Electronic Transition Oscillator Strength by the Extended Hückel Molecular Orbital Method

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Calculations of the oscillator strength of electronic dipole-induced transitions (EDITs) based on EHMO wave functions including all transition matrix elements offer a generally applicable method for computing intensities of all types of transitions found in molecules, clusters, and complexes. Application of this EHMO-EDIT procedure to formaldehyde, MnO$_4^-$, p-(N,N-dimethylamino)benzonitrile (DMABN), 2,2'-bipyridyl (bpy), Ru(bpy)$_3^{2+}$, and [Co(CO)$_4$(H$_2$Si$_4$O$_{12}$)] illustrates the versatility of this procedure and offers new insight into some "old problems". We find that the TICT state of DMABN is expected to live long enough to relax to a state described by the (b$_1$)$^1$(b$_3$)$^1$ configuration. Emission of a photon in this state is forbidden by symmetry. However, a small twist of the dialkylamino group by only 15° increases this oscillator strength along the z axis enormously. TICT emission has empirically been shown to be z-polarized and strong in intensity. The emission rates can be thermally activated. This is in good qualitative agreement with the oscillator strength calculation. We also find that the intensities of the two z-polarized π* ← π transitions depend relatively little on the amino group torsional angle. This dependence is indeed characteristic for the TICT state. EDIT calculations on bpy as a function of the torsional angle θ lead to a satisfactory interpretation of the two prominent π* ← π transitions of this very often used ligand. The 2π* ← 2n oscillator strength is very small for cis. However, the cis (2n)$^1$(2π*)$^1$ configuration correlates with the trans (1π)$^1$(1π*)$^1$ which bears a large 1π* ← 1n oscillator strength. The cis 2π* ← 1n transition retains its π* ← π character but loses intensity with increasing θ and becomes symmetry-forbidden at θ = 180°. The first intense band which is broad, featureless, and very similar in different organic solvents is the result of a superposition of bands arising from an equilibrium Boltzmann distribution over the whole range of angles θ from 0° to 180°. This causes a hypochromatic shift of the maximum of the first intense band, because the 1π* ← 1n transition energies of the species with angles different from θ ≈ 180° and θ ≈ 0° appear at larger energy. The bathochromic shift of the first 1π* ← 1n transition of the protonated bpy is due to the predominance of the cis isomer and hence a narrow Boltzmann distribution of the θ region close to 0°. The number of possible Ru(bpy)$_3^{2+}$ excited-state configurations in the HOMO/LUMO region give rise to 143 different one-electron spin-allowed transitions. Even though a few of them are forbidden by symmetry, most are allowed, but many are of low intensity. They can be grouped according to the usual classification MLCT(π* ← d), MC(d* ← d), LC(π* ← π,π* ← n), and LMC(d* ← π,d ← n), which is based on the orbitals engaged and on the specific parts of the complex involved. However, the absorption around 40 000 cm$^{-1}$ is composed of a LC(π* ← π)-type and a LMC(d* ← n,π* ← 1n)-type transition. Thus, the often encountered opinion that this region has to be attributed to a MLCT transition should be revised. The HOMO of [Co(CO)$_4$(H$_2$Si$_4$O$_{12}$)] consists of oxygen lone pairs localized on H$_2$Si$_4$O$_{12}$, and the LUMO is identical with the LUMO of Co(CO)$_4$. The first electronic transitions observed in the near-UV are the of H$_2$Si$_4$O$_{12}$ (oxygen lone pair) to Co(CO)$_4$ fragment charge-transfer type.

I. Introduction

Electronic transitions are usually classified according to the orbitals engaged or to specific parts of the molecule involved. Common types of electronic transitions in organic compounds are π* ← π, σ* ← σ, π* ← n, and π* (acceptor) ← π (donor), the latter leading to so-called locally excited (LE) states. Metal-centered (MC), ligand-centered (LC), ligand-to-metal charge-transfer (LMCT), and metal-to-ligand charge-transfer (MLCT) transitions are commonly observed in coordination compounds. The basic theoretical conception for calculating intensities of electronic dipole-induced transitions is the same in all these cases and was outlined by R. S. Mulliken more than 50 years ago.1 Calculations of oscillator strengths for π* ← π transitions based on the PPP² method have long been a useful tool for spectroscopic and photochemical studies. Wolfsberg and Holz were the first to explain why the tetrahedral ions MnO$_4^-$ and CrO$_4^{2-}$ are colored while the isoelectronic ClO$_4^-$, SO$_4^{2-}$, and PO$_4^{3-}$ are not, based on LCAO-MO calculations of the extended Hückel type and on computed oscillator strengths.² Oscillator strength calculations on different levels of sophistication are often used. However, a general procedure which can be applied to compute or estimate intensities of all types of electronic dipole-induced transitions (EDITs) of large molecules and complexes has still been missing. The simplest generally applicable method bearing the potential to fill this gap is the extended Hückel molecular orbital (EHMO) theory.⁴ One of the most fascinating aspects of this transparent method is that it can be successfully applied to study molecules, clusters, complexes, solids, and the interaction of molecules on surfaces.⁵,⁷ We have therefore developed an EDIT program to calculate oscillator strengths of even very large molecules and complexes based on Slater-type MOs. Calculations of the two-center

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integrals involved have recently been described by J. J. P. Stewart.\textsuperscript{8} In this article, we report the application of EDiT to a number of representative examples based on EHMO wave functions. We focus on the description of electronic charge-transfer transitions, which are actually of great interest and cannot be treated with the different popular ZDO (zero differential overlap) approaches. To warm up, we first consider formaldehyde and MnO$_4^-$\textsuperscript{-}.$^{3,9}$ We then discuss the oscillator strengths as a function of the torsional angle of p-(N,N-dimethylamino)benzonitrile (DMABN), which has become noted for its so-called twisted intramolecular charge-transfer (TICT) state.$^{10,11}$ An investigation of 2,2$'$-bipyridyl (bpy) as a function of the torsional angle serves as a starting point to discuss the Ru(bpy)$_3^{2+}$ spectrum. This will clarify some features of the spectrum of this extensively studied complex. The first monosubstituted octasilasesquioxane with a silicon–metal bond has recently become available, namely, [Co(CO)$_4$(H$_2$SiO$_4$)$_2$]$^{12}$ It bears oxygen lone pair to cobalt charge-transfer transitions, which are discussed. The compounds under consideration are displayed in Figures 1 and 2 and in Chart 1.  

