

Bond Angle and Twist Angle Calculation of Aniline and Its Reaction Products

AMRENDRA KUMAR SINGH

Department of Physics, M.L.K. (P.G.) College, Balrampur, Uttar Pradesh

Abstract- We have calculated Bond angle and twist angle of aniline, acetanilide, benzanilide and diphenyl urea with the help of molecular orbital package (MOPAC) software. The results obtained are summarised.

I. INTRODUCTION

The growth of computational chemistry has generally followed advances in computer technology and it has become an essential tool in chemical research. It is used both as a guide to new avenues of research and as a way to understand fundamental chemical process. Computational chemistry is used in areas as diverse as material science to Pharmaceutical research where most companies have a computational chemistry division that helps guide the development of new drugs.

If all the areas in computational chemistry, calculations that solve Schrodinger's equations are the most prevalent. Almost any property associated with where electrons are in the molecule and how those electrons behave can be calculated.

II. METHOD OF CALCULATION

A semi empirical molecular orbital package (MOPAC) software is used to calculate bond angle and twist angle of aniline, diphenyl urea, acetanilide, benzanilide. In this calculation we have used MINDO/3 semi-empirical method. This method is modified form of intermediate neglect of differential overlap approximation. MINDO was developed by this group of Michel Dewar and was original method in the MOPAC program. This method actually be referred as MINDO/3.

III. RESULTS AND DISCUSSION

- **BOND ANGLE:** Bond angle is the angle between the bonding electron pairs in a given molecule. With the increase of lone pair on central atom the bond angle decreases. If any central atom has no lone pair then its bond angle will be maximum. If the density on central atom is more than other central atom then bp-bp repulsion will be greater. The increase in bp-bp repulsion, also increases the bond angle. The bond angle decreases with the decrease in magnitude of bp-bp repulsion. The bond angle also decreases with the decrease of electronegativity. The repulsion between different types of electron pair decreases in the order-(lp - lp) > (lp - bp) > (bp - bp)

If (lp-bp) repulsion is greater than (bp-bp) repulsion this reduces the bond angle. The MINDO/3 bond angle of aniline and its reaction products like diphenyl urea, acetanilide and benzanilide have been presented in the Table -1

The following points are drawn from these results:

1. In aniline, the C₅-N₇-H₁₃ bond angle is exactly equal to the C₅-N₂-H₁₄ bond angle because the (bp-bp) repulsion is same.
2. The N₇-C₅-C₄ bond angle is greater than the C₃-C₄-H₁₂ bond angle. Since the (bp-bp) repulsion in N₇-C₅-C₄ is greater than the (bp-bp) repulsion in C₃-C₄-H₁₂. Due to decrease in (bp-bp) repulsion in C₃-C₄-H₁₂ bond angle also decreases in aniline.
3. We find the bond angle between different bonds in aniline in the following order: C - N - H > C - C - N > C - C - C > C - C - H
4. The C₅-N₇-H₁₃ bond angle is about 124.06° which is the maximum while the C₄-C₅-C₆ bond angle is about 117.72 which is minimum. But according to above order the C-C-H bond angle should be minimum instead of C-C-C bond angle. This is due

