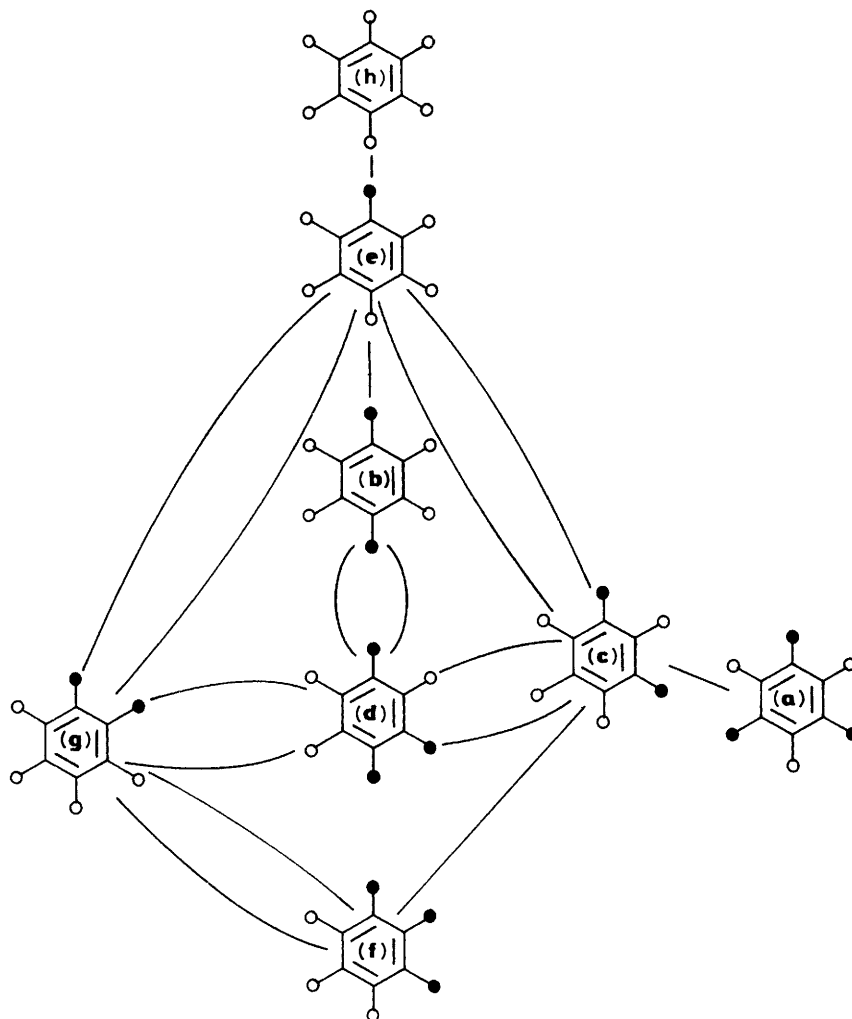


Figure 2. Graph showing symmetry non-equivalent pathways (edges) for the interconversion of the eight stereoisomers of (1)

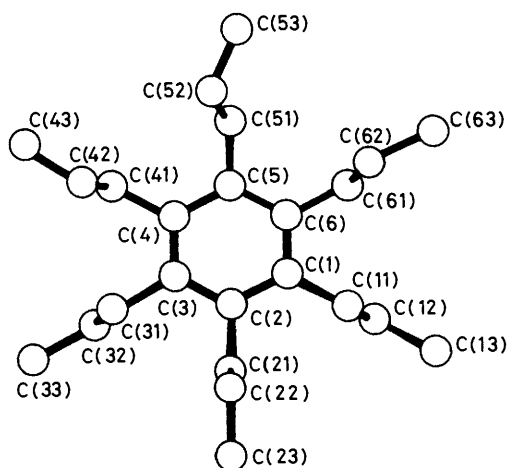


Figure 3. EFF-Calculated structure for stereoisomer (1c)

β -CH₂, and C_{arene} signals broaden and decoalesce, and each of these three signals is split into two at temperatures below 226 °K. The coalescence phenomenon reflects a topomerisation of the molecule in which the proximal and distal propyl groups undergo site exchange. Rates of exchange were obtained by line shape analysis using the program DNMR3⁸ and were not significantly different for the three decoalescences (see Table 3).

