MODELIZATION OF REACTION MECHANISM OF CHLORINATION OF ANILINE: A DFT (DENSITY FUNCTIONAL THEORY) STUDY

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ABSTRACT

The reaction mechanism of electrophilic substitution by chlorine on the benzene derivative (aniline) catalyzed by aluminium chloride has been studied theoretically by DFT (Density Functional Theory) calculations by taking CCSD(T) as reference method. The results obtained in the gas phase are consistent with the traditional description of this reaction: the orientation of the chlorination of aniline depends on the stability of a reaction intermediate (Wheland said). Taking out of consideration the reactants and products, four stationary points have been found in the potential surface energy of the reaction.

Key words: Aniline, Density functional theory (DFT), Modelization, Reaction mechanism, Chlorination.
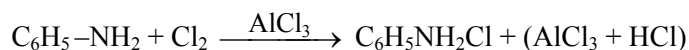
INTRODUCTION

The electrophilic aromatic substitution reactions is one of the most widely used reactions in organic chemistry[1-3], however, the mechanism has not been extensively studied theoretically. Olah and his colleagues studied his mechanism and, after much experimental works showed the influence of the solvent in the reactions of electrophilic substitution[4-7]. In electrophilic substitution reaction on the benzene derivatives, the orientation of the second substitution depends on the nature of the first substituent and not on the electrophile. This point is always rationalized by analyzing with mesomeric principles, the electronic structure of Wheland complex[8]. Experimental data have proved that Wheland complex exist and the orientation of the reaction depend on the stability of this complex[9-19]. Recent works have also proved that the solvent plays a major role to lower the energy barrier in electrophilic substitution reactions of substituted benzene[20,21] and on the other hand, to explain the mechanism of these reactions [22-24].

In this work, we have proposed to explore the potential surface energy of the reaction of choration of aniline in gas phase in order to validate or invalidate the Wheland interpretation, which said that the orientation of the second substituent depend on the stablity of the Wheland complex.

Computational methods

In the molecular orbital calculation, the chemical species participating in the chlorination reaction are assumed to be aniline (C_6H_5-NH_2), molecular chlorine (Cl_2) and Lewis acid, so that the reacting system

is considered to be neutral at the starting point and to be more realistic in describing the overall reaction pathway. The aluminium chloride monomer $AlCl_3$ is adopted as a Lewis acid catalyst in the present study. The overall reaction is formally written as follows;

$$C_6H_5-NH_2 + Cl_2 \xrightarrow{AlCl_3} C_6H_5NH_2Cl + (AlCl_3 + HCl)$$

The calculations of the wave function have been carried out at the hybrid Hartree-Fock density functional method B3LYP level[25-28] and CCSD(T) level[29-32] with the basis 6-31G** in Gaussian 03 software[33]. Stationary points on the potential surface were confirmed by calculation of harmonic vibrational frequencies, all positive for a minimum and one imaginary for a transition state (TS).
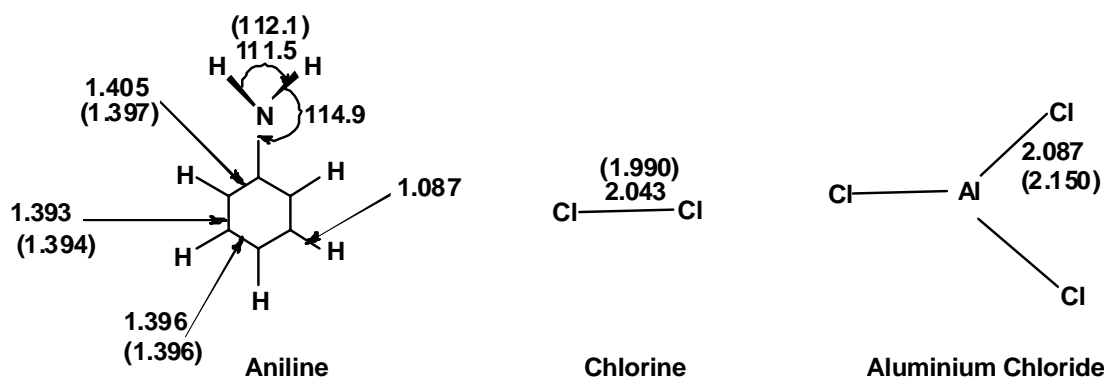
RESULTS AND DISCUSSION

The relative energies obtained for the chlorination of aniline in the presence of aluminium chloride in gaz phase are in Table 1.

