is formally the Diels–Alder adduct of **4** and tetra-*O*-methylconduritol A (**10**), but thermal retro-Diels–Alder reaction of **7** would not be expected to occur below 300 °C, since no activating groups are present on the dienophile.[11,12]

To liberate the protected C=C bond we relied instead on the remarkable "Evans accelerating effect" of the oxido group.[13,14] The requisite hydroxyl was revealed upon hydrolysis of the (benzyloxy)methyl protecting group (**7** → **8**). Treatment of a dioxane solution of **8** with potassium hydride generated the alkoxide, and fragmentation occurred *at room temperature*[15] to the potassium salt of anthrone (**9**)[16] and the olefin **10**.

To determine whether alcohol protecting groups[17] would survive the oxido-accelerated retro-Diels–Alder reaction, the pentol **11** was prepared (Scheme I), and the secondary hydroxyls were protected as the acetonide at C-4 and C-5 and the (benzyloxy)methyl ether at C-3 and C-6. Retro-Diels–Alder reaction gave the protected conduritol A derivative **13**. Either the acetonide or the (benzyloxy)methyl groups[18] could be removed from **13** selectively, and sequential deprotection afforded conduritol A (**3**) itself.[19] The overall yield of **3** from **1** was 39%.

Differentiation of the C-3 and C-6 carbonyl groups of **5** was achieved in two ways (Scheme II). Selective monoreduction of **5** using the tetrabutylammonium borohydride[21] gave a single hydroxy enone, **14**. The site of reduction was confirmed by acetylation, since the resulting acetoxy enone, **15**, showed a coupling pattern in the 360-MHz ^{1}H NMR spectrum consistent only with the structure shown. As an alternative, the enediol **6** was monosilylated using *tert*-butyldimethylsilyl triflate[22] at −100 °C, giving in 86% yield a 3:1 mixture of alcohols. Methylation of the major product afforded **16**, whose hydroxyls are now distinct and appropriately protected.

A variety of pathways may be formulated for transforming **14** or **16** to aminocyclitols **2**, and we are currently investigating these possibilities.

Acknowledgment. This research was supported by grants from PHS (AI-18703) and the Merck Foundation. We are grateful to Professor Joseph E. Sinsheimer for the IR spectrum of authentic **3** and the mass spectrum of its tetraacetate derivative. The 360-MHz ^{1}H NMR spectrum of **15** was obtained at the NMR facility, Department of Biochemistry and Biophysics, University of Pennsylvania.

Supplementary Material Available: Spectroscopic data (NMR, IR), melting points, and R_f's for new compounds (2 pages). Ordering information is given on any current masthead page.

---

(11) Recent reviews of the retro-Diels–Alder reaction: (a) Ripoll, J. L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19. (b) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(12) Recent use of the retro-Diels–Alder reaction in synthesis: (a) Siwapinyoyos, T.; Thebtaranonth, Y. *J. Org. Chem.* **1982**, *47*, 598. (b) Klunder, A. J. H.; Bos, W.; Zwanenburg, B. *Tetrahedron Lett.* **1981**, *22*, 4557. (c) Verlaak, J. M. J.; Klunder, A. J. H.; Zwanenburg, B. *Ibid.* **1982**, *23*, 5463. See also ref 11.

(13) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.

(14) For leading references see: Zoeckler, M. T.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 7661.

(15) The retro-Diels–Alder reaction studied by Grimme was accelerated by a factor of 10^6 or more by an oxido substituent. Papies, O.; Grimme, W. *Tetrahedron Lett.* **1980**, *21*, 2799.

(16) The recovered anthrone was contamined by varying amounts of anthraquinone.

(17) We tried unsuccessfully to remove all four methyl groups of **10** using iodotrimethylsilane (Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761). By ^{1}H NMR analysis, destruction of the alkene preceded replacement of the last methyl group by trimethylsilyl.

(18) Stork, G.; Isobe, M. *J. Am. Chem. Soc.* **1975**, *97*, 6260.