2. Experimental Section

EDT. The electronic transition–dipole moment ($\mu_{ed}$) between two wave functions $\psi_n$ and $\psi_m$ is defined as$^{13,14}$

$$\mu_{ed}^2 = \langle \psi_n | \mu_{ed} | \psi_m \rangle$$

The oscillator strength ($f$) of the transition $n \rightarrow m$ amounts to

$$f = \frac{8\pi^2 \nu c m_e}{3h^2} |\mu_{ed}|^2$$

Making use of the definition of the transition–dipole length ($D_{nm}$)

$$|D_{nm}|^2 = \frac{1}{\epsilon^2} |\mu_{ed}|^2$$

we find

$$f = l_0 |D_{nm}|^2$$

where $\epsilon$ is the elementary charge, $h$ is Planck's constant, $m_e$ is the electron mass, $c$ is the speed of the light in vacuum, $\nu$ are the electron position vectors, $\nu$ is the wavenumber in cm$^{-1}$ of the transition $n \rightarrow m$, and $l_0$ is equal to 1.085 $\times$ 10$^{-5}$ cmÅ$^{-1}$. $f$ is dimensionless. The relation between the molar decadic extinction coefficient ($\epsilon$) and the oscillator strength ($f$) can be expressed as follows:

$$f = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu$$

where $f$ is an intrinsic property of the species (molecule, compound, particle) under consideration and independent of the electromagnetic field responsible for the excitation. Typical $f$ values for electronic dipole-allowed transitions, further denoted as $f_{el}$, are in the range of 10$^{-3}$–1. The $f_{el}$ values for a single absorption or emission electron obey the sum rule\textsuperscript{1}

$$\sum_i \epsilon_{ed}^{n \rightarrow m} = 1$$

where $i$ runs over all excited states involved. For the strongest electronic transitions, $f_{el}$ may therefore be in the order of 1. Generalizing this result leads to the rule that the summed up
oscillator strength in an electronic spectrum must be equal to the number of electrons in the molecule.

The LCAO–MO wave functions are written as products of one-electron molecular orbitals that may contain two electrons each with antiparallel spin. In can be shown that all electrons residing in closed shells do not affect the $f_{ed}$ values. Therefore, we can restrict the discussion to the two MOs changing their occupation upon excitation. We denote the initial and final MOs with $\psi_i$ and $\psi_f$, respectively. $f_{ed}$ is proportional to the energy gap between the two MOs $\psi_i$ and $\psi_f$, $\tilde{\epsilon}$, and to $|D_{ij}|^2$, but the factor $l_0$ has to be doubled if $\psi_i$ is occupied by two electrons, and hence, the maximum $f_{ed}$ value possible for a transition between two nondegenerate molecular orbitals must be 2. Combining eqs 1 and 4, we find for the transition–dipole length

$$D_n = \langle \psi_f | \tilde{\epsilon} | \psi_i \rangle = \left( \sum_{k} c_{k}^{i} \langle \tilde{\epsilon} \rangle \langle \chi | \psi_i \rangle \sum_{l} c_{l}^{f} \langle \psi_f | \tilde{\epsilon} | \chi \rangle \right)$$

(8)

where $c_{k}^{i}$ and $c_{l}^{f}$ are the coefficients of the atomic orbitals $\chi$ constituting the MOs. This equation can be written as a matrix containing integrals over atomic orbitals. We distinguish between block-diagonal or one-center and off-block-diagonal or two-center integrals. The block-diagonal elements contain AOs located at the same atom, while the off-block-diagonal elements concern AOs that are located at different centers. The calculation of the matrix elements is cumbersome. Our treatment basically relies on the procedure described in ref 13. However, for the sake of easier and generally valid programming, some effort was necessary to accommodate this method. The calculation of the transition–dipole length reduces to the computations of overlap integrals with modified Slater exponents, $\xi$. We use the overlap subroutine of ICON18 and ICONC&INPUT12 to calculate the overlap integrals to which the right transformation properties are applied. Slater-type overlap integrals have recently been investigated by Stewart.3 Our computer program, which we name EDIT, has been restricted to FORTRAN 77 standards what makes it easily portable to most platforms.18 EDIT reads input files created by ICONC&INPUT.

We conclude this section by saying a few words about oscillator strengths of excitations between degenerate MOs. Any electron occupying the degenerate initial molecular orbital may be promoted to any molecular orbital of the degenerate final set. Hence, the formula for the $f_{ed}$ value takes the following form:

$$f_{ed} = 2l_0 \tilde{\eta} \sum_{G_l} \sum_{G_i} \left( \langle \psi_f | \tilde{\epsilon} | \psi_i \rangle \right)^2$$

(9)

where $G_l$ and $G_i$ indicate the degeneracy of the initial and the final MO, respectively. The averaged occupation number of the initial MO is denoted by $\tilde{\eta}$; the 2 in the denominator takes into consideration that the factor $2l_0$ is again calculated for fully occupied orbitals. As it is only possible to promote one electron at a time which may originate from any of the initial molecular orbitals, we have to divide the double sum by $G_i$.

**MO Calculations.** Molecular orbital calculations have been carried out by the extended Hückel method.4 The off-diagonal elements were calculated as

$$H_{ij} = 1/kS_{ij}(H_{ii} + H_{jj})$$

(10)

by using the weighted Wolfsberg–Helmholz formula19 with a

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### TABLE 1: Coulomb Integrals $H_{ii}$ and Slater Exponents $\xi$

<table>
<thead>
<tr>
<th>element</th>
<th>$H_{ii}$/eV</th>
<th>$\xi_1$</th>
<th>$\xi_2$</th>
<th>$c_1$</th>
<th>$c_2$</th>
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<tbody>
<tr>
<td>H</td>
<td>1s</td>
<td>-13.60</td>
<td>1.300</td>
<td></td>
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</tr>
<tr>
<td>C</td>
<td>2s</td>
<td>-21.40</td>
<td>1.710</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2s</td>
<td>-26.00</td>
<td>2.140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>4s</td>
<td>-10.03</td>
<td>1.650</td>
<td></td>
<td></td>
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<tr>
<td>Ru</td>
<td>5s</td>
<td>-13.10</td>
<td>1.950</td>
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### TABLE 2: Bond Lengths and Angles

