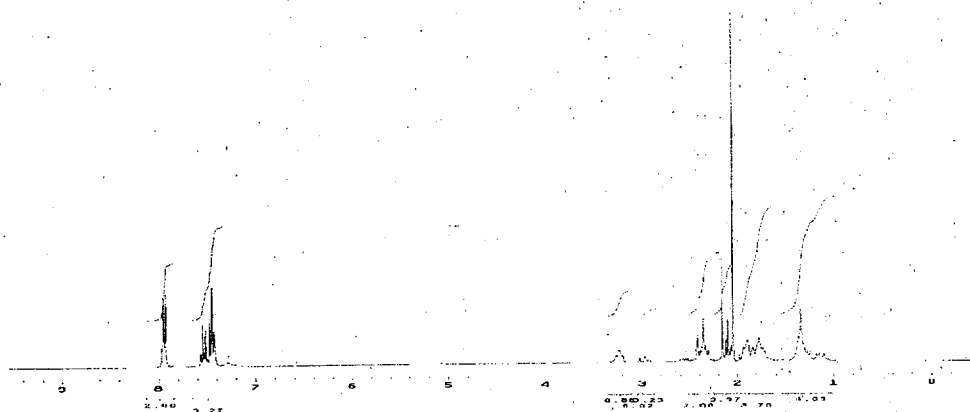
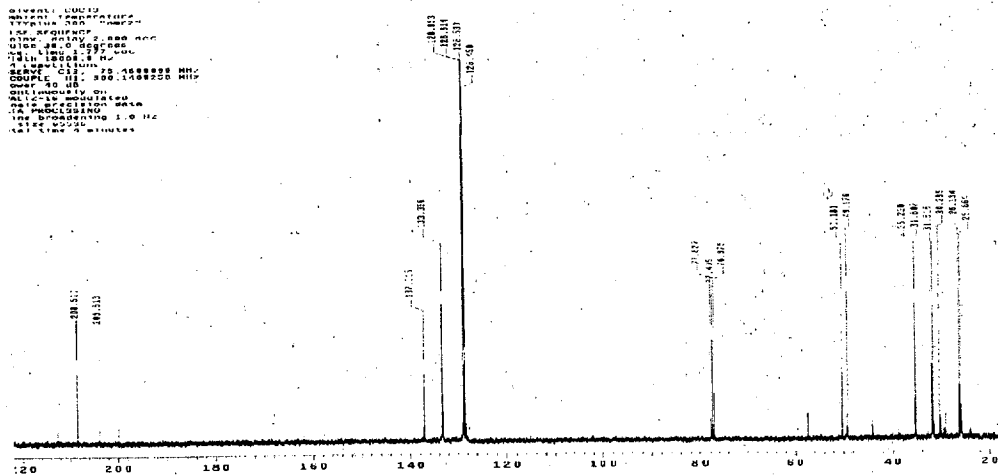
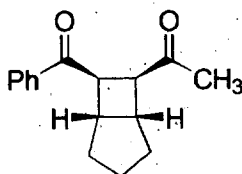


8b



C O B S E R V E

[illegible]

**8c****1-(3-Benzoyl-octahydro-pentalen-1-yl)-ethanone (8c).**

To a solution of Co(dpm)_2 (87 mg, 0.204 mmol, 10 mol%) in dichloroethane (0.45 M) at room temperature was added methylphenylsilane (1.1 mL, 8.0 mmol, 400 mol%). The reaction mixture was allowed to stir for 30 min., at which point a dichloroethane solution of 1-phenyl-2-deca-2,7-diene-1,9-dione (**8a**) (500 mg, 2.06 mmol) was added via syringe. The reaction progress was monitored by TLC. Upon complete consumption of starting materials, the reaction mixture was quenched with methanol/10% $\text{HCl}_{\text{(aq)}}$ and allowed to stir for 30 minutes. The reaction mixture was partitioned between ethyl acetate and $\text{NH}_4\text{Cl}_{\text{(aq)}}$. The aqueous layer was extracted and the combined organic extracts were dried (Na_2SO_4) and filtered. The solvent was evaporated and the reaction was purified via flash chromatography (SiO_2 : 9:1, hexanes:ethyl acetate) to provide **8b** (25mg) in 5% yield and **8c** (325mg) in 65% yield.

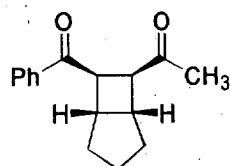
Mp = 77-78 °C.

^1H NMR (CDCl_3 , 300 MHz): δ 7.81 (m, 2H), 7.46 (m, 3H), 3.80 (dd, J = 5.1, 9.6 Hz, 1H), 3.02 (m, 3H), 2.02 (s, 3H), 1.79 (m, 6H).

^{13}C NMR (CDCl_3 , 75 MHz): δ 207.7, 199.4, 136.4, 133.1, 128.9, 128.2, 51.7, 48.3, 39.4, 38.7, 32.7, 32.5, 28.8, 25.4.

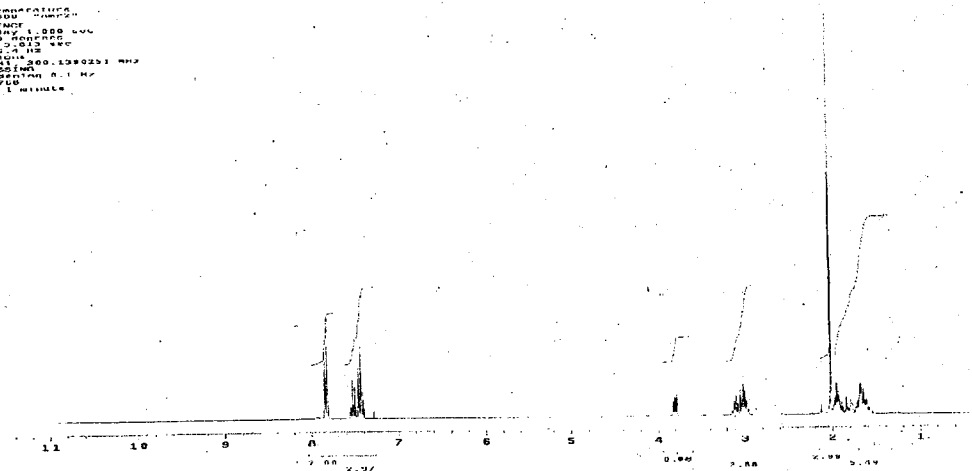
IR (neat): 3055, 2948, 2858, 1706, 1678, 1448, 1356, 1264, 1218, 739 cm^{-1} .

HRMS: Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ [$\text{M}+1$] 243.1385, found 243.1387.

