Molecular orbital study of fluoroaryl-substituted aminoalane dimers : Geometry and energetics

H. C. Tandon[a]* and Asha Tandon[b]

[a]Department of Chemistry, Sri Venkateswara College (University of Delhi), Dhaula kuan, New Delhi-110 021, India

E-mail : hctwave@yahoo.co.in

[b]Daulat Ram College (University of Delhi), Maurice Nagar, Delhi-110 007, India

Abstract : A large number of aluminium-nitrogen compounds obtained from the reactions of organoaluminium complexes with amines continually proved to be of great importance in material science, as precursors, for the deposition of thin films of aluminium nitride. In the present work, quantum chemical studies using semi-empirical Parametric Method 3 (PM3) at the level of unrestricted Hartree-Fock (UHF) framework on six dimeric aminoalanes of the formula : $[Me_2Al-\mu-N(H)Ar^F]_2$ (Ar^F = 4-C_6H_4F (1), 2-C_6H_4F (2), 3,5-$C_6H_3F_2$ (3), 2,3,4,5-C_6HF_4 (4), 2,3,5,6-C_6HF_4 (5) and C_6F_5 (6) have been carried out. Their geometrical parameters have been compared with the available X-ray data. Our calculated values are in good agreement with the experimental values. Further, the energetic parameters have also been calculated.

Keywords : Fluoroaryl-aminoalane dimers, dipole moment, HOMO-LUMO energy gap, heat of formation, PM3 method, atomic charges.

A large number of aluminium-nitrogen compounds obtained from the reactions of organoaluminium complexes with amines continually proved to be of great importance in material science, as precursors, for the deposition of thin films of aluminium nitride[1-4]. The fluoroaryl amino-alane dimers are used as potential reagents for preparing α-diimine, β-diimine and β-ketoimine ligands[5]. These ligand classes are assuming increasing importance in various catalytic processes[6] as well as for the stabilization of unusual oxidation states and bonding situation[7,8]. In order to develop catalytic systems with enhanced activities at the metal centres it has become increasing desirable to employ highly electron withdrawing substituents at the nitrogen atoms of such ligands[9]. The set approach to the synthesis of α-diimine, β-diimine ligands involves the reaction of an α- or β-diketone with the appropriate primary amine in the presence of an acid catalyst[10]. In view of the expectation that fluoro-substituted arylamines would be poor nucleophiles may play significant role as excellent reagents for effecting the desired transformation (due to weaker Al-N and N-H bonds as compared to Al-O and O-H). This is further supported from the report that lithium-aluminium amides will convert aldehydes and cyclic ketones into corresponding imines[11]. Recently, Shukla

et al.[12] synthesized the six fluoroaryl-substituted aminoalane dimers and characterized them by single crystal X-ray crystallography. In the present work, we have applied the semi-empirical Parametirc Method 3 (PM3) to all the six fluoroaryl-substituted primary aminoalanes of the type $[Me_2Al-\mu-N(H)Ar^F]_2$ (Ar^F = 4-C_6H_4F (1), 2-C_6H_4F (2), 3,5-$C_6H_3F_2$ (3), 2,3,4,5-C_6HF_4 (4), 2,3,5,6-C_6HF_4 (5) and C_6F_5 (6)) for their geometrical and electronic parameter calculations.

Method of calculations :

In the present study, structures **1-6** have been treated quantum chemically by using PM3 method[13-15] at the level of UHF approach[13,14]. The geometry optimization of the structures were performed by using MM^+ (molecular mechanics) method[16] and PM3 (UHF). The optimizations were done successively and iteratively till the desired precision and consistency was achieved (the optimizations were obtained by the application of the Steepest Decent method followed by conjugate-gradient method, Fletcher-Reeves and Polak-Ribiere consecutively (convergence limit of 0.0001 kcal/mol and RMS gradient of 0.001 kcal/Å mol). All these computations were achieved by using Hyperchem 7.5 program[17].

Results and discussion

Each of the six compounds exist in dimer form indicated by mass spectra and confirmation was provided by X-ray crystallography. Shukla et al.[12] divided the six compounds into three groups viz. (i) **1**, **2** and **4**, (ii) **3**, (iii) **5** and **6** on the basis of molecular structure. From energy and electronic structure perspective, we have divided them into four groups viz. (i) **1** and **2**, (ii) **3**, (iii) **4** and **5** and (iv) **6**.

