

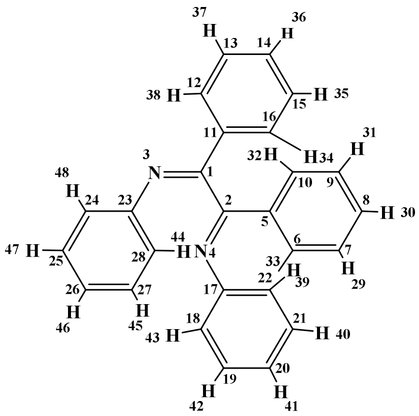
Synthesis, Theoretical Studies of *N¹*,*N²*,1,2-Tetraphenylethane-1,2-Diimine and Their Derivatives

Hanan M. Ali
Depart. of Chemistry, College of Education for Pure Sciences University of Basrah, Basrah, Iraq

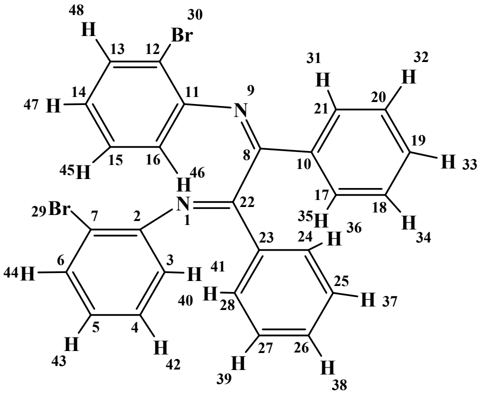
Abstract
*N¹,N²,*1,2-tetraphenylethane-1,2-diimine(1),*N¹*,*N²*-*bis*(2-bromophenyl)-1,2diphenylethane-1,2-diimine(2) and *N¹*,*N²*-*bis*(4-bromophenyl)-1,2-diphenylethane-1,2-diimine(3) were synthesised and studied theoretically. The bond lengths, bond angles, dihedral angles and close contact of atoms were calculated. There are variable results for each compound. Internal coordinate of the three compounds were showed that the atoms around the double bond were in R and S configuration and the angle type was dihedral in most of atoms. The molecular mechanics force field (MMFF94) energy and gradient for (1), (2) and (3) were also calculated. The results showed that the total energy for this frame were (746.902, 1223.418 and 1235.345) kcal/mol respectively and the RMS gradients were 80.761, 175.979 and 178.38 respectively. The MMFF94 minimization iteration was also calculated which equal to 455, 500 and 500 and the final energy for (1), (2) and (3) were (120.525, 153.35 and 117.306) kcal/mol respectively. Though, the molecular mechanics (MM2) minimization of (1), (2) and (3) were also calculated and the total energy were (78.4465, 85.3592 and 74.7126) kcal/mol. the results were showed the difference between the three compounds and the effect of substitution in their results, the compound (2) was gave high total energy higher than (1) and (3) because the bulky substituted Br in ortho position which near to the nitrogen of imine group can effective by steric effect and this can explain the high value of strain energy (E). High dipole/dipole value was observed in compound (2) which was also higher than (1) and (3) and the later was higher than (1) which explains the effect of substituted group and their position in the structure properties. The best minimization either use MMFF94 or MM2 were observed in compound (3) which gave lower total energy than (1) and (2). The MMFF94 minimization and MM2 minimization were indicated the steric effect of o-Br in compound (2).
Keywords: Internal coordinate, Molecular mechanics, ligand.

Introduction
Internal coordinates are an attractive alternative to the Cartesian coordinates of each atom when particular degrees of freedom are not of interest.[1] Internal coordinates such as bond lengths, bond angles, and torsion angles (BAT) are natural coordinates for describing a bonded molecular system.[2] Molecular modelling can be considered as a range of computerized techniques based on theoretical chemistry methods and experimental data that can be used either to analyse molecules and molecular systems or to predict molecular, chemical, and biochemical properties.[3] One of the major advantages of molecular mechanics compared to other computational techniques is the relative ease with which structures can be optimized via minimization of the corresponding potential energy functions.[4] Thomas[5] introduced MMFF94, the initial published version of the Merck molecular force field (MMFF). It describes the objectives set for MMFF, the form it takes, and the range of systems to which it applies. This study also outlines the methodology employed in parameterizing MMFF94 and summarizes its performance in reproducing computational and experimental data. The aim of this work is to study the effect of substation and their position in the phenyl ring in the formation of imine group.