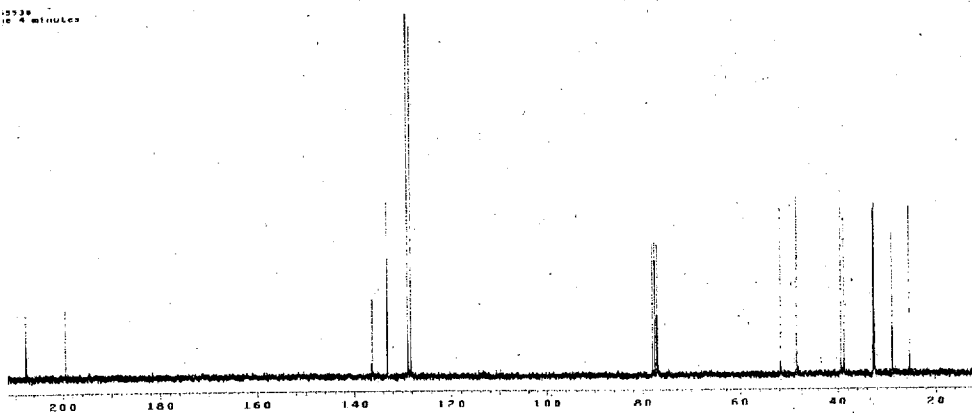


8c

1H NMR (400 MHz, CDCl₃)
 7.25 (d, 2H, ArH), 7.15 (d, 2H, ArH), 7.05 (d, 2H, ArH), 6.95 (d, 2H, ArH), 6.85 (d, 2H, ArH), 6.75 (d, 2H, ArH), 6.65 (d, 2H, ArH), 6.55 (d, 2H, ArH), 6.45 (d, 2H, ArH), 6.35 (d, 2H, ArH), 6.25 (d, 2H, ArH), 6.15 (d, 2H, ArH), 6.05 (d, 2H, ArH), 5.95 (d, 2H, ArH), 5.85 (d, 2H, ArH), 5.75 (d, 2H, ArH), 5.65 (d, 2H, ArH), 5.55 (d, 2H, ArH), 5.45 (d, 2H, ArH), 5.35 (d, 2H, ArH), 5.25 (d, 2H, ArH), 5.15 (d, 2H, ArH), 5.05 (d, 2H, ArH), 4.95 (d, 2H, ArH), 4.85 (d, 2H, ArH), 4.75 (d, 2H, ArH), 4.65 (d, 2H, ArH), 4.55 (d, 2H, ArH), 4.45 (d, 2H, ArH), 4.35 (d, 2H, ArH), 4.25 (d, 2H, ArH), 4.15 (d, 2H, ArH), 4.05 (d, 2H, ArH), 3.95 (d, 2H, ArH), 3.85 (d, 2H, ArH), 3.75 (d, 2H, ArH), 3.65 (d, 2H, ArH), 3.55 (d, 2H, ArH), 3.45 (d, 2H, ArH), 3.35 (d, 2H, ArH), 3.25 (d, 2H, ArH), 3.15 (d, 2H, ArH), 3.05 (d, 2H, ArH), 2.95 (d, 2H, ArH), 2.85 (d, 2H, ArH), 2.75 (d, 2H, ArH), 2.65 (d, 2H, ArH), 2.55 (d, 2H, ArH), 2.45 (d, 2H, ArH), 2.35 (d, 2H, ArH), 2.25 (d, 2H, ArH), 2.15 (d, 2H, ArH), 2.05 (d, 2H, ArH), 1.95 (d, 2H, ArH), 1.85 (d, 2H, ArH), 1.75 (d, 2H, ArH), 1.65 (d, 2H, ArH), 1.55 (d, 2H, ArH), 1.45 (d, 2H, ArH), 1.35 (d, 2H, ArH), 1.25 (d, 2H, ArH), 1.15 (d, 2H, ArH), 1.05 (d, 2H, ArH), 1.95 (d, 2H, ArH), 1.85 (d, 2H, ArH), 1.75 (d, 2H, ArH), 1.65 (d, 2H, ArH), 1.55 (d, 2H, ArH), 1.45 (d, 2H, ArH), 1.35 (d, 2H, ArH), 1.25 (d, 2H, ArH), 1.15 (d, 2H, ArH), 1.05 (d, 2H, ArH), 0.95 (d, 2H, ArH), 0.85 (d, 2H, ArH), 0.75 (d, 2H, ArH), 0.65 (d, 2H, ArH), 0.55 (d, 2H, ArH), 0.45 (d, 2H, ArH), 0.35 (d, 2H, ArH), 0.25 (d, 2H, ArH), 0.15 (d, 2H, ArH), 0.05 (d, 2H, ArH).



13C NMR (100 MHz, CDCl₃)
 199.1, 198.8, 198.5, 198.2, 197.9, 197.6, 197.3, 197.0, 196.7, 196.4, 196.1, 195.8, 195.5, 195.2, 194.9, 194.6, 194.3, 194.0, 193.7, 193.4, 193.1, 192.8, 192.5, 192.2, 191.9, 191.6, 191.3, 191.0, 190.7, 190.4, 190.1, 189.8, 189.5, 189.2, 188.9, 188.6, 188.3, 188.0, 187.7, 187.4, 187.1, 186.8, 186.5, 186.2, 185.9, 185.6, 185.3, 185.0, 184.7, 184.4, 184.1, 183.8, 183.5, 183.2, 182.9, 182.6, 182.3, 182.0, 181.7, 181.4, 181.1, 180.8, 180.5, 180.2, 179.9, 179.6, 179.3, 179.0, 178.7, 178.4, 178.1, 177.8, 177.5, 177.2, 176.9, 176.6, 176.3, 176.0, 175.7, 175.4, 175.1, 174.8, 174.5, 174.2, 173.9, 173.6, 173.3, 173.0, 172.7, 172.4, 172.1, 171.8, 171.5, 171.2, 170.9, 170.6, 170.3, 170.0, 169.7, 169.4, 169.1, 168.8, 168.5, 168.2, 167.9, 167.6, 167.3, 167.0, 166.7, 166.4, 166.1, 165.8, 165.5, 165.2, 164.9, 164.6, 164.3, 164.0, 163.7, 163.4, 163.1, 162.8, 162.5, 162.2, 161.9, 161.6, 161.3, 161.0, 160.7, 160.4, 160.1, 159.8, 159.5, 159.2, 158.9, 158.6, 158.3, 158.0, 157.7, 157.4, 157.1, 156.8, 156.5, 156.2, 155.9, 155.6, 155.3, 155.0, 154.7, 154.4, 154.1, 153.8, 153.5, 153.2, 152.9, 152.6, 152.3, 152.0, 151.7, 151.4, 151.1, 150.8, 150.5, 150.2, 149.9, 149.6, 149.3, 149.0, 148.7, 148.4, 148.1, 147.8, 147.5, 147.2, 146.9, 146.6, 146.3, 146.0, 145.7, 145.4, 145.1, 144.8, 144.5, 144.2, 143.9, 143.6, 143.3, 143.0, 142.7, 142.4, 142.1, 141.8, 141.5, 141.2, 140.9, 140.6, 140.3, 140.0, 139.7, 139.4, 139.1, 138.8, 138.5, 138.2, 137.9, 137.6, 137.3, 137.0, 136.7, 136.4, 136.1, 135.8, 135.5, 135.2, 134.9, 134.6, 134.3, 134.0, 133.7, 133.4, 133.1, 132.8, 132.5, 132.2, 131.9, 131.6, 131.3, 131.0, 130.7, 130.4, 130.1, 129.8, 129.5, 129.2, 128.9, 128.6, 128.3, 128.0, 127.7, 127.4, 127.1, 126.8, 126.5, 126.2, 125.9, 125.6, 125.3, 125.0, 124.7, 124.4, 124.1, 123.8, 123.5, 123.2, 122.9, 122.6, 122.3, 122.0, 121.7, 121.4, 121.1, 120.8, 120.5, 120.2, 119.9, 119.6, 119.3, 119.0, 118.7, 118.4, 118.1, 117.8, 117.5, 117.2, 116.9, 116.6, 116.3, 116.0, 115.7, 115.4, 115.1, 114.8, 114.5, 114.2, 113.9, 113.6, 113.3, 113.0, 112.7, 112.4, 112.1, 111.8, 111.5, 111.2, 110.9, 110.6, 110.3, 110.0, 109.7, 109.4, 109.1, 108.8, 108.5, 108.2, 107.9, 107.6, 107.3, 107.0, 106.7, 106.4, 106.1, 105.8, 105.5, 105.2, 104.9, 104.6, 104.3, 104.0, 103.7, 103.4, 103.1, 102.8, 102.5, 102.2, 101.9, 101.6, 101.3, 101.0, 100.7, 100.4, 100.1, 99.8, 99.5, 99.2, 98.9, 98.6, 98.3, 98.0, 97.7, 97.4, 97.1, 96.8, 96.5, 96.2, 95.9, 95.6, 95.3, 95.0, 94.7, 94.4, 94.1, 93.8, 93.5, 93.2, 92.9, 92.6, 92.3, 92.0, 91.7, 91.4, 91.1, 90.8, 90.5, 90.2, 89.9, 89.6, 89.3, 89.0, 88.7, 88.4, 88.1, 87.8, 87.5, 87.2, 86.9, 86.6, 86.3, 86.0, 85.7, 85.4, 85.1, 84.8, 84.5, 84.2, 83.9, 83.6, 83.3, 83.0, 82.7, 82.4, 82.1, 81.8, 81.5, 81.2, 80.9, 80.6, 80.3, 80.0, 79.7, 79.4, 79.1, 78.8, 78.5, 78.2, 77.9, 77.6, 77.3, 77.0, 76.7, 76.4, 76.1, 75.8, 75.5, 75.2, 74.9, 74.6, 74.3, 74.0, 73.7, 73.4, 73.1, 72.8, 72.5, 72.2, 71.9, 71.6, 71.3, 71.0, 70.7, 70.4, 70.1, 69.8, 69.5, 69.2, 68.9, 68.6, 68.3, 68.0, 67.7, 67.4, 67.1, 66.8, 66.5, 66.2, 65.9, 65.6, 65.3, 65.0, 64.7, 64.4, 64.1, 63.8, 63.5, 63.2, 62.9, 62.6, 62.3, 62.0, 61.7, 61.4, 61.1, 60.8, 60.5, 60.2, 59.9, 59.6, 59.3, 59.0, 58.7, 58.4, 58.1, 57.8, 57.5, 57.2, 56.9, 56.6, 56.3, 56.0, 55.7, 55.4, 55.1, 54.8, 54.5, 54.2, 53.9, 53.6, 53.3, 53.0, 52.7, 52.4, 52.1, 51.8, 51.5, 51.2, 50.9, 50.6, 50.3, 50.0, 49.7, 49.4, 49.1, 48.8, 48.5, 48.2, 47.9, 47.6, 47.3, 47.0, 46.7, 46.4, 46.1, 45.8, 45.5, 45.2, 44.9, 44.6, 44.3, 44.0, 43.7, 43.4, 43.1, 42.8, 42.5, 42.2, 41.9, 41.6, 41.3, 41.0, 40.7, 40.4, 40.1, 39.8, 39.5, 39.2, 38.9, 38.6, 38.3, 38.0, 37.7, 37.4, 37.1, 36.8, 36.5, 36.2, 35.9, 35.6, 35.3, 35.0, 34.7, 34.4, 34.1, 33.8, 33.5, 33.2, 32.9, 32.6, 32.3, 32.0, 31.7, 31.4, 31.1, 30.8, 30.5, 30.2, 29.9, 29.6, 29.3, 29.0, 28.7, 28.4, 28.1, 27.8, 27.5, 27.2, 26.9, 26.6, 26.3, 26.0, 25.7, 25.4, 25.1, 24.8, 24.5, 24.2, 23.9, 23.6, 23.3, 23.0, 22.7, 22.4, 22.1, 21.8, 21.5, 21.2, 20.9, 20.6, 20.3, 20.0, 19.7, 19.4, 19.1, 18.8, 18.5, 18.2, 17.9, 17.6, 17.3, 17.0, 16.7, 16.4, 16.1, 15.8, 15.5, 15.2, 14.9, 14.6, 14.3, 14.0, 13.7, 13.4, 13.1, 12.8, 12.5, 12.2, 11.9, 11.6, 11.3, 11.0, 10.7, 10.4, 10.1, 9.8, 9.5, 9.2, 8.9, 8.6, 8.3, 8.0, 7.7, 7.4, 7.1, 6.8, 6.5, 6.2, 5.9, 5.6, 5.3, 5.0, 4.7, 4.4, 4.1, 3.8, 3.5, 3.2, 2.9, 2.6, 2.3, 2.0, 1.7, 1.4, 1.1, 0.8, 0.5, 0.2, 0.0.