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<tr>
<th>compd</th>
<th>pt group</th>
<th>bond</th>
<th>lengthÅ</th>
<th>bond angle</th>
<th>angle/deg</th>
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<tr>
<td>H2CO</td>
<td>C2v</td>
<td>H1</td>
<td>1.220</td>
<td>H1-C-H2</td>
<td>120.00</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1.080</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO4-</td>
<td>Td</td>
<td></td>
<td>1.590</td>
<td>O1-Mn-O3</td>
<td>109.47</td>
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<tr>
<td>DMABN</td>
<td>C2v</td>
<td>C2</td>
<td>1.440</td>
<td>C1-C2-C3</td>
<td>120.00</td>
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<td></td>
<td></td>
<td></td>
<td>1.395</td>
<td>C2-C3-N4</td>
<td>120.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N1-C1</td>
<td>1.158</td>
<td>H1-C-N2</td>
<td>109.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N1-C2</td>
<td>1.426</td>
<td>C2-C1</td>
<td>120.00</td>
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<tr>
<td>bppy</td>
<td>C2v</td>
<td>C2v</td>
<td>1.392</td>
<td>C2v-C2v-C2v</td>
<td>120.00</td>
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<td></td>
<td>1.489</td>
<td>C2v-C2v-N4</td>
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<td></td>
<td>1.338</td>
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<tr>
<td>Ru(bppy)2+</td>
<td>D3</td>
<td></td>
<td>2.048</td>
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<td>1.390</td>
<td>C2v-C2v-N4</td>
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<td>1.335</td>
<td>H-C2v-C2v</td>
<td>120.00</td>
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</tbody>
</table>

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$^a$ The data of refs 10e and 49 have been used for the planar structure of DMABN and for Ru(bppy)$_2^{2+}$, respectively.

**distance-dependent Hückel constant**

$$k = 1 + [k + \Delta^2 - \Delta^{2e}]^{-1} e^{-\delta(R-R_0)}$$

$$\Delta = \frac{H_{ij} - H_{jj}}{H_{ii} + H_{jj}}$$

(11)

$H_{ii}$ and $H_{jj}$ are the Coulomb integrals of the $i$th and the $j$th atomic orbital, respectively. $R$ is the distance between the atoms where the $i$th and the $j$th atomic orbitals are located. $d_0$ is the sum of the $i$th and $j$th atomic orbital radii calculated from the corresponding Slater exponents; see eqs 13 and 14 in ref 20a. Standard $k = 1$ and $\delta = 0.35$ Å$^{-1}$ parameters were applied. To correct for the core–core repulsion, a two-body term as explained in ref 20a has been taken into account. The computations were carried out using the parameters in Table 1 and ref 12. For MnO$_4^{-}$, a population analysis based on ab initio calculations reveals that the population of the 3d orbitals is close to that of the Mn$^{2+}$ ion in which two electrons have been removed from the 4s orbital. We have therefore applied the STO basis sets of the Mn$^{2+}$ ion.21 If not stated otherwise, the bond lengths and angles used for the calculations are compiled in Table 2. For the EHMO parameters and the geometry of [Co(CO)$_3$(H$_2$Si$_2$O$_{13}$)], we refer to ref 12.

**Absorption Spectra.** Absorption spectra were measured at room temperature on a PHILIPS PU 8740 scanning spectrophotometer. A 10-mm quartz cell was used. Bandwidth and scan speed were chosen to be 0.2 nm and 125 nm/min, respectively. The [Ru(bppy)$_2^{2+}$](Cl$^-$)$_2$ complex has been synthesized as described in ref 22, and its spectrum was measured in water. The ligand was purchased at Fluka and measured in acetonitrile, cyclohexane, ethanol (Merck p.a.), 2 M NaOH, and 0.1 M HCl.
TABLE 3: Matrix Elements of $D_{ij}$ (in Å) for the $\pi^* - \pi$ Transition of Formaldehyde Calculated for Three Different Origins of the Coordinate System

<table>
<thead>
<tr>
<th>$z$</th>
<th>$0.5607(2p_{c})$</th>
<th>$+0.7164(2p_{o})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-0.8567(2p_{c})$</td>
<td>$+0.2930^a$</td>
<td>$+0.0120^a$</td>
</tr>
<tr>
<td>$-0.0000^b$</td>
<td>$0.0657^a$</td>
<td>$+0.0417^a$</td>
</tr>
<tr>
<td>$-0.5866^b$</td>
<td>$+0.3197^a$</td>
<td>$+0.0000^a$</td>
</tr>
<tr>
<td>$+0.7315(2p_{o})$</td>
<td>$-0.0983^b$</td>
<td>$+0.6393^a$</td>
</tr>
<tr>
<td>$-0.0624^c$</td>
<td>$+0.0000^c$</td>
<td>$+0.0000^c$</td>
</tr>
</tbody>
</table>

$^a$ The origin at the middle of the C=O bond. $^b$ and $^c$ Origin at the carbon and at the oxygen atom, respectively.

3. Results and Discussion

Formaldehyde. We consider the $z$-polarized $\pi^* - \pi$ transition of formaldehyde. The computed final and initial molecular orbitals ($\psi_1$ and $\psi_0$) are

$$
\psi_1 = -0.8567(2p_{c}) + 0.7315(2p_{o})
$$

$$
\psi_0 = 0.5607(2p_{c}) + 0.7164(2p_{o})
$$

with an energy separation of approximately 42,500 cm$^{-1}$. The transition dipole length ($D_{ij}$), eq 8, consists of four terms:

$$
D_{ij} = \left( \begin{array}{cc}
0.8567(0.5607)(2p_{c})(2p_{c}) & -0.8567(0.7164)(2p_{c})(2p_{o}) \\
0.7315(0.5607)(2p_{o})(2p_{c}) & 0.7315(0.7164)(2p_{o})(2p_{o}) \\
\end{array} \right)
$$

The diagonal elements are of one-center nature, while the off-diagonal terms contain AO's located at different atoms and are therefore of the two-center type. We have calculated these elements for three different origins of the coordinate system:

(a) origin in the middle of the C=O bond (Figure 1a);
(b) and (c) origin at the carbon and at the oxygen atom, respectively.

The results are reported in Table 3. We observe that the off-diagonal elements may become quite large, depending on the origin of the coordinate system. Because of the nature of the $\pi^* - \pi$ transition, they are of different sign and almost cancel. The transition dipole moment ($\mu_{\pi^*\pi}$) must be independent of the chosen origin of the coordinate system, as required by theory.

The oscillator strength of this transition amounts to

$$
f_{\text{ed},z} = (2 \nu_0 \text{cm}^2/\text{Å}^2)(42,500 \text{ cm}^{-1})(0.6067 \text{ Å})^2 = 0.34
$$

The reported experimental value of this $\pi^* - \pi$ excitation is 0.3. If we had chosen the ZDO approach, which neglects the off-block-diagonal elements, the three different $f_{\text{ed},z}$ values (a) 0.35, (b) 0.38, and (c) 0.32 would have been obtained. This means that the full calculation is independent of the origin of the coordinates, as it should be, while the ZDO approach is not.

