double bond character. The values obtained are ClNO[12] 48%, ClNO$_2$[2] 14%, ClNH$_2$[5] 9%, ClNHCH$_3$[6] 9%, with the partial negative charge on chlorine. In contrast, a partial positive charge on chlorine is obtained for ClNCO[10] with an ionic character of 10%.

Structure I has unsymmetrical methyl groups in which the CH bond parallel to the plane of symmetry is longer than the other two CH bonds by 0.02 and 0.03 Å, respectively. A long CH bond has also been reported for isobutane[21] (1.10 Å) and trimethylamine[22] (1.109 Å). On the other hand, in structure II, the methyl groups are symmetric (r(CH) = 1.094 Å) and each has an upward tilt of 4.1° toward the lone pair. Similar methyl tilts have been reported for a number of molecules[23] including methylamine,[24] trimethylamine,[22] and N-chloromethamine.[6] In the last three instances, tilt angles of ~3°, 1.3°, and ~3.5°, respectively, have been determined.

No appreciable difference is observed in the C–N bond length in structures I and II, which are 1.473 and 1.470 Å, respectively. In CH$_3$NHCl[6] the C–N bond distance was found to be 1.474 ± 0.005 Å. In each case the length of the C–N bond obtained from microwave studies appears to be in good agreement with the value of 1.47 Å which was reported for (CH$_3$)$_2$NCl and CH$_3$NCl$_2$ from electron diffraction studies.[11] The calculated value of the CNC bond angle (110.7° in structure I and 111° in structure II) is considerably larger than 108° which was assumed for this angle in the electron diffraction work.[11] However, the CNC angle presently obtained is consistent with the values of 110.9° and 111.6° which have been reported[22,25] for this angle in (CH$_3$)$_3$N and (CH$_3$)$_2$NH, respectively.

Of special interest is the N–Cl bond length. The N–Cl bond distance in (CH$_3$)$_2$NCl reported in the electron diffraction study[11] is 1.77 Å which is 0.04 Å longer than the sum of the covalent radii

of N and Cl (1.73 Å).[3] The N–Cl bond length obtained herein (1.742 Å in structure I and 1.749 Å in structure II) is smaller than the electron diffraction value and closer to the value predicted from the covalent radii of the two atoms. A comparison of this bond length with those reported for CH$_3$NCl$_2$ (1.74 Å)[11] and CH$_3$NHCl (1.750 Å)[6] shows that the N–Cl bond distance remains practically unchanged in this series of compounds. It should be noted, however, that the size of the ClNC angle in (CH$_3$)$_2$NCl (108.4° in structure I and 108.0° in structure II) is appreciably smaller than that reported[6] for CH$_3$NHCl (109.4°). The apparent contraction of the ClNC angle in (CH$_3$)$_2$NCl is to be expected considering the inductive effect due to the second methyl group in (CH$_3$)$_2$NCl which replaces the hydrogen atom in CH$_3$NHCl. The electron diffraction results[11] for the ClNC angles in (CH$_3$)$_2$NCl and CH$_3$NCl$_2$ are 107° ± 2° and 109° ± 2°, respectively. Despite the high degree of uncertainty in the electron diffraction measurements, these data correctly reflect the inductive effect of the methyl substituent.

It is interesting to note that the inductive effect of the methyl group on the corresponding carbon compounds results in a significant elongation of the carbon–chlorine bond length (see Table VII). For example, this distance in ethyl chloride[9] is 1.788 Å which is 0.007 Å longer than the corresponding distance in methyl chloride[7,8] but 0.010 Å shorter than the carbon–chlorine distance in isopropyl chloride.[27] Therefore, it is rather surprising that the nitrogen–chlorine distance remains so constant with the substitution of the methyl group for a hydrogen atom in the corresponding nitrogen compounds.