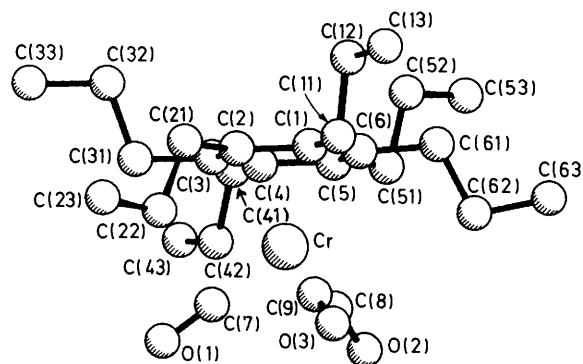


Figure 4. Molecular structure of tricarbonyl(η^6 -hexa-*n*-propylbenzene)chromium(0) (3)

A least-squares fit of the rate data to the Eyring equation yielded an average value of $\Delta G_{300}^* = 49.6 \pm 3.0$ kJ mol⁻¹.

The measured barrier to *n*-propyl group rotation in (3) is very close to that calculated for (1), even though complexation might be expected to lead to significantly increased steric energy in the arene ground state. Nevertheless, two major conclusions may be drawn: (i) *n*-propyl group rotations in (1) and (3) are uncorrelated; (ii) the barrier to *n*-propyl group rotation is sufficiently low in (1) that at ambient temperatures its ¹H n.m.r. spectrum must indeed be fully explained by the spin coupling

Table 1. Co-ordinates for the non-hydrogen atoms of (3)

Atom	x	y	z
Cr	0.232 3(1)	0.064 7(1)	0.169 6(1)
O(1)	0.323 1(6)	-0.056 3(3)	0.270 1(2)
O(2)	0.120 6(6)	-0.108 5(4)	0.106 0(2)
O(3)	0.522 2(5)	0.022 5(4)	0.132 0(2)
C(1)	0.270 9(6)	0.216 8(4)	0.149 6(2)
C(2)	0.267 5(6)	0.209 9(3)	0.209 0(2)
C(3)	0.142 5(6)	0.166 6(4)	0.229 0(2)
C(4)	0.022 4(6)	0.132 9(3)	0.190 1(2)
C(5)	0.030 7(6)	0.141 0(4)	0.130 3(2)
C(6)	0.154 0(6)	0.185 0(4)	0.110 6(2)
C(7)	0.286 5(6)	-0.009 3(4)	0.230 4(3)
C(8)	0.163 3(7)	-0.040 3(4)	0.130 7(3)
C(9)	0.408 5(7)	0.039 4(4)	0.146 4(3)
C(11)	0.403 3(7)	0.264 6(4)	0.127 7(3)
C(12)	0.378 3(9)	0.370 0(5)	0.119 1(3)
C(13)	0.500 9(12)	0.416 7(6)	0.089 8(5)
C(21)	0.390 4(6)	0.247 7(4)	0.251 5(3)
C(22)	0.511 9(7)	0.177 5(4)	0.271 9(3)
C(23)	0.623 2(8)	0.220 2(5)	0.317 7(3)
C(31)	0.133 8(6)	0.159 5(4)	0.291 7(2)
C(32)	0.062 5(7)	0.249 1(4)	0.313 8(3)
C(33)	0.055 4(10)	0.243 2(6)	0.377 3(3)
C(41)	-0.113 8(6)	0.093 1(4)	0.212 8(3)
C(42)	-0.107 7(7)	-0.012 1(4)	0.226 9(3)
C(43)	-0.238 1(9)	-0.042 6(5)	0.256 5(3)
C(51)	-0.096 4(6)	0.105 7(5)	0.088 6(3)
C(52)	-0.207 9(7)	0.183 4(5)	0.072 1(3)
C(53)	-0.321 6(8)	0.153 9(6)	0.024 0(3)
C(61)	0.157 0(7)	0.198 4(5)	0.047 3(2)
C(62)	0.230 3(8)	0.118 5(5)	0.017 0(3)
C(63)	0.248 5(9)	0.147 4(6)	-0.043 8(3)
C(71)	0.443 5(39)	0.019 1(23)	0.053 55(15)
C(72)	0.408 1(43)	0.052 2(22)	0.474 3(18)
C(73)	0.442 5(57)	0.065 0(32)	0.432 7(23)
C(74)	0.369 2(43)	0.055 9(26)	0.506 5(19)
C(75)	0.441 9(66)	0.024 0(40)	0.577 8(26)

non-equivalence of the α - and β -methylene protons, despite rapid exchange causing chemical equivalence.