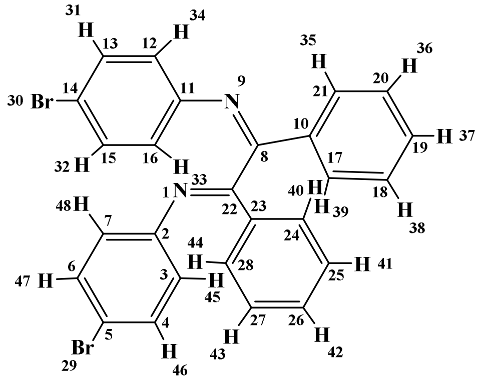
Result and discussion
*N¹,N²,*1,2-tetraphenylethane-1,2-diimine(1), *N¹*,*N²*-*bis*(2-bromophenyl)-1,2-di phenylethane-1,2-diimine (2) and *N¹*,*N²*-*bis*(4-bromophenyl)-1,2-diphenylethane-1,2-diimine (3), Figure (1) was synthesised.



(1)



(2)



(3)

Figure 1: *N^1^*,*N^2^*,1,2-tetraphenylethane-1,2-diimine (1), *N^1^*,*N^2^*-*bis*(2-bromophenyl)-1,2-di phenyl ethane-1,2-diimine (2) and *N^1^*,*N^2^*-*bis*(4-bromophenyl)-1,2-diphenylethane-1,2-diimine (3).

The ^1H NMR shows the shielding effective by the two carbonyl groups and the peak related to (NH_2) group were disappeared in each ligand. Though, the three ligands faced a strong shift in their peaks to high filed and this was clarified the formation of (C=N) group. The elemental analysis was also calculated for each ligand as shown in table 1.

Table 1: Elemental analysis of (1), (2) and (3)

No	Element	Percent by Weight					
		Theoretical			Actual		
		(1)	(2)	(3)	(1)	(2)	(3)
1	C	86.68%	60.26%	60.26%	86.70%	60.30%	60.23%
2	H	5.59%	3.50%	3.50%	5.55%	3.48%	3.52%
3	N	7.77%	5.41%	5.41%	7.76%	5.40%	5.43%
4	Br		30.84%	30.84%		30.85%	30.82%

The particular bond lengths and bond angles are provided in tables 2 and 3 respectively they are in accordance with already reported structures in figure 1.

Table 2: selected of bond length in (1), (2) and (3)

No	compounds			Bond Length (Å)		
	(1)	(2)	(3)	(1)	(2)	(3)
1	C(14)-C(15)	C(14)-C(15)	C(14)-Br(30)	1.395	1.395	1.881
2	C(12)-C(13)	C(12)-Br(30)	C(12)-C(13)	1.395	1.881	1.395
3	C(8)-C(9)	C(8)-N(9)	C(8)-N(9)	1.395	1.26	1.26
4	C(7)-C(8)	C(7)-Br(29)	C(7)-C(2)	1.395	1.881	1.395
5	C(5)-C(6)	C(5)-C(6)	C(5)-Br(29)	1.395	1.395	1.881
6	N(4)-C(17)	C(4)-C(5)	C(4)-C(5)	1.26	1.395	1.395
7	N(3)-C(23)	C(3)-C(4)	C(3)-C(4)	1.26	1.395	1.395
8	C(2)-N(4)	C(2)-C(7)	C(2)-C(7)	1.26	1.395	1.395
9	C(1)-N(3)	N(1)-C(22)	N(1)-C(22)	1.26	1.26	1.26
10	C(1)-C(2)	N(1)-C(2)	N(1)-C(2)	1.337	1.26	1.26

Table 3: Selected bond angles in (1), (2) and (3)