(21) Lide, D. R., Jr. J. Chem. Phys. 1960, 33, 1519.
(22) Wollrab, J. E.; Laurie, V. W. J. Chem. Phys. 1969, 51, 1580.
(23) Wollrab, J. E. Rotational Spectra and Molecular Structure; Academic: New York, 1967; Appendix 9.
(24) Lide, D. R., Jr. J. Chem. Phys. 1957, 27, 343.
(25) Wollrab, J. E.; Laurie, V. W. J. Chem. Phys. 1968, 48, 5058.
(26) Moore, G. E.; Badger, R. M. J. Am. Chem. Soc. 1952, 74, 6076.

(27) Tobiason, F. L.; Schwendeman, R. H. J. Chem. Phys. 1964, 40, 1014.
(28) Lide, D. R., Jr.; Jen, M. J. Chem. Phys. 1963, 38, 1504.

Luminescence from Nitrido Complexes of Osmium(VI). Evidence for a Nontotally Symmetric Excited-State Distortion

Michael D. Hopkins,[*1] **Vincent M. Miskowski,**[*2] **and Harry B. Gray**[*1]

Contribution No. 7373 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125, and the Applied Sciences and Microgravity Experiments Section, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109. Received February 24, 1986

Abstract: Vibronically resolved emission spectra have been obtained for the [Ph$_4$As][OsNX$_4$] (X = Cl, Br; C_{4v} ground state) complexes. The observation of long ($\tau > 10$ μs) emission lifetimes and very weak absorptions, together with a large geometric distortion along the OsN coordinate, supports assignment of the excited state to B$_1$, B$_2$ (^{3}E) ((d_{xy})^1(d_{xz},d_{yz})^1). Large distortions are also observed along a deformation vibrational coordinate of b$_1$ symmetry (ground-state vibrational frequency 151 cm^{-1} (X = Cl), 112 cm^{-1} (X = Br)) that is Jahn–Teller active. It is proposed that the ^{3}E excited states are strongly distorted toward a C_{2v} (equatorial nitrido) trigonal-bipyramidal geometry.

The electronic structures of high-valent transition-metal complexes containing multiple metal–ligand bonds have been the subject of numerous spectroscopic investigations.[3] Recent attention has been focused on 6-coordinate d^2 MO$_2$$^{n+}$ species, in part because of their solution luminescence properties.[4] One characteristic dynamic process of the emissive ^{3}E$_g$ excited state of each of these d^2 complexes is a distortion from the ground-state structure along symmetric coordinates, with the metal–oxo bond undergoing a particularly large displacement.[4] We have continued our investigations of d^2 metal–ligand multiply bonded species, and included in the present report are emission spectroscopic results that

(1) Arthur Amos Noyes Laboratory.
(2) Jet Propulsion Laboratory.
(3) Winkler, J. R.; Gray, H. B. Comments Inorg. Chem. 1981, 1, 257–263 and references therein.