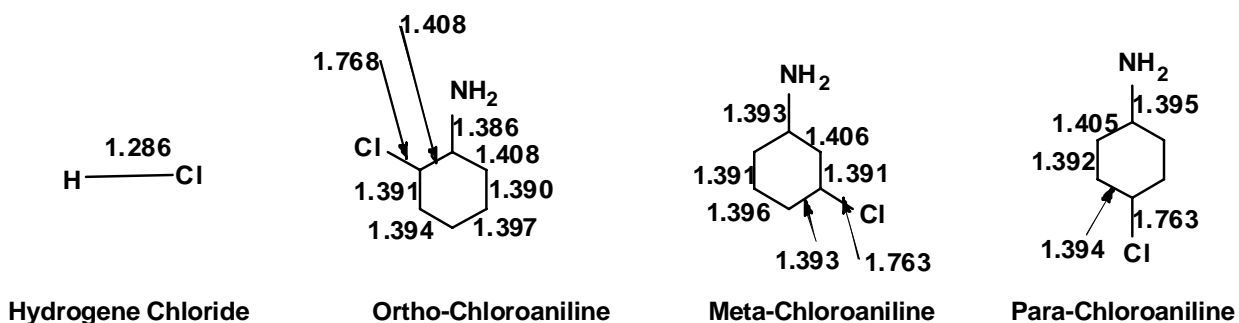**Table 1: Relative energies for chlorination of aniline in gas phase**

	B3LYP/6-31G** ΔE (Kcal/mol)			CCSD(T)/6-31G** ΔE(Kcal/mol)		
	Ortho	Meta	Para	Ortho	Meta	Para
Reactants	0.0	0.0	0.0	0.0	0.0	0.0
σ_1	-50.8	-27.7	-55.7	-59.0	-30.2	-62.9
σ_2	-53.8	-27.9	-56.9	-61.6	-30.6	-64.1
TS_2	-42.6	-27.0	-40.7	-47.0	-28.4	-44.4
Π_2	-42.9	-44.0	-41.9	-50.0	-48.9	-46.9
Products	-29.3	-29.0	-28.6	-34.1	-33.6	-33.2

Reactants and products

Aniline   Chlorine   Aluminium Chloride

The optimized geometric parameters obtained of reactants are in good agreements with the experimental values[34-36] in parentheses. Units of bond lengths and bond angles of all parameters are Å and degrees (°), respectively.

The optimized structures of products obtained are below:

Hydrogene Chloride   **Ortho-Chloroaniline**   **Meta-Chloroaniline**   **Para-Chloroaniline**

Units of bond lengths are in Å. The relative energies obtained for three products (ortho, meta and para) are equal to be between -28.6 and -29.3 kcal/mol; it means that the reaction is not in thermodynamic control. This result is also confirmed by CCSD (T) calculations where we have obtained the relative energies for the three products which are very close to each other.

Π_1 complex and TS_1

The structures corresponding to Π_1 complex (with fairly interaction between $AlCl_3-Cl_2$ and π system of substituted benzene and TS_1 (first transition state) does not exist in this reaction of chlorination of aniline in the presence of aluminium chloride. It was found that the reaction directly goes from the reactants to first σ_1 (sigma$_1$) complex without passing to Π_1 complex and TS_1. We have done the scan of dCl-Cl (see Fig. 1 in the case of para position) from the first σ_1 and the graph of the enegy in function of dCl-Cl (see Fig. 2), which showed the proof that these two complexes (Π_1 and TS_1) do not exist in the reaction pathway.
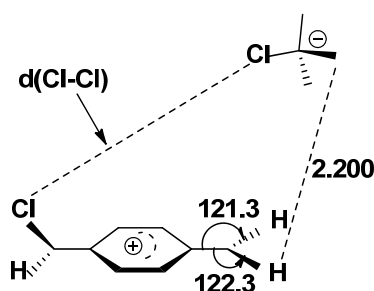

