Table I. Absorption and Emission Properties of Orthometalated Pt(IV) Complexes

complex	absorption[a]		emission				
			293 K[a]			77 K[b]	
	λ_{max}, nm	ϵ	λ_{max},[c] nm	τ,[d] μs	Φ[e]	λ_{max},[c] nm	τ,[d] μs
Pt(Phpy)$_2$(CH$_2$Cl)Cl	260 306	23000 15000	447	150	0.15	444	300
Pt(Phpy)$_2$(CHCl$_2$)Cl	261 307	26000 15000	446	100	0.10	444	360
Pt(Thpy)$_2$(CH$_2$Cl)Cl	287 344	22000 17000	513	200	0.05	507	340
Pt(Thpy)$_2$(CHCl$_2$)Cl	287 344	22000 16000	513	270	0.05	507	430

[a] In CH$_2$Cl$_2$. [b] In propionitrile–butyronitrile 4:5 v/v mixture. [c] λ of the high-energy feature of the phosphorescence emission. [d] Emission lifetime in deaerated solution; estimated error ±10%. [e] Luminescence quantum yield, based on the value 0.028 reported in water at room temperature for Ru(bpy)$_3^{2+}$ (Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697); estimated error ±20%.

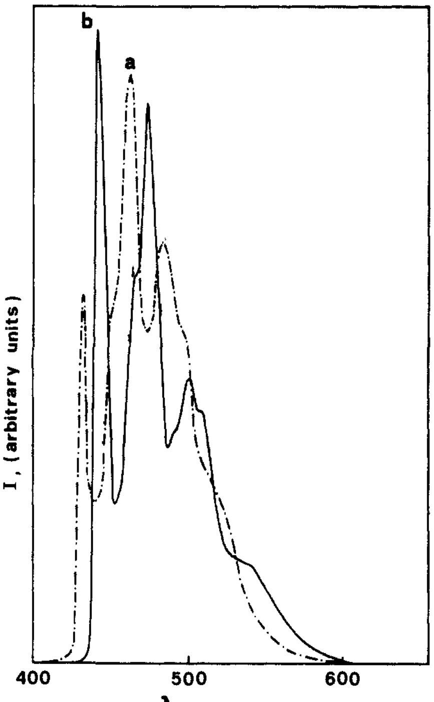


Figure 3. Emission spectra of PhpyH (a) and Pt(Phpy)$_2$(CH$_2$Cl)Cl (b) in propionitrile–butyronitrile 4:5 v/v mixture at 77 K.

region, red-shifted with respect to those of the "protonated" ligand.

A quite interesting property of these Pt(IV) complexes is their ability to give a strong and long-lived luminescence. The previously reported[7-9] oxidative addition products of Pt(II) complexes apparently do not exhibit this property and, to our knowledge, the Pt(IV) complexes discussed in this paper constitute the first example of luminescent Pt(IV) organometallic complexes. In rigid nitrile matrix at 77 K the emission spectra have structures similar to those of the phosphorescenee spectra of the free protonated ligands, with a small red shift (see, e.g., Figure 3). This suggests that the emitting excited state is the lowest triplet ligand centered excited state, perturbed by metalation. The relatively long emission lifetimes (Table I) are consistent with this assignment. It should also be noted that metal-to-ligand charge-transfer excited states (which are responsible for the emission of the starting Pt(II) complexes)[5] are expected to lie at very high energies in Pt(IV) complexes and that emission from metal centered (and likely also from ligand-to-metal charge transfer) excited states would give rise to broad and unstructured luminescence bands.[10,11]

Strong luminescence and long emission lifetime are also observed at room temperature in deaerated solution (Table I), which makes these Pt(IV) complexes interesting as potential photosensitizers. Another important point of interest of the reaction described in this paper is the following. One can envisage the addition, to the orthometalated Pt(II) complexes, of Cl–(CH$_2$)$_n$–X species, where X is an appropriate luminescent moiety. This would lead to the preparation of a new class of bichromophoric complexes suitable for the study of intramolecular energy- and electron-transfer processes.

