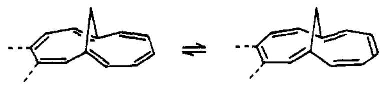
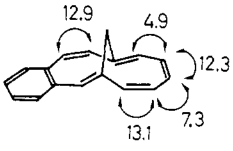
synthesis of hydrocarbon **3** accordingly provides a unique opportunity for direct NMR comparison between a paratropic [4*N*]annulene (**4**) and a monobenzo derivative thereof (**3**).

One important aspect of this comparison concerns the effect of benzannelation on the dynamic π-bond shift observed previously in the parent compound.[5] Of the two valence isomers **4a** and **4b**,



4a **4b**

the latter is now highly favored, as can be seen by examining the vicinal H,H coupling constants obtained from a 400-MHz ^{1}H NMR spectral analysis of **3**.



J_{vic} in Hz

These values, in fact, correspond quite closely to those estimated for **4** at −135 °C,[5] where the π-bond shift is slow on the NMR time scale (average difference <0.6 Hz). Thus, the geometric features of the [4*N*] perimeter must be comparable for the two compounds, and one may expect paratropic behavior also for the benzannelated system **3**. Indeed, several aspects of the ^{1}H NMR chemical shift data in Table I attest to the presence of a paramagnetic ring current in the [12]annulene moiety of **3**: (1) The bridge protons resonate at 2.2 ppm lower field than those of an atropic model.[15] (2) The benzo protons show the relation $\delta_\alpha < \delta_\beta$, which is typical for benzo rings fused to paratropic systems.[12] (3) Even the benzo β-protons are shielded by 0.23 ppm relative to δ(benzene). (4) The signals for the "olefinic" protons H-(1)–H(4) appear upfield by 0.6–0.9 ppm from the reference value for cyclic conjugated olefins (6.5 ppm[14b]).

It is equally apparent, however, that the benzene ring in **3** has caused a marked reduction of the paramagnetic ring current in the 12-electron π system relative to that in the parent homoheptalene **4**. The bridge protons in **4** resonate at even lower field than those in **3** by ca. 1.6 ppm,[16] and the "olefinic" protons in **4** resonate at higher field than those in **3** by ca. 0.4 ppm. Using a value of 2.2 ppm for the CH_2 resonance in an atropic system[15] and $\delta(CH_2)$ of **4**, we estimate that **3** sustains 50–60% of the paramagnetic ring current effect present in **4**. *Thus, benzannelation reduces the paramagnetic ring current of this* [*4N*]*-annulene by approximately the same percentage that benzannelation reduces the diamagnetic ring current of several rigid* [*4N + 2*]*annulenes.*[10,11] Quantitative effects of benzannelation on other [4*N*]annulenes have previously been reported only for dehydro systems.[14] The present study consequently represents an important step toward broadening our understanding of electron delocalization in bicyclic π systems.

Acknowledgment. We thank the U.S. National Science Foundation, the donors of the Petroleum Research fund, administered by the American Chemical Society, and the Fonds der Chemischen Industrie for financial support of this work.

Registry No. **1**, 65754-71-4; **3**, 84537-62-2; **4**, 40985-77-1; benzyne, 462-80-6.

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(15) *anti*-1,6,8,13-Bismethano[14]annulene: Vogel, E.; Haberland, U.; Günther, H. *Angew. Chem.* **1970**, *82*, 510; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 513.

(16) The possibility that this difference in $\delta(CH_2)$ between **3** and **4** might result mainly from through-space shielding by the benzene ring in **3** can be rejected on the following grounds: (1) the small shift difference between H(13) and H(14), with H(13) at the low-field side; (2) the location of the CH_2 protons in the deshielding rather than the shielding region of the simple anisotropy cone for benzene, as indicated by models.

Emission Spectroscopic Properties of Dioxorhenium(V) Complexes in Crystals and Solutions

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It is surprising how little attention has been paid to the emission spectroscopic behavior of transition-metal oxo complexes,[1,2] particularly in view of the widespread interest in their electronic structures.[3-10] Our interest in exploring excited-state oxygen atom transfer chemistry has led us to examine dioxorhenium(V) systems, and we have discovered that several of these complexes possess relatively long-lived emissive excited states in solution.