Fig. 1: Scan of of dCl-Cl in the case of para position

Units of bond lengths and bond angles of all parameters are Å and degrees (°)
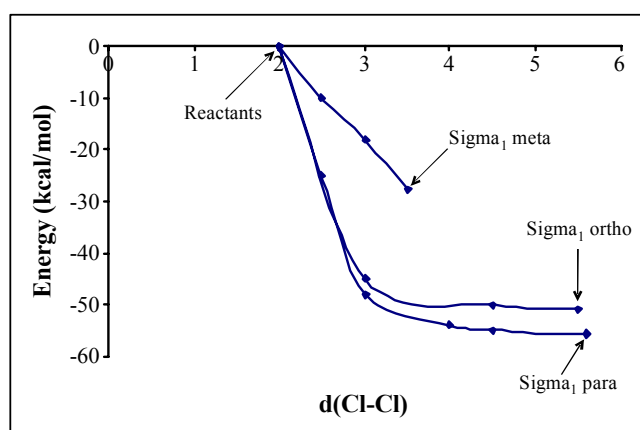

Fig. 2: Graph of the energy in function of d(Cl-Cl)

σ₁ and σ₂ complexes

One can easily expect that the system will reach to the σ complex, which has a C-Cl σ-bond. Geometry optimization gives the structure illustrated in Figures below. The system, which we call σ-complex consists of two parts cation being the traditional σ –complex C_6H_5Cl-NH_2^+ and the counter anion $AlCl_4^-$ part. Since these species are charged, Coulomb interaction between these two species stablizes the complexes. These two species are on the same side in the case of σ₁ (see Fig. 3) and in the different side in the case of σ₂ complex (see Fig. 4)
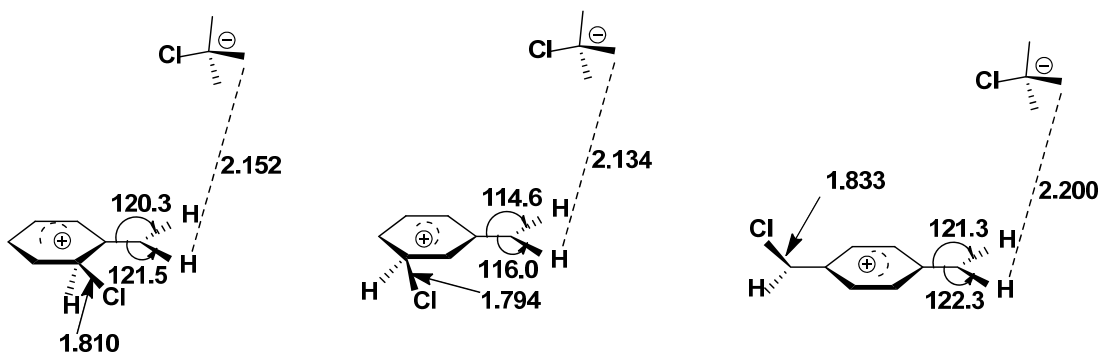

Fig. 3 - σ₁ (sigma₁) complexes in the cases of ortho, meta and para position, respectively

Units of bond lengths and bond angles of all parameters are Å and degrees (°)

Comparing these complexes to reactancts, the stabilization complexe σ₁ complex is equal to -55.7 (para) and -50.8 (ortho) kcal/mol ; -27.7 kcal/mol) in the case of meta complexe. This stabilisation is more high than the one obtained in the case of non substituted benzene (-20 kcal/mol)[37].
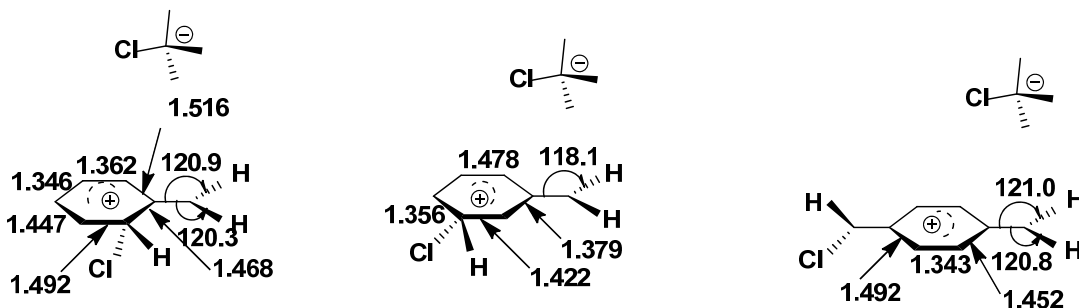