In conclusion, we have shown that new, strongly luminescent orthometalated Pt(IV) complexes can be easily prepared by a photochemical oxidative addition on the corresponding orthometalated Pt(II) complexes. The reported reaction, which represent the quite unusual case of a photochemical process that converts a luminescent complex into another luminescent complex, offers a promising route for the synthesis of complexes containing distinct emitting units.

Acknowledgment. This work was supported by the Italian National Research Council, Ministero della Pubblica Istruzione, and Swiss National Science Foundation.

---

(10) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970.

(11) Crosby, G. A. *J. Chem. Educ.* **1983**, *60*, 791.

Tight, Oriented Binding of an Aliphatic Guest by a New Class of Water-Soluble Molecules with Hydrophobic Binding Sites

Timothy J. Shepodd,[1a] Michael A. Petti,[1b] and
Dennis A. Dougherty*[1c]

*Contribution No. 7337, Arnold and Mabel Beckman
Laboratory of Chemical Synthesis, California
Institute of Technology, Pasadena, California 91125*

Received December 13, 1985

There is much current interest in the design and synthesis of water-soluble organic molecules with hydrophobic binding sites.[2] A variety of interesting artificial receptors (hosts) based on cyclophane skeletons has been prepared and shown to bind flat, aromatic guests very efficiently.[3-6] In contrast, efforts to bind

---

(1) (a) Fellow of the W. R. Grace Foundation, 1985. (b) Fellow of the Atlantic Richfield Foundation, 1984. (c) Camille and Henry Dreyfus Teacher Scholar, 1984–1989.

(2) Tabushi, I.; Yamamura, K. *Top. Curr. Chem.* **1983**, *113*, 145–183.

(3) (a) Diederich, F.; Dick, K. *J. Am. Chem. Soc.* **1984**, *106*, 8024–8036. (b) Diederich, F.; Griebel, D. *J. Am. Chem. Soc.* **1984**, *106*, 8037–8046. (c) Diederich, F.; Dick, K. *Chem. Ber.* **1985**, *118*, 3817–3829. (d) Diederich, F.; Dick, K.; Griebel, D. *Chem. Ber.* **1985**, *118*, 3588–3619.

(4) (a) Odashima, K.; Itai, A.; Iitaka, Y.; Koga, K. *J. Am. Chem. Soc.* **1980**, *102*, 2504–2505. (b) Soga, T.; Odashima, K.; Koga, K. *Tetrahedron Lett.* **1980**, *21*, 4351–4354. (c) Odashima, K.; Soga, T.; Koga, K. *Tetrahedron Lett.* **1981**, *22*, 5311–5314.

(5) (a) Jarvi, E. T.; Whitlock, H. W. *J. Am. Chem. Soc.* **1982**, *104*, 7196–7204. (b) Miller, S. P.; Whitlock, H. W. *J. Am. Chem. Soc.* **1984**, *106*, 1492–1494.

(6) (a) Tabushi, I.; Yasuhisa, K.; Yoshio, K. *Tetrahedron Lett.* **1976**, *37*, 3327–3330. (b) Tabushi, I.; Kimura, Y.; Yamamura, K. *J. Am. Chem. Soc.* **1978**, *100*, 1304–1306. (c) Tabushi, I.; Kimura, Y.; Yamamura, K. *J. Am. Chem. Soc.* **1981**, *103*, 6486–6492.