Experimental

Synthesis.—Hexa-*n*-propylbenzene (1). This was prepared by the method of Hopff and Gati.² ¹³C-¹H N.m.r. spectrum in [²H₈]toluene at ambient temperature, δ 15.1 (Me), 25.3 (CH₂), 32.2 (CH₂), and 136.9 (C_{arene}) p.p.m.

Tricarbonyl(η^6 -hexa-*n*-propylbenzene)chromium(0) (3). This was prepared as previously described.⁷ ¹³C-¹H N.m.r. spectrum in [²H₈]toluene at ambient temperature δ 14.2 (Me), 25.6 (CH₂), 30.0 (CH₂), 109.6 (C_{arene}), and 233.5 (CO) p.p.m. At 226 K; δ 13.9 (Me), 23.1, 28.9, (CH₂), 29.3, 31.1, (CH₂), 105.2, 114.3 (C_{arene}), and 234.6 (CO) p.p.m.

Variable-temperature N.m.r. Measurements.—The variable-temperature n.m.r. spectrum of (3) was recorded at 90.56 MHz (¹³C) on a Bruker WH360 spectrometer operating in the Fourier transform mode. The n.m.r. sample was filtered under N₂ through a grade 3 glass sinter, freeze-thaw degassed, and sealed in a 10 mm (outsider diameter) tube. The temperature of the probe was measured by a thermocouple inserted in an n.m.r. tube filled with toluene to the same depth as the solution in the sample tube. Temperatures were considered accurate to ± 2 °C.

Empirical Force Field Calculations.—Input geometries were based on standard bond lengths and bond angles. These

Table 2. Selected bond distances (Å) and bond angles (°) for (3)

C(1)–Cr	2.238(6)	C(8)–Cr–C(7)	88.8(3)
C(2)–Cr	2.262(5)	C(9)–Cr–C(7)	87.8(3)
C(3)–Cr	2.246(6)	C(9)–Cr–C(8)	87.3(3)
C(4)–Cr	2.265(5)	C(11)–C(1)–C(2)	119.0(5)
C(5)–Cr	2.244(5)	C(11)–C(1)–C(6)	119.4(5)
C(6)–Cr	2.261(5)	C(3)–C(2)–C(1)	118.5(5)
C(7)–Cr	1.802(6)	C(21)–C(2)–C(1)	122.0(5)
C(8)–Cr	1.817(6)	C(21)–C(2)–C(3)	119.4(5)
C(9)–Cr	1.811(7)	C(4)–C(3)–C(2)	120.9(5)
C(7)–O(1)	1.168(8)	C(31)–C(3)–C(2)	120.0(5)
C(8)–O(2)	1.171(8)	C(31)–C(3)–C(4)	119.1(5)
C(9)–O(3)	1.165(8)	C(5)–C(4)–C(3)	118.7(5)
C(2)–C(1)	1.421(8)	C(41)–C(4)–C(3)	119.5(5)
C(6)–C(1)	1.401(7)	C(41)–C(4)–C(5)	121.7(5)
C(11)–C(1)	1.539(9)	C(6)–C(5)–C(4)	120.2(5)
C(3)–C(2)	1.435(8)	C(51)–C(5)–C(4)	119.1(5)
C(21)–C(2)	1.515(7)	C(51)–C(5)–C(6)	120.6(5)
C(4)–C(3)	1.431(7)	C(5)–C(6)–C(1)	120.0(5)
C(31)–C(3)	1.506(8)	C(61)–C(6)–C(1)	120.4(5)
C(5)–C(4)	1.438(8)	C(61)–C(6)–C(5)	119.6(5)
C(41)–C(4)	1.532(8)	O(1)–C(7)–Cr	179.1(5)
C(6)–C(5)	1.422(8)	O(2)–C(8)–Cr	179.1(5)
C(51)–C(5)	1.518(8)	O(3)–C(9)–Cr	179.3(5)
C(62)–C(6)	1.521(8)	C(12)–C(11)–C(1)	111.3(5)
C(12)–C(11)	1.515(9)	C(13)–C(12)–C(11)	111.9(7)
C(13)–C(12)	1.546(14)	C(22)–C(21)–C(2)	116.0(5)
C(22)–C(21)	1.526(8)	C(23)–C(22)–C(21)	111.7(5)
C(23)–C(22)	1.522(9)	C(32)–C(31)–C(3)	111.1(5)
C(32)–C(31)	1.547(8)	C(33)–C(32)–C(31)	111.4(5)
C(33)–C(32)	1.520(10)	C(42)–C(41)–C(4)	115.3(5)
C(42)–C(41)	1.522(8)	C(43)–C(42)–C(41)	111.5(5)
C(43)–C(42)	1.527(11)	C(52)–C(51)–C(5)	111.8(5)
C(52)–C(51)	1.519(9)	C(53)–C(52)–C(51)	112.2(6)
C(53)–C(52)	1.508(10)	C(62)–C(61)–C(6)	115.9(5)
C(62)–C(61)	1.539(10)	C(63)–C(62)–C(61)	110.7(6)
C(63)–C(62)	1.530(9)		

