2 and **5** deserve some comments. In both complexes, the palladium atoms are not directly bonded to each others through Pd–Pd bonds but linked by bridging ligands. Whereas the five-electron donor ligands μ_3-OH in **2** and μ_3-Cl in **5** are of a conventional type, the μ_3-[$Ph_2PCHC(O)OC_2H_5$] and μ_3-[$Mo(CO)_3Cp$] bridges also have to be described as five-electron donors in order to account for the structures of **2** and **5** involving three square-planar Pd(II) centers. Although this bonding mode could be predicted in the former case, and is easily rationalized with localized two-electron–two-center bonds, it was not so in the latter case. Indeed, **5a** is the only example known of such a bonding situation for the organometallic fragment $Mo(CO)_3Cp$. The question remains open as to what extent the electrons from the three carbonyls and the d electrons from the molybdenum are involved in the bonding of the $Mo(CO)_3Cp$ fragment to the three Pd(II) centers.

Acknowledgment. We thank the Centre National de la Recherche Scientifique for financial support.

Registry No. 1, 79086-58-1; **2**, 87862-44-0; **3**, 87862-45-1; **4**, 87862-47-3; **5a**, 87862-49-5; **5b**, 87935-86-2; **6**, 79061-46-4; Na[$Mo(CO)_3$(η^5-C_5H_5)], 12079-69-5; [Pd(8-mq)Cl]$_2$, 28377-73-3; $AgBF_4$, 14104-20-2; $AgPF_6$, 26042-63-7.

Supplementary Material Available: Least-squares planes of the quinoline rings for compounds **2** and **5a** (Tables SI and SII), anisotropic thermal parameters for **2**, **5a**, and **6** (Tables SIII, SIV, and SV), and observed and calculated structure factors for **2**, **5a**, and **6** (Tables SVI, SVII, and SVIII) (60 pages). Ordering information is given on any current masthead page.

Communications to the Editor

α vs. *β* Protonation of Pyrrole and Indole

J. Catalán and M. Yáñez*

Departamento de Química Física y Química Cuántica
Centro Coordinado CSIC-UAM
Facultad de Ciencias, C-XIV
Universidad Autónoma de Madrid
Cantoblanco(Madrid, 34), Spain

Received July 13, 1983

α vs. β protonation of five-membered rings has been the subject of considerable attention,[1-6] in particular regarding pyrrole and its derivatives. It is well established, at least in solution, that electrophilic substitution of these compounds takes place predominantely at the α position,[1,5] although all theoretical calculations,[7] both at the semiempirical and the "ab initio" levels, assign a larger electronic charge to the β than to the α position. Moreover, the corresponding molecular electrostatic potentials[2] indicate a favorable β attachment, and as a consequence, some complicated mechanisms involving a simultaneous bending of the $C_\alpha H$ and the NH bonds out of the molecular plane or the behavior of the nitrogen atom as a charge transducer have been proposed[2] to explain the predominance of the α substitution in pyrrole.

It is worth noting however that when this five-membered ring is fused to a six-membered one, as in indole, both the experimental evidences[8] and the theoretical calculations[9] indicate that C_3 (β position) is the most reactive center toward electrophilic reagents.

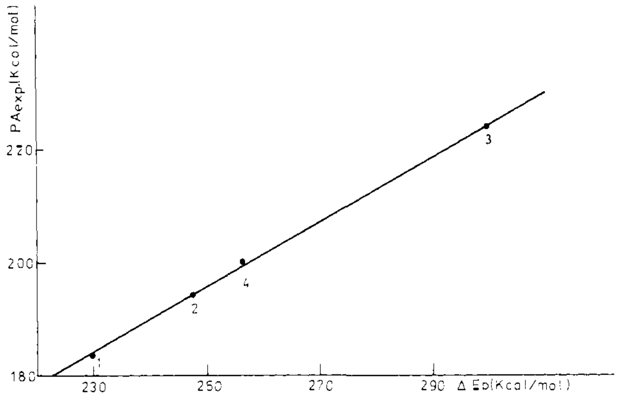

Figure 1. Experimental PA vs. calculated protonation energies.