Permanganate Ion. The permanganate ion can be regarded as the classical charge-transfer interaction. Its electronic spectrum has been reported by many individuals and is still the focus of recent publications. Three major absorption bands lie below 50,000 cm$^{-1}$, namely at 18,500, 32,200, and 44,000 cm$^{-1}$. We aim at the description of the oscillator strength of the long-wavelength band, responsible for the violet color. The highest occupied molecular orbital is of $t_1$ symmetry and thus 3-fold degenerate. The LUMO spans an E representation at the $T_d$ point group, and thus, the first symmetry-allowed band is caused by a $e - \pi$ transition between

| TABLE 4: Oscillator Strength of the First Electronic Transition (LUMO — HOMO) of MnO$_4^-$ |

<table>
<thead>
<tr>
<th>$n$</th>
<th>$n_f$</th>
<th>$f_{\text{ed},z}$</th>
<th>$f_{\text{ed},z}$</th>
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<tbody>
<tr>
<td>1</td>
<td>14</td>
<td>17</td>
<td>3.6687E+05</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>17</td>
<td>4.8758E-02</td>
</tr>
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<td>3</td>
<td>16</td>
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</tr>
<tr>
<td>4</td>
<td>14</td>
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<td>1.2233E-03</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>18</td>
<td>1.6257E-02</td>
</tr>
<tr>
<td>6</td>
<td>16</td>
<td>18</td>
<td>1.6833E-02</td>
</tr>
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</table>

$$
\sum_{n=1}^{6} \frac{\Delta E}{n} = 15 \text{ 450  cm}^{-1}
$$

$^a$ $\Delta E_{\text{ed}} = 15 \text{ 450  cm}^{-1}$

$^b$ $\Delta E_{\text{ed}} = 15 \text{ 450  cm}^{-1}$

TABLE 5: First Electronic Dipole-Allowed Transition (T$_2$ $=$ 1A$_1$) of MnO$_4^-$

<table>
<thead>
<tr>
<th>$\Delta E$/eV</th>
<th>$f_{\text{ed},z}$</th>
<th>$f_{\text{ed},z}$</th>
<th>$f_{\text{ed},z}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.29</td>
<td>1.68</td>
<td>2.48</td>
<td>1.92</td>
</tr>
<tr>
<td>0.032</td>
<td>0.076</td>
<td>0.069</td>
<td>0.046</td>
</tr>
</tbody>
</table>

the oxygen t$_1$ orbitals and the e orbitals exhibiting mainly metal d character. Hence, this $\text{T}_2$ $\rightarrow$ $\text{A}_1$ transition is of the LMCT type. By group theoretical reasoning

$$
E \otimes T_1 \supseteq T_2 \quad \Gamma_{x,y,z} = T_2
$$

(15)

the transition is equally allowed in any of the three directions $x$, $y$, and $z$. The total transition dipole moment ($\mu_{\text{tot}}$) must be independent of the chosen origin of the coordinate system, as we have already pointed out. This does not hold for its projections to the axes. Applying the proposition of Pythagoras, we get

$$
\mu_{\text{ed},x}^2 = (\mu_{\text{ed},x})^2 + (\mu_{\text{ed},y})^2 + (\mu_{\text{ed},z})^2
$$

(16)

However, considering the choice of our coordinates as motivated by group theory—the three axes coincide with the 2-fold symmetry axis (Figure 1b)—we expect $f_{\text{ed},x} = f_{\text{ed},y} = f_{\text{ed},z}$. This is correct, as we see by inspection of the computations compiled in Table 4.

The initial MO is 3-fold-degenerate and the final MO is 2-fold-degenerate, respectively, giving rise to six transitions. These values are summed up and divided by three; see eq 9. The experimental absorption energy of the LUMO $-$ HOMO transition in MnO$_4^-$ is 18,470 cm$^{-1}$. Our calculation yields a HOMO/LUMO separation of 15,450 cm$^{-1}$ or 1.92 eV, which is too small and could be adjusted. We have not done this since it is natural for the orbital energy difference which does not contain the exchange integral to be smaller than the energy difference between the ground state and the excited state. The experimental $f_{\text{ed}}$ values projected to the axes (i.e., $f_{\text{ed},x}$, $f_{\text{ed},y}$, $f_{\text{ed},z}$) of the first electronic transition in permanganate lie at 0.032. Our calculated $f_{\text{ed}}$ value is 0.046 by taking the full transition matrix into account. The ZDO approach, which considers only the one-center elements, yields 0.057. This means that the off-block-diagonal elements correct the ZDO $f_{\text{ed}}$ value significantly.

To our knowledge, we are the first to calculate the oscillator strength of the long-wave transition ($\text{T}_2$ $\rightarrow$ $\text{A}_1$) in MnO$_4^-$, applying an exact treatment within the extended Hückel method. Wolfsberg and Helmholtz neglected the oxygen 2s AO's to reduce the computational burden and obtained a wrong ordering of the $t_1$ and $e$ levels in the LUMO region. They computed a projected oscillator strength of 0.076 considering only the block-diagonal elements. An $f_{\text{ed}}$ value of 0.069 was obtained in a
more recent ab initio study in which $\psi_{A_1}$ and $\psi_{T_1}$ were built from occupied and virtual orbitals of a ground-state calculation.21 These results are compiled in Table 5.

DMABN. The phenomenon of the dual fluorescence of $p$-(N,N-dimethylamino)benzotriazole (DMABN) and structurally related compounds in polar solvents has given rise to scientific controversy over its origin which has been going on for the last 4 decades.10,11 While Majumdar et al. were to stress the relevance of full ground-state geometry optimization in their study on DMABN,10c Calzaferri et al.11 pointed out that the relaxation of the $S_1 \rightarrow S_0$ Franck-Condon (FC) excitation leads to a lengthening of the C-N bond by an amount of about 0.1 Å, allowing the cyano-group-centered $\pi^*$ orbital to contribute significantly to the developing locally excited (LE) state which has been reported to be important for the description of the evolving TICT state. This is the starting point for an EDT oscillator strength calculation of the $\pi^*(\text{A_1}) \rightarrow \pi_0$ charge-transfer transition between intramolecular $\pi$-acceptor/$\pi$-donor groups.