x-Ray Crystallographic Material for 1b.

X-ray Experimental.

Table 1. Crystallographic Data for **1b**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$) for the non-hydrogen atoms of **1b**.

Table 3. Bond Lengths ($\text{\AA}$) and Angles ($^\circ$) for the non-hydrogen atoms of **1b**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of **1b**.

Table 5. Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the hydrogen atoms of **1b**.

Table 6. Observed and calculated structure factor amplitudes for **1b**. Values for F_o , F_c and $\sigma(F_o)$ have been multiplied by 10.

Figure 1. View of **1b** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms are drawn to an arbitrary size.

Figure 2. View of the H-bound dimer formed by **1b**. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms are drawn to an arbitrary size. Dashed lines indicate the H-bonding interactions. The two molecules are related by a crystallographic inversion center at 0, 0, $\frac{1}{2}$. The geometry of the interaction is: O1-H1O $\cdots$ O2 (related by $-x, -y, 1-z$), O $\cdots$ O 2.859(1) $\text{\AA}$, H $\cdots$ O 1.99(2) $\text{\AA}$, O-H $\cdots$ O 161(2) $^\circ$.

Figure 3. Unit cell packing diagram for **1b**. The view is approximately down the **b** axis.

X-ray Experimental for $C_{13}H_{16}O_2$: Crystals grew as colorless prisms by slow evaporation from ethylacetate and hexanes. The data crystal was cut into a trigonal prism that had approximate dimensions; 0.33 x 0.33 x 0.10 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 309 frames of data were collected using ω -scans with a scan range of 1° and a counting time of 39 seconds per frame. The data were collected at -120°C using a Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.¹ The structure was solved by direct methods using SIR92² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.³ The hydrogen atom positions were located in a ΔF map and refined with isotropic displacement parameters. The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0472*P)^2 + (0.1494*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.100, with $R(F)$ equal to 0.0386 and a goodness of fit, S , = 1.033. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁴ The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_o/[1 + (2.7(5) \times 10^{-5}) * F_o^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁵ All figures were generated using SHELXTL/PC.⁶ Tables of positional and thermal parameters, bond lengths and angles, figures and lists of observed and calculated structure factors are located in tables 1 through 6.

References

- 1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, *Methods in Enzymology*, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweet, Editors, Academic Press.
- 2) SIR92. (1993). A program for crystal structure solution. Altomare, A., Casciarano, G., Giacovazzo, C. & Guagliardi, A. *J. Appl. Cryst.* **26**, 343-350.
- 3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
- 4) $R_w(F^2) = \{ \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2) \}^{1/2}$ where w is the weight given each reflection.
 $R(F) = \sum (|F_o| - |F_c|) / \sum |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
- 5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for **1b**.

Empirical formula	C13 H16 O2	
Formula weight	204.26	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 9.9320(4) Å	$\alpha = 90^\circ$
	b = 9.2240(4) Å	$\beta = 92.967(3)^\circ$
	c = 12.1770(5) Å	$\gamma = 90^\circ$
Volume	1114.07(8) Å ³	
Z	4	
Density (calculated)	1.218 Mg/m	
Absorption coefficient	0.081 mm ⁻¹	
F(000)	440	
Crystal size	0.33 x 0.33 x 0.10 mm ³	
Theta range for data collection	3.02 to 27.49°	
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 11, -15 ≤ l ≤ 15	
Reflections collected	4501	
Independent reflections	2483 [R(int) = 0.0198]	
Completeness to theta = 27.49°	97.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2483 / 0 / 201	
Goodness-of-fit on F ²	1.033	
Final R indices [I > 2σ(I)]	R1 = 0.0386, wR2 = 0.0902	
R indices (all data)	R1 = 0.0614, wR2 = 0.1002	
Extinction coefficient	2.7(5) × 10 ⁻⁵	
Largest diff. peak and hole	0.177 and -0.184 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O1	-662(1)	-26(1)	6708(1)	31(1)
O2	1997(1)	643(1)	5376(1)	36(1)
C1	-390(1)	1407(1)	7101(1)	25(1)
C2	586(1)	2216(1)	6363(1)	24(1)
C3	-117(1)	2620(1)	5255(1)	29(1)
C4	-1373(1)	3527(2)	5420(1)	35(1)
C5	-2356(1)	2708(2)	6113(1)	35(1)
C6	-1674(1)	2293(2)	7219(1)	32(1)
C7	1840(1)	1322(1)	6225(1)	26(1)
C8	2920(1)	1257(1)	7132(1)	26(1)
C9	2870(1)	2071(1)	8092(1)	29(1)
C10	3912(1)	1984(2)	8899(1)	35(1)
C11	5001(1)	1087(2)	8747(1)	39(1)
C12	5060(1)	275(2)	7798(1)	41(1)
C13	4027(1)	356(2)	6993(1)	34(1)

Table 3. Bond lengths [Å] and angles [°] for **1b**.

