# Microwave Spectrum, Structure, and Dipole Moment of Bicyclo[2.1.1]hex-2-ene

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**Abstract:** The microwave spectra of four isotopic species of bicyclo[2.1.1]hex-2-ene have been observed and analyzed. From these data a "substitution" ($r_s$) structure has been obtained for the carbon skeleton. The internuclear distances have been found to be (in Å): $C_1$-$C_2$ = 1.529 ± 0.002, $C_2$-$C_3$ = 1.341 ± 0.002, $C_1$-$C_5$ = 1.568 ± 0.001; the dihedral angle of the four-membered ring is 126.7 ± 0.2°, and $\angle C_1C_2C_3$ is 103.3 ± 0.1°. Stark effect measurements have yielded a dipole moment of $\mu$ = 0.299 ± 0.008 D for the $C_{2v}$ molecule.

During the past several years we have been carrying on a systematic study of the structural properties of small polycyclic hydrocarbons, including bicyclobutane,[1,2] 1-chlorobicyclo[1.1.1]pentane,[3] bicyclo[2.1.0]pentane,[4] and benzvalene.[5,6] The general aim of these studies has been to provide a sound quantitative understanding of the molecular structures of this class of strained hydrocarbons, and the relationship of the structural features to other chemical and physical properties.

The bicyclo[2.1.1]hex-2-ene molecule (see Figure 1) is of particular interest because of its structural similarity to the tricyclic benzvalene molecule, which has one additional C-C bond (between carbon atoms 5 and 6 of Figure 1). Since removal of this bond is expected to lower the ring strain appreciably, it was expected that the structural parameters of bicyclohexene would revert more nearly to the values appropriate for the less-strained monocyclic systems of which it is composed.

In addition to comparison of the similar bicyclic and tricyclic systems, it was hoped that additional information could be obtained concerning an apparent constancy of the *average* C-C bond lengths in the cyclobutyl ring moiety.[4,6] This average bond length constancy is similar to one observed also for the cyclopropyl ring moiety,[5] but is perhaps less-well substantiated at this time.

An electron diffraction structural study of the bicyclo[2.1.1]hex-2-ene molecule has been reported previously.[7] Although the reported structure seemed reasonable, we felt that a microwave study was desirable in view of the difficulties encountered in the electron diffraction study of bicyclo[2.1.0]pentane.[4] In particular, the $C_1$-$C_4$ and $C_5$-$C_6$ nonbonded distances of Figure 1 are very similar, as are also the $C_1$-$C_3$ and $C_2$-$C_5$ distances. Consequently it seemed quite possible that the least-squares analysis of the scattering data might have converged to a false structure.

## Experimental Section

The sample of bicyclo[2.1.1]hex-2-ene ($C_6H_8$) used in these studies was provided by Professor Robert G. Carlson of the University of Kansas. It had been purified previously[8] by VPC and was used without further treatment for the microwave studies.

Microwave spectra for the normal isotopic species were obtained on a 5 kHz Stark-modulated spectrometer of conventional design.[9] Spectra of the three monosubstituted $^{13}C$ species were observed in natural abundance using a Hewlett-Packard 8460A microwave spectrometer. At dry ice temperature, signal-to-noise ratios of 5/1 or better were achieved for the isotopic species, each of which is present in approximately 2% abundance.

Dipole moment measurements were performed on the normal species using the 5 kHz spectrometer. Stark shifts were measured as a function of the ground-to-base modulation voltage, and the Stark cell was calibrated using OCS.[10]

## Observed Spectrum and Analysis

Preliminary spectral predictions were performed using the published electron diffraction structure[7] for the molecule. Although these predictions were not very precise, the expected a-type, R-branch clusters of lines were observed and assigned for the normal isotopic species using the characteristic Stark effects. Table I presents the observed spectrum and the rotational transition assignments. As usual for these rigid polycyclic molecules, the spectrum is very well defined by the rigid rotor approximation, which was used to obtain the rotational constants listed in Table II. The uncertainties listed in Table II represent at least one standard deviation for the least-squares fit, and the observed minus calculated frequencies in Table I are seen to be satisfactory.