The geometry of these compounds have been optimized and the selected bond lengths and bond angles are given in Table 1. It can be seen from the table that the calculated values are in good agreement with the experimental results. N–Al–N angle which ranges from 84.6° to 87.6° in all six compounds and is more acute than in Al–N–Al (91.5° to 95.4°).

The average N–Al bond distance, for **1** (1.93 Å) and **4** (1.89 Å) are in close proximity with X-ray structural data obtained for other dimeric aminoalanes[18-22]. The geometries at Al- and N- are both tetrahedral (see Table 1). The angle between the N–C^F and Al$_2$N$_2$ mean plane range from 125.3° in **2** to 126.5° in **4** compared to experimentally reported[12] 130.5° in **2** to 134.4° in **4**, compounds **1** and **4** are found to have *trans*-orientation with arene substitutents arranged in parallel fashion (see Figs. 1, 2) consistent with the experimental finding[12]. How-

ever compound **2** is found to have *cis*-orientation in contrast with the reported *trans*-orientation which may be due to overlapping of the orbitals on F-atom at *ortho*-position and H-atom of one of the methyl groups attached to Al-atom, making partial F----H hydrogen bond and
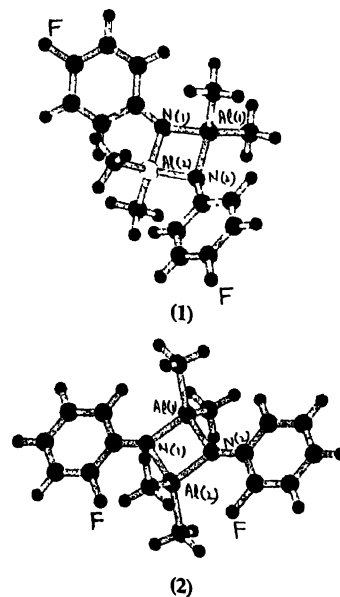

Fig. 1

	Table 1. Selected bond lengths (Å) and angle (°) for 1-6					
	1	**2**	**3**	**4**	**5**	**6**
Al–N	1.930 (1.993)	1.935 (1.981)	1.930 (1.971)	1.899 (1.992)	1.877 (2.008)	1.901 (2.009)
	1.933 (1.973)	1.945 (1.988)	1.935 (1.989)	1.893 (1.995)	1.799 (1.994)	1.899 (1.999)
		1.933 (1.982)				
		1.931 (1.993)				
Al–C	1.950 (1.950)	1.951 (1.945)	1.951 (1.937)	1.977 (1.952)	2.006	1.962
		1.950 (1.946)	1.948 (1.939)		2.053	
					2.006	
N–C$_F$	1.337 (1.441)	1.320 (1.436)	1.332 (1.425)	1.330 (1.437)	1.345 (1.406)	1.321 (1.424)
Al–Al (non-bonded)	2.852 (2.866)	2.852	2.851	2.767	2.705	3.202
N–N (non-bonded)	2.601 (2.742)	2.601	2.601	2.492	2.451	2.038
N–Al–N	86.7 (87.5)	86.8 (87.3)	87.1 (87.6)	86.1 (86.7)	84.6 (85.6)	87.6 (85.8)
Al–N–Al	92.3 (92.5)	92.3 (92.8)	91.5 (92.2)	95.2 (93.2)	95.4 (92.0)	92.4 (92.4)
					92.2 (93.1)	
C–Al–C	109.5 (117.6)	109.5 (120 4)	109.5 (123.1)	108.2 (122.6)	109.5 (120.2)	117.6 (124.1)
N–Al–N–Al	10 0	0.7 (1.8)	0.0 (4.0)	1.1 (1.8)	11.5 (14.0)	0.11 (14)