Table 3. Rate constants for the topomerisation of (3)^a

T/K	(i) k/s ⁻¹	(ii) k/s ⁻¹	(iii) k/s ⁻¹
226	70.0	50.0	25.0
243	215.0	220.0	200.0
253	500.0	400.0	510.0
268	1 700.0	1 600.0	1 850.0
283	5 500.0	5 000.0	4 000.0
298	12 000.0	—	14 500.0

^a Obtained from the coalescences of the ¹³C signals in the subspectra of (i) the aromatic carbon atoms; (ii) the α -methylene carbon atoms; (iii) the β -methylene carbon atoms.

structures were then optimised by the program BIGSTRN-3⁴ using the MM2 force field.⁵ Geometry optimisations were routinely begun with the variable-metric method and concluded with the full-matrix Newton-Raphson method. Analytical second derivatives were used at both stages. The final convergence criteria for the Newton-Raphson stage were as follows: r.m.s. gradient less than 10⁻⁶ kcal mol⁻¹ Å⁻¹ and r.m.s. movement less than 10⁻⁶ Å. Final structures were characterised as minima by the absence of negative eigen values in the matrix of analytical second derivatives.

For the calculation of the rearrangement pathways, the torsion angle ϕ was held fixed at a given value (ϕ_0) by imposing a large quadratic potential, $E_{\text{FIX}} = 10\,000 (\phi - \phi_0)$ kcal mol⁻¹. This is a modified version of a published technique.⁹

Crystallography.—Amber-yellow crystals of (3) were grown from n-heptane-toluene solution. Preliminary photographs showed that the compound diffracted sharply but with few reflections apparent beyond θ 40° (Cu radiation).

Crystal Data.— $C_{27}H_{42}CrO_3$, $M = 466.6$. Monoclinic, space group $P2_1/n$, $a = 9.197(2)$, $b = 14.120(2)$, $c = 23.776(3)$ Å, $\beta = 97.23(1)^\circ$, $V = 30.62$ Å³, $Z = 4$, D_c (no lattice solvent) = 1.01 g cm⁻³, $F(000) = 1008$, Mo radiation, $\lambda = 0.71069$ Å, $\mu = 3.6$ cm⁻¹.

Data Collection.—A crystal of dimensions *ca.* 0.25 × 0.25 × 0.25 cm was sealed into a capillary and mounted on an Enraf-Nonius CAD-4F diffractometer. Cell dimensions were refined from the setting angles of 25 reflections with θ *ca.* 13°. Data were collected by ω , 2 θ scans in the range $1 \leq \theta \leq 20^\circ$ over one quadrant of reciprocal space (4308 reflections, 241 systematically absent, 3747 unique). The intensity of a standard reflection showed no significant change.

Structure Solution.—The approximate position of the Cr atom was obtained from a Patterson synthesis, and the C and O atoms were located from difference syntheses alternating with cycles of least-squares refinement. These atoms were allowed anisotropic thermal parameters in the last cycles. Hydrogen atoms were included at calculated 'riding' positions, after the approximate positions of 32 out of 42 had been located (peak heights similar to strong background peaks). Also, a number of peaks in the intermolecular void near $\frac{1}{2}, 0, \frac{1}{2}$ were assigned as C atoms of disordered solvent molecules (no plausible molecule could be distinguished) and refined with isotropic thermal parameters; the strongest peaks (*ca.* 0.5 e Å⁻³) in the final difference synthesis were in this region; site occupancy factors (s.o.f.) were 0.5 for C(71) and C(72) and 0.25 for C(73), C(74), and C(75). These s.o.f. were not refined, as the e.s.d.s were large in positional and thermal parameters for 'solvent' atoms. Block-matrix refinement converged at R 0.058, R' 0.068, R_w {=

$[\sum w(\Delta F)^2 / \sum w F^2]^{1/2}$ 0.099 [2526 data with $|F| \geq 3\sigma(F)$], 300 parameters, $w = 0.169 [\sigma^2(F) + 0.0185F^2]^{-1}$ in last cycle. The SHELX 76 program¹⁰ system was used in all calculations.

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