Using the experimental rotational constants for the normal species and the expected isotope shift for $^{13}C$ substitution, spectral predictions were performed for each of the three monosubstituted $^{13}C$ species. The expected transitions were located within 10-20 MHz of the predicted values, and were assigned on the basis of relative intensity, Stark effects, and consistency of fit. Tables I and II list the observed spectral lines and derived rotational constants, respectively.

Additional evidence for the correctness of the assignment is provided in Table III. For a perfectly rigid $C_{2v}$ structure (see Figure 1), the moments of inertia of each of the $^{13}C$ species must satisfy the relation,

$$\Delta I_i + \Delta I_j - \Delta I_k = 0 \qquad (1)$$

In this expression i and j label the axes in the plane of substitution and $\Delta I$ is the difference in moments of inertia of the $^{12}C$ and the $^{13}C$-substituted molecule in question. In Table III we have tabulated the left side of eq 1 using the moments of Table II. The values deviate from zero, as expected, because of zero-point vibrational effects, but the small magnitudes indicate clearly the correctness of the isotopic identifications and the $C_{2v}$ molecular symmetry.

## Structure

Since each of the unique carbon atoms (e.g., atoms 1, 2, and 5 of Figure 1) has been isotopically substituted, a complete $r_s$ ring structure for the carbon skeleton can be obtained using the method of Costain[11] and Kraitchman's[12] equations. This is the best structural technique for the available data and its application has been discussed numerous times, e.g., by Suenram and Harmony in the recent benzvalene study.[6]

Table IV presents the $r_s$ coordinates which are obtained by this procedure. The sign choices for the coordinates are the only reasonable ones and since there are no very small

Table I. Microwave Spectra of Bicyclo[2.2.1]hex-2-ene[a]

| | $^{12}C$ | | 1-$^{13}C$ | | 2-$^{13}C$ | | 5-$^{13}C$ | |
|---|---|---|---|---|---|---|---|---|
| Transition | Obsd[b] | Obsd − calcd[c] | Obsd | Obsd − calcd | Obsd | Obsd − calcd | Obsd | Obsd − calcd |
| $0_{00} \rightarrow 1_{01}$ | 8 979.22 | −0.02 | | | | | | |
| $1_{11} \rightarrow 2_{12}$ | 17 558.43 | −0.05 | | | | | | |
| $1_{01} \rightarrow 2_{02}$ | 17 869.75 | 0.04 | | | | | | |
| $2_{12} \rightarrow 3_{13}$ | 26 287.22 | 0.08 | | | | | | |
| $2_{02} \rightarrow 3_{03}$ | 26 608.32 | 0.04 | | | | | | |
| $2_{21} \rightarrow 3_{22}$ | 26 937.62 | 0.03 | 26 805.03 | 0.04 | 26 552.67 | 0.00 | 26 331.39 | 0.03 |
| $2_{20} \rightarrow 3_{21}$ | 27 266.94 | 0.04 | 27 202.58 | −0.01 | 26 881.73 | 0.03 | 26 889.86 | 0.03 |
| $2_{11} \rightarrow 3_{12}$ | 27 474.58 | 0.06 | 27 381.03 | 0.02 | 27 097.11 | 0.03 | 27 105.98 | 0.02 |
| $3_{13} \rightarrow 4_{14}$ | 34 970.94 | −0.04 | 34 691.52 | 0.05 | 34 448.23 | 0.01 | 34 696.55 | −0.02 |
| $3_{03} \rightarrow 4_{04}$ | 35 209.55 | −0.04 | 34 909.14 | −0.01 | 34 694.71 | 0.01 | 34 939.64 | 0.01 |
| $3_{22} \rightarrow 4_{23}$ | 35 846.92 | −0.05 | 35 653.86 | −0.04 | 35 333.93 | −0.03 | 35 454.62 | 0.01 |
| $3_{31} \rightarrow 4_{32}$ | 36 062.51 | −0.05 | 35 915.06 | −0.05 | 35 549.31 | −0.01 | 35 623.57 | −0.02 |
| $3_{30} \rightarrow 4_{31}$ | 36 135.85 | −0.05 | 36 016.29 | −0.04 | 35 621.40 | 0.00 | 35 674.05 | −0.01 |
| $3_{12} \rightarrow 4_{13}$ | 36 497.70 | −0.01 | 36 337.05 | 0.01 | 35 995.29 | −0.01 | 36 039.67 | −0.03 |
| $3_{21} \rightarrow 4_{22}$ | 36 552.66 | 0.00 | 36 482.44 | 0.06 | 36 041.36 | −0.02 | 36 022.55 | −0.01 |

