^{3}MLCT Lifetimes of Tris(2,2'-bipyridine)ruthenium(II). Position-Dependent Deuterium Effects

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Studies of polypyridine complexes of ruthenium(II) have intensified greatly in recent years.[1] Three major deactivation pathways of the excited (^{3}MLCT) state have been identified: radiative (k_r), direct nonradiative (k_{nr}), and nonradiative via crossover into thermally accessible (energy of ΔE) d-d excited states (k_{dd}).[2] The observed lifetime has been expressed as

$$\Upsilon^{-1} = k_r + k_{nr} + k^{0\prime} \exp[-\Delta E/RT] = k_r + k_{nr} + k_{dd} \quad (1)$$

Meyer and co-workers[2e] have shown that approximately 70% of the excited state energy is dissipated via vibrational relaxation (k_{nr}) at room temperature in aqueous solution.

The study of deuteration effects on measured lifetimes of excited states can provide insight into the precise mechanisms of nonradiative decay processes.[3-5] For example, the observed substantial increases in the triplet-state lifetimes of naphthalene[6] and benzene[7] upon perdeuteration were interpreted in terms of the Robinson/Frosch theory[3] of radiationless deactivation, i.e., as a result of the decreased overlap of (lower frequency) C-D modes relative to C-H modes for the same energy gap. Extensions of this approach demonstrated a lifetime dependence not only on the number of deuterium substituents but also on the position of substitution.[5d,f,g]

Van Houten and Watts[9] have previously reported that perdeuteration of the bipyridine ligands of the title complex causes an increase (from 580 to 690 ns) in the lifetime of the ^{3}MLCT state. Although the effect of ligand deuteration is relatively small, it is appropriate to investigate the issue of selective deuteration effects. Herein we report results which clearly demonstrate experimentally distinguishable lifetime differences for three such isotopically substituted analogues of $Ru(bpy)_3^{2+}$ (i.e., complexes of bpy-*3,3'-d*$_2$, bpy-*6,6'-d*$_2$, and partially deuterated bpy-*3,3',5,5'-d*$_4$).

The syntheses of the dideuterated and perdeuterated ligand complexes have been reported.[10] As shown previously, the Ru(bpy-*3,3'-d*$_2$)$_3^{2+}$ complex can be prepared directly from the natural abundance complex by reaction with CH_3O^2H/CH_3ONa in dimethyl-d_6 sulfoxide according to the method of Constable and Seddon.[11b] The extent of $^1H/^2H$ exchange is easily monitored by ^{1}H NMR. Greater than 95% deuteration at the 3,3'-positions is observed after about 24 h. We now note that partial deuteration at the 5,5'-positions also occurs if the exchange reaction is extended for prolonged periods. After 1 week, we observe approximately 70% deuterium exchange at the 5,5'-positions, as determined from the NMR spectrum, with no evidence for exchange at the 4,4'- or 6,6'-positions. Experiments are now under way to optimize solution conditions to enhance the exchange rate at the 5,5'-positions. This not only will provide samples of bipyridine-*3,3',5,5'-d*$_4$ but also will facilitate preparation of the bipyridine-*5,5'-d*$_2$ complex via 24-h exchange of the 3,3'-deuterons in $CH_3OH/CH_3ONa/Me_2SO$. Lifetimes were measured in N_2-purged (15 min) aqueous solutions at room temperature by using time-correlated single photon counting techniques as previously described.[11c]

Table I. ^{3}MLCT Lifetimes and k_{nr} Values of Complexes in Aqueous Solution[a]

complex	lifetime, ± 10 ns	k_{nr} s^{-1}
$Ru(bpy)_3^{2+}$	580	12.2×10^5
$Ru(bpy\text{-}d_8)_3^{2+}$	690	9.45×10^5
Ru(bpy-*3,3'-d*$_2$)$_3^{2+}$	580	12.2×10^5
Ru(bpy-*6,6'-d*$_2$)$_3^{2+}$	645	10.5×10^5
Ru(bpy-*3,3',5,5'-d*$_4$)$_3^{2+}$	655[b]	10.3×10^5

[a] Approximately 10^{-5} M solutions at 22 ± 3 °C. [b] Estimated 70% deuteration at 5,5'-positions.