To explain the calculations, we first consider the frontier orbitals depicted in Figure 3. On the left-hand side, we start from the planar $S_0$ ground state of DMABN with the first two sets of $\pi^* \rightarrow \pi$ transitions. Set I represents the $\chi$-polarized $\pi^*(a_2) \rightarrow \pi(b_2)$ and $\pi^*(b_2) \rightarrow \pi(a_1)$ excitations, giving rise to the $S_1$ state of B1 symmetry. Set II represents the $\gamma$-polarized $\pi^*(b_2) \rightarrow \pi(b_1)$ and $\pi^*(a_1) \rightarrow \pi(a_2)$ excitations, giving rise to the $S_2$ state of A1 symmetry.10c CI treatment to create the desired transitions between electronic states, namely, the $\gamma$-allowed $S_1(B_1) \rightarrow S_0(A_1)$ and the $\gamma$-allowed $S_2(A_1) \rightarrow S_0(A_1)$ transitions, would not be a difficult problem mathematically,13 but there is no way to circumvent appropriate parameterization. We therefore prefer to discuss the results on a one-electron basis, which leads to an interesting pictorial interpretation. We present the results within the $C_2v$ point group; thus, the $z$ axis coincides with the 2-fold rotational axis $C_2$, and $x$ lies in the plane of the aromatic ring. This allows a simplified discussion without losing important information.

In the ground-state geometry on the left side of Figure 3, $\pi^*(b_2)$ is too high in energy to be directly attainable in a FC excitation. However, occupation of the C-N antibonding $\pi_1$ orbital causes weakening of this bond. As the FC geometry relaxes by stretching the C-N bond, the energy of the $b_1$ symmetry in-plane orbital $\pi_1$ decreases rapidly, by as much as 1.2 eV during stretching of 0.1 Å. Thus, $\pi^*$ becomes the superlance LUMO. As a result, its contribution to the developing partial CT state increases rapidly and the molecule ends up in the LE state displayed in Figure 3, with broken arrows indicating electronic-dipole-forbidden relaxation pathways.

Starting from the LE state, we now consider torsion of the dialkylamino group 90° out-of-plane. The main event observed

Table 6: Results of the Oscillator Strength Calculation of DMABN

<table>
<thead>
<tr>
<th>$\Delta(TICT,\text{floss})^{\pi^* \rightarrow \pi}$</th>
<th>$\pi^* \rightarrow \pi(TICT)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>torsion angle</td>
<td>$\langle b_2 \rangle \rightarrow \langle b_1 \rangle$</td>
</tr>
<tr>
<td>90°</td>
<td>4.468E-03</td>
</tr>
<tr>
<td>75°</td>
<td>4.324E-03</td>
</tr>
<tr>
<td>60°</td>
<td>3.988E-03</td>
</tr>
<tr>
<td>45°</td>
<td>3.738E-03</td>
</tr>
<tr>
<td>30°</td>
<td>2.533E-03</td>
</tr>
<tr>
<td>15°</td>
<td>8.850E-04</td>
</tr>
<tr>
<td>0°</td>
<td>2.393E-38</td>
</tr>
</tbody>
</table>

The symmetry labels refer to MO symmetries in the ideal TICT geometry (torsion angle 90°).

The weight of the low-energy excited configurations of A1 symmetry increases from left to right in Figure 3, due to the large stabilization of the $\pi^*$ orbital, the destabilization of the $\pi_1$ orbital, and the change in character of the $\pi_1$ orbital from $b_2$ to $b_1$. A $\gamma$-polarized ($b_1 \rightarrow b_2$) transition is symmetry-allowed. Calculating the oscillator strengths shows, however, that it is low in intensity. This is evident from the data in Table 6 where we report EDT oscillator strengths for the four relevant transitions ($b_1 \rightarrow b_2$, $b_2 \rightarrow b_1$, $b_2 \rightarrow b_2$, and $a_2 \rightarrow a_2$) at different values of the amino group torsional angle. The low intensity of the $a_2$-allowed transition ($b_1 \rightarrow b_2$) is not surprising and can be explained by the poor overlap of the $\pi^*$ and $\pi_1$ orbitals. The intrinsic emissive lifetime ($\tau_0$) for the $f \rightarrow i$ emission is

$$1/\tau_0 = \frac{64\pi^4\nu^2}{3h} |\langle \psi_f | \mathbf{e} \mathbf{r} | \psi_i \rangle|^2$$

where $\nu$ is the wavenumber in cm$^{-1}$ of the luminescence $f \rightarrow i$ and $\mathbf{r}$ is the electron position vector.13 Substituting Eq 3 in Eq 17 leads to

$$1/\tau_0 = \frac{8\pi^2\nu^2e^2}{cm_{e}fed}$$

Hence, the TICT state is expected to live long enough to relax to a state described by the ($b_2)^2(b_1)^0$ configuration. Emission of a photon in this state is forbidden by symmetry; see Table 6. However, a small twist of only 15° increases this oscillator strength along the $z$ axis enormously. TICT emission has empirically been shown to be $\gamma$-polarized and strong in intensity, and the emission rates can be activated thermally.10 This is in good qualitative agreement with the oscillator strength calculations. We note that the two $\gamma$-polarized $\pi^* \rightarrow \pi$ transitions depend relatively little on the amino group torsional angle. This dependence is indeed characteristic for the TICT state.
without a large activation barrier upon coordination to a metal center. We calculated $\Delta E^a = 0.24$ eV for the trans-to-cis conversion. This is only half of, e.g., the boat-to-chair interconversion barrier of cyclohexane. Fielding and Le Fevre have carried out dipole moment measurements of bpy in benzene from which they conclude that its geometry is near-trans with a ring—plane twist of about 28° or $\theta = 152°$. The $\theta = 0°$ refers to the cis-planar geometry. Our EHMO calculations give no evidence for a local minimum in the range of 90° to 180°. We observe a local minimum at $\theta = 14°$ and the global minimum at $\theta = 180°$, in qualitative agreement with recently published ab initio studies on the torsional potential of the 4,4'-bipyridimine. It is therefore most likely that Fielding's experimental results have to be interpreted as caused by a mixture of trans and cis isomers. Because of the shallow potential along the angle $\theta$, it appears probable that intermediate angles are populated to a certain degree depending on the solvent and on the temperature. This conclusion is supported by results from UV/vis spectroscopy.

Nakamoto was the first to report the pH dependence of the electronic absorption spectrum of bpy. In acidic solution, two bands are observed, one at 33 200 cm$^{-1}$ and another one at 41 500 cm$^{-1}$. Krumholz, and later also Weinstein and Brey, showed that the monocation predominates in 2 N HCl. In basic solution, the authors reported two peaks at 35 850 and 43 100 cm$^{-1}$, respectively, which they assigned to the trans isomer. It was argued that the monocation favors a not completely planar cis geometry, while in basic solution the planar trans isomer is the most stable form. Some further aspects of the UV/vis spectrum of bpy have been discussed based on PPP calculations by Gondo and by Hanazaki and Nagakura.