[a] All values in MHz. [b] Measurement accuracy approximately ±0.05 MHz. [c] Computed using rotational constants of Table II.

Table II. Rotational Constants and Moments of Inertia of Bicyclo[2.1.1]hex-2-ene

| | $^{12}C$ | 1-$^{13}C$ | 2-$^{13}C$ | 5-$^{13}C$ |
|---|---|---|---|---|
| $A$ | 5820.653 ± 0.121[a] | 5752.524 ± 0.103 | 5792.950 ± 0.058 | 5748.483 ± 0.079 |
| $B$ | 4689.605 ± 0.007 | 4685.847 ± 0.006 | 4627.840 ± 0.003 | 4612.760 ± 0.004 |
| $C$ | 4289.591 ± 0.007 | 4249.150 ± 0.007 | 4223.050 ± 0.003 | 4264.360 ± 0.004 |
| $\kappa$ | −0.477462 | −0.419044 | −0.484311 | −0.530497 |
| $I_a$ | 86.8246[b] | 87.8529 | 87.2398 | 87.9147 |
| $I_b$ | 107.7652 | 107.8156 | 109.2034 | 109.5604 |
| $I_c$ | 117.8145 | 118.9358 | 119.6708 | 118.5116 |

[a] Rotational constants have units of MHz, and the uncertainties represent one standard deviation. [b] Moments of inertia computed using conversion factor of 505 376 amu Å$^2$ MHz.

Table III. Moment of Inertia Differences for Isotopic Species

| Molecule | $\Delta I_a + \Delta I_c - \Delta I_b$ (amu Å$^2$) | $\Delta I_a + \Delta I_b - \Delta I_c$ (amu Å$^2$) |
|---|---|---|
| 1-$^{13}C$ | — | −0.0066 |
| 2-$^{13}C$ | — | −0.0029 |
| 5-$^{13}C$ | −0.0082 | — |

Table IV. Carbon Atom Coordinates

| Atom[a] | $a$ | $b$ | $c$ |
|---|---|---|---|
| 1 | 0.2934 ± 0.0020[b] | 1.0225 ± 0.0005 | 0 |
| 2 | −1.1933 ± 0.0005 | 0.6704 ± 0.0008 | 0 |
| 3 | −1.1933 ± 0.0005 | −0.6704 ± 0.0008 | 0 |
| 4 | 0.2934 ± 0.0020 | −1.0225 ± 0.0005 | 0 |
| 5 | 0.8262 ± 0.0007 | 0 | 1.0626 ± 0.0006 |
| 6 | 0.8262 ± 0.0007 | 0 | −1.0626 ± 0.0006 |

[a] See Figure 1 for atomic labeling scheme. [b] All values in Å; uncertainties represent one standard deviation for the rotational constants.

coordinates there are no ambiguities. Note that atoms 4, 3, and 6 are related by symmetry to atoms 1, 2, and 5, respectively. The listed uncertainties represent only the statistical uncertainties (one standard deviation) in the experimental rotational constants.