Table I gives the observed lifetimes of the ^{3}MLCT excited states and the corresponding k_{nr} values derived from eq 1 for the parent and perdeuterated complexes as well as those for the specifically deuterated compounds. Reliable estimates of k_{nr} are obtained from eq 1 for the deuterated analogues inasmuch as the k_r and k_{dd} values, carefully determined by Meyer and co-workers for the parent compound, are relatively insensitive to isotopic substitution effects.[2e]

The measured lifetimes of the natural abundance complex and perdeuterated analogue are in agreement with those reported by Van Houten and Watts.[9] As can be seen in the table, deuteration at the 3,3'-positions has no measurable effect on k_{nr}, whereas the complex of the other dideuterated ligand (i.e., Ru(bpy-*6,6'-d*$_2$)$_3^{2+}$) exhibits a lifetime that is significantly longer than that of the parent compound. A relatively large effect on k_{nr} is observed for the complex of bpy-*3,3',5,5'-d*$_4$ even though the exchange was only 70% complete at the 5,5'-positions.

These preliminary results provide encouraging evidence that such studies may be of substantial value in probing nonradiative relaxation processes in these systems in that they are consistent with the "active H atom" theory of Robbins and Thomson.[12] These workers argue that increased electron density in the region of the atoms whose vibrations act as promoting modes should lead to greater efficiency of radiationless decay. Similar predictions have been made by Henry and Siebrand[4] and this effect has been observed semiquantitatively in studies involving selectively deuterated *trans*-stilbine and anthracenes.[5a,k] In the present case, it is noted that 3,3'-deuteration has no measurable effect on k_{nr}; these are positions of low electron density as judged by the fact that base-catalyzed $^1H/^2H$ exchange occurs readily on the metal complex at these positions.[11] There is no evidence for exchange at the 6,6'-positions. Second, the results given in the table agree qualitatively with ^{1}H NMR data. Measured chemical shifts show the lowest electron density at the 3,3'-positions with increased electron density at the 6,6'-positions. For the metal complex, the order of increasing chemical shift is 5,5' < 6,6' < 4,4' < 3,3'[13] while for the free ligand the order is 5,5' < 4,4' < 3,3' < 6,6'.[14]

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(1) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159 and references therein.
(2) (a) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853. (b) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17*, 3381. (c) Hoggard, P. E.; Porter, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 1457. (d) Porter, G. B.; Sparks, R. H. *J. Photochem.* **1980**, *13*, 123. (e) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803. (f) Gleria, P. J.; Minto, F.; Beggiato, G.; Bortolus, P. J. *J. Chem. Soc., Chem. Commun.* **1978**, 285.
(3) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962; *38*, 1187.
(4) Henry, B. R.; Siebrand, W. *J. Chem. Phys.* **1971**, *54*, 1072.
(5) (a) Henry, B. R.; Charlton, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 2782. (b) Lim, E. C.; Laposa, J. D. *J. Chem. Phys.* **1964**, *41*, 3257. (c) Simpsom, J. D.; Offen, H. W.; Burr, J. G. *Chem. Phys. Lett.* **1968**, *2*, 383. (d) Hirota, N.; Hutchinson, C. A., Jr. *J. Chem. Phys.* **1967**, *46*, 1561. (e) Lin, S. H.; Bersohn, R. *J. Chem. Phys.* **1968**, *48*, 2732. (f) Watts, R. J.; Strickler, S. J. *J. Chem. Phys.* **1968**, *49*, 3867. (g) Gierke, T. D.; Watts, R. J.; Strickler, S. J. *J. Chem. Phys.* **1969**, *50*, 5425. (h) Martin, T. E.; Kalantar, A. H. *J. Chem. Phys.* **1968**, *48*, 4996. (i) Thomas, T. R.; Watts, R. J.; Crosby, G. A. *J. Chem. Phys.* **1973**, *59*, 2123. (j) Griesser, H. J.; Wild, U. P. *Chem. Phys.* **1980**, *52*, 117. (k) Heinrich, V. G.; Gusten, H.; Mark, F.; Olbrich, G.; Schutle-Frohlinde, D. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 103.
(6) Hutchison, C. A., Jr.; Mangum, B. W. *J. Chem. Phys.* **1960**, *32*, 1261.
(7) Wright, M. R.; Frosch, R. P.; Robinson, G. W. *J. Chem. Phys.* **1960**, *33*, 934.
(8) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272.
(9) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 3843.
(10) McClanahan, S.; Kincaid, J. *J. Raman Spectrosc.* **1984**, *15*, 173.
(11) (a) McClanahan, S.; Hayes, T.; Kincaid, J. *J. Am. Chem. Soc.* **1983**, *103*, 4486. (b) Constable, E. C.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 34. (c) McClanahan, S.; Dallinger, R. F.; Holler, F. J.; Kincaid, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 4853.
(12) Robbins, D. J.; Thomson, A. J. *Mol. Phys.* **1973**, *25*, 1103.
(13) McClanahan, S. F. Ph.D. Thesis, University of Kentucky, Lexington, KY, 1984.

