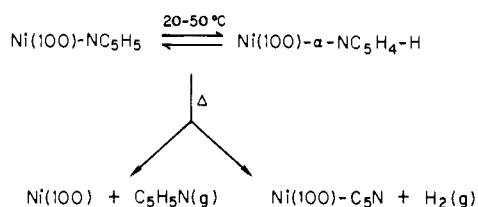Scheme I

explain the uniquely high regiospecificity of nickel catalysts and the general features of the catalytic studies of Moyes and Wells[10] with full consistency of mechanistic interpretation. We cannot mechanistically interpret the higher temperature decomposition processes for adsorbed pyridines because of possible kinetic isotope effects and because two or more processes may be operative.

The pyridine chemistry of the (100), (111), and 6(111) × (111) surfaces of platinum was similar to that of Ni(100) except that reversible C–H bond breaking (i.e., H–D exchange) was not detected. Other nickel surfaces like Ni(111) and Ni[9(111) × (111)] showed only single broad $H_2(D_2)$ decomposition spectra and no evidence of H–D exchange between C_5H_5N and C_5D_5N. The unique features of Ni(100) may be due to a geometric factor,[26] but further studies with other surfaces are required before this tentative proposal can be seriously advanced. Presently, the conceptual features of this experimental study are being applied to thiophene and furan surface chemistry.

Registry No. Pyridine, 110-86-1; Ni, 7440-02-0; Pt, 7440-06-4.

Supplementary Material Available: Figures of complete thermal desorption and thermal decomposition spectra for C_5H_5N, 2,6-$C_5H_3D_2N$, 3,5-$C_5H_3D_2N$, and 4-C_5H_4DN adsorption states on Ni(100) (Figures 2–6), experimental procedures for the synthesis of the deuterium-labeled pyridines, and thermal desorption data for 4-$CH_3C_5H_4N$ (8 pages). Ordering information is given on any current masthead page.

(21) We present here no spectroscopic data that provide direct information about the structure and stereochemistry of chemisorbed molecular pyridine. A planar C_5H_5N molecule bound in a π (η^3) fashion is a possible chemisorbed state. An η^6 form by its nature would have a stereochemistry (all hydrogen atoms at the same, relatively large distance from surface metal atoms) that would not necessarily lead to regiospecific C–H bond scission at elevated temperatures. In contrast, a molecular state in which pyridine is bound largely through the nitrogen atom (σ-donor and π-acceptor interactions with the ring plane either normal to the surface or slightly tipped) could, through a rocking mode, bring either of the two α-CH hydrogen atoms close to the surface atoms—a stereochemistry that seems to invariably[23-25] lead to C–H bond scission on these metal surfaces. We favor the latter form for Ni(100)–N-C_5H_5.

(22) The coordination chemistry of 4-methylpyridine on Ni(100) was essentially identical with that of pyridine (see Supplementary Material). This fact is supportive of our characterization of the molecular pyridine chemisorption state. Were pyridine bonded as an η^6 ligand in a plane parallel to the surface plane, the methyl substituent in 4-methylpyridine should significantly perturb the surface chemistry of the substituted pyridine as in the qualitative difference between benzene and toluene surface chemistry on nickel reported by Friend and Muetterties.[8]

(23) Muetterties, E. L. *ACS Symp. Ser.* **1981**, *155*, 273.

(24) Gavin, R. M.; Reutt, J.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 3981.

(25) Muetterties, E. L. *Proc. Int. Conf. Organomet. Chem. 10th* **1981**, August. Muetterties, E. L. *Pure Appl. Chem.* **1982**, *54*, 83.

(26) The diagonal distance of the nickel(100) unit cell is nearly ideal for the conversion of a chemisorbed pyridine molecule, initially bound through the nitrogen atom at a single metal atom, to a μ-η^2-α-pyridyl state. This diagonal separation is structurally optimal for an α-pyridyl species. The distances used for Ni–N and Ni–C interactions for an α-pyridyl complex were 1.91 and 1.85 Å, respectively.

