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The X-ray Crystal and Molecular Structure of 2-Methylpiperidinepentacarbonyltungsten

JAMES D. KORP, IVAN BERNAL*

Chemistry Department, University of Houston, Houston, Tex. 77004, U.S.A.

JERRY L. MILLS and HARRY T. WEAVER, Jr.

Chemistry Department, Texas Tech University, Lubbock, Tex. 79409, U.S.A.

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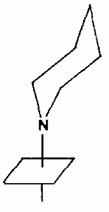
The X-ray crystal structure of 2-methylpiperidinepentacarbonyltungsten has been determined from single crystal diffraction data. The compound crystallizes in the monoclinic space group $P2_1$ *with four molecules in a unit cell having dimensions* a = *8.565(3),* b = *11.617(4),* c = *13.925(4) Å, and* β = *91.84°. The structure was solved by the Patterson method and refined to a final* R *value of 4.6%. The chirality of the molecule is (*S*) at position 2 and (*S*) at the prochiral N, for the enantiomer which preferentially precipitates as a diastereoisomeric salt with (*R,R*)-tartaric acid. The ring is in the chair conformation. The equatorial carbonyls are all bent away from the 2-Me-Pip ring such that W is 0.08 Å out of the plane of the carbons. The average W–C(axial) distance is about 0.1 Å shorter than the W–C(eq) average, indicative of carbonyl having a greater affinity for the metal electrons than piperidine. A CD spectrum showed no optical rotation induced on the visible-UV bands of the complex, probably due to dissociation of the piperidine ligand in solution.*

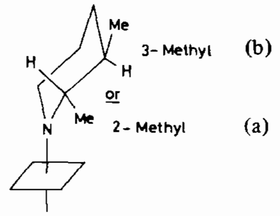
Introduction

If a molecule such as $Mo(CO)_6$ reacts with piperidine [1] one can isolate the carbonyl monosubstituted species (I) which, in solution and for two explicit orientations of the N–H moiety (eclipsing or bisecting carbonyls of the basal plane), has a mirror plane passing through the metal atom.

However, if one uses the 2- or 3-methylpiperidine derivative, the monosubstituted products (II) are optically active diastereoisomeric species containing asymmetric centers at the chiral carbon (C2 or C3), the piperidine N (which is a prochiral center in the free ligand), and the metal atom. An important and interesting question, thus far never probed to our knowledge, is, 'How much of a rotational strength is induced at the metal center upon using the enantiomeric 2- or 3-methylpiperidine ligand as the reagent?' That is, 'What is the rotational strength of a CD band associated with this system, as compared to (zero) in the piperidine derivative?'



(I)



(II)

In order to answer such a question, we resolved 2-methylpiperidine (*vide infra*) and prepared (*II, a*), determined its structure and absolute configuration, and also measured its CD spectrum. We determined also the absolute configuration of 2-methylpiperidine in the process, which, to our knowledge, had not been determined before, even though its chiro-optical properties are well known.

Experimental

The solvent tetrahydrofuran (THF) was checked for peroxides, and was distilled from calcium hydride

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*Author to whom correspondence should be addressed.

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and stored over molecular sieves. Tungsten hexacarbonyl was sublimed prior to use. The optically pure amine was resolved by selective precipitation of the *d*-tartaric acid adduct salt. The amine was recovered from its tartrate salt by dissolving the salt in aqueous NaOH, followed by extraction in ether. The organic layer was dried over $CaSO_4$ and vacuum distilled. IR spectra were recorded on a Nicolet FT model MS-X spectrophotometer.