We aim at showing, in this paper, that this question can be clarified from a theoretical point of view.

First, it must be indicated that the different theoretical approaches reported in the literature to evaluate proton affinities or to predict preferred protonation sites can be classified in two different categories: those that would furnish information on the most active center for kinetically controlled processes and those that would indicate which protonated species is thermodynamically the most stable.

It is well-known that (a) the molecular electrostatic potentials or (b) the linear correlation between gas-phase proton affinities (PA) and 1s binding energies[10] (or 1s "ab initio" orbital energies[3]) provides, in general, good tools to predict the preferred protonation site of a given compound. However, it must be taken into account that, for instance, the molecular electrostatic potential furnished information on the most favorable approaching path to the isolated molecule of a unit positive charge, but the corresponding substitution does not lead necessarily to the most stable isomer. Similarly, procedure b yields the *intrinsic basicity* of a given center of the isolated molecule, but quite frequently protonation induces dramatic changes in both the structure and the charge distribution of the system. As a consequence, not always does protonation on the most basic center lead to the most stable protonated form.

---

[1] Katrizky, A. R.; Lagowski, J. M. "The Principles of Heterocyclic Chemistry"; Academic Press: New York, 1968. Jones, R. A. *Adv. Heterocycl. Chem.* **1970**, *11*, 383. Gossauer, A. "Die Chemie der Pyrrole"; Springer-Verlag: Berlin, 1974. Jones, R. A.; Bean, G. P. "The Chemistry of Pyrroles"; Academic Press: London, 1977.

[2] Politzer, P.; Weinstein, H. *Tetrahedron* **1975**, *31*, 915. Chou, D.; Weinstein, H. *Ibid.* **1978**, *34*, 275.

[3] Catalán, J.; Yáñez, M. *J. Chem. Soc., Perkin Trans. II* **1979**, 1627.

[4] Houriet, R.; Schwarz, H.; Zummack, W.; Andrade, J. G.; Schleyer, P. v. R. *Nouv. J. Chim.* **1981**, *5*, 505.

[5] Gassner, R.; Krumbholz, E.; Steuber, F. W. *Leibigs Ann. Chem.* **1981**, 789.

[6] (a) Angelini, G.; Sparapani, C.; Speranza, M. *J. Am. Chem. Soc.* **1982**, *104*, 7084. (b) Angelini, G.; Lilla, G.; Speranza M. *Ibid.* **1982**, *104*, 7091. (c) Angelini, G.; Laguzzi, G.; Margonelli, A.; Speranza M. Euchem Conference Ion Chemistry: Gaseous vs. Solvated Ions, Lido di Ostia, Rome, Italy, sep, 1982.

[7] Hermann, R. B. *Int. J. Quantum. Chem.* **1968**, *2*, 165. Preston, H. J. T.; Kaufmann, J. J. *Int. J. Quantum. Chem., Symp.* **1973**, *7*, 207. Kaufmann, J. J.; Preston, H. J. T.; Kerman, E.; Cusach, L. C. *Ibid.* **1973**, *7*, 249. Kao, J.; Hinde, A. L.; Radon, L. *Nouv. J. Chim.* **1979**, *3*, 473. Cordell, F. R.; Boggs, J. E. *J. Mol. Struct.* **1981**, *85*, 163.

[8] Hinnan, R. L.; Whipple, E. B. *J. Am. Chem. Soc.* **1962**, *84*, 2534. Hinnan, R. L.; Lang, J. *Ibid.* **1964**, *86*, 3796. Chen, H. J.; Hakka, L. E.; Hinnan, R. L.; Kresge, A. J.; Whipple, E. B. *Ibid.* **1971**, *93*, 5102.

[9] Catalán, J.; Perez, P.; Yáñez, M. *Tetrahedron* **1982**, *38*, 3693.

[10] Martin, R. L.; Shirley, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 5299. Davis, D. W.; Rabalais, J. W. *Ibid.* *96*, 5305. Brown, R. S.; Tse, a. *Ibid.* **1980**, *102*, 5222. Buschek, J. M.; Jorgensen, F. S.; Brown, R. S. *Ibid.* **1982**, *104*, 5019. Catalán, J.; Mó, O.; Perez, P.; Yáñez, M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1409.