Orbital Rotation in the Lowest Triplet State of Benzophenone

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An orbital is a mathematical function, a solution of the wave equation describing a bound state of a single electron. We also use this term to refer to eigenfunctions of the Hartree–Fock effective Hamiltonian, as in the SCF LCAO–MO approximation for many-electron systems. The atomic orbitals we use in this approach have no objective significance. However, they are convenient "building blocks" for constructing approximate molecular orbitals because they allow us to visualize the electron density in the molecule by breaking it down into the more familiar contributions of each of its component parts. Thus, when we speak of an "$n\pi^*$" state[1] of benzophenone, we are clearly referring to an excited state derived from a single configuration in which an electron is promoted from the oxygen 2p-type "lone-pair" orbital to an antibonding π^* orbital. The currently accepted view is that this is, in fact, an accurate description of the lowest excited states of many aromatic carbonyls, including triplet benzophenone.[2] However, recent experimental results on this prototype system,[3] summarized herein, suggest that this is not the case and further reveal new properties of such excited states which may be of chemical importance.

Our experiments were performed on a single crystal of 4,4'-dibromodiphenyl ether (DDE) containing ~0.1 mol % of an enriched perdeuterio[^{17}O]benzophenone (^{17}O-BP-d_{10}) guest, which was immersed in pumped liquid helium at 1.2 K, excited with a filtered Hg arc, and examined by optically detected magnetic resonance (ODMR) and electron–nuclear double resonance (ODENDOR) spectroscopy at both zero and high magnetic fields (zf and hf).[4] In contrast to the behavior of ^{16,18}O-BP-h_{10} or -d_{10}, each of the electron spin transitions in the zf ODMR spectrum of ^{17}O-BP-d_{10} is split into several components by the combined effect of the ^{17}O ($I = {}^5/_2$) quadrupole and second-order hyperfine interactions. Direct measurements of the nuclear sublevel splittings in each of the three electron spin manifolds were made with an accuracy of $\leq$400 kHz by the zf ODENDOR technique. Figure 1 shows some representative spectra obtained for the T_z–T_y transition. First-order ^{17}O hyperfine splittings were observed in the hf ODMR experiments; in this case, the presence of a well-defined quantization axis made possible measurements of these splittings, which vary from 0 to 150 MHz, as a function of the angles between the laboratory field and the crystallographic axes of the host with a precision of ±3 MHz and ±2°. Additional structure in each of the hyperfine components, produced by the ^{17}O nuclear quadrupole and Zeeman interactions, was revealed by hf ODENDOR experiments at selected orientations of the crystal.

A treatment[3] of these data using the full spin Hamiltonian of the $S = 1$, $I = {}^5/_2$ system yields the principal values of the electron fine-structure ($\mathbf{D'}$), oxygen hyperfine ($\mathbf{A''}$), and oxygen quadrupole ($\mathbf{Q''}$) tensors and the relative orientation of their principal axes. Of particular interest are the diagonal forms of the quadrupole

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(2) See, for example, N. J. Turro, "Modern Molecular Photochemistry", Benjamin-Cummings, Menlo Park, CA, 1978.

(3) G. Wäckerle, M. Bär, H. Zimmermann, K.-P. Dinse, S. Yamauchi, R. J. Kashmar, and D. W. Pratt, *J. Chem. Phys.*, in press. For preliminary results, see S. Yamauchi and D. W. Pratt, *Chem. Phys. Lett.* **60**, 145 (1978).

(4) For a review, see D. W. Pratt in "Excited States", Vol. 4, E. C. Lim, Ed., Academic Press, New York, p 137.
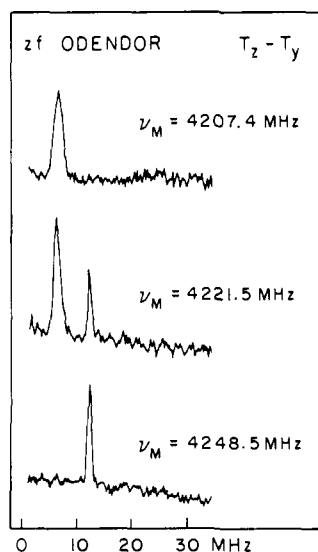
Communications to the Editor