From the atomic coordinates of Table IV we have computed values for the pertinent structural parameters, and have presented these results in Table V. Note that a minimum of five parameters suffice for a complete structural specification of the polycyclic ring. We have chosen these as the three bond distances, $\angle C_1C_2C_3$, and a dihedral angle of the four-membered ring. Some additional redundant parameters have also been computed for convenience.

The listed uncertainties are again the standard deviations of the fit. As previously discussed,[6] the uncertainties due to neglected vibration–rotation interactions are expected to exceed the pure experimental errors. Also, the $a$ coordinate of $C_1$ is rather small, and will consequently transmit a somewhat greater uncertainty to the related structural parameters. Nevertheless, as shown previously in some detail for benzvalene,[6] the distance parameters in Table V are likely to have uncertainties no greater than 0.003–0.004 Å due to vibration–rotation interactions; for the angle variables the corresponding value is 0.3–0.4°.

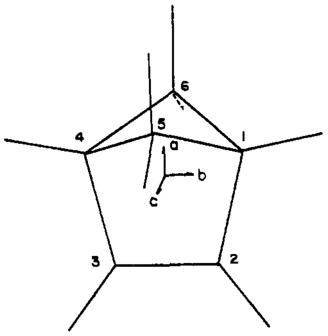

**Figure 1.** Bicyclo[2.1.1]hex-2-ene structure with principal axis and carbon atom identifications. Hydrogen atoms are unnumbered.

## Dipole Moment

Second-order Stark effect measurements have been performed on several low-J transitions, and the data have been analyzed by the method of Golden and Wilson[13] to obtain the molecular electric dipole moment. Table VI summarizes the measurements and gives the dipole moment resulting from a least-squares fit.

## Discussion

A comparison of the microwave and electron diffraction

Table V. Structural Parameters of Bicyclo[2.1.1]hex-2-ene[a]

| Parameter[b] | This work | ED[c] |
|---|---|---|
| $C_1-C_2$ | 1.528 ± 0.002[d] | 1.537 ± 0.010 |
| $C_2-C_3$ | 1.341 ± 0.002 | 1.332 ± 0.003 |
| $C_1-C_5$ | 1.568 ± 0.001 | 1.548 ± 0.005 |
| $\angle C_1C_2C_3$ | 103.3 ± 0.1 | 108.4 ± 0.4 |
| $\theta$ | 126.7 ± 0.2 | 123.5 ± 1.2 |
| $\angle C_5C_1C_2$[e] | 100.4 ± 0.1 | |
| $\angle C_5C_1C_6$[e] | 85.33 ± 0.05 | |
| $\angle C_1C_5C_4$[e] | 81.40 ± 0.05 | |

[a] Distances in Å, angles in degrees. [b] See Figure 1 for parameter identification. $\theta$ is the four-membered ring dihedral angle formed by intersection of $C_4C_5C_1$ and $C_4C_6C_1$ planes. [c] Reference 7 electron diffraction results. Uncertainties are stated to be three standard deviations. [d] Uncertainties are those arising from one standard deviation in the rotational constants. [e] Redundant parameters.

Table VI. Stark Shifts and Dipole Moment of Bicyclo[2.1.1]hex-2-ene

| | | $(\Delta\nu/E^2) \times 10^5$ | |
|---|---|---|---|
| Transition | $M$ | Obsd[a] | Calcd |
| $1_{11} \rightarrow 2_{12}$ | 0 | 0.0311 | 0.0320 |
| | 1 | 1.3318 | 1.3893 |
| $2_{12} \rightarrow 3_{13}$ | 1 | 0.0500 | 0.0470 |
| | 2 | 0.1987 | 0.1937 |
| $\lvert\mu_T\rvert = \lvert\mu_a\rvert = 0.299 \pm 0.008$ D | | | |

[a] Units are MHz/(V/cm)$^2$. Stark cells calibrated using $\mu = 0.7152$ for OCS.