(19) Conduritol A (**3**): mp 139.5–140 °C (lit.[6a] 142–143 °C, lit.[6b] 145.5–145.7 °C). Conduritol A monoacetonide: mp 101–103 °C (lit.[20] 101–102 °C). Synthetic **3** had ^{1}H NMR and IR spectra identical with those published.[6b] Acetylation of synthetic **3** gave the tetracetate, whose ^{1}H NMR and mass spectra matched those published.[6b]

(20) Dangschat, G.; Fischer, H. O. L. *Naturwisenschaften* **1939**, *45*, 756.

(21) (a) Raber, D. J.; Guida, W. C. *J. Org. Chem.* **1976**, *41*, 690. (b) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H. A.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095.

(22) Corey, E. J.; Cho, H.; Rücker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455.

Two-Photon Excitation of d → d* Transitions in a Rhodium(III) Complex

M. Johnson Hassinger and F. E. Lytle*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received February 7, 1983

One of the challenging aspects of the study of second- and third-row transition series metal chelate complexes is the assignment of bands in absorption spectra. In particular, transitions to excited states of gerade microsymmetry, such as the metal-localized d → d*'s, are forbidden by symmetry arguments and are often obscured by symmetry-allowed (ungerade) bands of greater intensity. Since the determination of d → d* energies is of photophysical and photochemical importance, a technique that can probe these bands is of great interest. Two-photon excitation (TPE) is a nonlinear spectroscopic technique that selectively accesses gerade excited states by absorbing two photons of light simultaneously. TPE has been applied in studies of f → f* transitions in rare-earth metals[1-3] and d → d* bands in crystalline K_2PtCl_6.[4] We report the first TPE spectrum of d → d* bands in a metal chelate dissolved in a vitreous solvent, that of *cis*-dicyanobis(4,4′-dimethyl-2,2′-bipyridine)rhodium(III) chloride ($Rh(CN)_2(dmb)_2^+$).

A ~0.01 M solution of $Rh(CN)_2(dmb)_2^+$ in 4:1 ethanol–methanol was degassed by three freeze–pump–thaw cycles and sealed in a 4-mm o.d. glass capillary. An argon ion laser at 514.5 nm synchronously pumped a ring dye laser, providing a 96-MHz train of excitation pulses with peak powers of ~0.3–0.8 kW. The dye laser was continuously tunable from 570 to 620 nm, corresponding to excitation energies of 35 090–32 260 cm^{-1}. Laser light was focused on the sample, after cooling to 77 K, and phosphorescent emission from the chelate was collected at right angles, filtered with a double monochromator, and detected with an EMI 9558 cooled photomultiplier. A picoammeter voltage proportional to the photomultiplier current was sampled with a computer. Initially, the luminescence spectrum of the sample was measured by using single-photon excitation at 297 nm (obtained by frequency doubling the dye laser output). All spectral data agreed with that presented by Julander.[5] Subsequently, the one- and two-photon excited luminescence spectra were compared to confirm the origin of the emission. To generate an excitation spectrum, TPE intensities ($\lambda_{\text{emission}}$ = 471 nm) were measured at 1-nm intervals. At each wavelength the laser power was varied from zero to maximum in five evenly spaced steps. The resultant data were subjected to a linear regression of signal/average laser power vs. average laser power to verify the quadratic dependence of the luminescence intensity. An ancillary advantage of this approach is the ability to separate the total detector current into its one- and two-photon contributions.[6] The one-photon contribution was independent of the nature of the solute and was identified as residual laser scatter on the basis of polarization and optical filtering experiments. Spectral data resulting from regressions having a correlation coefficient less than 0.95 were rejected. The final TPE signal was corrected for laser pulse structure variations by utilizing a reference correction scheme.[7] Sequential two-photon processes involving real states with lifetimes greater than a few picoseconds were ruled out by ascertaining that the signal grew

---

(1) Fritzler, U.; Schaack, G. *J. Phys. C* **1976**, *9*, L23–L26.

(2) Dagenais, M.; Neumann, R.; Downer, M.; Bloembergen, N. J. *J. Opt. Soc. Am.* **1980**, *70*, 1392–1393.

(3) Bleijenberg, K. C.; Kellendonk, F. A.; Struck, C. W. *J. Chem. Phys.* **1980**, *73*, 3586–3588.