(4) (a) Winkler, J. R.; Gray, H. B. Inorg. Chem. 1985 24, 346–355. (b) Winkler, J. R.; Gray, H. B. J. Am. Chem. Soc. 1983, 105, 1373–1374.
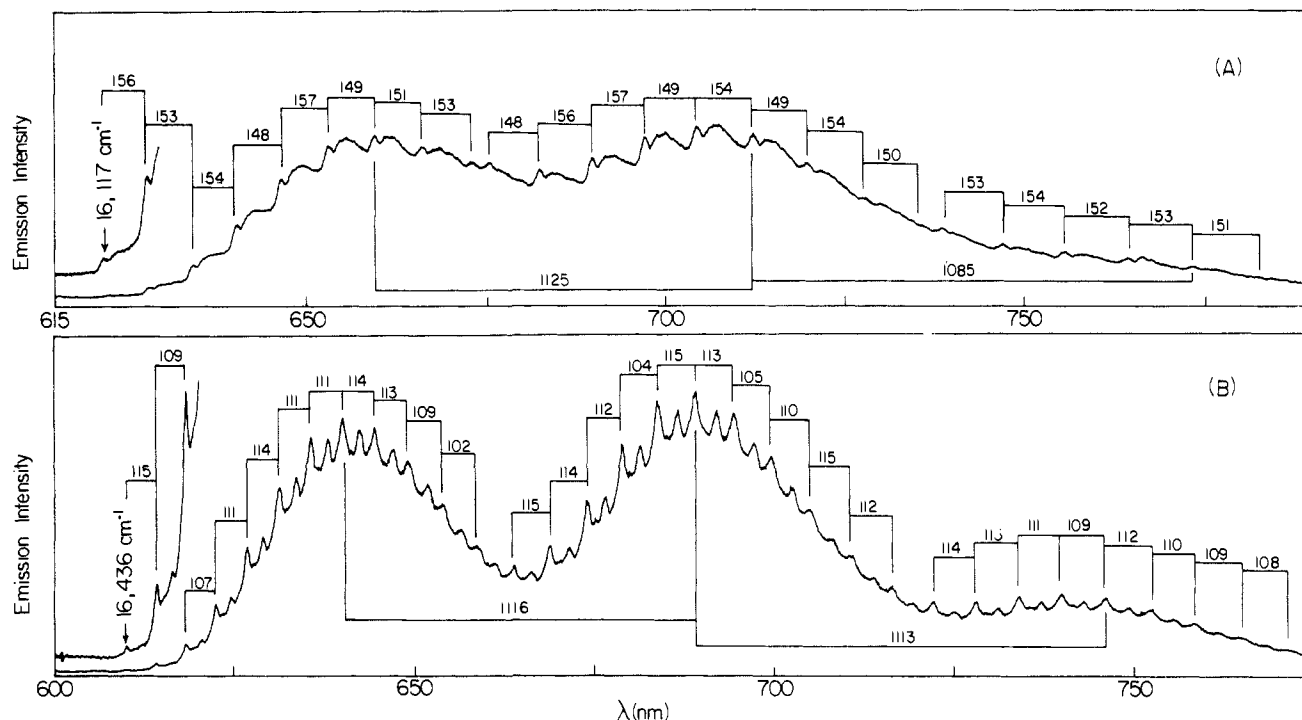
Figure 1. Emission spectra of polycrystalline [Ph$_4$As][OsNX$_4$] at ca. 5 K (uncorrected for spectrometer response): (a) X = Cl; (b) X = Br. The $\nu_1(\nu$OsN) and $\nu_5(\delta_{as}$OsX$_4$) modes are identified.

Table I. Luminescence Lifetimes of [OsNX$_4$]$^{-a}$

	τ	
compound	T = 300 K ns	77 K μs
[Ph$_4$As][OsNCl$_4$]	500	20^b
[Ph$_4$As][OsNBr$_4$]	940	34
[n-Bu$_4$N][OsNBr$_4$]	<10	11

^{a} Excited with the second harmonic (532 nm) of a Nd:YAG laser. Emission was monitored at 650 nm. ^{b} Also determined to be 20 μs at 5 K.

indicate the nature of the excited-state distortions of 5-coordinate Os≡N complexes.

Experimental Section

The osmium(VI)–nitrido complexes were prepared as described previously.[5,6] Data reported here are for samples that were freshly recrystallized from acetonitrile.

The instruments and procedures used for high-resolution emission spectra[7] and lifetime measurements[8] have been described in detail elsewhere. Polarized single-crystal absorption spectra were recorded with a Cary 17 spectrophotometer equipped with dual Glan-Thompson air-spaced calcite polarizers. Samples for these latter experiments consisted of crystals mounted on quartz flats, the area around the crystal being carefully masked with heat-conducting grease. Crystal faces were identified by examination with a polarizing microscope. Temperature control for low-temperature experiments was achieved with an Oxford Instruments Ltd. Model CF-204 continuous-flow cryostat equipped with a Model 3120 temperature controller, a Model VC30 flow regulator, and a Rh/Fe thermocouple.

Results and Discussion

Compounds containing [OsNX$_4$]$^-$ (X = Cl, Br) exhibit intense red luminescence.[5b] As indicated in Table I, there is some cation

(5) (a) Cowman, C. D.; Trogler, W. C.; Mann, K. R.; Poon, C. K.; Gray, H. B. *Inorg. Chem.* **1976**, *15*, 1747–1751. (b) Cowman, C. D. Ph.D. Thesis, California Institute of Technology, 1974. (c) Collison, D.; Garner, C. D.; Mabbs, F. E.; Salthouse, J. A.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1812–1819.