Preparations

2-methylpiperidinepentacarbonyltungsten, (2-Me-Pip)$W(CO)_5$, was prepared photochemically [1]. In a typical reaction, approximately 2.0 g (5.7 mmol) of $W(CO)_6$ was dissolved in 75.0 ml of THF solvent. The solution was irradiated in a quartz reaction vessel under a nitrogen atmosphere with a 750-watt Hg lamp (Hanovia) for 1 hr. Then 7.0 ml (or 5.2 mmol) 2-methylpiperidine was added and the solution was irradiated for an additional 2 hrs, resultin in a bright orange solution. The solvent was removed by a dynamic vacuum and the unreacted $W(CO)_6$ was removed by sublimation at 50 °C. The product was extracted with n-hexane and recrystallized under nitrogen with the same solvent. The IR carbonyl stretching vibrations, as expected for a mono-substituted species [1], occurred at $A_1^{(2)}$, 2071 cm^{-1}; $A_1^{(1)}$, 1917 cm^{-1}; E, 1928.5 cm^{-1}. The product slowly decomposes in solution, with the rate of decomposition apparently being related to the purity of the amine. The isolated orange crystals of (2-Me-Pip)$W(CO)_5$ are reasonably stable.

Visible-UV Spectra

These were recorded on a Cary 17 and showed absorption maxima at 365 nm ($\epsilon = 100$), 289 nm ($\epsilon = 360$), and 240 nm ($\epsilon = 1600$), the latter being a shoulder buried in the tail-off of the 2-methylpiperidine absorption. Given the absorption coefficients of the first two bands, it is clear that they are tungsten 5d-orbital centered transitions. However, it is difficult to judge the nature of the third one since it is riding on the shoulder of the amine UV absorption.

CD Spectra

There is no optical rotation induced upon the two visible-UV bands listed above, as determined with a computer-controlled JASCO CD instrument (belonging to Professor G. Palmer, Rice University, whom we thank for these measurements). The two traces recorded in that instrument (500 to 300 nm; using a 1 cm cell and corrected for solvent; and 400 to 230 nm using a 1 mm path cell and uncorrected for solvent) show no evidence of rotational strength even though the instrument is capable of recording rotational strengths of millidegrees at the gains used. These traces have been deposited with the Editor and are available to the interested reader from him or from the authors.

TABLE I. Data Collection and Processing Parameters.

Space group	$P2_1$, monoclinic
Cell constants	a = 8.565(3) Å
	b = 11.617(4)
	c = 13.925(4)
	β = 91.84(3)°
	V = 1385 $Å^3$
Molecular formula	$WC_{11}H_{13}NO_5$
Molecular weight	423.1
Molecules per cell	$Z = 4$
Density	$\rho = 2.03$ g-cm^{-3}
Absorption coefficient	$\mu = 79.9$ cm^{-1}
Transmission factor range	0.05 to 0.13
Radiation (MoKα)	$\lambda = 0.71073$ Å
Collection range	$4° < 2\theta < 65°$
Scan width	$\Delta\theta = (1.10 + 0.35 \tan\theta)°$
Maximum scan time	240s
Scan speed range	0.4 to 5.0° min^{-1}
Total data collected	5367
Independent data with $I > 3\sigma(I)$	2525
Total variables	164
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.046
$R_W = [\Sigma W(\lvert F_o - F_c \rvert)^2 / \Sigma W \lvert F_o \rvert^2]^{1/2}$	0.044
Weights	$\sigma(F)^{-2}$
Goodness-of-fit	1.53

X-ray Studies

The crystal used for the X-ray study was a small, irregularly shaped polyhedron having nine distinct faces, the longest dimension being about 0.53 mm. All measurements were made on an Enraf-Nonius CAD-4 automatic diffractometer using MoKα radiation monochromatized by a dense graphite crystal, assumed for all purposes to be ideally imperfect. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table I. The Laue symmetry was determined to be 2/m, and from the systematic absences noted the space group was shown to be either $P2_1/m$ or the noncentrosymmetric $P2_1$. Intensity data were collected using the θ–2θ scan technique, with two standard reflections being collected after every 2 h of X-ray exposure time. In reducing the data, Lorentz and polarization factors were applied, as well as an analytical absorption correction based on crystal geometry.