O1-C1	1.4270(15)	C5-H5A	0.985(14)
O1-H1O	0.91(2)	C5-H5B	0.997(15)
O2-C7	1.2256(14)	C6-H6A	0.991(15)
C1-C6	1.5271(17)	C6-H6B	0.992(14)
C1-C2	1.5474(16)	C7-C8	1.5006(15)
C1-H1	1.006(12)	C8-C9	1.3916(17)
C2-C7	1.5099(16)	C8-C13	1.3958(17)
C2-C3	1.5322(16)	C9-C10	1.3926(17)
C2-H2	0.982(13)	C9-H9	0.978(13)
C3-C4	1.5238(18)	C10-C11	1.3818(19)
C3-H3A	0.990(14)	C10-H10	0.987(15)
C3-H3B	1.015(15)	C11-C12	1.380(2)
C4-C5	1.524(2)	C11-H11	0.985(15)
C4-H4A	1.008(16)	C12-C13	1.3842(19)
C4-H4B	0.996(16)	C12-H12	1.004(17)
C5-C6	1.5248(18)	C13-H13	0.967(15)
C1-O1-H1O	110.6(11)	C2-C3-H3B	108.4(8)
O1-C1-C6	112.49(10)	H3A-C3-H3B	107.8(11)
O1-C1-C2	111.45(9)	C5-C4-C3	110.70(11)
C6-C1-C2	110.40(10)	C5-C4-H4A	109.7(8)
O1-C1-H1	104.8(7)	C3-C4-H4A	110.4(8)
C6-C1-H1	108.7(7)	C5-C4-H4B	110.5(9)
C2-C1-H1	108.8(7)	C3-C4-H4B	110.9(9)
C7-C2-C3	112.07(10)	H4A-C4-H4B	104.5(12)
C7-C2-C1	110.27(9)	C6-C5-C4	110.22(11)
C3-C2-C1	110.94(9)	C6-C5-H5A	110.0(8)
C7-C2-H2	109.0(7)	C4-C5-H5A	109.7(7)
C3-C2-H2	108.6(7)	C6-C5-H5B	109.5(8)
C1-C2-H2	105.8(7)	C4-C5-H5B	111.0(8)
C4-C3-C2	110.87(10)	H5A-C5-H5B	106.4(11)
C4-C3-H3A	110.3(7)	C5-C6-C1	112.70(10)
C2-C3-H3A	109.2(7)	C5-C6-H6A	109.3(8)
C4-C3-H3B	110.2(8)	C1-C6-H6A	107.6(7)

C5-C6-H6B	111.3(7)
C1-C6-H6B	106.2(8)
H6A-C6-H6B	109.6(11)
O2-C7-C8	118.90(10)
O2-C7-C2	120.96(10)
C8-C7-C2	120.15(10)
C9-C8-C13	119.07(11)
C9-C8-C7	122.77(11)
C13-C8-C7	118.16(11)
C8-C9-C10	120.28(12)
C8-C9-H9	120.2(7)
C10-C9-H9	119.5(8)
C11-C10-C9	119.85(13)
C11-C10-H10	120.4(8)
C9-C10-H10	119.7(8)
C12-C11-C10	120.33(12)
C12-C11-H11	120.7(8)
C10-C11-H11	119.0(9)
C11-C12-C13	120.09(13)
C11-C12-H12	119.6(10)
C13-C12-H12	120.3(10)
C12-C13-C8	120.37(13)
C12-C13-H13	121.4(8)
C8-C13-H13	118.2(8)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	39(1)	26(1)	29(1)	3(1)	-4(1)	-5(1)
O2	36(1)	43(1)	30(1)	-12(1)	0(1)	3(1)
C1	29(1)	27(1)	20(1)	0(1)	-2(1)	-2(1)
C2	29(1)	22(1)	22(1)	-2(1)	-1(1)	-2(1)
C3	36(1)	27(1)	24(1)	3(1)	-1(1)	0(1)
C4	44(1)	31(1)	30(1)	1(1)	-7(1)	8(1)
C5	31(1)	41(1)	33(1)	-5(1)	-5(1)	9(1)
C6	30(1)	39(1)	27(1)	-3(1)	2(1)	1(1)
C7	29(1)	24(1)	25(1)	-1(1)	3(1)	-5(1)
C8	25(1)	25(1)	28(1)	1(1)	2(1)	-4(1)
C9	25(1)	33(1)	30(1)	-2(1)	2(1)	-2(1)
C10	32(1)	44(1)	30(1)	-5(1)	-2(1)	-5(1)
C11	28(1)	49(1)	38(1)	3(1)	-7(1)	-3(1)
C12	29(1)	44(1)	50(1)	-2(1)	-2(1)	6(1)
C13	31(1)	35(1)	37(1)	-6(1)	1(1)	1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1b**.

	x	y	z	U(eq)
H1O	-1051(18)	-3(19)	6017(16)	63(5)
H1	66(11)	1269(13)	7850(10)	24(3)
H2	836(11)	3112(15)	6758(10)	24(3)
H3A	-359(12)	1722(16)	4846(10)	28(3)
H3B	544(14)	3183(16)	4810(12)	41(4)
H4A	-1121(13)	4476(17)	5786(11)	39(4)
H4B	-1817(14)	3810(17)	4700(13)	48(4)
H5A	-2676(12)	1832(16)	5719(11)	31(3)
H5B	-3172(14)	3305(16)	6236(11)	41(4)
H6A	-1422(12)	3185(16)	7635(11)	33(3)
H6B	-2275(13)	1688(15)	7656(11)	36(4)
H9	2107(13)	2717(14)	8200(10)	31(3)
H10	3876(13)	2578(15)	9571(12)	39(4)
H11	5732(15)	1040(16)	9323(12)	44(4)
H12	5859(17)	-368(19)	7695(13)	58(5)
H13	4041(13)	-216(15)	6328(13)	38(4)

Figure 1. View of **1b** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms are drawn to an arbitrary size.