Table VII. Structural Parameters in Related Molecules[a]

| | Bicyclo[2.1.1]-hex-2-ene[b] | Benzvalene[c] | Cyclopentene[d] |
|---|---|---|---|
| $C_1-C_2$ | 1.528 | 1.503 | 1.519 |
| $C_2-C_3$ | 1.341 | 1.339 | 1.342 |
| $C_1-C_5$ | 1.568 | 1.529 | 1.546 |
| $\angle C_1C_2C_3$ | 103.3 | 105.7 | 111.0 |
| Dihedral angle[e] | 116.6 | 127.2 | 151.2 |

[a] Distances in Å, angles in degrees. [b] Present study. [c] Reference 6. [d] M. I. Davis and T. W. Muecke, *J. Phys. Chem.*, 74, 1104 (1970). [e] This dihedral angle is that of the five-membered ring, and is consequently equal to $(360 - \theta)/2$, where $\theta$ is the four-membered ring dihedral angle described in footnote *b* of Table V.

results in Table V indicates that several of the parameters differ by amounts considerably outside the experimental uncertainties, even if the additional microwave uncertainties due to vibration-rotation interactions are considered. The principal discrepancies seem to lie in the two angle variables, $\angle C_1C_2C_3$ and the dihedral angle $\theta$. An interesting result of this is that the nonbonded $C_5 \cdots C_6$ distance is predicted by the electron diffraction data to be very short, viz., 1.826 Å, while the microwave result is 2.125 Å. The electron diffraction value for this distance would make it even shorter than the well-substantiated value of 1.850 Å[3,14] for the nonbonded CC distance in the more strained bicyclo[1.1.1]pentane molecule, and all evidence would argue against such a short distance.

The synthesized radial distribution function[7] shows no less than 8 nonbonded atom pairs leading to an unresolved principal peak in the region 2.27 Å. Consequently it seems likely that the electron diffraction data are incapable of an unambiguous resolution of the molecular structure. This is entirely analogous to the situation for bicyclo[2.1.0]pentane.[4]

In Table VII structural parameters for several molecules have been presented for comparison. Comparing the present data to that of benzvalene, it is seen that removal of the $C_5-C_6$ bond in benzvalene has produced major changes as expected, except in the unsaturated end of the molecule where the double bond is virtually unchanged. In particular, $C_1-C_2$ has increased by 0.025 Å and $C_1-C_5$ by 0.019 Å. Thus the entire C–C single-bond system has loosened appreciably, which probably reflects the rehybridization occurring upon removal of the $C_5-C_6$ bridgehead bond. Removal of the $C_5C_6$ bridge bond has, of course, also permitted the five-membered ring dihedral angle to drop from 127.2° to 116.6°, which decreases the repulsive interactions between the previously mentioned atoms 5 and 6.

Comparison of the bicyclohexene and cyclopentene data indicates that the cyclopentene moiety is still appreciably perturbed in the former molecule. The decrease in cyclopentene dihedral angle is, of course, necessary to reduce nonbonded repulsion between atoms 5 and 6. In addition, the bridging methylene group (carbon $C_6$, e.g.) forces $\angle C_1C_2C_3$ to decrease appreciably from 111.0° to 103.3°. This has the concomitant effect of increasing p character in the $C_2-C_1$ bond, which in turn produces a slight lengthening of this bond.

Perhaps the most startling feature is that the cyclobutyl bond length has become 0.02 Å longer than in cyclobutane[15] itself. We had observed earlier[4] that, in the absence of strong perturbing substituents such as -CN, the average C-C bond lengths in cyclobutyl groups remained at or somewhat shorter than the value in cyclobutane itself. We must conclude now that either this principle is not generally viable, or the bridging alkene ($C_2{=}C_3$) enters into a particularly strong interaction with the ring. Such an interaction is possible since the pertinent symmetry of the highest filled molecular orbital of cyclobutane is the same as that of the lowest unfilled molecular orbital ($\pi^*$) of the alkene group.[16] Consequently, a slight shift of electron density out of the cyclobutane ring into the $\pi^*$ alkene orbital is likely. Since the pertinent cyclobutane orbital is C–C bonding, such a transfer of electron density would lead to a lengthening of cyclobutyl C–C bonds. It seems likely that it is this mechanism which causes the apparent violation of our earlier generalization.