(6) Collin, R.; Griffith, W. P.; Pawson, D. *J. Mol. Struct.* **1973**, *19*, 531–544.

(7) Nocera, D. G.; Winkler, J. R.; Yocom, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5145–5150.

(8) Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571–4575.

Table II. Vibronically Active Modes of [OsNX$_4$]$^-$

		frequency/cm^{-1}		
compound		ground state (IR/Raman)^a	ground state (emission)	excited state (absorption)^b
[Ph$_4$As][OsNCl$_4$]	ν_1	1123	1125	~800
	ν_2	184		
	ν_5	149	151	160
[Ph$_4$As][OsNBr$_4$]	ν_1	1119	1116	~1000
	ν_2	122		
	ν_5	110	112	110

^{a} Reference 6. ^{b} Excited-state ν_1 values are imprecise (±150 cm^{-1}) because of severe spectral congestion (see ref 5).

dependence of the emission lifetime at room temperature, although at low temperature all the emissions are nearly equally long lived. At 5 K, the emission spectra of [Ph$_4$As][OsNX$_4$] display beautifully resolved vibronic structure (Figure 1, Table II). These spectra bear a strong resemblance to each other: both are dominated by a progression in a high-frequency (~1120 cm^{-1}) mode that corresponds to ν(OsN) (IR/Raman:[6] X = Cl, ν = 1123 cm^{-1}; X = Br, ν = 1119 cm^{-1})[9] as well as a long, well-defined subprogression in a mode of lower frequency (X = Cl, ν = 151 cm^{-1}; X = Br, ν = 112 cm^{-1}). The spectra of these complexes also contain phonon sidebands to the main progressions, but these are well resolved only for the bromide derivative (Figure 2).[10]

The absorption systems corresponding to emission were located for a thick (0.54 mm) single crystal[11] of [Ph$_4$As][OsNCl$_4$] (Figure