0002-7863/86/1508-6085$01.50/0 © 1986 American Chemical Society

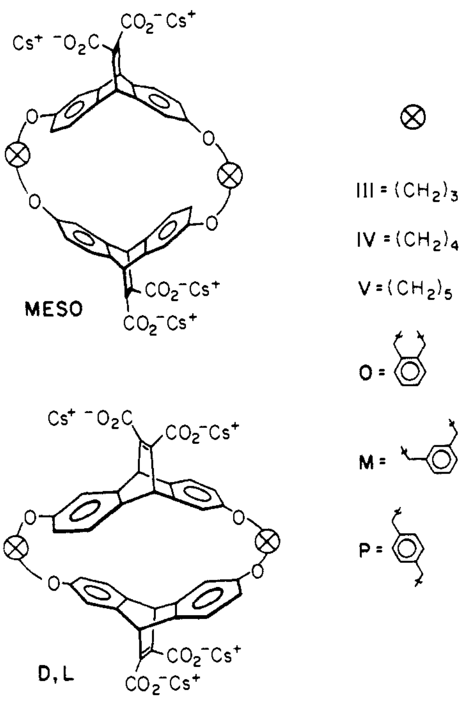


Figure 1.

Table I. K_a and Δ Values for Binding of ATMA to Several Hosts[a]

host	Δ*A*	Δ*B*	Δ*C*	ΔD_1	ΔD_2	K_a, M^{-1} [b]
meso-IV	0.92	1.00	1.02	1.09	1.10	7500[c]
d,l-IV	0.73	0.64	0.61	0.80	0.88	1300[c]
meso-V	2.52	2.80	0.95	1.08	0.97	2500[c]
d,l-V	2.42	2.83	1.41	1.52	1.34	1900[c]
meso-P	1.82	2.76	1.16	1.21	0.69	240000[d]
d,l-P	1.83	2.90	1.19	1.30	0.76	120000[d]

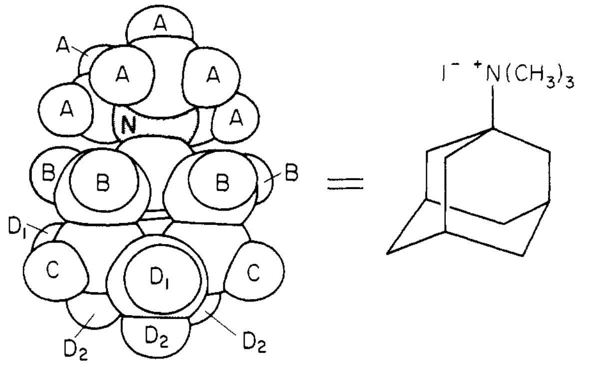
[a] The Δ values for each proton are in ppm. [b] Average of the values calculated for each of the five protons of ATMA. [c] ±15%. [d] These values represent lower limits. Large variation in the percent ATMA bound is not possible for such large K_a values over the concentration ranges studied. Δ values are calculated for these lower limit K_a values.

other types of guests, such as derivatives of polycyclic aliphatic systems, have been less successful. We report herein that a new class of receptor molecules, which we have designed and synthesized,[7] binds a guest of this second type very effectively. Two binding modes are seen: one in which the guest is bound in a relatively random orientation and one which involves very much stronger binding with a very precise orientation of the guest in the binding site.

Twelve host structures—six *meso*/*d,l* pairs—have been prepared and characterized (Figure 1).[7] CPK models suggested a complementary fit between our receptor site and an adamantyl system. We therefore prepared adamantyltrimethylammonium iodide (ATMA) as a water-soluble adamantane derivative suitable for ^1H NMR studies.

On addition of host to an aqueous solution of ATMA, all guest signals show substantial upfield shifts.[8] By performing such studies over a range of concentrations, standard fitting techniques[9] provide values for the upfield shift of completely bound ATMA relative to free (Δ) and for the association constant (K_a). The results of these studies are summarized in Table I.