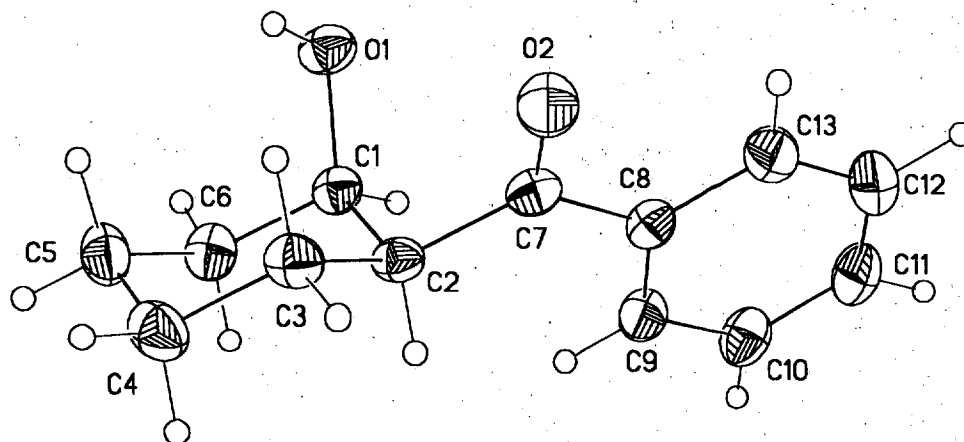


Figure 2. View of the H-bound dimer formed by **1b**. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms are drawn to an arbitrary size. Dashed lines indicate the H-bonding interactions. The two molecules are related by a crystallographic inversion center at 0, 0, ½. The geometry of the interaction is: O1-H1O $\cdots$ O2 (related by $-x, -y, 1-z$), O $\cdots$ O 2.859(1)Å, H $\cdots$ O 1.99(2)Å, O-H $\cdots$ O 161(2)°.

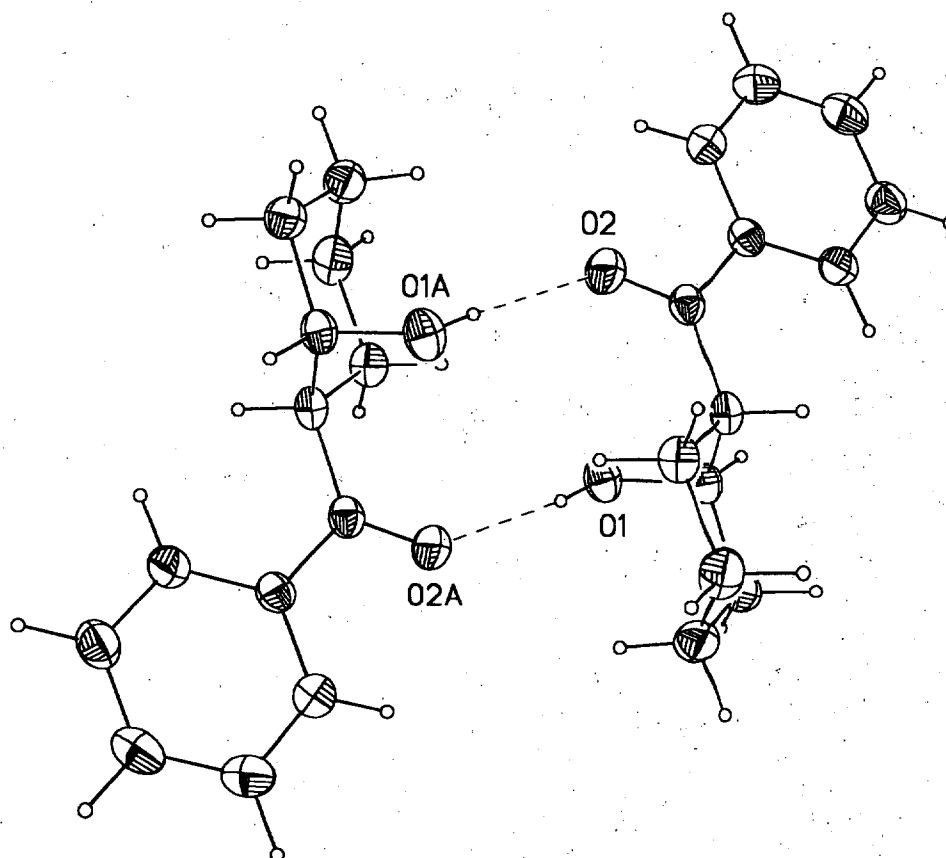
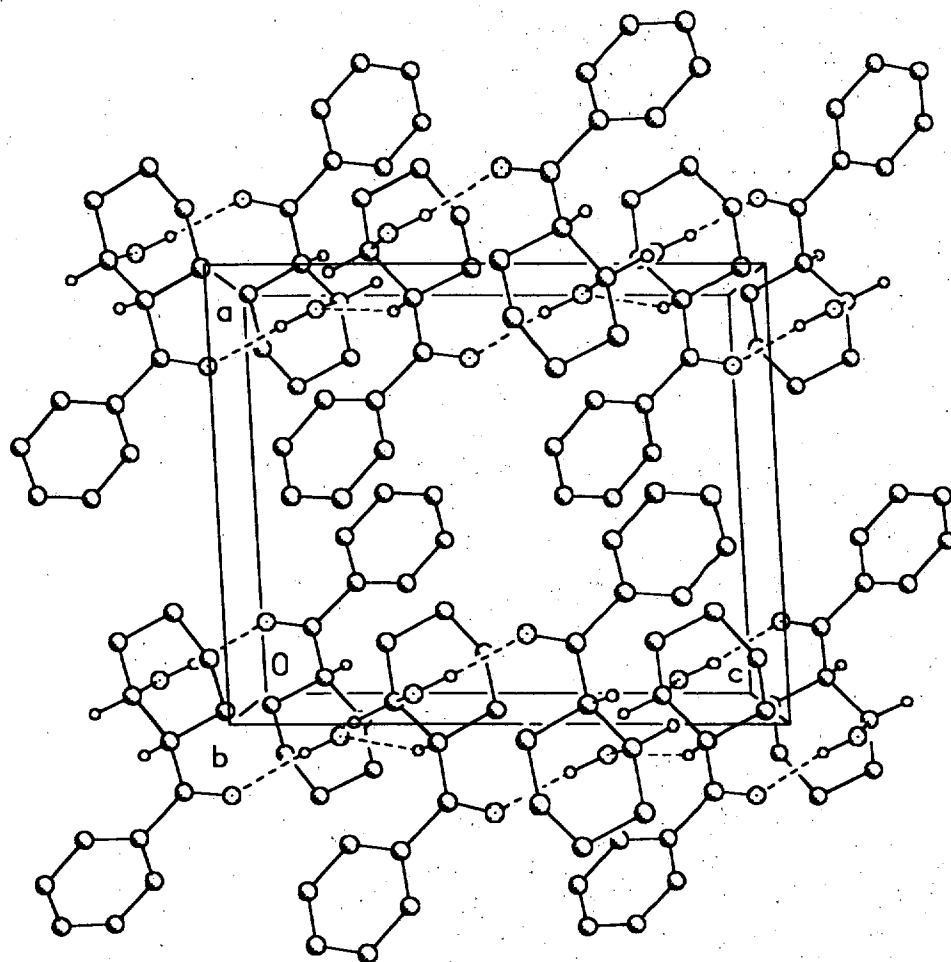


Figure 3. Unit cell packing diagram for **1b**. The view is approximately down the **b** axis.



Crystallographic Material for Co(dpm)₂.

X-ray Experimental

Table 1. Crystallographic Data for Co(dpm)₂.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$) for the non-hydrogen atoms of Co(dpm)₂.

Table 3. Bond Lengths ($\text{\AA}$) and Angles ($^\circ$) for the non-hydrogen atoms of Co(dpm)₂.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of Co(dpm)₂.

Table 5. Fractional coordinates and isotropic thermal parameters ($\text{\AA}^2$) for the hydrogen atoms of Co(dpm)₂.

Table 6. Observed and calculated structure factor amplitudes for Co(dpm)₂. Values for F_o , F_c and $\sigma(F_o)$ have been multiplied by 10.

Figure 1. View of Co(dpm)₂ showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

Figure 2. Unit cell packing diagram for Co(dpm)₂. The view is approximately down the **a** axis.