(9) The corrected (Parker, C. A.; Rees, W. T. *Analyst* **1960**, *85*, 587–600) emission spectra show relative intensities of the ν(OsN) vibronic progression members of 1/1.8/1.3 for both compounds. A Franck–Condon calculation with these intensities and the ground- and excited-state ν(OsN) values of Table II yields an excited-state Os≡N bond distortion of 0.09 Å (diatomic approximation).
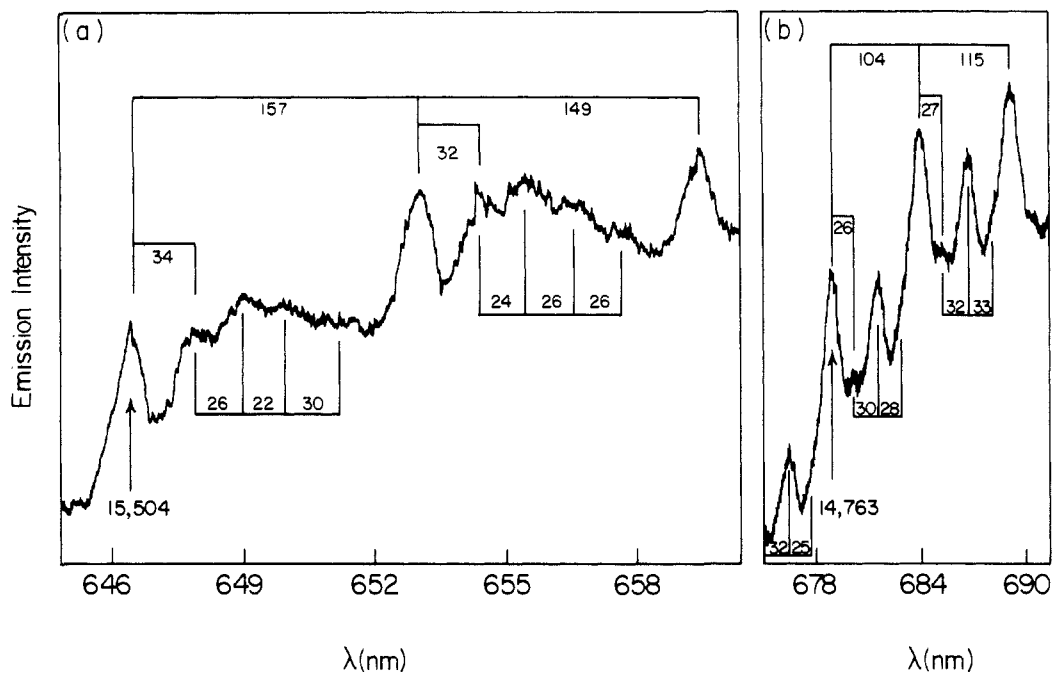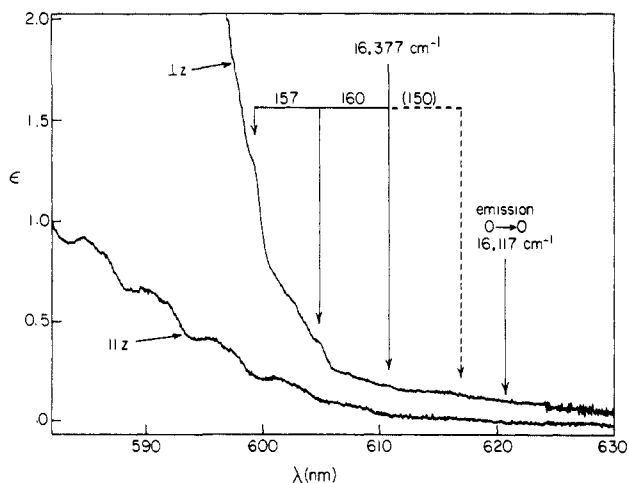
(10) An alternative explanation of these weak features is the possibility of multiple electronic origins (as opposed to vibronic) from the presumably closely spaced B$_1$, B$_2$ (^{3}E) states (vide infra). We did not see any changes in relative intensities of the various lines with temperature, however, as expected[4a] for this hypothesis; invariance of the low-temperature emission lifetime over the range 4.2–77 K was also noted. On one occasion we observed an essentially total collapse of the vibronic fine structure of the subprogressions of [Ph$_4$As][OsNCl$_4$] emission as the temperature was lowered to 4 K, which was reversed as the temperature increased to 15 K. This observation could not be reproduced with a different sample, however, so its significance is unclear.

Figure 2. Expanded view of Figure 1 showing the phonon subprogressions of [Ph$_4$As][OsNX$_4$]: (a) X = Cl; (b) X = Br.

Figure 3. Polarized single-crystal absorption spectrum of [Ph$_4$As]-[OsNCl$_4$] at ca. 5 K. The crystal thickness was 0.54 mm. The ⊥z spectrum is vertically offset from the ϵ = 0 base line.

3, Table II). These features are extremely weak, consistent with the long emission lifetime. In ‖z polarization, the very weak band can be followed out to ~540 nm (one quantum of excited state ν(OsN) $\simeq$ 800 cm^{-1} was observed), while in ⊥z polarization the weak features are obscured by a much stronger absorption band[5] below ~595 nm. It is this latter polarization that seems to bear a mirror-image relationship to the emission; the ‖z polarization shows only the broad phonon sidebands and lacks the relatively sharp lines of the subprogression observed in emission. The lowest energy absorption feature that is firmly established is at 16 377 cm^{-1}, although there appears to be a trace of a lower energy feature at about 16 277 cm^{-1}.[12] Even assuming that this last line is real, there is still a gap of ~110 cm^{-1} between the absorption and emission origins, suggesting that a vibronic intensity-allowing mechanism is operative for the electronic transition; a completely forbidden pure electronic origin presumably lies midway between the absorption and emission vibronic origins. The single-crystal

(11) The space group is tetragonal (P_4/n: Phillips, F. L.; Shapski, A. C. *J. Cryst. Mol. Struct.* **1975**, *5*, 83–92, ref 5c) and imposes rigorous C_{4v} site symmetry on the anion. A {h00} face was studied, which yields spectra parallel and perpendicular to molecular z (OsN coordinate).