Model-building studies suggested that the preferred binding orientation would have the C_3 axis of ATMA passing directly through the binding cavity, running roughly parallel to the etheno bridges. The A and B protons of ATMA each form a ring that lies perpendicular to this axis. Interestingly, C and D_1 are in very similar environments and together form a third ring of protons. The D_2 protons, however, are in a very different environment and point approximately parallel to the C_3 axis. Thus, in the proposed binding orientation, the A, B, C and D_1 protons all point out toward the aromatic rings of the host and should be substantially shielded. Importantly, C and D_1 should be comparably shielded. However, D_2 points away from the aromatic rings and should be the least shielded.



ATMA

The data of Table I show that all the hosts studied bind ATMA well, considering that before the present work a K_a of 740 M^{-1} was the largest previously reported[3c] for a host–guest combination of this type.[10] However, the characteristic shift pattern predicted above is not exhibited for all hosts. When bound to *meso*- or *d,l*-IV, all ATMA resonances shift upfield to roughly the same extent. This must indicate that complexation does not require a specific guest orientation. We suggest that these hosts can collapse out of the idealized conformations shown in Figure 1 to some other form that does not enforce a particular binding orientation. The expected shift pattern is also absent with hosts *meso*- and *d,l*-V.

When the aliphatic "linker" groups (⊗ in Figure 1) are replaced by the rigid, *p*-xylyl group to give *meso*- and *d,l*-P, two significant changes occur (Table I). The binding constant increases by roughly 2 orders of magnitude, and the characteristic shift pattern indicative of oriented binding emerges. Evidently, the rigid linkers oppose host collapse, and this leads to highly oriented binding with higher association constants.

Comparing our hosts to previously reported synthetic systems, the major design feature that could be responsible for the marked improvement in binding ability is the ethenoanthracene unit. This dissymmetric, concave building block is very rigid, and it has been amply demonstrated[11] that "flexibility is the enemy"[12] in the design of synthetic receptors. Additionally, the ethenoanthracenes enforce a clear-cut separation of the hydrophilic (charged) and hydrophobic regions. One might expect that this also enhances hydrophobic binding. Further studies are under way to probe the influences of these and related effects on the binding phenomenon.

---

(7) Petti, M. A.; Shepodd, T. J.; Dougherty, D. A. *Tetrahedron Lett.* **1986**, *27*, 807–810.

(8) The concentrations of the stock host solutions, in 10 mM cesium phosphate buffer (D_2O, pD ≃7.5), were determined by integration against four internal standards. All NMR spectra were obtained under fast-exchange conditions on a JEOL GX400 spectrometer with all chemical shifts being relative to external DSS. All NMR experiments were performed significantly below the cmc's of these hosts.[7] The host/guest ratio varied from 2:1 to 1:4 with typical [host] = 40–500 μM and [guest] = 100–800 μM. The ATMA reference spectrum was recorded at 450 μM in D_2O. Control studies with cesium maleate and ATMA or the "half-molecule" (2,6-diethoxy-9,10-dihydro-9,10-(1,2-dicarboxy)ethenoanthracene, dicesium salt) and ATMA were performed. In each case only very small ATMA shifts were seen, which are attributable to ionic interactions.

(9) See, for example: de Boer, J. A. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1985**, *107*, 5347–5351. Deranleau, D. A. *Ibid.* **1969**, *91*, 4044–4049.

(10) Cyclodextrins and their derivatives are also effective at binding adamantane derivatives. See, for example: (a) Emert, J.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 670–672. (b) Tabushi, I.; Shimokawa, K.; Shimizu, N.; Shirakata, H.; Fujita, K. *J. Am. Chem. Soc.* **1976**, *98*, 7855–7856. (c) Cromwell, W. C.; Byström, K.; Eftink, M. R. *J. Phys. Chem.* **1985**, *89*, 326–332.

(11) See, for example: Cram, D. J. *Science (Washington, D.C.)* **1983**, *219*, 1177–1183.

(12) Breslow, R. *Isr. J. Chem.* **1979**, *18*, 187–191.

In addition, it remains to be determined whether the strong connection between the ability of a host to orient a guest and the magnitude of K_a, apparent from the present work, is a general phenomenon.