0002-7863/86/1508-3840$01.50/0

For the latter species, the results of HMO calculations[15] show decreasing π-electron densities in the same order.

Inasmuch as the theory[4,12] invokes a critical dependence of k_{nr} on π-electron densities and relative atom displacements of particular vibrational modes, more meaningful interpretation of such data will require reliable normal mode formulations. Thus, an extension of this approach will involve a determination of the lifetime of a large number of specifically deuterated analogues and an intensive effort to obtain a realistic force field via normal coordinate calculations based on extensive vibrational spectroscopic data. Such studies and efforts are currently under way in our laboratory.

(14) (a) Kramer, F. A.; West, R. *J. Phys. Chem.* **1965**, *69*, 673. (b) Castellano, S.; Gunther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166. (c) Gil, V. M. S. *Mol. Phys.* **1965**, *9*, 97.
(15) Sinha, S. P. *Rev. Roum. Chim.* **1973**, *18*, 777.

Enantiospecific Total Synthesis and Absolute Configurational Assignment of (-)-Punctatin A (Antibiotic M95464)

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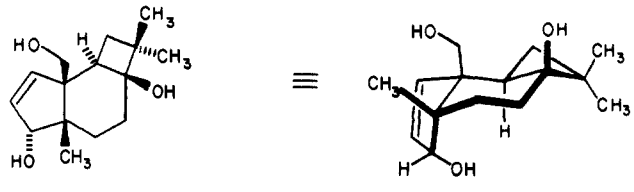
In 1984, Anderson and his associates[1] reported the isolation from the dung fungus *Poronia punctata* (Linnaeus ex Fries) of a trishydroxylated sesquiterpene possessing a previously unknown caryophyllene-related tricyclic framework. The crystalline levorotatory substance, originally known as antibiotic M95464, was assigned the trivial name punctatin A.[2,3] The biological activity of **1** and particularly the presence within its structure of a



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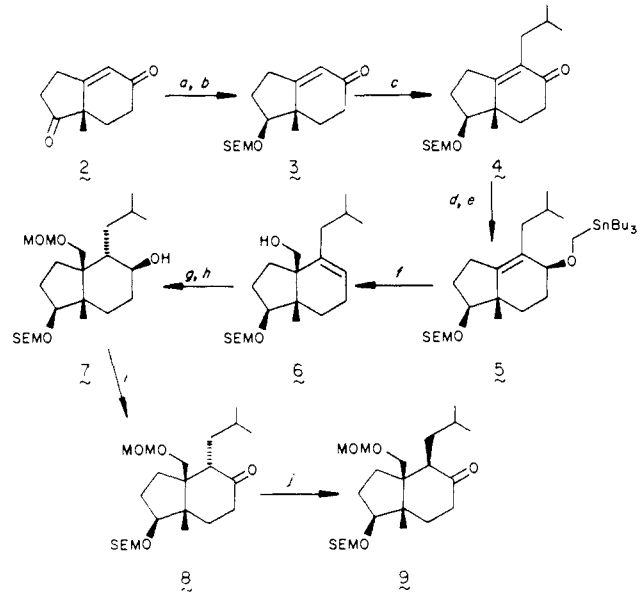
trans-fused tertiary cyclobutanol aroused our interest in its laboratory preparation. We herein describe an enantiospecific route to (-)-**1** that permits the assignment of absolute configuration and showcases several interesting synthetic facets including (a) utilization of the Still rearrangement[4] as a viable means for elaborating an angular hydroxymethylated *cis*-perhydroindane system and (b) construction of the completely functionalized four-membered ring in proper stereochemical disposition by application of Norrish Type II photochemistry.[5]