- to presence of $-NH_2$ group at the C_5 decreases its bond angle inside the ring.
- In diphenyl urea, the maximum angle is formed between $C_2-N_1-C_{10}$ and this $-NH$ group is attached with the C_{10} of first ring carbon therefore the $N_1-C_{10}-C_{11}$ bond angle is minimum. The maximum bond angle is found about 135.78° while the minimum bond angle is found about 117.86° .
 - In diphenyl urea, the other $-NH$ group is attached with C_4 of second ring carbon which reduces the $N_3-C_4-C_5$ bond angle. This bond angle is less than the all other bond angle of second ring carbon.
 - The $C_8-C_9-H_{28}$ bond angle is least in diphenyl urea. This trend is similar as in case of aniline.
 - We also find that $C-N-C$ bond angle is the maximum which is 135.78° while $N-C-N$ bond angle is the minimum which is about 113.90° .
 - In acetanilide the $N_1-C_2-C_3$ bond angle, $C_2-N_1-C_4$ bond angle and $C_2-N_1-H_{15}$ bond angle are found the same which is equal to 180° . Thus the atoms C_4 , N_1 , C_2 , C_3 and H_{15} lie in the same straight line. The $C_3-C_2-O_{16}$ bond angle is found to 90° which is minimum. This oxygen atom attached to the C_2 .
 - In this molecule since bond angles $N-C-C$, $C-N-C$ and $C-N-H$ are same. Thus this trend is totally different from other molecules. The bond angle $N_1-C_4-C_6$ and $C_4-C_6-C_7$ are also same which is equal to 133.60° .
 - The $-CH_3$ group is attached to the C_2 so bond angles $C_2-C_3-H_{18}$ and $C_2-C_3-H_{19}$ are exactly same but the bond angle $C_2-C_3-H_{17}$ is slightly less than the bond-angle $C_2-C_3-H_{18}$ in acetanilide.
 - In benzanilide, $C_2-N_1-H_{20}$ bond angle is less than the $N_1-C_2-C_3$ bond angle. Since central atom N_1 has one lone pair while C_2 has no lone pair therefore $C_2-N_1-H_{20}$ bond angle is less than $N_1-C_2-C_3$ bond angle. Thus if the number of lone pair increases then bond angle decreases.
 - The bond angle $C_9-N_1-C_2$ is maximum which is equal to the 141.48° in benzanilide. Since the density on central atom N_1 is maximum which increases the bp-bp repulsion. So bond angle $C_9-N_1-C_2$ is maximum.
 - In benzanilide the bond angle in decreasing order is given below: $C-N-C > C-C-N > C-C-C > C-C-H > C-N-H$ In this case the bond angle $C-N-H$ is found minimum while in the aniline molecule this bond angle is found to be maximum.
- TIWIST ANGLE:** Any deviation of bond angle from the normal value would impose a condition of internal strain on the ring. All the cyclic were planar and thus calculated the angles through which each of the valency bonds was deflected from the normal direction in the formation of various rings. This is called angle strain which determines the stability of the ring. The twist angle of aniline, diphenyl urea, acetanilide the benzanilide are reported in Table - 2 using MINDO/3. If the twist angle is positive then it shows that the C-C bonds have to be compressed to satisfy the geometry of the ring. If the twist angle is negative then this indicates that C-C bonds have to be widened to satisfy this geometry of the ring. Whether the twist angle be positive or negative, its magnitude determines the extent of the strain in ring. The magnitude of twist angle between C-C-C in aniline is greater than the twist angle between C-C-C in diphenyl urea. So aniline is unstable and more reactive than the diphenyl urea. In diphenyl urea the magnitude of twist angle between $C_6-C_7-C_8-C_9$ is the minimum. This shows that the greater stability. In acetanilide the twist angle either 180° or zero degree except the twist angle between $N-C-C-H$. The twist angle between $N_1-C_2-C_3-H_{18}$ is -59.998° while the twist angle between $N_1-C_2-C_3-H_{19}$ is 59.998° . Thus except the atoms H_{18} and H_{19} all the atoms lie in the same plane. In benzanilide the maximum twist angle is found between $C_9-C_{11}-C_{12}-H_{19}$ which is about -179.910° while the minimum twist angle is found between $C_9-C_{11}-C_{12}-C_{13}$ which is $.351^\circ$. If all the ring carbons are not forced into one plane then rings in which can become absolutely free of strain. Such non-planar strainless rings in which the ring carbon atoms can have normal tetrahedral angles are also possible for larger ring compounds. For the formation of bond two atoms must be involved so that an orbital of one atom overlap with an orbital of the other atom. For a given pairs of atoms the greater the overlapping of atomic orbitals, the stronger the bond. When carbon is bounded to four other atoms its bonding orbital, the stronger the bond. When carbon is bounded to four other atoms its bonding orbitals are directed to the corners of a regular tetrahedron. Formation of a C-C bond involves the overlapping of sp^3 orbital of one carbon overlaps with a sp^3 orbital of the other

carbon atom to a maximum extent. This will happen only if the sp^3 orbitals overlap along their axes. The deviation from normal value increases continuously with increase in the number of carbon atoms in the ring.