Since an optically pure amine was used in the synthesis, the possibility of space group $P2_1/m$ was ruled out from the start. Interpretation of a Patterson map yielded the positions of both W atoms, one in each of the two crystallographically independent molecules in the asymmetric unit. Difference Fourier syntheses revealed all remaining nonhydrogen atoms,

TABLE II. Atomic Coordinates and Thermal Parameters (×1000, W × 10000).

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0.5228(1)	0.1360(0)	0.6115(1)	450(5)	372(7)	418(7)	−13(6)	71(5)	−44(7)
W′	0.0084(1)	0.4202(1)	0.8969(1)	452(5)	477(9)	415(7)	5(6)	104(5)	−37(7)
O1	0.861(2)	0.208(2)	0.664(1)	78(6)					
O2	0.640(2)	−0.119(2)	0.603(1)	65(5)					
O3	0.497(2)	0.125(2)	0.839(1)	92(6)					
O4	0.433(2)	0.403(2)	0.620(1)	84(6)					
O5	0.625(2)	0.172(2)	0.396(1)	71(5)					
N	0.265(1)	0.085(1)	0.571(1)	32(4)					
C1	0.732(2)	0.175(2)	0.653(1)	43(6)					
C2	0.591(3)	−0.023(2)	0.605(2)	44(6)					
C3	0.496(2)	0.125(2)	0.752(2)	53(6)					
C4	0.465(3)	0.304(2)	0.618(2)	44(6)					
C5	0.581(2)	0.155(2)	0.470(2)	59(7)					
C6	0.213(2)	−0.034(2)	0.595(1)	46(6)					
C7	0.043(2)	−0.051(2)	0.568(1)	53(6)					
C8	−0.001(3)	−0.020(2)	0.467(2)	81(9)					
C9	0.052(2)	0.100(2)	0.446(2)	60(7)					
C10	0.222(2)	0.118(2)	0.470(1)	60(7)					
C11	0.239(3)	−0.067(3)	0.697(1)	62(7)					
O1′	−0.260(2)	0.471(2)	0.751(1)	72(5)					
O2′	0.171(2)	0.272(2)	0.739(1)	80(6)					
O3′	0.160(2)	0.653(2)	0.824(2)	104(7)					
O4′	−0.185(2)	0.550(2)	1.051(1)	84(6)					
O5′	−0.174(2)	0.191(2)	0.935(1)	87(6)					
N′	0.204(2)	0.392(2)	1.015(1)	47(5)					
C1′	−0.157(2)	0.451(2)	0.807(2)	48(6)					
C2′	0.115(2)	0.325(2)	0.799(2)	42(6)					
C3′	0.104(3)	0.562(3)	0.853(2)	70(8)					
C4′	−0.110(3)	0.510(2)	0.995(2)	48(6)					
C5′	−0.104(3)	0.278(3)	0.928(2)	62(8)					
C6′	0.359(2)	0.345(2)	0.988(2)	62(7)					
C7′	0.462(3)	0.323(2)	1.074(1)	75(9)					
C8′	0.390(3)	0.255(2)	1.153(2)	83(9)					
C9′	0.243(3)	0.314(3)	1.181(2)	88(10)					
C10′	0.136(3)	0.322(2)	1.094(2)	88(10)					
C11′	0.429(2)	0.427(2)	0.919(2)	59(6)					
H1	0.198(1)	0.136(1)	0.620(1)	100(0)					
H6	0.285(2)	−0.089(2)	0.552(1)	100(0)					
H7A	−0.024(2)	0.002(2)	0.615(1)	100(0)					
H7B	0.015(2)	−0.140(2)	0.579(1)	100(0)					
H8A	−0.126(3)	−0.025(2)	0.457(2)	100(0)					
H8B	0.053(3)	−0.079(2)	0.419(2)	100(0)					
H9A	0.032(2)	0.117(2)	0.370(2)	100(0)					
H9B	−0.015(2)	0.159(2)	0.488(2)	100(0)					
H10A	0.250(2)	0.208(2)	0.460(1)	100(0)					
H10B	0.290(2)	0.067(2)	0.422(1)	100(0)					
H11A	0.360(3)	−0.041(3)	0.701(1)	100(0)					
H11B	0.227(3)	−0.151(3)	0.729(1)	100(0)					
H11C	0.170(3)	−0.006(3)	0.736(1)	100(0)					
H1′	0.238(2)	0.478(2)	1.037(1)	100(0)					
H6′	0.344(2)	0.263(2)	0.953(2)	100(0)					
H7A′	0.499(3)	0.405(2)	1.104(1)	100(0)					
H7B′	0.563(3)	0.276(2)	1.051(1)	100(0)					
H8A′	0.470(3)	0.250(2)	1.214(2)	100(0)					
H8B′	0.363(3)	0.169(2)	1.128(2)	100(0)					
H9A′	0.188(3)	0.266(3)	1.236(2)	100(0)					
H9B′	0.271(3)	0.400(3)	1.207(2)	100(0)					