The values in parantheses are X-ray data, taken from Ref. 12.
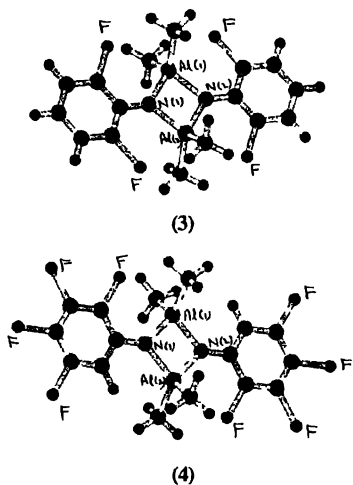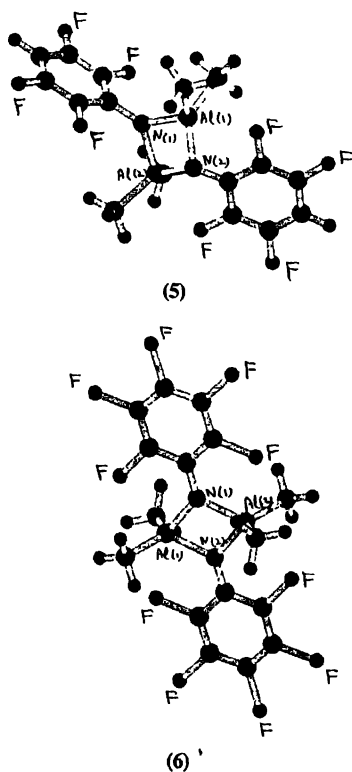
(3)

(4)

Fig. 2

(5)

(6)

Fig. 3

restricts the spatial orientation of the phenyl group. The *cis*-form of 3 of arene substituents is observed which is consistent with the X-ray data (Fig. 2). For the structures 5 and 6, compound 5 is found to have twisted aryl substituents with dihedral angle of 82.7° and the longer N–

C^F bond (1.345 Å), which is in contrast with the reported compound 6. In our work, 6 is found to be coplanar evident from the $N–C^F$ bond (1.321 Å) consistent with the structure 1, 2, 3 and 4. A further consequence of aryl *ring twisting* is that the central Al_2N_2 core of 5 is markedly folded along the Al----Al vector (Fig. 3).

Energy and electronic parameters :

The calculated energy parameters are given in Table 2. It can be seen from the results that compounds 1-6 are found to be exothermic with 2, the least and 6, the most. The theoretical efforts seem to provide a simple principle in chemistry for understanding the structure and reactivity of molecules and explored that the energetic behaviour and alteration in the electron population density distribution. The change of symmetry of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), on distortion of molecular structure largely determine the equilibrium geometries of the molecules. Fukui[23] established that the frontier orbitals govern chemical reactions and solely determine the reaction path. Further investigations have revealed that the energy gap between HOMO and LUMO is an important stability index for molecules and the most stable electronic structure has the largest HOMO-LUMO energy gap[24,25]. Hence, it follows that when the geometry of a molecule transforms from equilibrium to non-equilibrium geometry, its HOMO-LUMO energy gap decreases and the molecule becomes unstable and chemically more reactive. On the other hand, when the molecule evolves from unstable non-equilibrium form towards the equilibrium geometry, its HOMO-LUMO gap increases and becomes maximum. In the light of this view, we have focussed on the internal stability among the compounds mentioned here. From *isoelectronic perspective*, we have divided the six compounds into four catagories (i) 1, 2, (ii) 3, (iii) 4, 5, (iv) 6. Compound 1 is more exothermic than 2 and moreover has large HOMO-LUMO energy gap (see Table 2). In a similar way, 4 is stable than 5 on the basis of heat of formation and comparatively large HOMO-LUMO energy gap. These are the theoretical findings *with no experimental result available for comparison*. However, Shukla *et al.*[12] observed experimentally that 5 and 6 have lower melting points than the other compounds due to less H----F interaction. In our opinion, the lower melting points of 5 and 6 may be due to the least HOMO-LUMO energy gap in comparison to other compounds. Along the same line 3 is predicted to have the moderate melting point closer to the melting point of 1, on the basis of close proximity of HOMO-LUMO energy gap.

Table 2. Calculated energy parameters for **1-6**

Parameters	1	2	3	4	5	6
Total Energy (kcal mol^{-1})	–80948.29	–80945.18	–100544.63	–139732.15	–139703.54	–159323.72
Binding energy (kcal mol^{-1})	–4267.42	–4264.31	–4287.56	–4322.67	–4294.05	–4338.03
Heat of formation (kcal mol^{-1})	–68.38	–65.27	–154.94	–322.90	–294.29	–404.68
–HOMO (eV)	9.311	9.114	9.125	9.730	9.897	9.747
–LUMO (eV)	1.779	1.646	1.671	2.422	2.774	2.470
$\Delta\epsilon$ (eV) (LUMO-HOMO)	7.532	7.468	7.454	7.308	7.123	7.277
No. of valence electrons	114	114	126	150	150	162

1, 2 and **4, 5** are isoelectronic.