X-ray Experimental for $C_{22}H_{38}CoO_4$: Crystals grew as beautiful violet prism by sublimation. The data crystal was cut from a larger crystal and had approximate dimensions; .20 x .20 x .15 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with $MoK\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). A total of 310 frames of data were collected using ω -scans with a scan range of 1.0° and a counting time of 38 seconds per frame. The data were collected at -120°C using a Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.¹ The structure was solved by direct methods using SIR92² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.³ The hydrogen atom positions were observed in a ΔF map and refined with isotropic displacement parameters. The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0349 \cdot P)^2 + (1.3386 \cdot P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0674, with $R(F)$ equal to 0.0248 and a goodness of fit, S , = 1.040. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁴ Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁵ All figures were generated using SHELXTL/PC.⁶ Tables of positional and thermal parameters, bond lengths and angles, figures and lists of observed and calculated structure factors are located in tables 1 through 6.

References

- 1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.
- 2) SIR92. (1993). A program for crystal structure solution. Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. J. Appl. Cryst. **26**, 343-350.
- 3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
- 4) $R_w(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^4)\}^{1/2}$ where w is the weight given each reflection.
 $R(F) = \sum(|F_o| - |F_c|) / \sum |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
- 5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for Co(dpm)₂.

Empirical formula	C ₂₂ H ₃₈ Co O ₄	
Formula weight	425.45	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I4 ₁ /a	
Unit cell dimensions	a = 10.4718(2) Å	α = 90°.
	b = 10.4718(2) Å	β = 90°.
	c = 21.7983(3) Å	γ = 90°.
Volume	2390.37(7) Å ³	
Z	4	
Density (calculated)	1.182 Mg/m ³	
Absorption coefficient	0.739 mm ⁻¹	
F(000)	916	
Crystal size	0.20 x 0.20 x 0.15 mm ³	
Theta range for data collection	3.3 to 27.5°.	
Index ranges	-13 ≤ h ≤ 13, -9 ≤ k ≤ 9, -28 ≤ l ≤ 22	
Reflections collected	2351	
Independent reflections	1376 [R(int) = 0.0111]	
Completeness to theta = 27.49°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1376 / 0 / 100	
Goodness-of-fit on F ²	1.040	
Final R indices [I > 2σ(I)]	R ₁ = 0.0248, wR ₂ = 0.0655	
R indices (all data)	R ₁ = 0.0286, wR ₂ = 0.0674	
Largest diff. peak and hole	0.24 and -0.22 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Co(dpm)_2 . $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Co	5000	7500	6250	23(1)
O1	4450(1)	6249(1)	6847(1)	26(1)
C1	5000	7500	7713(1)	27(1)
C2	4536(1)	6400(1)	7428(1)	23(1)
C3	4044(1)	5287(1)	7820(1)	30(1)
C4	2753(1)	5689(2)	8088(1)	42(1)
C5	4973(2)	4978(2)	8343(1)	49(1)
C6	3856(2)	4097(2)	7424(1)	53(1)

Table 3. Bond lengths [Å] and angles [°] for Co(dpm)₂.

Co-O1#1	1.9334(8)	C2-C1-H1	116.48(7)
Co-O1	1.9334(8)	C2#1-C1-H1	116.48(8)
Co-O1#2	1.9334(8)	O1-C2-C1	124.56(11)
Co-O1#3	1.9334(8)	O1-C2-C3	115.79(11)
O1-C2	1.2794(13)	C1-C2-C3	119.61(11)
C1-C2	1.3972(14)	C6-C3-C4	108.99(14)
C1-C2#1	1.3972(14)	C6-C3-C5	109.24(14)
C1-H1	0.86(3)	C4-C3-C5	109.57(12)
C2-C3	1.5345(16)	C6-C3-C2	110.30(11)
C3-C6	1.530(2)	C4-C3-C2	107.49(10)
C3-C4	1.5314(18)	C5-C3-C2	111.21(11)
C3-C5	1.5333(19)	C3-C4-H4A	110.3(11)
C4-H4A	0.94(2)	C3-C4-H4B	110.5(11)
C4-H4B	0.99(2)	H4A-C4-H4B	106.9(15)
C4-H4C	0.99(2)	C3-C4-H4C	109.5(12)
C5-H5A	0.98(2)	H4A-C4-H4C	107.6(16)
C5-H5B	0.95(2)	H4B-C4-H4C	112.1(15)
C5-H5C	0.98(2)	C3-C5-H5A	110.8(11)
C6-H6A	0.99(2)	C3-C5-H5B	110.4(14)
C6-H6B	1.05(2)	H5A-C5-H5B	108.0(16)
C6-H6C	0.99(2)	C3-C5-H5C	111.8(12)
		H5A-C5-H5C	107.6(16)
O1#1-Co-O1	95.46(5)	H5B-C5-H5C	108.1(18)
O1#1-Co-O1#2	116.90(3)	C3-C6-H6A	107.7(12)
O1-Co-O1#2	116.90(3)	C3-C6-H6B	108.8(12)
O1#1-Co-O1#3	116.90(3)	H6A-C6-H6B	112.0(16)
O1-Co-O1#3	116.90(3)	C3-C6-H6C	108.3(11)
O1#2-Co-O1#3	95.46(5)	H6A-C6-H6C	108.9(15)
C2-O1-Co	124.17(8)	H6B-C6-H6C	111.0(16)
C2-C1-C2#1	127.03(15)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+3/2,z #2 -y+5/4,x+1/4,-z+5/4 #3 y-1/4,-x+5/4,-z+5/4

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Co(dpm)_2 . The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co	29(1)	29(1)	12(1)	0	0	0
O1	31(1)	32(1)	16(1)	2(1)	-2(1)	-3(1)
C1	32(1)	37(1)	12(1)	0	0	7(1)
C2	20(1)	34(1)	17(1)	5(1)	2(1)	7(1)
C3	28(1)	38(1)	25(1)	11(1)	3(1)	5(1)
C4	27(1)	58(1)	43(1)	18(1)	8(1)	4(1)
C5	34(1)	69(1)	45(1)	35(1)	-4(1)	3(1)
C6	79(1)	33(1)	47(1)	10(1)	13(1)	-5(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)
for Co(dpm)_2 .

	x	y	z	U(eq)
H1	5000	7500	8110(12)	41(6)
H4A	2188(18)	5919(18)	7772(9)	53(5)
H4B	2353(18)	4965(18)	8311(8)	55(5)
H4C	2870(19)	6449(19)	8355(9)	62(6)
H5A	4679(18)	4235(19)	8577(9)	54(5)
H5B	5800(20)	4790(20)	8184(10)	79(7)
H5C	5060(20)	5690(20)	8631(9)	64(6)
H6A	4700(20)	3852(18)	7256(9)	61(6)
H6B	3200(20)	4310(20)	7077(10)	74(6)
H6C	3538(18)	3396(19)	7690(9)	57(5)

Figure 1. View of $\text{Co}(\text{dpm})_2$ showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. The Co atom lies on a crystallographic four-fold inversion center at $1/2, 3/4, 5/8$.