No	Atom			Bond Angle (°)		
	(1)	(2)	(3)	(1)	(2)	(3)
1	C(21)-C(22)-C(17)	C(8)-C(22)-N(1)	C(8)-C(22)-N(1)	120	120	120
2	C(18)-C(17)-N(4)	C(18)-C(17)-C(10)	C(18)-C(17)-C(10)	119.999	120.002	119.997
3	C(15)-C(14)-C(13)	C(13)-C(12)-Br(30)	Br(30)-C(14)-C(13)	120.003	120.002	119.998
4	C(13)-C(12)-C(11)	Br(30)-C(12)-C(11)	C(6)-C(5)-Br(29)	119.997	120.002	119.998
5	C(16)-C(11)-C(1)	C(16)-C(11)-N(9)	C(16)-C(11)-N(9)	120.942	119.999	119.999
6	C(12)-C(11)-C(1)	C(12)-C(11)-N(9)	C(12)-C(11)-N(9)	113.762	119.999	119.999
7	C(9)-C(8)-C(7)	C(11)-N(9)-C(8)	C(11)-N(9)-C(8)	120.003	115	115
8	C(22)-C(21)-C(20)	C(22)-C(8)-C(10)	C(22)-C(8)-C(10)	119.997	120	120
9	C(10)-C(9)-C(8)	C(22)-C(8)-N(9)	C(22)-C(8)-N(9)	119.997	120	120
10	C(10)-C(5)-C(2)	C(10)-C(8)-N(9)	C(10)-C(8)-N(9)	119.999	120	120
11	C(7)-C(6)-C(5)	Br(29)-C(7)-C(6)	C(6)-C(5)-C(4)	119.997	120	120.003
12	C(9)-C(8)-C(7)	Br(29)-C(7)-C(2)	Br(29)-C(5)-C(4)	120.003	120	119.998
13	N(4)-C(2)-C(1)	C(7)-C(2)-C(3)	C(7)-C(2)-C(3)	120	120.003	120.003
14	C(11)-C(1)-N(3)	C(7)-C(2)-N(1)	C(7)-C(2)-N(1)	120	119.999	119.999
15	N(3)-C(1)-C(2)	C(3)-C(2)-N(1)	C(3)-C(2)-N(1)	120	119.999	119.999
16	C(22)-C(17)-N(4)	C(22)-N(1)-C(2)	C(22)-N(1)-C(2)	119.999	115	115

Tables (2) and (3) shows that the bond lengths and bond angles are different in some atoms for each ligand due to the dihedral angles may be beneficial to be calculated because internal coordinates naturally deliver a correct separation of internal and overall motion, which was found to be vital for the construction and clarification of the free energy of these ligands. Table (3) also displayed that the bond angles of C(22)-C(17)-N(4), C(22)-N(1)-C(2) and C(22)-N(1)-C (2) were equal to 119.99°, 115° and 115° respectively and this corresponding to N-C=C, C=N-C and C=N-C which explain the different in the values of the three angles. The dihedral angles and close contact of atoms for these ligands were calculated in order to study the effect of substation and their position in the phenyl ring in the formation of imine group, see table (4) and (5) below.

Table 4: The dihedral angles for (1) and their derivatives (2) and (3)

No	compounds			Dihedral Angle		
	(1)	(2)	(3)	(1)	(2)	(3)
1	**N(3)-C(23)-C(28)-C(27)**	**C(22)-C(23)-C(28)-C(27)**	**C(22)-C(23)-C(28)-C(27)**	**179.998**	**179.999**	**179.999**
2	**C(20)-C(21)-C(22)-C(17)**	**C(24)-C(23)-C(22)-N(1)**	**C(24)-C(23)-C(22)-N(1)**	**-0.004**	**-90**	**-90**
3	**C(11)-C(12)-C(13)-C(14)**	**Br(30)-C(12)-C(13)-C(14)**	**Br(30)-C(14)-C(15)-C(16)**	**-0.006**	**179.994**	**-179.996**
4	**C(1)-C(11)-C(16)-C(15)**	**N(9)-C(11)-C(16)-C(15)**	**N(9)-C(11)-C(16)-C(15)**	**-152.703**	**179.999**	**179.999**
5	**C(22)-C(17)-C(18)-C(19)**	**C(22)-C(8)-N(9)-C(11)**	**C(10)-C(8)-N(9)-C(11)**	**0.006**	**0**	**-180**
6	**C(2)-C(5)-C(6)-C(7)**	**C(5)-C(6)-C(7)-Br(29)**	**C(5)-C(6)-C(7)-H(48)**	**-179.994**	**179.997**	**179.997**
7	**C(1)-N(3)-C(23)-C(28)**	**N(1)-C(2)-C(7)-Br(29)**	**N(1)-C(2)-C(7)-C(6)**	**90**	**-0.001**	**179.999**
8	**N(4)-C(2)-C(5)-C(10)**	**N(1)-C(2)-C(3)-C(4)**	**N(1)-C(2)-C(3)-C(4)**	**-90**	**-179.994**	**-179.994**
9	**C(5)-C(2)-N(4)-C(17)**	**C(7)-C(2)-C(3)-C(4)**	**C(7)-C(2)-C(3)-C(4)**	**0**	**0.006**	**0.006**
10	**C(2)-C(1)-C(11)-C(12)**	**C(2)-N(1)-C(22)-C(8)**	**C(2)-N(1)-C(22)-C(8)**	**60.444**	**-180**	**-180**
11	**C(2)-C(1)-C(11)-C(16)**	**C(2)-N(1)-C(22)-C(23)**	**C(2)-N(1)-C(22)-C(23)**	**-145.275**	**0**	**0**
12	**N(3)-C(1)-C(11)-C(12)**	**C(22)-N(1)-C(2)-C(3)**	**C(22)-N(1)-C(2)-C(3)**	**-119.555**	**0**	**0**
13	**N(3)-C(1)-C(11)-C(16)**	**C(22)-N(1)-C(2)-C(7)**	**C(22)-N(1)-C(2)-C(7)**	**34.726**	**-180**	**180**
14	**C(2)-C(1)-N(3)-C(23)**			**0**		
15	**C(11)-C(1)-N(3)-C(23)**			**180**		
16	**N(3)-C(1)-C(2)-N(4)**			**180**		
17	**N(3)-C(1)-C(2)-C(5)**			**0**		
18	**C(11)-C(1)-C(2)-N(4)**			**0**		
19	**C(11)-C(1)-C(2)-C(5)**			**-179.999**		