Table I. 1s Orbital Energies (au) for the α and β Positions of Pyrrole, Indole, and Cyclopentadiene

	C_α	C_β
pyrrole	−11.0387	−10.992
indole	−11.0646	−10.998
cyclopentadiene	−11.0104	−11.013

One can conclude, therefore, that these approaches must be included in the first category indicated above (kinetically controlled processes).

Obviously, among the procedures to be included in the second category, the simplest one would be, in principle, to evaluate the energy of the different protonated forms. However, this magnitude is basis-set dependent, and only if one employs a very large basis set, including polarization and correlation effects,[11] can one have some confidence on the reliability of the energy obtained. Unfortunately, for molecules as big as pyrrole and indole, such calculations are unfeasible. A possible alternative would be to obtain a linear correlation between the calculated protonation energy (ΔE_p), defined as the energy difference between the protonated and the nonprotonated forms, and the measured gas-phase proton affinity. Since we aim at comparing C_α vs. C_β protonation of the compounds under study, we have selected for this purpose a set of compounds–benzene (**1**), naphthalene (**2**), azulene (**3**), and cyclopentadiene (**4**)–that are carbon basis and whose gas-phase PA's have been measured with high accuracy.[12] To have confidence on the goodness of the corresponding linear relationship, the calculated protonation energy was obtained using INDO fully optimized geometries, conveniently scaled as indicated elsewhere.[9] All ab initio calculations were performed using a STO-3G minimal basis set.

The linear correlation obtained (see Figure 1) obeys the equation

$$\mathrm{PA} = -0.572\Delta E_p + 52.5 \qquad r^2 = 0.999$$
$$\sigma_{\mathrm{PA}} = 0.5\ \mathrm{kcal/mol} \tag{1}$$

When eq 1 is used to predict the gas-phase PA's of pyrrole, for α and β protonation, the values obtained are 208.9 with and 205.2 kcal/mol, respectively. The first value is identical with the experimental one,[12a,c] and the second one is only a little smaller than the lower limit proposed by Houriet et al.,[4] from thermodynamic data obtained in a ion cyclotron double-resonance experiment.

The values obtained for indole (202.1 kcal/mol for α protonation and 207.1 kcal/mol for β protonation) indicate that, in contrast with pyrrole, in this particular case the β-protonated form is more stable than the α-protonated one.

If one considers now the C_{1s} orbital energies of the α and β positions (see Table I), it is evident that, in pyrrole, C_β is the most basic center and therefore the one that should undergo protonation in a process where conditions favor a kinetic control. This theoretical result is in agreement with the conclusion of Angelini et al.[6a,c] who have shown, by means of a kinetic analysis of gas-phase electrophilic substitutions of pyrrole by CH_3-F-CH_3^+, HeT^+, and t-$C_4H_9^+$ ions, that formation of the β-substituted compound predominates under all experimental conditions. Besides, the subsequent isomerization of the resulting excited intermediates to the thermodynamically more stable α-protonated form proposed by these authors is also in agreement with our previous discussion.

The values obtained for indole indicate also that the β position is the preferred protonation site from a kinetic point of view. Therefore one can conclude that (a) if the pyrrolic ring is either isolated or fused to a six-membered one protonation should take place on the β position and (b) in indole the corresponding protonated form is also the most stable one from a thermodynamic point of view, while in pyrrole the α-protonated isomer is more stable than the β-protonated one. Consequently, in the latter case a subsequent isomerization involving a C_β–C_α proton shift might take place. The different behavior predicted for these two compounds is easily explained. In indole (and related systems) charge migrations between the six- and the five-membered rings[9,13] and polarizability effects[14] (both absent in pyrrole) contribute to extra stabilize the β-protonated form.