(continued overleaf)

TABLE II. *(continued)*

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H10A′	0.028(3)	0.362(2)	1.115(2)	100(0)					
H10B′	0.112(3)	0.236(2)	1.068(2)	100(0)					
H11A′	0.536(2)	0.380(2)	0.911(2)	100(0)					
H11B′	0.452(2)	0.505(2)	0.960(2)	100(0)					
H11C′	0.381(2)	0.450(2)	0.849(2)	100(0)					

TABLE III. Average Intramolecular Bond Distances and Angles.

Distances (Å)			
W–N	2.34(1)	C–N	1.49(2)
W–Cl	1.90(2)	C6–C11	1.49(2)
W–C(2–5)	1.99(2)	C–C	1.50(2)
C–O	1.17(2)		
Angles (°)			
W–C–O	175(2)	C–C–N,C	112(2)
N–W–Cl	176(1)	W–N–C6	119(1)
N–W–C	92(1)	W–N–C10	110(1)
C–W–C	175(1)	N–C6–C11	111(1)
C–W–C	89(1)	C7–C6–C11	111(1)
Torsion Angles (°)			
N–C6–C7–C8	51(1)	C2–W–N–C6	21(1)
C6–C7–C8–C9	–54(1)	C3–W–N–C6	–72(1)
C7–C8–C9–C10	56(1)	W–N–C6–C11	57(1)
C8–C9–C10–N	–58(1)	C4–W–N–C10	69(1)
C9–C10–N–C6	54(1)	C5–W–N–C10	–22(1)
C10–N–C6–C7	–50(1)		

however hydrogens could not be located and were instead entered at ideally calculated positions. Attempts to allow the nonhydrogens other than tungsten to refine anisotropically resulted in non-positive definite thermal parameters, and so they had to remain isotropic. The correct absolute configuration was determined from the analysis of 9 Bijvoet pairs [2] of reflections, each of which specified the same handedness. After all shift/esd ratios were less than 0.4, convergence was reached at the agreement factors listed in Table I. Final positional and thermal parameters are presented in Table II, according to the atom labelling scheme of Fig. 1. The atomic scattering factors for the nonhydrogen atoms were computed from numerical Hartree-Fock wave functions [3]; for hydrogen those of Stewart, Davidson, and Simpson [4] were used. The anomalous dispersion coefficients of Cromer and Liberman [5] were used for W. All calculations were made with the SHELX-76 series of programs [6]. Intramolecular bond lengths, angles, and torsion angles are presented in Table III, based on the positions of Table II.