In Figure 4, we show the ultraviolet absorption spectra of bpy in acetonitrile, cyclohexane, ethanol, and 2 M NaOH and in Figure 5 the spectrum of Ru(bpy)$_3^{2+}$ in water along with the bpy spectrum in 0.1 M HCl. We notice that the first band of bpy appears at the same position and is of similar shape in cyclohexane, acetonitrile, ethanol, and 2 M NaOH and that it is very broad and featureless in each case. Three main bands at about 35 500, 41 100, and 42 200 cm$^{-1}$ are observed in organic solvents and only two at 35 500 and 42 600 cm$^{-1}$ in 2 M NaOH. The main absorptions in 0.1 M HCl appears at 33 200 and 41 500 cm$^{-1}$, and we also note the much less intense band at 37 500 cm$^{-1}$, Figure 5.

The results of EDIt calculations on bpy as a function of the angle $\theta$ are compiled in Table 7 and in Figure 6. In Figure 7, we show the correlation diagram of the frontier MOs of trans- and cis-bpy. The two prominent $\pi^* \rightarrow \pi$ absorptions of the cis isomer can be assigned to the $1\pi^* \rightarrow 1\pi$ and the $2\pi^* \rightarrow 1\pi$ transitions with calculated oscillator strengths of 0.853 and 0.376. The $2\pi^* \rightarrow 2\pi$ transition is very weak ($I_{2\pi^*} = 10^{-3}$) for cis, but becomes the prominent $1\pi^* \rightarrow 1\pi$ band for trans. We follow the $1\pi^* \rightarrow 1\pi$ transition, circles in Figure 6, along the angle $\theta$ starting at $\theta = 0°$. The orbital energy difference between the $1\pi^*$ and $1\pi$ levels increases with increasing $\theta$. At the same time, the oscillator strength decreases rapidly at angles larger than about 30°. If we surpass $\theta = 90°$, it correlates with the $2\pi^* \rightarrow 2\pi$ transition of the trans isomer and its energy leaves the spectral region considered here. Instead a new $1\pi^* \rightarrow 1\pi$ transition develops out of the former $2\pi^* \rightarrow 2\pi$ which gains much intensity at $\theta > 90°$ and almost reaches the $1\pi^* \rightarrow 1\pi$ oscillator strength of the cis-planar conformation, while the orbital energy difference decreases to approximately the same value. The reverse is true for the cis $2\pi^* \rightarrow 1\pi$ (squares in Figure 6) which retains its $\pi^* \rightarrow \pi$ character but loses intensity with increasing $\theta$ and becomes symmetry-forbidden at $\theta = 180°$. The second excited $\pi^*$ state of the trans isomer has to be regarded as a mixture of the $(b_2\pi\pi^*)(a_1\pi^*$) and the $(b_3\pi\pi^*)(a_1\pi^*)$ configurations which have the same symmetry, similar oscillator strength, and similar energy and can therefore interact. They correlate, however, only with high-energy configurations at decreasing $\theta$ and are therefore not indicated in Figure 6 but are reported in Table 7.

If we accept the results of our calculations and conclusions of previous studies that trans is the stable isomer but that the potential along the angle $\theta$ is very shallow, then it is easy to understand why the first intense band in Figure 4 is broad, featureless, and similar in all four solvents. It is caused by a superposition of bands arising from an equilibrium Boltzmann distribution over the whole range of angles $\theta$ from 180° to 0°. This causes a hypochromic shift of the maximum of the first intense band, because the $1\pi^* \rightarrow 1\pi$ transition energies of the species with angles different from $\theta \approx 180°$ to $\theta \approx 0°$ appear at larger energy; see Figure 6. The reason for the bathochromic shift of the first $1\pi^* \rightarrow 1\pi$ transition by 2300 cm$^{-1}$ of the protonated bpy is due to the predominance of the cis isomer and hence a narrow Boltzmann distribution of the $\theta$ region close to 0°.

We now investigate if this explanation is consistent with the other observations. Let us remark that the calculated orbital energy differences are always smaller than the experimental electronic transition energies, for the same reason as explained for MnO$_2$-, but it is generally observed that the energy differences between the first and the second transitions are well reproduced as long as CI plays a minor role.

The second intense band of bpy appears at about the same position, $\approx 42$ 200 cm$^{-1}$, and is of similar shape in cyclohexane, acetonitrile, ethanol, and 2 M NaOH. It is broad, featureless,
and of about half the intensity of the first $\pi^* - \pi$ transition. In addition, there is a weaker bathochromically shifted band at 41 100 cm$^{-1}$ the intensity of which decreases in the order cyclohexane > acetonitrile > ethanol > 2 M NaOH and becomes the prominent band in 0.1 M HCl. Based on our calculations, both bands have to be interpreted as the second $\pi^* - \pi$ transition, the higher energetic one belonging to the trans and the lower energetic to the cis isomer. This means that the ratio of the intensities of these bands is an indicator for the ratio of the cis conformation, prefered by the protonated bppy, and the trans isomer. Different bppy—solvent interactions affect the Boltzmann population of the angle $\theta$. One can speculate that detailed experimental investigations of the bppy spectra in different solvents and in suficiently large temperature range would allow us to determine this Boltzmann distribution experimentally. At present, we can only deduce that the concentration of the cis form decreases in the order 0.1 M HCl > cyclohexane > acetonitrile > ethanol > 2 M NaOH. The small peak at 37 500 cm$^{-1}$ observed in 0.1 M HCl can probably be assigned to the $\pi^* - \pi$ transition of the cis isomer with a calculated oscillator strength of 0.018, see Table 7, but this remains uncertain.

The first electronically-excited-state configuration of bppy is of the $(1n)^{-1}(1\pi)^{2}$ type. According to the results reported in Table 7, a $\pi^* - n$ transition should appear as a long-wavelength shoulder of the $1\pi^* - 1\pi$ band. However, it is well-known that the energy of the $\pi^* - n$ transitions strongly depends on the solvent polarity, which has been investigated for the comparable terpyridyl (tpy) molecule by Fink and Ohnesorge. They have observed the solvent dependence of the long-wavelength tail of the tpy absorption spectrum as typically expected for $\pi^* - n$ transitions. The tpy $\pi^* - n$ absorption starts at 420 nm in cyclohexane and nearly disappears below the $\pi^* - \pi$ band in chloroform. We have therefore investigated the long-wavelength tail of bppy below 32 000 cm$^{-1}$. The onset in Figure 4 shows a shoulder at 31 500 cm$^{-1}$ in cyclohexane, which we could not observe in the other solvents. It is therefore
likely that this shoulder can be assigned to the $13\pi_e \rightarrow \pi$ transition of the trans isomer with an oscillator strength in the order of $3 \times 10^{-4}$.