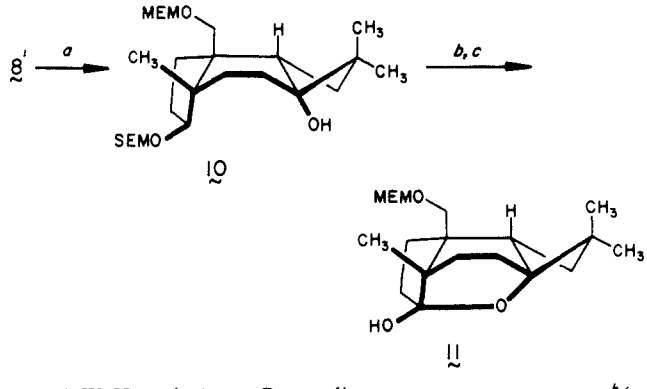
(1) Anderson, J. R.; Briant, C. E.; Edwards, R. L.; Mabelis, R. P.; Poyser, J. P.; Spencer, H.; Whalley, A. J. S. *J. Chem. Soc., Chem. Commun.* **1984**, 405.
(2) Care should be exercised not to confuse punctatin A with punctatin, a germacradienolide obtained from *Liatris punctata* Hook (Herz, W.; Wahlberg, I. *Phytochemistry* **1973**, *12*, 1421). This substance was later renamed punctaliatrin (Herz, W.; Wahlberg, I. *Phytochemistry* **1974**, *13*, 315). An even earlier use of the name for a group of homoisoflavones has turned up (Heller, W.; Tamm, C. *Prog. Chem. Org. Nat. Prods.* **1981**, *40*, 105).
(3) Two additional metabolites that are coproduced with **1** and assigned the names punctatin B and C have more recently been structurally characterized (Anderson, J. R.; Edwards, R. L.; Freer, A. A.; Mabelis, R. P.; Poyser, J. P.; Spencer, H.; Whalley, A. J. S. *J. Chem. Soc., Chem. Commun.* **1984**, 917.
(4) (a) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1480. (b) Still, W. C.; Mitra, A. *Ibid.* **1978**, *100*, 1927.

Scheme I



[a] $LiAlH(O\text{-}t\text{-}Bu)_3$, ether. [b] $Me_3SiCH_2CH_2OCH_2Cl$, $(i\text{-}Pr)_2NEt$. [c] $CH_3SOCH_2^-Na^+$, $(CH_3)_2CHCH_2I$, Me_2SO. [d] $LiAlH_4$, ether. [e] KH, ICH_2SnBu_3, THF. [f] *n*-BuLi, hexane, -78 → 0 °C. [g] CH_3OCH_2Cl, $(i\text{-}Pr)_2NEt$. [h] BH_3·THF, diglyme; H_2O_2, NaOH, H_2O. [i] PCC, CH_2Cl_2. [j] $NaOCH_3$, CH_3OH.

Scheme II



[a] 450-W Hanovia lamp, Pyrex, dioxane, room temperature. [b] $(n\text{-}Bu)_4N^+F^-$, 60 °C, 2 mmHg. [c] PCC, CH_2Cl_2.

(+)-Diketone **2**, readily available in an enantiomeric purity of 99.6%,[6] underwent regio- and stereocontrolled hydride reduction[7] together with conversion[8] to SEM ether **3** in 88% yield (Scheme I). Alkylation of the thermodynamic enolate of **3**[9] with 1-iodo-2-methylpropane provided **4** (54%) with the intention that the alkyl side chain ultimately become the carbocyclic backbone of the four-membered ring. As expected,[10] **4** was reduced by $LiAlH_4$ exclusively to the β-alcohol (97%). Deprotonation and alkylation of this intermediate with (iodomethyl)tributyltin afforded the allyl stannylmethyl ether **5** which was treated with excess *n*-butyllithium in hexane. Smooth [2,3]-sigmatropic rearrangement ensued to deliver homoallylic alcohol **6** ($[\alpha]^{22}$ +59.3° (*c* 4.0, C_6H_6)) with complete transfer of chirality[11] (34% overall).

Careful conformational analysis of the MOM ether of **6** revealed that its hydroboration should be less encumbered from the

(5) (a) Fleming, I.; Kemp-Jones, A. V.; Long, W. E.; Thomas, E. J. *J. Chem. Soc., Perkin Trans 2* **1976**, 7. (b) Fleming, I.; Long, W. E. *Ibid.* **1976**, 14 and relevant references cited in these papers.
(6) Hajos, Z. G.; Parrish, D. R. *Org. Synth.* **1984**, *63*, 26.
(7) Hajos, Z. G.; Parrish, D. R.; Oliveto, E. P. *Tetrahedron* **1968**, *24*, 2039.
(8) Lipshutz, B. H.; Pegram, J. J. *Tetrahedron Lett.* **1980**, 3343.
(9) Hajos, Z. G.; Micheli, R. A.; Parrish, D. R.; Oliveto, E. P. *J. Org. Chem.* **1967**, *32*, 3008.
(10) Marshall, J. A.; Ellison, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 4312.
(11) Midland, M. M.; Kwon, Y. C. *Tetrahedron Lett.* **1985**, 5013 and relevant references cited therein.

0002-7863/86/1508-3841$01.50/0