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Figure 1. Zero field optically detected electron nuclear double resonance (i.e., ^{17}O NMR) spectra of photoexcited [^{17}O]benzophenone-d_{10} in a single-crystal host of 4,4'-dibromodiphenyl ether at 1.2 K. The spectra were obtained by monitoring radiofrequency-induced changes in the intensities of the three allowed ($\Delta m_I = 0$) components of the T_z-T_y electron spin microwave transition at $\nu_M = 4207.4$, 4221.5, and 4248.5 MHz and show, respectively, transitions between the ($|m_I|$, $|m_I|$) = ($^1/_2$, $^3/_2$), ($^1/_2$, $^3/_2$) and ($^3/_2$, $^5/_2$), and ($^3/_2$, $^5/_2$) ^{17}O nuclear spin sublevels of the T_y spin manifold, at frequencies of 6.2, 6.2 and 12.0, and 12.0 MHz.

tensor, $Q'' = (8.7 \pm 2.0, -7.8 \pm 2.0, -0.86 \pm 0.40)$ MHz, the hyperfine tensor, $A'' = (\pm 2 \pm 10, \pm 150 \pm 3, 26 \pm 3)$ MHz, and the transformations relating the (assumed coincident) principal axes of A'' and Q'' to those of D' and the molecular frame. An analysis of the ^{17}O quadrupole data for both the ground[5] and first excited triplet states of BP by the Townes and Dailey approach[6] shows that the changes in the "π-type" $2p_x$ and "n-type" $2p_y$ atomic orbital populations on excitation are $\Delta a = a_{T_1} - a_{S_0} \simeq 0.43$ and $\Delta b = b_{T_1} - b_{S_0} \simeq -0.67$. The corresponding (normalized) orbital spin densities derived from A'' are, assuming $A_{xx}'' > 0$ and $A_{yy}'' < 0$ (as suggested by INDO calculations),[3] $\rho_{2s}{}^O \simeq 0.01$, $\rho_{2px}{}^O \simeq 0.06$, $\rho_{2p_y}{}^O \simeq 0.41$, and $\rho_{2p_z}{}^O \simeq 0$. Both of these sets of results conform, at least qualitatively, to expectations for an "nπ*" state. However, we also find, quite unexpectedly, that *the principal axes of A'' do not conform to the local C_{2v} symmetry of the carbonyl group*. Specifically, if we define xyz as the coordinate system of the planar[7] $-C_1-C(O)-C_1'-$ fragment of BP (with z parallel to the carbonyl bond, y in the plane and perpendicular to the carbonyl bond, and x normal to the fragment plane), then *independent* fits of the zf and hf ODMR data show that D' and A'' share a common principal axis ($z = z' = z''$) but that x'' and y'' (the principal transverse axes of A'') are rotated by angles of $-38 \pm 5°$ away from x' and y' (the corresponding principal axes of D'). It is known from hf ODENDOR experiments on carbonyl-labeled ^{13}C-BP-d_{10}[7] that x' and y' make angles of $\phi_{xx'(yy')} = 18 \pm 2°$ with x and y (the corresponding *molecular* axes). Thus, the angle between $x''(y'')$ and $x(y)$ is $\phi_{xx''(yy'')} = -20 \pm 5°$. Note that $\phi_{xx'}$ and $\phi_{xx''}$, although similar in magnitude, have *opposite* signs; i.e., the sense of rotation of $x''(y'')$ from the carbonyl plane is opposite to that of the corresponding fine-structure axis.

The rotation of the principal transverse axes of D', observed in many triplet BP's,[8] has its origin in electron spin dipolar interactions arising from spin density in the ring π orbitals[8d,9] which,

because of a twisting of the rings in a conrotatory fashion, are off-diagonal in the xyz coordinate system. This rotation fixes the orientation of the rings relative to the carbonyl plane for a given molecule in the unit cell. Given that fact, the fact that A is expected to be diagonal in the representation of the oxygen $2p_x$, $2p_y$, and $2p_z$ orbitals, and the discussion of the previous paragraph, we are led to the inescapable conclusion that the "n-type" $2p_y$ orbital is rotated out of the carbonyl plane by an angle of $\sim 20°$, as shown in the sketch. Clearly, this rotation allows for a more
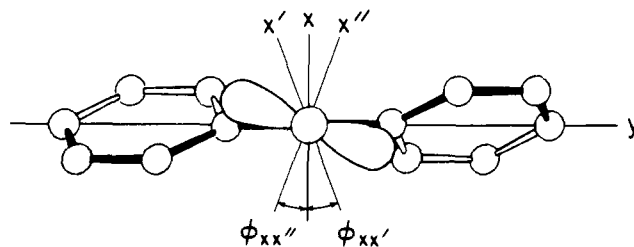
favorable overlap of the "n" orbital with the ring π orbitals and is, in our view, a direct consequence of nπ*/$\pi\pi$* configurational mixing. The low overall symmetry of the molecule could be an important factor in determining the degree of this mixing.[3] However, one can also argue that the major driving force for orbital rotation is the relief of antibonding character between the "π-type" $2p_x$ orbitals of the carbonyl carbon and oxygen atoms.[10] Thus, "planar" aromatic carbonyls might also exhibit this behavior. Whatever the cause, rotation of the "n" orbital out of the plane also requires rotation of the oxygen $2p_x$ orbital. Consequently, although such mixing is also possible in the ground state of BP, it should be small because of the higher carbonyl bond order in that state.