(4) Kozikowski, B. A.; Keiderling, T. A. *Chem. Phys. Lett.* **1982**, *86*, 463–466.

(5) Julander, H. P. M.S. Thesis, Washington State University, Pullman, WA, 1980.

(6) Birge, R. R. In "Ultrasensitive Laser Spectroscopy"; Kliger, D. S., Ed.; Academic Press: New York, 1983; Chapter 2.

(7) Johnson, M. C.; Lytle, F. E. *J. Appl. Phys.* **1980**, *51*, 2445–2449.

0002-7863/83/1505-5495$01.50/0

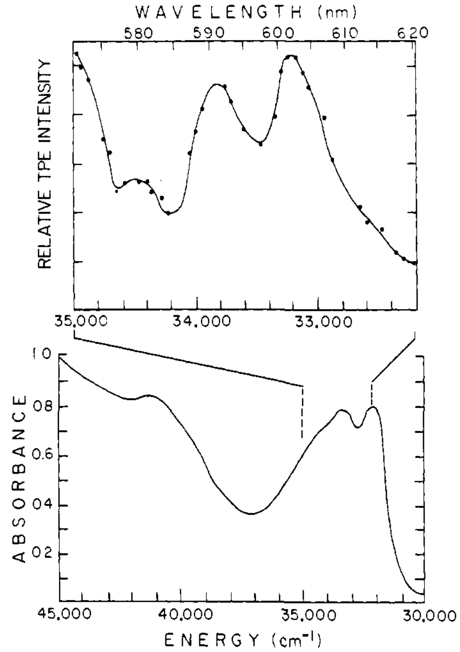

Figure 1. Lower trace: absorption spectrum of $Rh(CN)_2(dmb)_2^+$, $\sim 10^{-6}$ M in 4:1 ethanol-methanol at room temperature. The hatch marks indicate the energy range of correspondence between the absorption spectrum and the two-photon spectrum. Upper trace: two-photon excitation spectrum of $Rh(CN)_2(dmb)_2^+$ at 77 K. The upper x-axis scale represents the laser wavelengths (nm) used to generate the spectrum, and the lower x-axis scale corresponds to the actual energies (cm^{-1}) of excitation. $Rh(CN)_2(dmb)_2^+$ emission monitored at 471 nm.

with an increased peak-to-average power ratio.

The TPE spectrum and the absorption spectrum of $Rh(CN)_2(dmb)_2^+$ are shown in the upper and lower half of Figure 1, respectively. The corresponding profiles of the two spectra are entirely different, indicating that unique bands are accessed. We believe that the origin of the structure seen in the TPE spectrum is attributable to metal-localized d → d* transitions rather than to ligand-localized transitions. The absorption spectra of tris(4,4′-dimethyl-2,2′-bipyridine)rhodium(III) and $Rh(CN)_2(dmb)_2^+$ are almost identical, since the major bands in both spectra are intraligand $\pi \rightarrow \pi^*$ transitions that are not greatly perturbed by the change in the crystal field splitting between the two ions. However, TPE of $Rh(dmb)_3^{3+}$ was not observed, although the two complexes have similar luminescence intensities when viewed under single-photon excitation. Thus, it appears in $Rh(CN)_2(dmb)_2^+$ that the increased crystal field splitting due to the substitution of the cyano groups for a bipyridine has moved a d → d* band(s) into the energy region we are accessing. Estimation of the positions of d → d* transitions via crystal field considerations supports the above conclusion.

$Rh(CN)_2(dmb)_2^+$ is a pseudooctahedral d^6 complex with the low-spin configuration t_2^6. The excited state configuration t_2^5e gives rise to a pair of singlet d → d*'s and a pair of triplet d → d*'s that are split due to the C_{2v} symmetry of the complex. The states are not strictly gerade, thus the two-photon excited d → d* transitions are less allowed than similar TPE transitions would be for an octahedrally symmetric molecule. We have estimated experimentally that the TPE efficiency for the transitions falls at least an order of magnitude below a "forbidden" two-photon transition (the vibronically coupled $A_{1g} \rightarrow B_{2u}$ transition in naphthalene). This suggests that they are due to the triplet d → d* states, where the spin-forbidden nature of the triplet state transition and loss of gerade character have greatly decreased the TPE intensity. Extension of the $Rh(CN)_2(dmb)_2^+$ spectrum and excited-state symmetry studies of the spectral features via two-photon techniques are necessary before absolute assignments can be made.