Acknowledgment. We thank the 3M Corporation and the Arco Foundation for partial support of this work.

Discrete-Variational-Xα Electronic Structure Studies of the Spherical C_{60} Cluster: Prediction of Ionization Potential and Electronic Transition Energy

Paul D. Hale

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received April 22, 1986

Recent carbon vaporization studies by Smalley and co-workers[1] have provided evidence for the existence of a remarkably stable C_{60} species. It has been proposed that this cluster may be nearly spherical in shape, with a truncated icosahedral structure made up of 12 pentagonal rings and 20 hexagonal rings. The stability of this molecule has been discussed in terms of a simple Hückel model[2] and Herndon–Simpson resonance theory,[3] and the electronic structure has been studied in considerable detail using a three-dimensional Hückel scheme.[4] Very recent MNDO calculations[5] have also investigated the stability of C_{60} and have provided an estimate of the ionization potential of this species.

The present paper describes preliminary results of discrete-variational-Xα (DV-Xα) electronic structure calculations[6] for this soccerball-shaped carbon cluster. This method has been used to study a wide range of molecules, from small hydrocarbons[7] to large aromatic systems,[8] and the accuracy of the Slater transition-state technique[9] in calculating optical transition energies and ionization potentials is well-documented.[7,8]

For the C_{60} molecule, ground-state calculations and transition-state calculations for the lowest allowed optical transition and the first ionization energy were performed. In order to simplify the computations, it was assumed that all carbon–carbon bond lengths are equal. Two cases were considered: (a) C–C bond length of graphite (1.421 Å) and (b) C–C bond length of benzene (1.395 Å). The atomic basis functions were determined from a separate Hartree–Fock–Slater calculation; in this, an effective configuration of $1s^2 2s^2 2p^2 3s^0 3p^0$ was used for carbon. Also, a potential well[7,10] was placed on the C atom to localize the virtual 3s and 3p orbitals, which would otherwise be unreasonably diffuse in the ground-state potential. Finally, for convenience, the calculations were performed under D_3 symmetry rather than under the full I_h symmetry of the molecule.

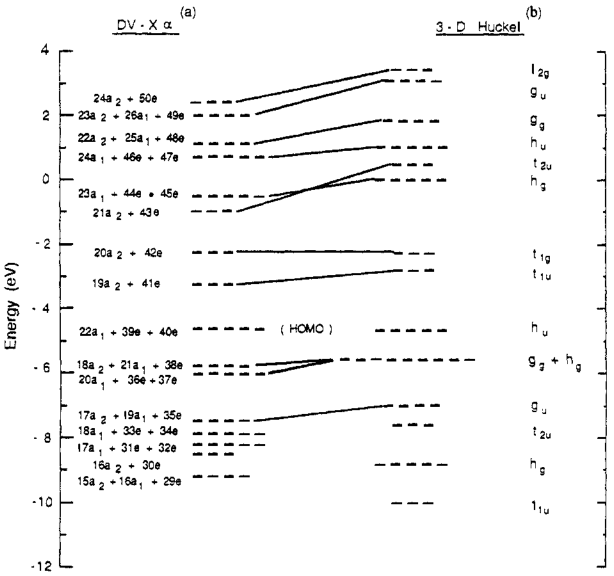


Figure 1. Orbital energy level diagram for the C_{60} cluster: (a) DV–Xα calculations assume D_3 symmetry; the results shown are for a uniform carbon–carbon bond distance of 1.421 Å (graphite). (b) Hückel results are from ref 4. In the diagram, β has been given a value of −2.52 eV.

Table I

	case A[a]	case B[a]
first IP[b]	6.42 eV	6.38 eV
optical transition[c]	2.52 eV	2.65 eV

[a] Case A: C–C bond length = 1.421 Å. Case B: C–C bond length = 1.395 Å. [b] $22a_1 + 39e + 40e$ under D_3 symmetry; h_u under I_h symmetry. [c] $22a_1 + 39e + 40e \rightarrow 20a_2 + 42e$ under D_3 symmetry; $h_u \rightarrow t_{1g}$ under I_h symmetry.