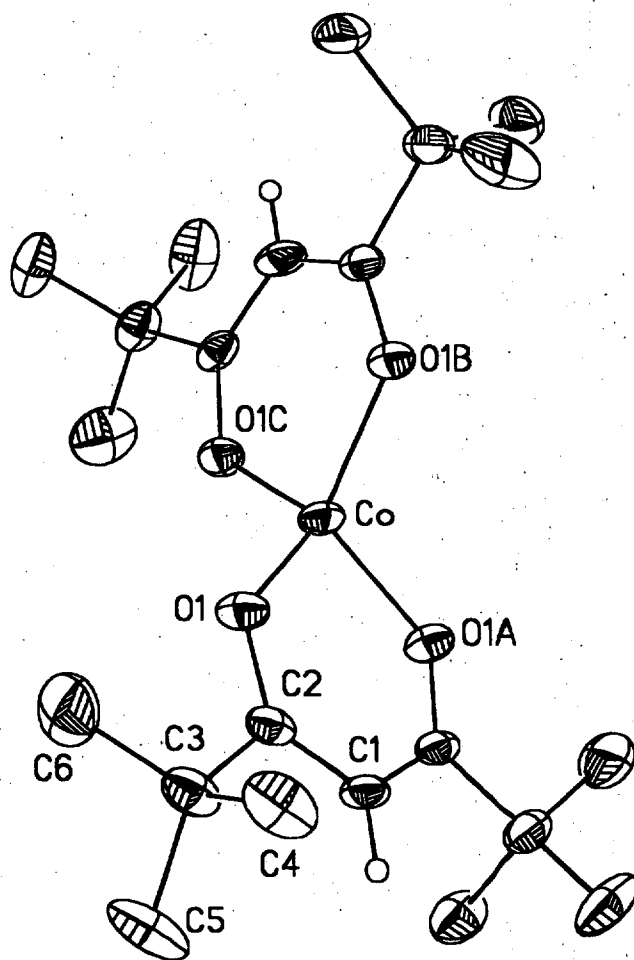
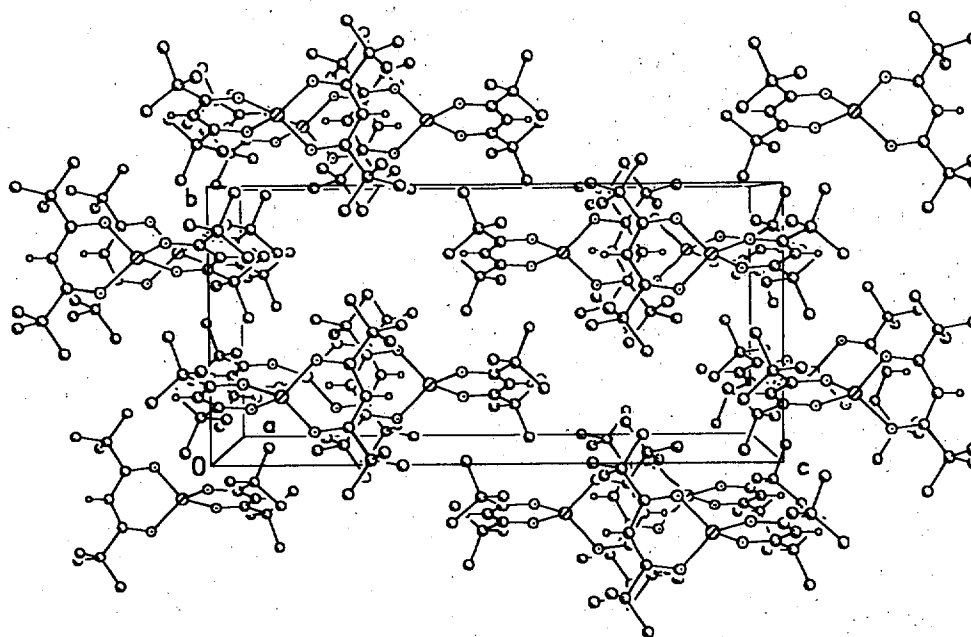


Figure 2. Unit cell packing diagram for Co(dpm)_2 . The view is approximately down the a axis.



Neutron structure determination of $C_{13}H_{15}D_1O_2$ (1b) at 20 K. Neutron diffraction data were collected from a single crystal of (1b) (26.2 mg, $3.9 \times 3.2 \times 1.7$ mm³) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. The single-crystal diffractometer (SCD) is a time-of-flight (TOF) instrument with a time- and position-sensitive detector. Neutrons were produced by the pulsed (30 Hz) spallation source at IPNS, and the SCD instrument used the entire thermal spectrum of neutrons from each pulse. The SCD position-sensitive neutron detector contained a ⁶Li glass scintillator with dimensions of 30×30 cm². For a given crystal setting, data were stored in a three-dimensional histogram in which each point had coordinates x , y , and t . These quantities were the horizontal and vertical detector positions and the TOF, respectively. t is related to the neutron wavelength λ by the de Broglie equation $\lambda = (h/m)(t/l)$, in which h is Planck's constant, m is the neutron mass, and l is the path length traversed in time t . There were 120 time-of-flight channels in each histogram, constructed in such a way that $\Delta t/t$ had a constant value of 0.015. Each histogram comprised measurements of a three-dimensional block of reciprocal space, from neutrons in the wavelength range of 0.71–4.2 Å. A detailed description of the SCD instrument and data collection and analysis procedures has been published.^{1,2} The sample temperature is controlled at 20 K by a Displex® closed-cycle helium refrigerator (Air Products and Chemicals, Inc., Model CS-202).

An auto-indexing algorithm³ was used to obtain an initial orientation matrix from the peaks in one histogram. For intensity data collection, a total of 25 histograms were measured - each for a different crystal setting - in order to cover a quartet of reciprocal space. Bragg peaks were integrated in three dimensions about their predicted locations and were corrected for the incident neutron spectrum, detector efficiency, and dead-time loss. Lorenz and absorption corrections were also applied. Non-hydrogen atomic coordinates from X-ray analysis was used as starting solution for the neutron structure. The GSAS software package⁴ was used for structural analysis. The refinement was based on F using 2966 reflections with $|F_o| > 2\sigma(F_o)$ and a minimum d spacing of 0.65 Å. Weights were assigned as $wF_o = (1/(\sigma(F_o)^2 + (0.002 F_o^2)^2))^2$ where $\sigma^2(F_o^2)$ is the variance based on counting statistics. Hydrogen atoms at β -position of 1b, namely H(3A) and H(3B), were refined as fully occupied at the beginning, which gave a high residual R

values of $R_w(F) = 0.135$ and $R(F) = 0.094$. In addition, the thermal parameters for these two hydrogen atoms were 10 times greater than those of hydrogen atoms in the adjacent positions. Subsequent refinement has deuterium atoms included at β -position, with the total occupancy of each site being constraint to unity. The refinement used 307 variables and converged successfully to $R_w(F) = 0.088$ and $R(F) = 0.071$. All atoms were refined with anisotropic atomic displacement parameters at the final stage. Here we are able to distinguish hydrogen from deuterium easily because the neutron scattering lengths of hydrogen and deuterium are significantly different (-3.739 for H and $+6.671$ for D).

A summary of parameters related to the neutron diffraction analysis is presented in Table 1. Selected bond distances and angles are listed in Table 2. Table 3 lists the site occupancies of H and D atoms at the β -position. The ratio of hydrogen to deuterium at the β -position with respect to the carbonyl is found to be $0.976(9)$ from neutron diffraction data, corresponding to $1.012(9)$ deuterium being incorporated into the product. Neutron structural analysis also shows that the product is a mixture of stereo isomers with 52% of the deuterium up and 48% down. A plot of the molecules of **1b** is shown in Figure 1.

References

- (1) Schultz, A. J.; Van Derveer, D. G.; Parker, D. W.; Baldwin, J. E. *Acta Crystallogr., Sect. C* **1990**, *C46*, 276.
- (2) Schultz, A. J. *Trans. Am. Cryst. Assoc.* **1993**, *29*, 29.
- (3) Jacobson, R. A. *J. Appl. Cryst.* **1986**, *19*, 283.
- (4) Larson, A. C.; Von Dreele R. B. *GSAS General Structural Analysis System*. Los Alamos National Laboratory, New Mexico, 2000.