(12) We have not been able to obtain significantly thicker crystals of good optical quality to test this point.
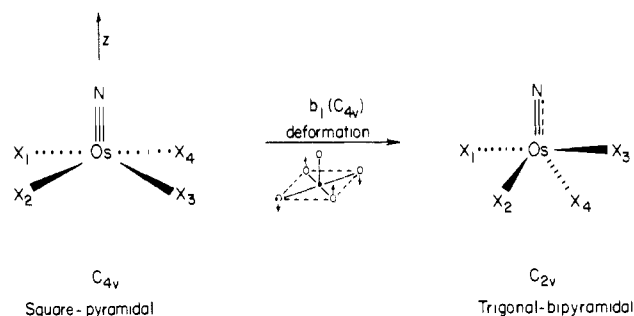
Figure 4. Proposed excited-state (^{3}E) distortion of [OsNX$_4$]$^-$. The ground-state (C_{4v}) NOsX angle is[5,11] ~105°.

absorption spectrum of [Ph$_4$As][OsNBr$_4$] (not shown) is qualitatively similar in these regards.

The observed photophysical and vibronic characteristics of these d^2 systems are consistent with previous work,[4,5] indicating that the lowest electronic transitions are the spin–orbit components of the ^{3}E←^{1}A$_1$[(d$_{xy}$)^2→(d$_{xy}$)^1(d$_{xz}$,d$_{yz}$)^1] ligand-field transition. Both simple [4a] and more complicated[5c] spin–orbit treatments indicate that the lowest energy excited states will be the B$_1$, B$_2$ components, which are degenerate to first order; ^{3}E←^{1}A$_1$-[(d$_{xy}$)^2→(d$_{xy}$)^1(d$_{xz}$,d$_{yz}$)^1] transitions to these states from the ground state are dipole-forbidden, which accounts for the long excited-state lifetime. The large distortion of the Os≡N bond[9] is attributed to the π-antibonding (OsN) nature of the d$_{xz}$,d$_{yz}$ orbitals; similarly large distortions have been inferred for absorption transitions to other ^{3}E spin–orbit components.[5]

The electronic spectra of [OsNX$_4$]$^-$ clearly show that there is also a large excited-state distortion along a low-frequency deformation coordinate in both absorption and emission. Absorption studies earlier had indicated[5] that this mode is the totally symmetric umbrella deformation (ν_2, Table II); however, the ground-state frequency seen in emission is not in accord with this interpretation. The observed frequency is, in fact, in excellent agreement with a nontotally symmetric deformation of b$_1$ symmetry (ν_5, Table II).

We believe that the origin of the implied nontotally symmetric excited-state distortion is straightforward. The ^{3}E excited state is Jahn–Teller unstable, and the active modes for this distortion in C_{4v} symmetry are b$_1$ and b$_2$. That a b$_1$ deformation mode should be strongly active is intuitively pleasing, since this mode is exactly the one that can carry the molecule between C_{4v} (square-pyram-

idal) and C_{2v} (pseudo-trigonal-bipyramidal, with an equatorial nitrido ligand) geometry, as shown in Figure 4 . From an electronic standpoint, this is the geometry that would be expected to result from the weakened OsN π-bonding of the excited state, since this distortion allows one component of d_{xz}, d_{yz} (the one unoccupied in the excited state) to be destabilized by increased σ-interaction with the X ligands, while the occupied component is stabilized by decreased σ-interaction. If there were no π-bonding at all, electrostatic considerations would favor a trigonal-pyramidal geometry.