**Tris(2,2'-bipyridyl)ruthenium(II).** The excited-state chemistry of Ru(bpy)$_3^{2+}$ has attracted intense interest in recent years, and as a consequence, its electronic spectrum has been investigated in great detail. It is therefore difficult to add relevant new information. However, EHMO–EDIT calculations offer new insight which helps to improve our understanding of this interesting complex, the one-electron levels of which are depicted in Figure 8. The comparison of the Ru(bpy)$_3^{2+}$ frontier orbitals with those of the ligand and the metal has been obtained by means of the fragment molecular orbital (FMO) technique. The subscripts $x$ and $y$ ($x+y=1$) in the $d_{x^2}$ and $d_{y^2}$ labels are the populations of these orbitals per electron as derived from a Mulliken population analysis. The Ru 4d orbitals mix strongly with the n-type ligand orbitals to form the metal–ligand bond and at the same time to push the (d$^5$) levels above the first four π* ligand orbitals which are only slightly perturbed. We name the (d$^5$) wave function d$^{-n}$ orbital based on the $d_{x^2}$,$d_{y^2}$, population. Each ligand π* orbital is split into a degenerate e set and a MO of either a$_1$ or a$_2$ symmetry upon coordination to the metal center. The nondenerate component of these orbitals can be classified to be either symmetric a$_1$ or antisymmetric a$_2$ with respect to the C$_2$ axis retained in the complex. Weak interaction of the Ru 12p-(d) orbitals with the 3τ and 1τ MOs of bpy split them by 250 cm$^{-1}$ into an a$_1$(d) and an e(d) component, respectively, a$_1$(1d$_{x^2,0}(0,10)$) and e(2d$_{x^2,0}(0,14)$), upon symmetry reduction from O$_h$ to D$_3$. The experimental value for the a$_1$(d)-to-e(d) splitting is 200 cm$^{-1}$.40

The electronic spectrum of Ru(bpy)$_3^{2+}$ can be grouped into four regions phenomenologically by visual inspection of the spectrum in Figure 5 and also based on the MO diagram in Figure 8. However, the number of possible excited-state configurations in the HOMO/LUMO region go rise to $13 \times 11 = 143$ different one-electron transitions in any of the three directions. Even though a few of them are forbidden by symmetry, most are allowed, but many are of low intensity. Transitions with oscillator strengths larger than $1.0 \times 10^{-2}$ and energies smaller than 45,000 cm$^{-1}$ are compiled in Table 8. We have grouped them according to the usual classifications MLCT($\pi^* \rightarrow d$), MC(d$^* \rightarrow d$), LC(π$^* \rightarrow \pi$, π$^* \rightarrow n$), and LMCT(d$^* \rightarrow \pi$, d$^* \rightarrow n$). It is obvious that a very detailed analysis in which spin–orbit and CI interactions would have to be included is complicated. Being aware of the danger of oversimplification, we nevertheless deduce a general pattern.

The first two electronic transitions are of the π$^* \rightarrow d$ type with similar oscillator strength. They are polarized perpendicular with respect to the C$_2$ axis and lead to the so often investigated MLCT(π$^* \rightarrow d$) states. Taking a closer look at the MLCT transitions in the HOMO/LUMO region, see Table 9, we find that the first band is strongly polarized perpendicular to the C$_2$ axis, which is not surprising as this is the direction of the transition metal to ligand. The calculated intensity ratio $I_{d}/I_{\pi}$ of this long-wavelength part of the MLCT transition is 17.3. Palmer and Piper measured polarized spectra of single crystals and reported a ratio of 26.5 at 300 K.22 The good agreement between the calculated energy range of 22,065 to 23,070 cm$^{-1}$ and the accepted experimental value of 22,120 cm$^{-1}$ of this first MLCT transition should not be overemphasized but gives us some confidence that the parameters in Table 1 are reasonable.

<table>
<thead>
<tr>
<th>Table 8: Calculated Transition Energies (in cm$^{-1}$) and Oscillator Strengths for the Ru(bpy)$_3^{2+}$ Complex</th>
<th>Table 9: First Electronic MLCT Transitions in Ru(bpy)$_3^{2+}$</th>
</tr>
</thead>
</table>
| **Type** | **Table 8:**<br>**MLCT**<br>22 312<br>23 070<br>29 905<br>30 152<br>30 287<br>33 307<br>34 025<br>34 272<br>30 130<br>30 377<br>31 000<br>31 137<br>31 759<br>31 759<br>31 896<br>36 282<br>38 841<br>38 975<br>38 978<br>43 036<br>43 036<br>43 364<br>43 498<br>39 066<br>39 202<br>43 036<br>43 036<br>43 261<br>43 261<br>43 588<br>43 588 | **Table 9:**<br>**MLCT**<br>$\Delta E_{\text{MLCT}}$
| **trans** | **E**
| **f$_{\text{MLCT}}$** | **total**
| 22 312 | $2d_{x^2,0}(0,14)$ | E | 0.06 | 0.13 (1)
| 23 070 | $2d_{x^2,0}(0,14)$ | E | 0.07 | 0.07
| 29 905 | $2d_{x^2,0}(0,14)$ | E | 0.07 | 0.07
| 30 152 | $2d_{x^2,0}(0,14)$ | A$_2$ | 0.09 | 0.16 (1 + 2)
| 30 287 | $2d_{x^2,0}(0,14)$ | E | 0.06 | 0.06
| 33 307 | $2d_{x^2,0}(0,14)$ | A$_2$ | 0.07 |
| 34 025 | $2d_{x^2,0}(0,14)$ | E | 0.03 | 0.08 (2)
| 34 272 | $2d_{x^2,0}(0,14)$ | A$_2$ | 0.01 |
| 30 130 | $2d_{x^2,0}(0,14)$ | E | 0.01 |
| 30 377 | $2d_{x^2,0}(0,14)$ | A$_2$ | 0.02 (2)
| 31 000 | $1\pi_e \rightarrow \pi$ | E | 0.08 |
| 31 137 | $1\pi_e \rightarrow \pi$ | A$_2$ | 0.54 |
| 31 759 | $1\pi_e \rightarrow \pi$ | A$_2$ | 0.52 (1.3 (2)
| 31 759 | $1\pi_e \rightarrow \pi$ | E | 0.10 |
| 31 896 | $1\pi_e \rightarrow \pi$ | E | 0.21 |
| 36 282 | $2d_{x^2,0}(0,14)$ | E | 0.04 |
| 38 841 | $2d_{x^2,0}(0,14)$ | E | 0.10 (3)
| 38 975 | $2d_{x^2,0}(0,14)$ | E | 0.12 (4)
| 38 978 | $2d_{x^2,0}(0,14)$ | E | 0.18 |
| 43 036 | $2d_{x^2,0}(0,14)$ | E | 0.05 |
| 43 036 | $2d_{x^2,0}(0,14)$ | E | 0.01 |
| 43 364 | $2d_{x^2,0}(0,14)$ | E | 0.04 |
| 43 498 | $2d_{x^2,0}(0,14)$ | A$_2$ | 0.04 |
| 39 066 | $1\pi_e \rightarrow \pi$ | E | 0.04 |
| 39 202 | $1\pi_e \rightarrow \pi$ | E | 0.03 |
| 43 036 | $1\pi_e \rightarrow \pi$ | E | 0.17 |
| 43 036 | $1\pi_e \rightarrow \pi$ | A$_2$ | 0.07 |
| 43 588 | $1\pi_e \rightarrow \pi$ | E | 0.51 |