The results of the ground-state calculation are shown in Figure 1 for the case where the C–C bond distance of graphite was used. The results of the calculation using the shorter C–C bond length of benzene are very similar, with the ground-state orbital energies shifted to higher values by less than 0.10 eV for the occupied orbitals and by less than 0.20 eV for the unoccupied, compared to the diagram in Figure 1. For comparison, the orbital energies from the three-dimensional Hückel studies of Raghavachari and co-workers[4] are also displayed. In that work, the energy of the lowest allowed electronic transition ($h_u \rightarrow t_{1g}$) was found to be equal to $-\beta$. In Figure 1, the value of β was taken from matching the DV-Xα calculation of this transition energy (see Table I and the discussion below). Also, in the schematic energy level diagrams, the energy of the highest occupied molecular orbital of the Hückel study (h_u) was set equal to that found in the DV-Xα work ($22a_1 + 39e + 40e$) in order to allow a straightforward comparison. The DV-Xα results correspond quite well with those of the simple Hückel model. This correspondence is shown in Figure 1 by lines connecting the two energy level schemes. It is clear from the diagrams that the lowest energy allowed electronic transition under D_3 symmetry is $22a_1 + 39e + 40e \rightarrow 20a_2 + 42e$, which corresponds to the $h_u \rightarrow t_{1g}$ transition under the full I_h symmetry of the molecule.

Since Koopmans' theorem is not valid in local density, the transition-state method[9] was used to calculate the first ionization potential and the energy of the first electronic transition. This method is known to take into account electron relaxation effects which occur upon ionization or optical excitation.[7,11] The results of these calculations are listed in Table I. The calculated ionization potential (6.4 eV) differs substantially with the results of previous studies, where values of 7.45–8.41 eV[5] and 8.1–9.1 eV[4] were obtained. It is also interesting to note that this lower value for the ionization potential raises the possibility that a near-resonance ionization process may be an important factor in the production of C_{60}^+ ions when an ArF laser (6.42-eV photon energy) is used as the ionizing source.[12] Finally, it is apparent that changing

---

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162.

(2) Haymet, A. D. J. *J. Am. Chem. Soc.* **1986**, *108*, 319.

(3) Klein, D. J.; Schmalz, T. G.; Hite, G. E.; Seitz, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 1301.

(4) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459.

(5) Newton, M. D.; Stanton, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 2469.

(6) Delley, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949 and references within.

(7) (a) Grant, J. L.; Hale, P. D.; Stair, P. C. *J. Electron Spectrosc. Relat. Phenom.*, in press. (b) Doris, K. A.; Delley, B.; Ratner, M. A.; Marks, T. J.; Ellis, D. E. *J. Phys. Chem.* **1984**, *88*, 3157.

(8) (a) Pietro, W. J.; Ellis, D. E.; Marks, T. J.; Ratner, M. A. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 273. (b) Ciliberto, E.; Doris, K. A.; Pietro, W. J.; Reisner, G. M.; Ellis, D. E.; Fragala, I.; Herbstein, F. H.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7748.

(9) Slater, J. C. *Adv. Quantum Chem.* **1972**, *6*, 1.

(10) (a) Anderson, P. R.; Ellis, D. E.; Ratner, M. A. *Chem. Phys.* **1979**, *41*, 209. (b) Berkovitch-Yellin, Z.; Ellis, D. E.; Ratner, M. A. *Chem. Phys.* **1981**, *62*, 21.

(11) Rosen, A.; Ellis, D. E.; Adachi, H.; Averill, F. W. *J. Chem. Phys.* **1976**, *65*, 3629.

0002-7863/86/1508-6087$01.50/0