Franck–Condon calculations (employing reported[10] bending force constants and neglecting **F** and **G** matrix mixing) indicate that the b_1 distortion is on the order of 8°, which places the excited-state structure approximately midway between the limiting square-pyramidal and pseudo-trigonal-bipyramidal geometries. That the barrier to this distortion is fairly small for this class of complexes may be inferred from the fact that the valence-isoelectronic species [ReNCl$_2$(PPh$_3$)$_2$] possesses a ground-state geometry[13] very similar to that proposed here for the emissive excited state of [OsNX$_4$]$^-$.

In support of our interpretation of [OsNX$_4$]$^-$ excited-state structure, 6-coordinate valence-isoelectronic complexes such as [ReO$_2$(CN)$_4$]$^{3-}$ show much smaller distortions along the deformation coordinates, in both absorption and emission, for the analogous electronic transitions.[4] It seems likely to us that the short progressions in low-frequency modes observed for this type of compound[14] represent excited-state Jahn–Teller distortions that are of small magnitude because there is no highly favorable geometry toward which the molecule can distort.

(13) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204–210.

(14) We have also examined two examples of weak axial adducts of [OsNCl$_4$]$^-$, the compounds [*n*-Pr$_4$N][OsNCl$_4$(OH$_2$)] and K$_2$[OsNCl$_5$]. Luminescence is extremely weak for both even at low temperature, and we have not yet been able to characterize it further.

Structural Control of the Triplet–Singlet Equilibrium in Cyclophane Diarylcarbenes

R. Alt,[1a] I. R. Gould,[1b] H. A. Staab,*[1a] and N. J. Turro*[1b]

Contribution from the Abteilung Organische Chemie, Max-Planck-Institute für Medizinishe Forschung, Jahnstrasse, D-6900 Heidelberg, West Germany, and the Chemistry Department, Columbia University, New York, New York 10027. Received April 4, 1986

Abstract: The absolute reactivities of [1.*n*]paracyclophane analogues of diphenylcarbene have been investigated by using the technique of laser flash photolysis. The results are consistent with theoretical predictions that the relative stabilities of the triplet and singlet states of these species can be controlled by changing the hybridization at the carbenic center and the torsional angle of the aryl rings.

Significantly different chemical reactivity is observed from singlet and triplet carbenes,[2,3] and thus the relationship between molecular structure and the relative energies of these two states is very important. Of particular interest is the possibility of controlling the relative stabilities of the singlet and triplet states of carbenes, and consequently the reaction products. However, the absolute energy difference between these states has been investigated for very few carbenes. In this regard diphenylcarbene (DPC, **2**) is exceptional in that both the energy difference between the ground triplet and corresponding singlet states (ΔE_{ts} = *E*(triplet) − *E*(singlet)), and the dynamics of their interconversion have been extensively studied.[4,5] This is because the carbene is the archetype arylcarbene and is amenable to time-resolved spectroscopic techniques.[4,5]

(1)
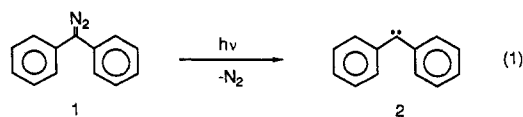
Recently the preparation of the [1.*n*]paracyclophane carbenes **4** was reported, together with ESR studies of these species.[6] These carbenes are of significant interest as analogues of diphenylcarbene. Theoretical evidence suggests that for DPC, the energies of the triplet and singlet states depend to differing extents upon the angle (α) between the two aryl carbon–carbenic carbon bonds and the torsional angle (θ) by which the two aryl rings are twisted with respect to a plane defined by the bonds on the carbenic center.[7] It is predicted that the singlet state should be stabilized with respect to the triplet as a function of decreasing α and

(1) (a) Max-Planck-Institute. (b) Columbia University.

(2) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971.

(3) *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley Interscience: New York, 1975; Vol. 1 and 2.

(4) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(5) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543.

(6) (a) Alt, R.; Staab, H. A. *Tetrahedron Lett.* **1984**, 633. (b) Staab, H. A.; Alt, R. A. *Chem. Ber.* **1984**, *117*, 850.

(7) (a) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485. (b) Metcalfe, J.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 634.

(8) These results for diphenylcarbene have previously been reported (ref 5).