**Calzaferri and Rytz**
Figure 9. Correlation diagram for H$_7$Si$_8$O$_{12}$ + Co(CO)$_4$ $\rightarrow$ [(H$_7$Si$_8$O$_{12}$)Co(CO)$_4$]. The energy levels of [(H$_7$Si$_8$O$_{12}$)Co(CO)$_4$] are split into three parts. Parts A and C contain the orbitals localized on the H$_7$Si$_8$O$_{12}$ and on the Co(CO)$_4$ fragment, respectively. The MOs of region B are delocalized over the whole molecule.

The third MLCT($\pi^* \rightarrow d$) bands are buried by the intense LC transitions and are therefore expected to affect the dipolar character of the spectral region 2. This is in good agreement with recently measured Stark absorption spectra of the bpy ligand and the corresponding Zn$^{2+}$, Fe$^{2+}$, Ru$^{2+}$, and Os$^{2+}$ complexes. Hug and Boxer have found that the intraligand transitions of the complexes lead to excited states with much larger dipole moments than expected for purely ligand-centered transitions.

The LC region spans from 31 000 cm$^{-1}$ to the far-UV. The most intense part is centered around 31 137 cm$^{-1}$ and indicated with the label 2 in Figure 5 and Table 8. It is expected to be of similar shape and energy as the $1\pi^* \rightarrow 1\sigma^*$ transition of cis-bpy. The bathochromic shift can be explained by the weak but not negligible interaction of the metal orbitals with the $1\pi^*$ and $1\sigma^*$ orbitals of the ligand. The direct through-space interaction between the three bpy ligands is very weak as indicated by the reduced overlap population between the N atoms; see Chart 2. We should not ignore, however, that this first LC($\pi^* \rightarrow \pi$) band consists of five significant contributions, while there is only one $1\pi^* \rightarrow 1\sigma^*$ transition in the cis-planar ligand.

The next intense part of the LC region groups around 38 975 cm$^{-1}$. It is indicated with the label 3 in Figure 5 and Table 8. At about the same energy, we observe two relatively intense LMCT ($d-\pi^* \rightarrow 1\sigma$; $d-\pi^* \rightarrow 3\pi^*$)-type transitions. The spectrum in Figure 5 shows two bands in this region. Because of the small energy difference, it is difficult to know if these transitions have to be attributed to the shoulder at 39 400 cm$^{-1}$, but it seems probable if we take the relative oscillator strength into account. In any case, however, we feel that the often encountered opinion that this region has to be attributed to a MLCT transition should be revised. We add that the calculated ratio of the oscillator strength of regions 2 and 3 is 2.56 for the complex and 2.27 for the ligand. This and the comparison with the spectrum of the bpy monocation in Figure 5 support our interpretation. Region 4 in Figure 5 lies very high for a frontier orbital description. However, a LMCT($d-\pi^* \rightarrow \pi$)-type transition seems to contribute significantly to this absorption. This means that its similarity with the ligand spectrum should not be overemphasized. The two intense LMCT transitions are calculated to lie at 43 261 and 43 588 cm$^{-1}$ with oscillator strengths of 0.17 and 0.51, respectively. The transferred charge is of $\sigma$ origin and the large intensity is due to the extended overlap between the donor and acceptor MOs.

**Monosubstituted Octanuclear Silasesquioxane.** The electronic structure of this complex which has recently been synthesized can be best understood by splitting it into three parts as shown in Figure 9. The orbitals localized on the H$_7$Si$_8$O$_{12}$ and on the Co(CO)$_4$ fragments are denoted by A and C; those delocalized over the whole molecule are denoted by B. The main correlations between the fragments and the delocalized molecular orbitals of region B are indicated with dotted lines. The orbitals of region B are responsible for the bonding and antibonding interactions between H$_7$Si$_8$O$_{12}$ and Co(CO)$_4$; see ref 12. Experimentally, the UV/vis spectrum of [Co(CO)$_4$(H$_7$Si$_8$O$_{12}$)] measured in n-hexane at room temperature starts with a long tail at about 380 nm which develops after some weak shoulders to a first maximum below 200 nm. Since the HOMO region consists of oxygen lone-pair orbitals, we can attribute the first transitions to be of the charge-transfer type in which an electron of the HOMO region A is transferred to the LUMO region of C:

$$[\text{H}_7\text{Si}_8\text{O}_{12}][\text{Co(CO)}_4]^+ \xrightarrow{\text{hv}} [\text{H}_7\text{Si}_8\text{O}_{12}]^+ [\text{Co(CO)}_4]^-$$

(19)

Individual oscillator strengths for the long-wavelength tail A-to-C charge-transfer transitions have been calculated to be at best $1.5 \times 10^{-3}$. The two highest occupied orbitals of region B belong mainly to the H$_7$Si$_8$O$_{12}$ fragment and are about 90% oxygen lone pair character with some Co contribution. This means that the shorter wavelength B-to-C transitions are of the same H$_7$Si$_8$O$_{12}$ (oxygen lone pair) to Co(CO)$_4$ fragment charge-transfer type. The individual oscillator strengths of these B-to-C charge-transfer transitions, however, have been calculated to be up to 0.03.
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