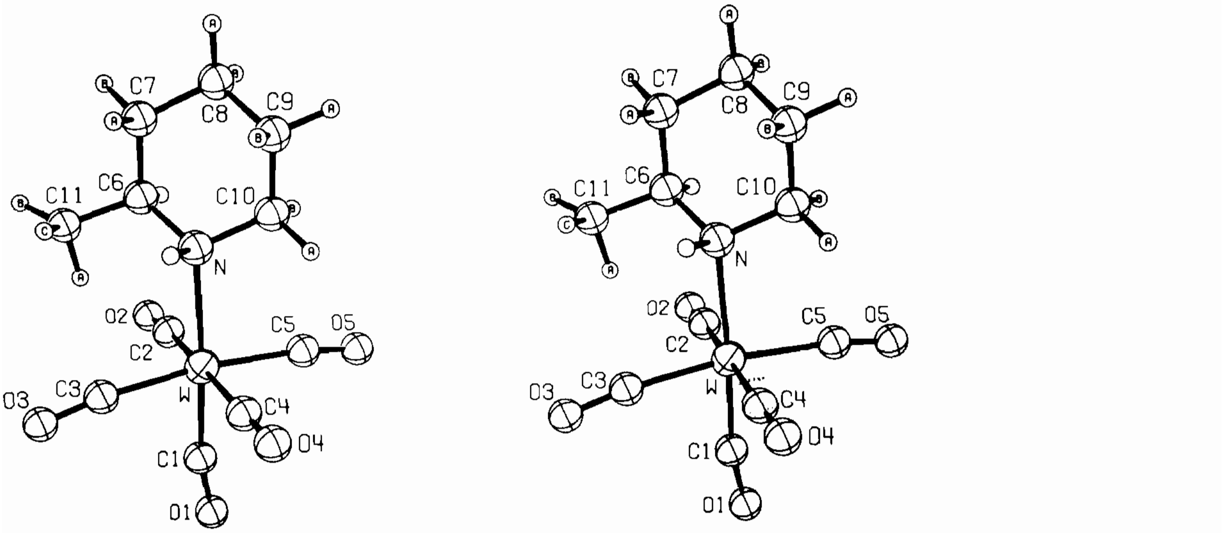

Fig. 1. Stereoscopic view of one molecule showing the atom labelling scheme. All atoms are shown as spheres of arbitrary diameter.

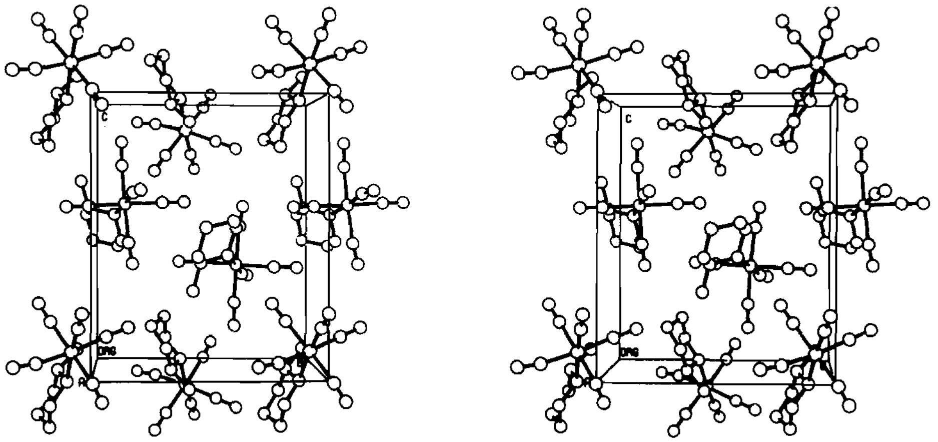

Fig. 2. Stereoscopic view of the molecular packing in the unit cell, as viewed into the *a* axis. Hydrogens are omitted for clarity.