Table - 1: Bond Angle

Molecule	Bond	Bond angle (degree)	
Aniline	C ₁ -C ₂ -C ₃	118.76	
	C ₂ -C ₃ -C ₄	121.07	
	C ₃ -C ₄ -C ₅	120.67	
	C ₄ -C ₅ -C ₆	117.72	
	C ₄ -C ₅ -N ₇	121.18	
	C ₅ -C ₆ -H ₈	120.59	
	C ₂ -C ₁ -H ₉	119.82	
	C ₃ -C ₂ -H ₁₀	120.89	
	C ₂ -C ₃ -H ₁₁	119.94	
	C ₃ -C ₄ -H ₁₂	118.59	
	C ₅ -N ₇ -H ₁₃	124.06	
	C ₅ -N ₇ -H ₁₄	124.06	
	Diphenyl urea	N ₁ -C ₂ -N ₃	113.904
		C ₂ -N ₃ -C ₄	133.376
N ₃ -C ₄ -C ₅		118.530	
C ₄ -C ₅ -C ₆		121.078	
C ₅ -C ₆ -C ₇		121.390	
C ₆ -C ₇ -C ₈		117.440	

Molecule	Bond	Bond angle (degree)
	C7-C8-C9	121.959
	C2-N1-C10	135.782
	N1-C10-C11	117.865
	N1-C10-C12	125.106
	C10-C12-C13	120.599
	C12-C13-C14	121.642
	C13-C14-C15	118.377
	C13-C14-H16	120.903
	C14-C15-H17	120.177
	C10-C11-H18	120.622
	C10-C12-H19	122.761
	C12-C13-H20	118.628
	C2-N1-H21	114.84
	N3-C2-O22	122.566
	C2-N3-H23	116.372
	C4-C5-H24	120.949

	C5-C6-H25	119.69
	C6-C7-H26	121.633
	C7-C8-H27	119.518
	C8-C9-H28	116.528

Molecule	Bond	Bond angle (degree)
Acetanilide	N ₁ -C ₂ -C ₃	180.000
	C ₂ -N ₁ -C ₄	180.000
	N ₁ -C ₄ -C ₅	115.565
	N ₁ -C ₄ -C ₆	133.602
	C ₄ -C ₆ -C ₇	133.602
	C ₆ -C ₇ -C ₈	131.855
	C ₇ -C ₈ -C ₉	99.125
	C ₇ -C ₈ -H ₁₀	125.514
	C ₈ -C ₉ -H ₁₁	117.662
	C ₄ -C ₅ -H ₁₂	121.429
	C ₄ -C ₆ -H ₁₃	102.707
	C ₆ -C ₇ -H ₁₄	117.512
	C ₂ -C ₂ -H ₁₅	180.000
	C ₃ -N ₁ -O ₁₆	90.000
Benzanilide	C ₂ -C ₃ -H ₁₇	109.000
	C ₂ -C ₃ -H ₁₈	110.000
	C ₂ -C ₃ -H ₁₉	110.000
	N ₁ -C ₂ -C ₃	121.718
	C ₂ -C ₃ -C ₄	123.664
	C ₂ -C ₃ -C ₅	120.407
	C ₃ -C ₄ -C ₆	122.684
	C ₄ -C ₆ -C ₇	119.718

Molecule	Bond	Bond angle (degree)
	C ₆ -C ₇ -C ₈	119.344
	C ₂ -N ₁ -C ₉	141.48
	N ₁ -C ₉ -C ₁₀	124.77
	N ₁ -C ₉ -C ₁₁	118.451
	C ₉ -C ₁₁ -C ₁₂	120.785
	C ₁₁ -C ₁₂ -C ₁₃	121.77
	C ₁₂ -C ₁₃ -C ₁₄	118.084
	C ₁₂ -C ₁₃ -H ₁₅	120.944
	C ₁₃ -C ₁₄ -H ₁₆	120.121
	C ₉ -C ₁₀ -H ₁₇	121.055
	C ₉ -C ₁₁ -H ₁₈	121.088
	C ₁₁ -C ₁₂ -H ₁₉	118.611
	C ₂ -N ₁ -H ₂₀	110.849
	C ₃ -C ₂ -O ₂₁	119.845
	C ₃ -C ₄ -H ₂₂	119.274