Fig. 4: σ₂ (sigma₂) complexes in the cases of ortho, meta and para position respectively

Units of bond lengths and bond angles of all parameters are Å and degrees (°)

These σ₂ are little more stable than σ₁ but in respect to the order of stability concerning the positions ortho, meta and para. The relative energies obtained are -53.8 kcal/mol for the ortho complex, -27.9 kcal/mol for the meta postion and -56.9 kcal/mol for the para complex. This order of stability has also been confirmed with CCSD(T) calculations, where we have obtained -61.6 kcal/mol(ortho), -30.6 kcal/mol (méta) and -64.1 kcal/mol (para).

TS₂ and Π₂ complex

From σ₂ complexes, the elimination process of hydrogen atom is done in a concerted manner as in the case of chlorination of non-substituted benzene : the breaking of C-H bond of σ₂ complex is done at the same time with the formation of H-Cl bond of the π₂ complex.

The optimized structures of transition states TS$_2$ obtained in the case of ortho, meta and para are below (See Fig. 5):
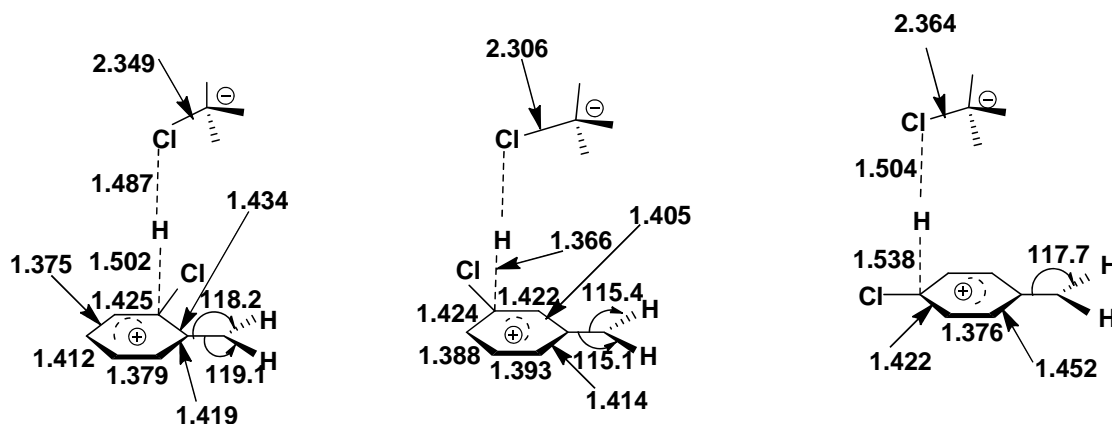

Fig. 5: Transition states TS$_2$ in the cases of ortho, meta and para position respectively

Units of bond lengths and bond angles of all parameters are Å and degrees (°)

The relative energies of transition states are equal to -42.3 kcal/mol in the case of ortho approach, -27.0 kcal/mol for the meta and -40.7 kcal/mol in the case of para position. The calculated activation barrier are 11.2 kcal/mol (ortho), 0.9 (meta) and 16.2 kcal/mol (para). This activation barrier is very small for meta position compared to other two approach.

The CCSD (T) calculations gives the relative energies of -47.0 kcal/mol for TS2 ortho, -28.4 kcal/ mol for TS2 meta and -44.2 kcal/mol for para; the activation barrier of meta remain smaller (2.2 kcal/mol) than the one of ortho (14.6 kcal/mol) and para position (19.9 kcal/mol) with this reference method.
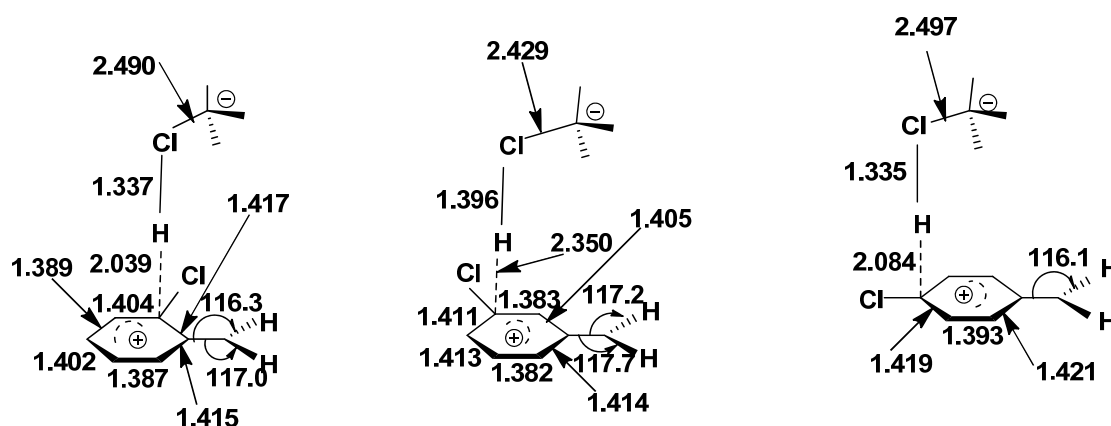