There is nothing in these results that suggests that triplet BP is not a radical-like electrophilic species having as its principal electron deficiency a half-vacant orbital on oxygen. Indeed, our experiments provide a striking confirmation of the interpretation of earlier work that showed that the relative reactivities of C–H bonds toward H atom abstraction by triplet BP and by *tert*-butoxy radical are very similar.[11] However, the present results also demonstrate that the "n" orbital does not lie in the plane of the carbonyl function in triplet BP, at least in the DDE host crystal. Recognition of this fact could contribute to our understanding of stereoelectronic factors in photochemical reactions,[12] particularly since the orientation of orbitals containing "nonbonding" electrons might be affected by the surrounding environment. The concept of orbital rotation is closely related to that of bent bonds[13] and incomplete orbital following,[14] for which there is mounting theoretical and experimental evidence.[15] However, by the latter we usually mean that directed valence orbitals can lag behind the nuclei during vibrational motions, whereas orbital rotation refers to the possibility that the orientation of orbitals might change during a purely electronic transition. This possibility could have important photophysical consequences as well. For example, it could explain the high efficiency of the S_1-T_1 intersystem-crossing process in BP[16] since the magnitude of rotation, and thus the degree of mixing between nπ* and $\pi\pi$* configurations, might be

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(10) A similar effect is thought to be responsible for the twisting of ethylene in its $\pi\pi$* states. For a review, see A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

(11) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **86**, 3902 (1964); **87**, 3361 (1965); A. Padwa, *Tetrahedron Lett.*, **1964**, 3465.

(12) See, for example, W. C. Agosta and S. Wolff, *J. Am. Chem. Soc.*, **98**, 4316 (1976); **99**, 3355 (1977); P. Livant and R. G. Lawler, *ibid.*, **98**, 6044 (1976); A. L. J. Beckwith and C. Easton, *ibid.*, **100**, 2913 (1978); **103**, 615 (1981); D. Griller, J. A. Howard, P. R. Marriott, and J. C. Scaiano, *ibid.*, **103**, 619 (1981).

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(16) P. M. Rentzepis, *Science (Washington, D.C.)*, **169**, 239 (1970).

significantly different in the two electronic states. Quantum beats[17] should also be observable in the excitation and decay of triplet BP since the angle between the principal transverse axes of **D'** and the oxygen $2p_x$ and $2p_y$ orbitals is nearly 45°. And, finally, we note that there is no reason to suppose that orbital rotation is unique to this system; analogous behavior might be awaiting discovery in other aromatic carbonyls, N-heterocyclics, and a variety of transition-metal ions. Investigations of some of these systems are in progress.[18]

Registry No. BP, 119-61-9.

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Luminescence of a Series of Pentacarbonylpyridinomolybdenum(0) Complexes in Fluid Solution

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Of current interest is the photochemistry of substituted group 6B metal carbonyls having low-lying metal to ligand charge-transfer (MLCT) excited states.[1-7] Luminescence assigned to be from a low-lying MLCT excited state has been observed from complexes of the general formulas $M(CO)_5L$ and $M(CO)_4L_2$, where M = Mo, W, and L = n-electron donor, either in rigid glasses at 77 K[3,8] or in methane and argon matrices at 12 K.[9] The absence of literature reports concerning emission from group 6B carbonyl complexes in fluid solution has been attributed to the relatively high photoreactivity and efficient nonradiative decay of the excited states of these complexes. In this paper, we report electronic absorption, emission, and excitation spectra obtained from a series of $Mo(CO)_5L$ complexes in room-temperature solution. These complexes appear to represent the first class of molybdenum carbonyls that emit under fluid conditions.