Table 1. Neutron Crystal Data and Structural Refinement Parameters for **1b**.

formula	C ₁₃ H ₁₅ O ₂ D ₁
fw	205.271
temperature, K	20(2)
crystal system	<i>monoclinic</i>
space group	<i>P2₁/c</i>
<i>a</i> , Å	9.842(1)
<i>b</i> , Å	9.236(1)
<i>c</i> , Å	12.168(2)
α , °	90
β , °	92.31(1)
γ , °	90
<i>V</i> , Å ³	1105.2(6)
<i>Z</i>	4
<i>d</i> _{calc} , g cm ⁻³	1.234
size, mm ³	3.9 × 3.2 × 1.7
radiation	neutrons
data collection technique	time-of-flight Laue
$\mu(\lambda)$, cm ⁻¹	1.445 + 1.048 λ
no. of reflns. (<i>I</i> > 2 σ (<i>I</i>))	2966
no. of parameters refined	307
refinement method	Full-matrix least-squares on <i>F</i>
<i>R</i> indices <i>Rw</i> (<i>F</i>) ^a <i>R</i> (<i>F</i>) ^b	0.088, 0.071
goodness-of-fit	1.97

$$^a R_w(F) = \left\{ \sum [w(F_o - F_c)^2] / \sum [w(F_o)^2] \right\}^{1/2}$$

$$^b R(F) = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$$

Table 2. Selected Bond Distances (Å), Bond Angles (°) for **1b**.

O1—C1	1.4357(26)	C7—C2	1.5172(23)
O2—C7	1.2407(26)	C7—C8	1.5066(23)
C1—O1	1.4357(26)	C8—C9	1.4085(25)
C1—C2	1.5637(24)	C8—C13	1.4140(24)
C1—C6	1.5311(25)	C9—C10	1.3994(25)
C3—C2	1.5419(25)	C10—C11	1.4049(24)
C3—C4	1.5299(25)	C11—C10	1.4049(24)
C4—C5	1.5361(25)	C11—C12	1.4092(26)
C5—C6	1.5399(26)	C12—C13	1.3967(25)
H1O—O1	0.989(5)	H6A—C6	1.124(4)
H1—C1	1.101(4)	H6B—C6	1.108(5)
H2—C2	1.108(4)	H9—C9	1.095(4)
H3A—C3	1.126(8)	H10—C10	1.093(5)
H3B—C3	1.087(10)	H11—C11	1.092(5)
H4A—C4	1.105(4)	H12—C12	1.082(4)
H4B—C4	1.113(4)	H13—C13	1.087(5)
H5A—C5	1.101(4)	D3A—C3	1.126(8)
H5B—C5	1.100(4)	D3B—C3	1.087(10)
O1—C1—C2	111.79(15)	C6—C5—H5B	109.31(28)
O1—C1—H1	105.18(26)	H5A—C5—H5B	106.3(4)
C2—C1—H1	108.86(25)	C1—C6—C5	112.72(15)
C1—C2—C3	110.95(14)	C1—C6—H6A	107.49(26)
C1—C2—C7	110.54(13)	C1—C6—H6B	108.72(27)
C1—C2—H2	106.04(25)	C5—C6—H6A	109.51(26)
C3—C2—C7	111.68(14)	C5—C6—H6B	110.56(27)
C3—C2—H2	108.48(26)	H6A—C6—H6B	107.7(4)
C7—C2—H2	108.95(25)	O2—C7—C2	121.33(17)
C2—C3—C4	110.71(15)	O2—C7—C8	119.06(17)
C2—C3—H3A	110.8(4)	C2—C7—C8	119.61(14)
C2—C3—H3B	108.0(6)	C7—C8—C9	122.85(15)
C2—C3—D3A	110.8(4)	C7—C8—C13	117.94(15)
C2—C3—D3B	108.0(6)	C9—C8—C13	119.21(16)
C4—C3—H3A	108.3(4)	C8—C9—C10	120.39(16)
C4—C3—H3B	111.9(5)	C8—C9—H9	120.75(28)
C4—C3—D3A	108.3(4)	C10—C9—H9	118.82(27)
C4—C3—D3B	111.9(5)	C9—C10—C11	119.98(16)
H3A—C3—D3B	107.0(7)	C9—C10—H10	120.04(28)
H3B—C3—D3A	107.0(7)	C11—C10—H10	119.97(28)
C3—C4—C5	110.83(14)	C10—C11—C12	120.15(17)
C3—C4—H4A	109.95(28)	C10—C11—H11	119.82(30)
C3—C4—H4B	109.73(27)	C12—C11—H11	120.03(30)
C5—C4—H4A	108.52(29)		

C5—C4—H4B	111.85(27)	C11—C12—C13	119.69(16)
H4A—C4—H4B	105.8(4)	C11—C12—H12	120.76(29)
C4—C5—C6	110.49(14)	C13—C12—H12	119.55(29)
C4—C5—H5A	109.52(29)	C8—C13—C12	120.57(16)
C4—C5—H5B	110.92(28)	C8—C13—H13	119.17(28)
C6—C5—H5A	110.23(27)	C12—C13—H13	120.26(28)

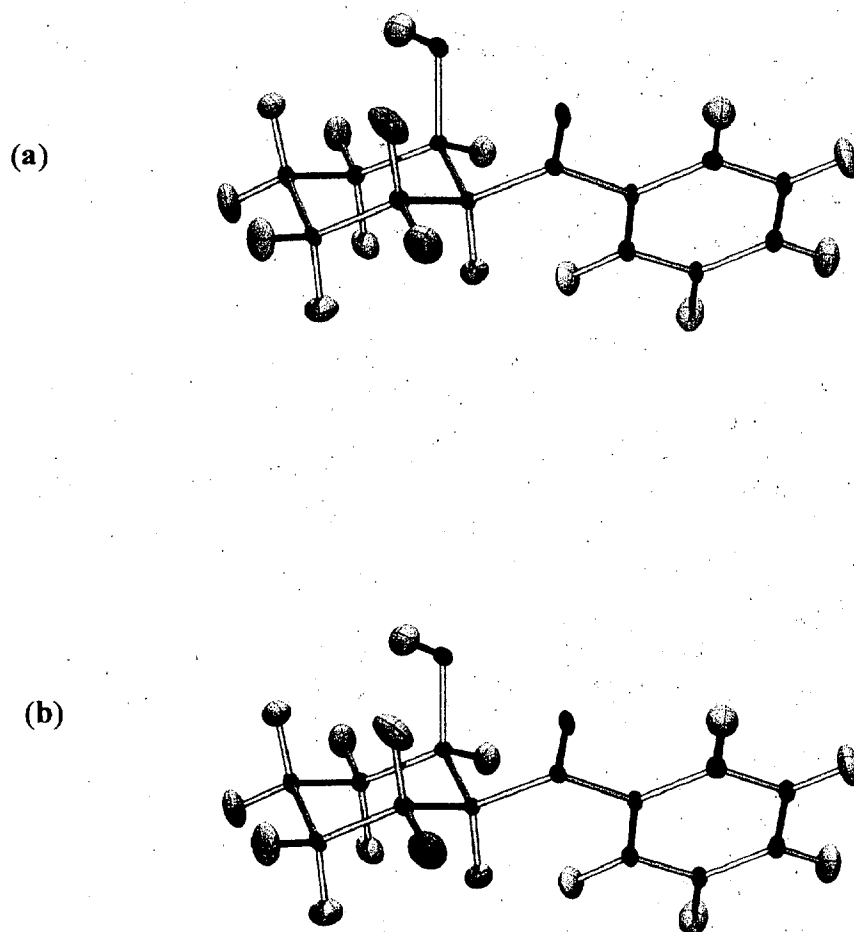


Figure 1. Perspective view of the molecules of $C_{13}H_{15}D_1O_2$ in (1b). Atoms are drawn at their 50% probability level. (a) Deuterium atom at up position. (b) Deuterium atom at down position (D3B)

Table 3. Site occupancies of H and D atoms at the β -position

Name	Occupancy	Total	Total H/D ratio	site H/D ratio	D(up)/D(down) ratio
H3A	0.476(6)	0.988(9)		0.908(9)	
H3B	0.512(6)			1.049(9)	
D3A	0.524(6)	1.012(9)			0.518 (up)
D3B	0.488(6)				0.482 (down)
			0.976(9)		