Finally, it is interesting to note that the bicyclohexene electric dipole moment of 0.30 D is 0.58 D smaller than in benzvalene.[5] Hence we see that destruction of the bicyclobutane moiety present in benzvalene drops the dipole moment by an amount approximately equal to the moment of bicyclobutane itself, vis., 0.68 D.[1] Consequently, the polarity of the bicyclohexene molecule is little larger than the cyclopentene value of 0.22 D.[17]

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## References and Notes

(1) M. D. Harmony and K. W. Cox, *J. Am. Chem. Soc.*, **88**, 5049 (1966).
(2) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).
(3) K. W. Cox and M. D. Harmony, *J. Mol. Spectrosc.*, **36**, 34 (1970).
(4) R. D. Suenram and M. D. Harmony, *J. Chem. Phys.*, **56**, 3837 (1972).
(5) R. D. Suenram and M. D. Harmony, *J. Am. Chem. Soc.*, **94**, 5915 (1972).
(6) R. D. Suenram and M. D. Harmony, *J. Am. Chem. Soc.*, **95**, 4506 (1973).
(7) D. L. Zebelman, S. H. Bauer, and J. F. Chiang, *Tetrahedron*, **28**, 2727 (1972).
(8) K. D. May, Ph.D. Dissertation, University of Kansas, 1974.
(9) R. H. Hughes and E. B. Wilson, Jr., *Phys. Rev.*, **71**, 562 (1947).
(10) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

(11) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).
(12) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).
(13) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).
(14) J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 1614 (1970).
(15) A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).
(16) For descriptions of these molecular orbitals, see W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973.
(17) G. W. Rathjens, Jr., *J. Chem. Phys.*, **36**, 2401 (1962).

# Interpretation of the Electronic Spectra of Low-Spin $d^6$ $M(CO)_5X$ Complexes. Primary Excited State Decay Paths in $Re(CO)_5X$ Complexes

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**Abstract:** The electronic spectra of $Re(CO)_5X$ (X = Cl, Br, I), $[M(CO)_5NH_2CH_3]Cl$ (M = Mn, Re), and $[(C_2H_5)_4N][M(CO)_5Br]$ (M = Cr, W) have been measured. The emission spectra and photochemistry of the $Re(CO)_5X$ complexes have also been investigated. The new electronic spectral studies along with data in the literature allow definitive assignment of the lowest absorptions as ligand field (LF) $^1A_1(e^4b_2^2) \rightarrow {}^{1,3}E(e^3b_2^2a_1^1)$ for a large class of low-spin $d^6$ $M(CO)_5X$ complexes. Emission from $Re(CO)_5X$ occurs from the $^3E(e^3b_2^2a_1^1)$ state and is strongly dependent on temperature in the range 20-100 K. Quantitative emission measurements have been made for the pure solids. Photochemistry of $Re(CO)_5X$ at 298 K involves substitution of CO with a quantum yield of up to 0.76 depending on X and the excitation wavelength. The observed chemistry and variable quantum yields accord well with the electronic nature of the lowest excited states.