$Mo(CO)_5L$ complexes, where L is 4-ACpyr (4-acetylpyridine), 4-BNpyr (4-benzoylpyridine), 4-CNpyr (4-cyanopyridine), and 4-FMpyr (4-formylpyridine), were prepared via the tetrahydro-furan complex $Mo(CO)_5(THF)$ according to a procedure described previously.[5,10] The main impurities present, unreacted $Mo(CO)_6$

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Table I. Electronic Absorption and Emission[a] Spectral Features for $Mo(CO)_5L$ Complexes in Benzene at 298 K[b]

L	absorption max[c]	emission max, nm	half-width,[d] $\times 10^3$ cm^{-1}	quantum yield[e] $\times 10^{-4}$
4-ACpyr	394 (7650), ~440 (sh)	632	4.1	1.6
4-BNpyr	393 (7460), ~438 (sh)	647	3.7	4.3
4-CNpyr	392 (6300), ~435 (sh)	630	4.4	1.3
4-FMpyr	392 (5710), ~447 (sh)	668	3.8	1.9

[a] The excitation wavelength is 436 nm. Emission spectra were corrected for variation in instrumental response as a function of wavelength. [b] 8×10^{-5} to 2×10^{-4} M deaerated solutions. [c] λ, nm; (ε), M^{-1} cm^{-1}. [d] Width of emission band at half-height. [e] Relative to the luminescence of $Ru(bpy)_3{}^{2+}$;[14] accurate to within ±10%.
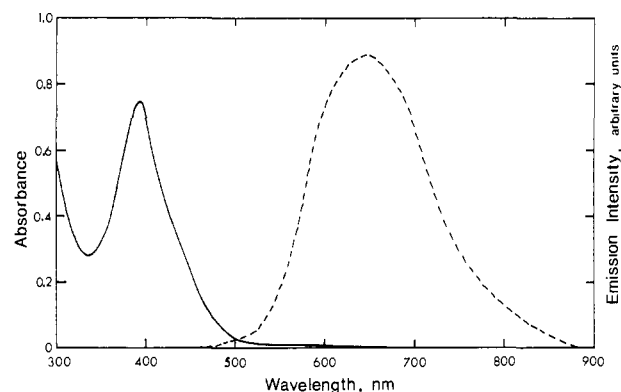

Figure 1. Electronic absorption (—) and emission (- - -) spectra of 10^{-4} M $Mo(CO)_5$(4-BNpyr) in benzene at 298 K. The emission spectrum is corrected for variations in instrumental response as a function of wavelength, and the excitation wavelength is 436 nm.
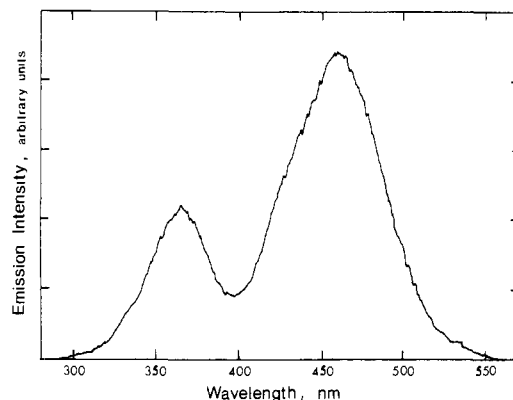

Figure 2. Excitation spectrum of 10^{-4} M $Mo(CO)_5$(4-BNpyr) in benzene at 298 K (emission monitored at 640 nm).

and L, were removed by column chromatography on alumina, followed by recrystallization from isooctane/benzene solution. Emitting or quenching impurities in the solvents (spectroscopic grade) were removed by several distillations. Carbonyl-containing impurities in the solvents were removed according to a literature procedure.[11]

The electronic absorption spectra recorded from filtered[12] solutions of $Mo(CO)_5$(4-ACpyr), $Mo(CO)_5$(4-BNpyr), Mo-

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(12) The $Mo(CO)_5L$ solutions were stringently filtered (at least twice through 0.22-μm millipore filters) to avoid the effects of particulate matter in the absorption and emission experiments.