Finally, it must be noted that the other five-membered ring, cyclopentadiene, fits eq 1 very well when α protonation is assumed, indicating that, as in pyrrole, the α-protonated form is the most stable one. However, in contrast with pyrrole and indole, the kinetic protonation of cyclopentadiene must take place at C_α, which is the position that exhibits a higher 1s orbital energy (see Table I). This is a consequence of substituting an NH by a CH_2 group within the ring, which affects the charge distribution of the system. To confirm this point, we have obtained the charge distribution of this molecule using the YSP population analysis[15,16] which, as it has been shown elsewhere[17], reproduces well the inductive effects of alkyl substituents and is practically unsensitive[15] to the basis set used to expand the corresponding wave function. Our results indicate that, in contrast with pyrrole and indole, C_α in cyclopentadiene is not only the center with the higher intrinsic basicity but also the one that presents a higher electronic density.

Acknowledgment. All calculations were performed at the UAM/IBM Center, Madrid.

Registry No. Pyrrole, 109-97-7; indole, 120-72-9.

---

(11) Del Bene, J. E.; Frisch, M. J.; Raghavachari, K.; Pople, J. A. *J. Phys. Chem.* **1982**, *86*, 1529.

(12) (a) Aue, D. H.; Bowers, M. T. In "Gas Phase ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2. (b) Meot-Ner (Mautner), M. *J. Phys. Chem.* **1980**, *84*, 2716. (c) Taft, R. W. *Prog. Phys. Org. Chem.* **1982**, *14*, 247. (d) All PA's referred to $PA(NH_3)$ = 205.0 kcal/mol.

(13) Catalān, J.; Mō, O.; Pērez, P.; Yāñez, M. *Tetrahedron* **1983**, *39*, 2851.

(14) Brauman, J. J.; Riveros, J. M.; Blair, L. K. *J. Am. Chem. Soc.*, **1971**, *93*, 2914. Wolf, J. F.; Abboud, J. L. M.; Taft, R. W. *J. Org. Chem.* **1977**, *42*, 3316. Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1979**, *101*, 2396. Catalān, J.; Elguero, J.; Flammang, R.; Maquestiau, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 323.

(15) Yāñez, M.; Stewart, R. F.; Pople, J. A. *Acta Crystallogr., Sect. A* **1978**, *A34*, 641.

(16) Escudero, F.; Yāñez, M. *Mol. Phys.* **1982**, *45*, 617.

(17) Catalān, J.; Escudero, F.; Laso, J.; Mo, O.; Yāñez, M. *J. Mol. Struct.* **1980**, *69*, 217.

Intramolecular Exciplex Emission from Aqueous β-Cyclodextrin Solutions

G. Sidney Cox and Nicholas J. Turro*

Chemistry Department, Columbia University
New York, New York 10027

Nien-chu C. Yang* and Ming-Jang Chen

Chemistry Department, University of Chicago
Chicago, Illinois 60637

Received August 15, 1983

Cyclodextrins provide a unique environment for organic compounds in aqueous media and are known to promote a variety of organic reactions.[1,2] The complexing of two chromophores with cyclodextrins has been demonstrated by excimer emission with naphthalene or pyrene by both intermolecular and intramolecular probes.[3-7] Hamai recently reported the formation of an electron donor–acceptor complex consisting of 2-methoxynaphthalene, *o*-dicyanobenzene, and β-cyclodextrin in a molar ratio of 1:1:2 on the basis of its absorption and emission spectra and suggested

---

(1) Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry", 1st ed.; Springer-Verlag: Berlin, 1978.

(2) Saenger, W. *Angew, Chem., Int. Ed. Engl.* **1980**, *19*, 344–346.

(3) Turro, N. J.; Okubo, T.; Weed, G. C. *Photochem. Photobiol.* **1982**, *35*, 325–329.

(4) Ueno, A.; Takahashi, K.; Osa, T. *J. Chem. Soc., Chem. Commun.* **1980**, 921–922.

(5) Emert, J.; Kodal, D.; Catena, R. *J. Chem. Soc., Chem. Commun.* **1981**, 758–759.

(6) Hamai, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2721–2729.

(7) Kano, K.; Takenoshita, I.; Ogawa, T. *Chem. Lett.* **1982**, 321–324.

0002-7863/84/1506-0422$01.50/0