Acknowledgment. The work was partially supported by the National Science Foundation. We are indebted to G. A. Crosby for providing the rhodium complex used in this research and thank the F. K. Fong group for the loan of the Dewar. Additionally, we thank R. F. Dallinger and D. R. McMillin for helpful discussions.

Static Distortion of ^2E Molecular Cations of Cyclobutane at 4.2 K Giving $^2B_2$ with C_{2v} Symmetry and Its Dynamic Average at $\gtrsim$77 K: ESR Evidence

Kiminori Ushida and Tadamasa Shida

Department of Chemistry, Faculty of Science
Kyoto University, Kyoto 606, Japan

Machio Iwasaki,* Kazumi Toriyama, and Keichi Nunome

Government Industrial Research Institute, Nagoya
Hirate, Kita, Nagoya 462, Japan

Received February 21, 1983

Highly symmetric molecular radical cations of simple alkanes often provide important examples of Jahn–Teller (J–T) active species, and the elucidation of the J–T distorted structure must be of fundamental significance in chemistry. However, little is known about the static distortion of these J–T active σ radical cations. Recent development of radiolytic production of radical cations in $CFCl_3$[1] and in other halogenated matrices[2,3] has made it possible to study electronic and geometrical structures of such J–T active species by electron spin resonance spectroscopy.[2,4-7] These results suggest that direct experimental information on static distoriton of J–T active species can be gathered at quite low temperatures even for small molecules with near orbital degeneracy.[2,7] In the present work, joint research by the two groups has been undertaken to elucidate a distorted structure of $c\text{-}C_4H_8^+$, one of the most important J–T active species.

The molecular cations were radiolytically produced at 77 or 4.2 K in a frozen solution of $CFCl_3$ containing a dilute solute of $c\text{-}C_4H_8$ (1:423 by volume).[1] Figure 1, parts a–d, demonstrates the ESR spectra measured at temperatures attainable by the instrument in Kyoto for the samples γ-irradiated at 77 K. At temperature above 77 K the fairly isotropic nine-line spectral feature indicates that the possible Jahn–Teller distortion is averaged out at these temperatures to result in an average splitting constant of about 15–16 G. Upon lowering the temperature the outer peaks are broadened as shown in Figure 1, parts a–d.

Shown in Figure 2 are the spectra obtained from the sample X irradiated at 4.2 K in Nagoya. The 4 K spectrum observed immediately after irradiation (Figure 2a) consists of three lines with the separation of 49 G, which further splits into three lines with the separation of 14 G. After annealing the sample at 77 K for 2 min, the coupling constants of the 3 × 3 line spectrum irreversibly changed into 44 and 22 G with a considerable narrowing of the line width giving a substructure of about 5 G (Figure

---

(1) (a) Shida, T.; Kato, T. *Chem. Phys. Lett.* **1979**, *68*, 106. (b) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963.

(2) (a) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Am. Chem. Soc.* **1981**, *103*, 3591. (b) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Chem. Phys.* **1982**, *77*, 5891.

(3) (a) Symons, M. C. R.; Smith, I. G. *J. Chem. Res., Synop.* **1979**, 382. (b) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Phys. Chem.* **1981**, *85*, 2149.

(4) Takemura, Y.; Shida, T. *J. Chem. Phys.* **1980**, *73*, 4133.

(5) (a) Kubodera, H.; Shida, T. 23rd Symposium of Radiation Chemistry, B202, October 1980, Kyoto. (b) Kubodera, H.; Shida, T. 19th ESR Symposium, 22A05, October 1980, Yokohama. (c) Shida, T.; Takemura, Y. *Radiat. Phys. Chem.* **1983**, *21*, 157.

(6) Ohta, K.; Nakatsuji, H.; Kubodera, H.; Shida, T. *Chem. Phys.* **1983**, *76*, 271.

(7) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 202.

0002-7863/83/1505-5496$01.50/0