Discussion

As shown in Fig. 1, the molecules contain W atoms having nearly octahedral geometry. The main points of interest are: (a) the plane defined by the four equatorial carbonyl carbons (C2–C5) does not contain the metal, which is, on the average, displaced by 0.08 Å in the direction of the piperidine N (b) the carbonyls are all bent, with those in the equatorial girth bent away from the piperidine ligand partly in order to avoid undesirable steric contacts [it is clear, however, that steric factors alone are not responsible for the bending since the *trans* carbonyl ligand is also bent (W–C1–O1 = 167°) which is surely an electronic effect] (c) finally, the piperidine ligand is oriented such that the two carbons *ortho* to the nitrogen ligand (C6 and C10) are oriented in between carbonyls. This phenomenon is not associated with an effort on the part of the ligand to avoid undesirable ligand contacts between the methyl group at the 2-position of the piperidine since we have recently determined the structures of pyridinepentacarbonylchromium(0) and *cis*-bispyridinetetracarbonylchromium(0) in both of which the plane of the pyridines more or less exactly bisects the OC–Cr–CO angles [7]. The same is true in the case of piperidinepentacarbonylchromium(0), studied recently by Cotton *et al.*, in which the H_2C–N–CH_2 plane of the piperidine ligand bisects the angles defined by pairs of carbonyls in the basal plane of the complex [8].

Concerning the chirality of the molecule, the piperidine ligand has an (*S*) carbon at position 2 (see Fig. 1, which is in the correct absolute configuration determined by the Bijvoet test; *vide infra*) while the prochiral N atom of the free molecule is now chiral and has the absolute configuration (*S*) also. The W atom itself is not a chiral center. Since the piperidine ligand was isolated as the enantiomer which preferentially precipitates as a diastereoisomeric salt with (*R*,*R*)-tartaric acid (*d*-tartaric acid), we have now established that the preferred pair is (*S*)-[(+)]-2-methylpiperidine with (*R*,*R*)-tartaric acid. This was unknown to people such as Craig [9] who recorded a rotation $[(+)]_D$ for this 2-methylpiperidine enantiomer without knowing for sure to which absolute configuration such an optical rotation corresponded; however, his assumption that it was (*S*) is correct.

As expected, the piperidine ring has the classical chair conformation (see Fig. 1) with average values for the C–C distances of 1.50(2) Å, C–N of 1.49(2) Å and C(ring)–C(Me) = 1.49(2) Å. The absolute values of the torsional angles within the piperidine ring average 54°. All of these values are normal and are not sufficiently precise to warrant a comparison against better quality structures of derivatives of the uncomplexed ligand.

The W–C(O) distances average 1.99(2) Å for the carbonyl ligands in the basal plane and 1.90(2) Å for the axial carbonyls, which supports the expectation that the weaker piperidine ligand does not compete successfully with the axial carbonyls for the metal electrons. This is in accord with the observed carbonyl stretching frequencies recorded for this substance and described in the Experimental section. In this regard, we reported the structures of some $W(CO)_4$ derivatives of bidentate dithioethers for which the W–C distances were 2.10(3) and 2.01(3) Å, respectively, for those carbonyls *trans* to each other and for those *trans* to the thioether S ligands [10]. Note that the difference in W–C distances in both cases is *ca.* 0.1 Å, whether the weak ligand in question is S or N. A more detailed discussion of this *trans* effect in metal carbonyls has been given in our three previous papers [10–12].

Finally, we must comment on the 'negative' result of observing no optical induction at the visible-UV bands of the complex as a result of having the proximal N and C chiral centers. It should be clear that the presence of ligands such as N and carbonyl is sufficient to give rise to very large CD rotational strengths [13, 14] *when the metal itself is a chiral center.* However, with a freely rotating and probably photodissociating ligand in solution (as must certainly be the case with this compound), the asymmetry at W must be minimal and the mere fact that the N and 2-C are chiral is not enough to induce a noticeable rotational strength in the two visible-UV bands of the compound under consideration.

Acknowledgements

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