	C ₄ -C ₆ -H ₂₃	119.785
	C ₆ -C ₇ -H ₂₄	120.25
	C ₇ -C ₈ -H ₂₅	120.227
	C ₃ -C ₅ -H ₂₆	119.691

Table – 2: Twist Angle

Molecule	Bond	Twist angle (degree)	
Aniline	C1-C2-C3-C4	-1.474	
	C2-C3-C4-C5	1.896	
	C3-C4-C5-C6	-1.396	
	C3-C4-C5-N7	177.898	
	C4-C5-C6-H8	-179.668	
	C3-C2-C1-H9	-179.632	
	C1-C3-C2-H10	-179.243	
	C1-C2-C3-H11	179.607	
	C2-C3-C4-H12	-179.121	
	C4-C5-N7-H13	176.133	
	C4-C5-N7-H14	4.452	
	Diphenyl urea	N1-C2-N3-C4	-172.365
		C2-N3-C4-C5	-144.973
		N3-C4-C5-C6	-178.925
C4-C5-C6-C7		0.367	
C5-C6-C7-C8		0.539	
C6-C7-C8-C9		-0.078	
N3-C2-N1-C10		-175.549	
C2-N1-C10-C11	-177.829		

Molecule	Bond	Twist angle (degree)
	C2-N1-C10-C12	2.331
	N1-C10-C12-C13	-179.969
	C10-C12-C13-C14	0.386
	C12-C13-C14-C15	-0.424

	C12-C13-C14-C16	179.662
	C13-C14-C15-H17	179.537
	N1-C10-C11-H18	-0.469
	N1-C10-C12-H19	0.274
	C10-C12-C13-H20	-179.336
	N3-C2-N1-H21	3.84
	N1-N3-C2-O22	-179.537
	N1-C2-N3-H23	10.545
	N3-C4-C5-H24	0.954
	C4-C5-C6-H25	179.833
	C5-C6-C7-H26	-179.478
	C6-C7-C8-H27	179.541
	C7-C8-C9-H28	178.022
	C3-C2-N1-C4	180.00
	C2-N1-C4-C5	0.00

Molecule	Bond	Twist angle (degree)
	C2-N1-C4-C6	180.00
	N1-C4-C6-C7	180.00
	C4-C6-C7-C8	0.00
	C6-C7-C8-C9	0.00
	C6-C7-C8-H10	180.00
	C7-C8-C9-H11	180.00
	N4-C4-C5-H12	0.00
	N1-C4-C6-H13	0.00
	C4-C6-C7-H14	180.00
	C3-C2-N1-H15	180.00

	N1-C3-C2-O16	180.00
	N1-C2-C3-H17	180.00
	N1-C2-C3-H18	-59.998
	N1-C2-C3-H19	59.998
Benzanilide	N1-C2-C3-C4	-78.697
	N1-C2-C3-C5	105.848
	C2-C3-C4-C6	-176.088
	C3-C4-C6-C7	-0.064
	C4-C6-C7-C8	0.78

Molecule	Bond	Twist angle (degree)
	C3-C2-N1-C9	-7.359
	C2-N1-C9-C10	-28.592
	C2-N1-C9-C11	153.398
	N1-C9-C11-C12	178.715
	C9-C11-C12-C13	0.352
	C11-C12-C13-C14	-0.755
	C11-C12-C13-H15	179.741
	C12-C13-C14-C16	-179.436
	N1-C9-C10-H17	0.666
	N1-C9-C11-H18	-0.856
	C9-C11-C12-H19	-179.91
	C3-C2-N1-H20	172.953
	N1-C3-C2-O21	177.976
	C2-C3-C4-H22	3.689
	C3-C4-C6-H23	-179.873
	C4-C6-C7-H24	-179.662

	C6-C7-C8-H25	179.429
	C2-C3-C5-H26	-4.187

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