Fig 6: π$_2$ complex in the cases of ortho, meta and para approach, respectively

Units of bond lengths and bond angles of all parameters are Å and degrees (°).

In these π$_2$ complexes (see Fig. 6), we noted the formation of H-Cl bond and there exist a π hydrogen bond between HCl and aniline. The relative energies of these second π complexes are equal to -42.9 kcal/mol for the ortho product, -44.4 kcal/mol for meta and -41.9 kcal/mol for para.

π$_2$ meta is more stable than the two other complexes.

With CCSD (T) method, we noted that the energies of ortho and meta complexes are very close.

The mechanism obtained for the reaction of chlorination of aniline in the presence of aluminium chloride as catalyst has been illustrated in the Fig. 7.
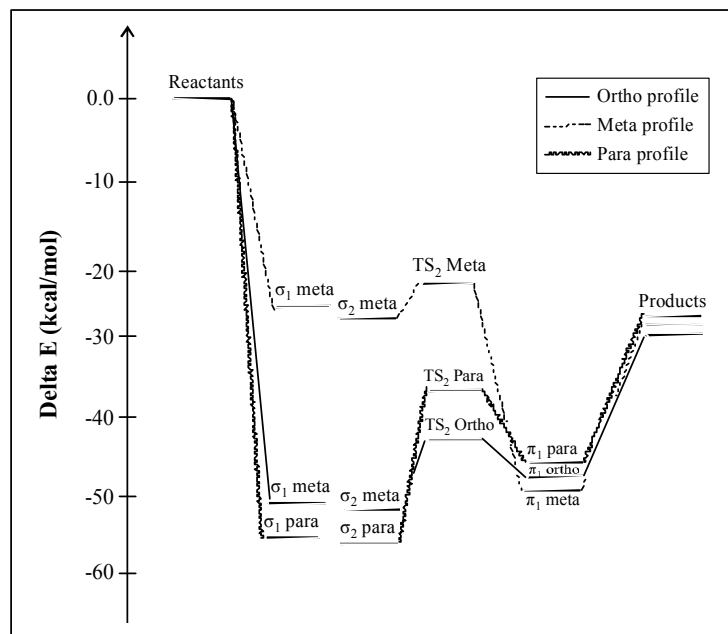

Fig. 7: Energy profiles of the reaction of chlorination of aniline in gas phase

CONCLUSION

At the end of this study, the reaction mechanism of chlorination of aniline in the presence of aluminium chloride in position ortho, meta and para has been studied theoretically by DFT (Density Functional Theory) method. It was concluded that in three cases, the limiting step of the reaction is the transformation of σ_2 (sigma$_2$) to π_2 (pi$_2$) via transition state TS$_2$. The results obtained proved that these reactions can be realized under the kinetic control.

The substitution in ortho and para positions has a priority than the meta one. This permits us to validate the Wheland classic interpretation given to this reaction: the orientation of the substitution reaction of this reaction in ortho and para position is governed by the relative stability of Wheland complex (σ_1 or σ_2).