Table 3. Selected electronic parameters for **1-6**

Parameters	1	2	3	4	5	6
Net charges on Al (1), Al (2)	0.303	0.294	0.347	0.304	0.322	0.355
Net charges N (1), N (2)	–0.043	–0.031	–0.065	–0.046	–0.026	–0.073
Dipole moment (μ) (Debye)	0.307	1.131	0.00	0.00	3.266	0.009

The net atomic charges on Al- and N- and the dipole moment values for **1-6** are given in Table 3. It is interesting to note that **1** (stable) bears more negative charge on nitrogen than **2**, similar to **4** which has more negative charge on nitrogen than **5**. We predict that **2** and **5** are chemically reactive than other compounds investigated here, due to higher values of dipole moment.

Conclusion :

It is well known that geometry of polyatomic molecule actually depends on many factors and there is no simple theory that can take all the relevant factors into account at once. So the most important contribution of quantum chemical methods, is to provide effective fundamental parameters like HOMO and LUMO and heats of formation. Hence, the semi-empirical methods like Parametric Method 3 (PM3), which requires very less computing time, can be used quite successfully in, not only predicting the geometrical structures but also the stability

and other physical qunatities like melting points, boiling points and vapour pressure on the basis of frontier orbitals.

Acknowledgement

References

1. S. Amir Khalili, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1979, 1206.

2. A. A. I. Al-Wassail, P. D. Hitchcock, S. Sarisaban, J. D. Smith and C. L. Wilson, *J. Chem. Soc., Dalton Trans.*, 1985, 1929.

3. K. M. Waggoner and P. P. Power, *J. Am. Chem. Soc.*, 1991, 113, 3385.

4. F. C. Sauls and L. V Interante, *Coord. Chem. Rev.*, 1993, 128, 193.

5. J. C. Gordon, P. Shukla, A. H. Cowely, J. N. Jones and B. L. Scott, *Chem. Commun.*, 2002, 2710.

6. S. D. Iteel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2002, **100**, 1169.

7. N. J. Hardman, B. F. Eicheer and P. P. Power, *Chem. Commun.*, 2000, 1491.

8. C. Cue, H. W. Roesky, H. G. Schmidt, H. Noltemeyer, H. Hao and F. Cimpoesu, *Angew Chem., Int Ed. Engl.*, 2000, **39**, 4274.

9. L. Johanson and M. Tilset, *J. Am. Chem. Soc.*, 2001, **123**, 739.

10. H. Tom Dieck, M Suoboda and T. Grieser, *Z. Nature Foroch B.*, 1981, **36**, 823.

11. A. Solladie-Cavallo, M Benchegroun and F. Bonne, *Synth. Commun.*, 1993, **23**, 1683.

12. P. Shukla, Alan H. Cowely, J. N. Jones, J. C. Gordon and B. L. Scott, *Dalton Trans.*, 2005, 1019.

13. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221.

14. I. N. Levine, "Quantum Chemistry", Prentice Hall, New Jersey, 2000.

15. A. R. Leach, "Molecular Modelling", Longman, Essex, 1997.

16. N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.

17. Hyper Chem, 7.5 version, Hyper Cube Inc., Florida, 2003.

18. D. C. Brodley, I. S. Harding, I. A. Maia and M. Motevalli, *J. Chem. Soc., Dalton Trans.*, 1997, 2969.

19. E. K. Styron, C. H. Lake, S. J. Schaur, C. L. Watkins and L. K. Kronnich, *Polyhedron*, 1999, **18**, 1595.

20. S. J. Schauer and G. H. Robinson, *J. Coord. Chem.*, 1993, **30**, 197.

21. M. G. Davidson, D. Elilo, S. L. Less, A Martin, P R. Raithby, R. Snaith and D. S. Wright, *Organometallics*, 1993, **12**, 1.

22. J. J. Byers, H. Lee and G. H. Robinson, *Polyhedron*, 1992, **11**, 967.

23. K. Fukui, *Science*, 1982, **218**, 747.

24. R. G. Pearson, *J. Org. Chem.*, 1998, **54**, 1423.

25. R. G. Parr and Z. Zhaou, *J. Am. Chem. Soc.*, 1989, **111**, 7371.