The electronic absorption spectrum of *trans*-$ReO_2L_4{}^z$ exhibits a weak band maximizing between 400 and 450 nm ($L = CN^-$, $z = -3$, $\lambda_{\max}$ 404 nm; L = pyridine (py), $z = +1$, $\lambda_{\max}$ 415 nm; $L = {}^1/_2$en, $z = +1$, $\lambda_{\max}$ 450 nm).[11] Straightforward electronic structural considerations suggest that the band be assigned to $^1E_g(b_{2g})^1(e_g)^1 \leftarrow {}^1A_{1g}(b_{2g})^2$ and that a less intense lower energy shoulder be attributed to the transition to ^3E_g.[12]

Luminescence is observed from crystalline samples containing *trans*-$ReO_2L_4{}^+$ (L = pyridine, pyridine-d_5, 4-picoline, and 4-*tert*-butylpyridine), $Re^{18}O_2(\text{pyridine})_4{}^+$, and $ReO_2(CN)_4{}^{3-}$. The emission maxima are all near 650 nm at 300 K, and at low temperature a great deal of vibrational fine structure is resolved. The 5 K single-crystal emission spectrum of $K_4ReO_2(CN)_4$ is very complex but does display a progression (865 cm^{-1}) corresponding to the symmetric Re–O stretching vibration. The 5 K emission spectrum of crystalline *trans*-$[ReO_2(py)_4]BPh_4$ is much less complex and exhibits progressions in a 900-cm^{-1} Re–O stretching mode as well as a 185-cm^{-1} vibration that probably corresponds to the symmetric Re–py stretching coordinate (Figure 1). A Franck–Condon analysis of this emission spectrum indicates a 0.1-Å excited state distortion of each Re–O bond (Re–O = 1.86 Å ($^1A_{1g}$), $[ReO_2(py)_4]Cl{\cdot}2H_2O$).[13] Both the estimated distortion and the relatively long radiative lifetimes (Table I) are consistent with an assignment of ^3E_g as the emissive excited state.[12]

Perdeuteration of the pyridine ligands in *trans*-$ReO_2(py)_4{}^+$ increases the excited-state lifetime in crystals by more than a factor of 4 (Table I). Oxygen-18 substitution, however, does not lead to a similar increase in lifetime. These data are consistent with a weak coupling model for radiationless decay in these systems where the rates of nonradiative deactivation are sensitive to the frequencies of the highest energy vibrations (C–H) in the molecule.[14] Chemical modification of the equatorial pyridine ligands (4-picoline, 4-*tert*-butylpyridine) shortens the excited-state lifetime by a factor of 3.

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(1) (a) Blasse, G.; Bril, A. *J. Lumin.* **1970**, *3*, 109. (b) Treadway, M. J.; Powell, R. G. *J. Chem. Phys.* **1974**, *61*, 4003.

(2) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015; **1980**, *102*, 198.

(3) Rappe, A. K.; Goddard W. A., III *J. Am. Chem. Soc.* **1980**, *102*, 5114.

(4) Rappe, A. K.; Goddard W. A. III *J. Am. Chem. Soc.* **1982**, *104*, 448.

(5) Collison, D.; Gahan, B.; Garner, C. D.; Mabbs, F. E. *J. Chem. Soc., Dalton Trans.* **1980**, 667.

(6) Sunil, K. K.; Rogers, M. T. *Inorg. Chem.* **1981**, *20*, 3283.

(7) Blyholder, G.; Head, J.; Ruette, F. *Inorg. Chem.* **1982**, *21*, 1539.

(8) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3771.

(9) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656.

(10) Winkler, J. R.; Gray, H. B. *Comments Inorg. Chem.* **1981**, *1*, 257.

(11) Sample preparations followed standard procedures: Beard, J. H.; Casey, J.; Murmann, R. K. *Inorg. Chem.* **1965**, *4*, 797. Crystal structure of $K_3[ReO_2(CN)_4]$: Murmann, R. K.; Schlemper, E. D. *Inorg. Chem.* **1971**, *10*, 2352.