REFERENCES

1.   R. O. C. Norman and R. Taylor, Electrophilic Substitution in Benzenoid Compound, Elesevier, Amsterdam (1965).

2.   L. M. Stock, Aromatic Substitution Reaction, Prentice-Hall, New Jersey (1968).

3.   R. Taylor, Electrophilic Aromatic Substitution, John-Wiley, New York (1990).

4.   G. A. Olah, J. Am. Chem. Soc., **4**, 240-253 (1971).

5.   G. A. Olah, Chem. Soc., **19**, 62-74 (1964).

6.   G. A. Olah, S. J. Kuhn, S. H. Flood and B. A. Hardie, Chem. Soc., **86**, 1035-1039 (1964).

7.   G. A. Olah, S. J. Kuhn and B. A. Hardie, Chem. Soc., **86**, 1055-1060 (1964).

8. G. G. Wheland, J. Am. Chem. Soc., **64**, 900-903 (1942).

9. G. Koleva, B. Galabov, J. I. Wu, H. F. Schaefer III and P. V. R. Schleyer, J. Am. Chem. Soc., **131**, 14722-14727 (2009).

10. F. A. Carey and R. J. Sundberg, Advanced Organic Chemistry Part A, Structure and Mechanisms, 4th Ed., Springer, New York (2000).

11. N. Isaacs, Physical Organic Chemistry, 2nd Ed. Longman, Singapore (1995).

12. M. B. Smith, Advanced Organic Chemistry Reactions: Mechanisms and Structure, 6th Ed. Wiley, New York (2006).

13. S. M. Hubig and J. K. Kochi, J. Am. Chem. Soc., **122**, 8279-8288 (2000).

14. J. Rosenthal and D. I. Schutser, J. Chem. Edu., **80**, 679-690 (2003).

15. P. J. Silva and M. J Ramos, J. Org. Chem., **74**, 6120-6129 (2009).

16. C. Boga, E. D. Vecchio, L. Forlani, A. Mazzanti, C. M. Lario, P. E. Todeso and S. Tozzi, J. Org. Chem., **74**, 5568-5575 (2009).

17. R. Corriu and C. Coste, Tetraedron, **25**, 4949-4965 (1969).

18. H. C. Brown and J. D. Brady, J. Am. Chem. Soc., **74**, 3570-3574 (1952).

19. J. M. Gnaim and R. A. Sheldon, Tetrahedron Lett., **46**, 4465-4468 (2005).

20. M. Zhang and C. R. F. Lund, J. Phys. Chem. A, **106**, 10294-10301 (2002).

21. Y. Wei, B. Wang, S. Hu, T. Chu, L. Tang, X. Liu, Y. Wang and X. Wang, J. Phys. Org. Chem., **18**, 625-631 (2005).

22. L. Chen, G. Chen and H. Xiao, J. Chinese Chem. Soc., **53**, 1005-1015 (2006).

23. S. Skovov and R. Wheeler, J. Phys. Chem., **103**, 4261-4269 (1999).

24. J. Morley and D. Roberts, J. Org. Chem., **62**, 7358-7363 (1997).

25. A. D. Becke, J. Chem. Phys., **98**, 5648-5652 (1993).

26. A. D. Becke, Phys. Rev., **A38**, 3098-3100 (1988).

27. C. Lee, Y. Yang and R. G. Parr, Phys. Rev., **B37**, 785-789 (1988).

28. B. Miehlich, A. Savin, H. Stoll and H. Preuss, Chem. Phys. Lett., **157**, 200-206 (1989).

29. N. Szabo and S. Ostlund, Modern Quantum Chemistry, McGraw-Hill, Nova New York (1989).

30. R. J. Bartlett and G. D. Purvis, Int. J. Quant. Chem., **14**, 561-581 (1978).

31. G. D. Purvis and R. J. Bartlett, J. Chem. Phys., **76**, 1910-1918 (1982).

32. G. E. Scuseria, C. L. Janssen and H. F. Schaefer III, J. Chem. Phys., **88**, 7382-7387 (1988).

33. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman et al., Gaussian 03, Revision A.1, Gaussian, Inc, Wallingford CT (2003).

34. W. B. Tzeng, K. Narayanan, K. C. Shieh and C. C. Tung, J. Mol. Struct. (Theochem), **428**, 231-240 (1998).

35. D. G. Lister, J. K. Tyler, J. H. Hog and N. W. Larsen, J. Mol. Struct., **23**, 253 (1974).

36. J. C. Jiang and C. E. Lin, J. Mol. Struct. (Theochem), **392**, 181-191 (1997).

37. Y. Osamura, K. Terada, Y. Kobayashi, R. Okazaki and Y. Ishiyama, J. Mol. Struct., **461**, 399-416 (1999).