Compelling spectroscopic[1-4] and photochemical[5-8] evidence supports the assignment of ligand field (LF) $^{1,3}E(e^3b_2^2a_1^1)$ to the lowest excited states in low-spin $d^6$ $M(CN)_5X^{n-}$ and $M(NH_3)_5X^{n+}$ (M = Co(III), Rh(III), Ir(III); X = $\pi$-donor, $\sigma$-donor) complexes. In these cases the energetic separation of the $d\sigma^*$ orbitals, $d_{x^2-y^2}(b_1)$ and $d_{z^2}(a_1)$, is relatively large. Thus, the lowest excited states involve population of one or the other of these orbitals with very little mixing via configuration interaction. Population of $d_{z^2}(a_1)$ increases the substitution lability of the ligands on the $z$ axis, and population of $d_{x^2-y^2}(b_1)$ labilizes the ligands on the $x$ and $y$ axes due to the directed $\sigma$-antibonding character of these orbitals.[9,10]

The electronic spectroscopy[11] and photosubstitution chemistry[12,13] of a series of $M(CO)_5X$ (X = $n$-electron donor; M = Mo, W) complexes, also of the $d^6$ low-spin electronic configuration, have been interpreted successfully by assigning the lowest excited states as $^{1,3}E(e^3b_2^2a_1^1)$.[11-13] Such an interpretation follows from the LF assignment[14] of lowest excited states in the $d^6$ $M(CO)_6$ species and the recognition that X is weaker in LF strength than CO. Recently, an extensive account of the electronic spectra of $d^6$, pentacarbonylhalogenometal complexes has appeared[15] where the $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1^1)$ interpretation was generally adopted. The matrix isolated $M(CO)_5$ (Cr, Mo, W) species have also been investigated,[16] and polarized spectral measurements[16b] of $Cr(CO)_5$ are in accord with the $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1^1)$ assignment for the lowest absorption band.

For *cis*-$M(CO)_4X_2$ (M = Cr, Mo, W; X = aliphatic amine) a LF assignment has also been given[17] for the lowest absorption bands. These complexes fall in the category *cis*-$ML_4X_2$,[18] with $X \ll L$ in LF strength as does *cis*-$Co(CN)_4$(ethylenediamine)$^-$, whose absorption spectrum has also been interpreted in this way.[19]

In the $d^6$ $Mn(CO)_5X$ (X = Cl, Br, I)[20] and corresponding Re complexes,[21] photoelectron spectra (PES) have revealed that the highest occupied orbital is one of e symmetry and principally halogen in character. Such PES data have influenced Blakney and Allen to assign[22] the lowest absorption bands in $Mn(CO)_5X$ as charge-transfer (CT) transitions involving depopulation of the highest occupied e level and population of a low lying orbital associated with mainly the carbonyl ligands. Several other investigators[23] have also regarded the lowest absorptions in $M(CO)_5X$ as involving CT excitation to the carbonyl groups. An account of the magnetic circular dichroism of $Mn(CO)_5Br$ has also recently appeared,[24] and the data were interpreted as consistent with an $e(Br) \rightarrow d_{z^2}$ CT lowest energy transition.

The aim of this paper is to examine critically all available electronic spectroscopic data on $d^6$ $M(CO)_5X$ complexes and also to report some new observations concerning $Re(CO)_5X$ (X = Cl, Br, I), $[M(CO)_5NH_2CH_3]Cl$ (M = Mn, Re), and $[(C_2H_5)_4N][M(CO)_5X]$ (M = Cr, W; X = Br). Absorption spectra for all of the complexes are reported, and emission spectral and photochemical studies have been carried out for $Re(CO)_5X$. These new data now allow definitive discussion of the electronic structure of the $d^6$ $M(CO)_5X$ complexes.

## Results

**a. Absorption Spectra.** The absorption spectra of $Re(CO)_5X$ (X = Cl, Br, I), $[M(CO)_5NH_2CH_3]^+$ (M = Mn, Re), $W(CO)_5NH_3$, and $[M(CO)_5Br]^-$ (M = Cr, W) have been measured. Electronic absorption spectral data for these complexes along with pertinent data from the literature[11-14,22] for other $d^6$ metal carbonyls are summarized in Table I. Figures 1, 2, and 3 show the spectra of some complexes investigated here. The Re and W complexes have remarkably similar spectra except for positions of the bands. The lowest absorption, band I, for these $C_{4v}$, $d^6$ Re carbon-

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