(12) The ligand field levels in *trans*-$ReO_2L_4{}^z$ would be expected[10] to be ordered b_{2g} $(xy) < e_g$ $(xz, yz) < b_{1g}$ $(x^2 - y^2) < a_{1g}$ (z^2), with a $^1A_{1g}$ $(b_{2g})^2$ ground state. The e_g orbitals possess $\pi^*(ReO_2)$ character, and as a result the Re–O bonds in both the ^1E_g and ^3E_g states should be slightly weaker than in the ground state.

(13) Lock, C. J. L.; Turner, G. *Acta Crystallogr., Sect. B* **1978**, *B24*, 923.

(14) Englman, R.; Jortner, J. *J. Mol. Phys.* **1970**, *18*, 145.

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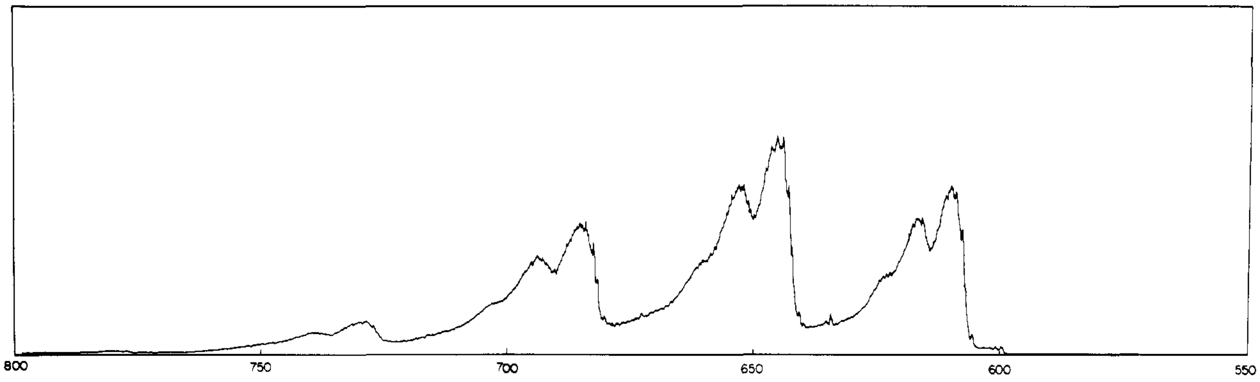

Figure 1. Emission spectrum of crystalline *trans*-$[ReO_2(py)\text{-}d_5)_4]BPh_4$ at 4.5 K (436-nm excitation, uncorrected for spectrometer response).

Table I. Photophysical Data for *trans*-$ReO_2L_4{}^z$ Complexes

complex	conditions[a]	$\lambda_{max}{}^{em}$, nm	τ, μs[b]
$K_3[ReO_2(CN)_4]$	crystal (300)	*c*	330
	crystal (30)	*c*	700
$[ReO_2(py)_4]BPh_4$	crystal (300)	*c*	32
	crystal (30)	*c*	66
	py soln (300)	655	17 (0.03)
	THF soln (300)	645	13 (0.03)
	CH_2Cl_2 soln (300)	670	4
$[ReO_2(py\text{-}d_5)_4]BPh_4$	crystal (300)	*c*	140
	THF soln (300)	645	9 (0.04)
$[Re^{18}O_2(py)_4]BPh_4$	crystal (300)	*c*	36
	py soln (300)	655	15 (0.03)
$[ReO_2(4\text{-pic})_4]BPh_4$	crystal (300)	*c*	11
	THF soln (300)	665	17 (0.02)
$[ReO_2(4\text{-}t\text{-Bu(py)})_4]BPh_4$	crystal (300)	*c*	11
	THF soln (300)	660	21 (0.03)

[a] Temperature (K) is given in parentheses. [b] Lifetimes measured with the second harmonic (532 nm) from a Nd:YAG laser (pulse width 8 ns fwhm). In parentheses are quantum yields measured relative to $[Ru(bpy)_3]Cl_2$ in degassed H_2O (Φ_{em}(436 nm) = 0.042 ± 0.002: van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* 1976, *98*, 4853. [c] Near 650 nm.

Several dioxorhenium(V) complexes also luminesce in aprotic solutions. The emission quantum yields measured with 436-nm excitation are about 0.03 for *trans*-$ReO_2(py)_4{}^+$ and its isotopically substituted derivatives. The excited-state lifetimes of these ions in solution vary from 4 to 17 μs, down by at least a factor of 2 from the solid-state values. Our observation that *trans*-$ReO_2(py\text{-}d_5)_4{}^+$ has a lifetime in THF solution nearly equal to that of the protonated form suggests that the dominant nonradiative solution decay pathway differs markedly from the one that is operative in crystals. Solvation of the cation as well as equatorial ligand dissociation[15] may contribute significantly to the observed decay rate.

None of the dioxorhenium(V) ions luminesces in aqueous solution. Addition of water to a pyridine solution of *trans*-$ReO_2(py)_4{}^+$ shifts both the absorption and emission bands to lower energy, decreases the emission quantum yield, and shortens the luminescence lifetime. Deuterated water produces identical spectral changes but reduces the excited-state lifetime less efficiently than H_2O. Methanol and ethanol also shorten the dioxorhenium(V) excited-state lifetime. The efficiency of the lifetime quenching by these alcohols is sensitive to deuteration at the hydroxyl though not at the alkyl positions. A cationic proton source, pyridinium ion, however, does not alter the absorption nor the emission spectrum of *trans*-$ReO_2(py)_4{}^+$ in pyridine solution, nor does it appreciably reduce the excited-state lifetime. These data suggest that protic media solvate the dioxorhenium(V) ions (perhaps via hydrogen bonding) to produce species that luminesce less efficiently and have shorter excited-state lifetimes than the isolated complexes.

In summary, we have found that the ^3E_g state of dioxorhenium(V) complexes lives 10–100 μs in crystalline samples and ~10 μs in aprotic solvents. Such relatively long-lived, highly energetic (~2-eV excited states) oxometal species are of potential interest as oxygen atom transfer agents in oxygenation reactions, and we are exploring this area at the present time.

Acknowledgment. J.R.W. thanks the Sun Company for a graduate fellowship. This research was supported by National Science Foundation Grants CHE78-10530 and CHE81-20419.

Registry No. $K_3[ReO_2(CN)_4]$, 19439-48-6; $[ReO_2(py)_4]BPh_4$, 84417-09-4; $[ReO_2(py\text{-}d_5)_4]BPh_4$, 84417-11-8; $[Re^{18}O_2(py)_4]BPh_4$, 84417-13-0; $[ReO_2(4\text{-pic})_4]BPh_4$, 84472-13-9; $[ReO_2(4\text{-}t\text{-Bu(py)})_4]BPh_4$, 84417-15-2.

---

[15] Beard, J. H.; Calhoun, C.; Casey, J.; Murmann, R. K. *J. Am. Chem. Soc.* **1968**, *90*, 3389.

Host–Guest Interactions in Amylose Inclusion Complexes: Photochemistry of Surfactant Stilbenes in Helical Cavities of Amylose[1]

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Received October 6, 1982

The control and modification of reactivity through incorporation of molecules into organized assemblies, functionalized polymers, and interfacial sites at solution–solid or gas–solid interfaces remain an area of considerable interest. A specific subarea that has been the focus of several recent investigations concerns reactivity of molecules incorporated into "host–guest" complexes, using as hosts such varied systems as zeolites, cyclodextrins, and various cryptates or crown ethers.[3-7] Most of the aforementioned reagents offer guest sites of relatively restricted dimensions; modifications of reactivity can occur for a variety of reasons including restriction of molecular motion, limited access of potential reaction partners, or hydrophilic–hydrophobic effects.

It has recently been shown that various amyloses and (carboxymethyl)amyloses can form inclusion compounds with a variety

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[1] Winkle, J. R.; Worsham, P. R.; Whitten, D. G. Photochemical Reactivity in Organized Assemblies. 33. Paper 32 submitted for publication.

[2] Visiting scientist from Shanghai Institute of Organic Chemistry, Academia Sinica, People's Republic of China.

[3] Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66.

[4] Emert, J.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 670.

[5] Mandelcorn, L., Ed. "Non Stoichiometric Compounds"; Academic Press: New York, 1964.

[6] Allcock, H. R. *Acc. Chem. Res.* **1978**, *11*, 81.

[7] Lehn, J.-M. *Acc. Chem. Res.* **1978**, *11*, 49.

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