Table 4 showed variable values of selected dihedral angles for (1) and their derivatives (2) and (3) and this correlated to different bonding in between the atoms. The atoms N(3)-C(23)-C(28)-C(27), C(22)-C(23)-C(28)-C(27) and C(22)-C(23)-C(28)-C(27) were gave 179.99°,179.99° and 179.999° respectively corresponding to N-C=C-C, C-C=C-C and C-C=C-C bonding, but the C(20)-C(21)-C(22)-C(17), C(24)-C(23)-C(22)-N(1) and C(24)-C(23)-C(22)-N(1) were gave -0.004°, -90° and -90° corresponding to C=C-C=C, C-C-C=N and C-C-C=N bonding and the bonding of all selected atoms were presented in figure 1. The explanation of the different values of dihedral angles which equal to 179.99° and -0.006° respectively between C(22)-C(23)-C(28)-C(27) and C(11)-C(12)-C(13)-C(14) atoms with same bonding C-C=C-C because the C(22) was bond with N(1) directly, but the C(11) was bond with C(1) which bond with N(3). Further, the table demonstrated that the dihedral angles of C(2)-C(1)-N(3)-C(23), C(11)-C(1)-N(3)-C(23), N(3)-C(1)-C(2)-N(4), N(3)-C(1)-C(2)-C(5), C(11)-C(1)-C(2)-N(4) and C(11)-C(1)-C(2)-C(5) which related to compound (1) were disappeared for their derivatives (2) and (3).

Table 5: Close contact of selected atoms in (1), (2) and (3)

No	compounds			Close contact		
	(1)	(2)	(3)	(1)	(2)	(3)
1	C(25)-C(28)	C(24)-C(27)	C(24)-C(27)	2.790	2.790	2.790
2	C(7)-C(28)	C(15)-C(27)	Br(30)-C(27)	2.574	1.961	3.227
3	C(6)-C(28)	C(14)-C(27)	C(15)-C(27)	2.082	2.319	1.961
4	C(5)-C(28)	C(16)-C(27)	C(14)-C(27)	2.472	2.574	2.319
5	C(24)-C(27)	C(15)-C(26)	C(16)-C(27)	2.790	2.443	2.574
6	C(8)-C(27)	C(14)-C(26)	Br(30)-C(26)	2.444	1.901	2.457
7	C(7)-C(27)	C(13)-C(26)	C(15)-C(26)	1.961	2.443	2.443
8	C(6)-C(27)	C(23)-C(26)	C(14)-C(26)	2.331	2.790	1.901
9	C(23)-C(26)	C(28)-C(25)	C(13)-C(26)	2.790	2.790	2.443
10	C(9)-C(26)	C(14)-C(25)	C(23)-C(26)	2.319	2.318	2.790
11	C(8)-C(26)	C(13)-C(25)	C(28)-C(25)	1.901	1.961	2.790
12	C(7)-C(26)	C(12)-C(25)	Br(30)-C(25)	2.319	2.574	3.227
13	C(10)-C(25)	C(15)-C(28)	C(14)-C(25)	2.331	2.331	2.318
14	C(9)-C(25)	C(16)-C(28)	C(13)-C(25)	1.961	2.082	1.961
15	C(8)-C(25)	C(11)-C(28)	C(12)-C(25)	2.444	2.589	2.574
16	C(10)-C(24)	C(3)-C(28)	C(15)-C(28)	2.082	2.402	2.331
17	C(9)-C(24)	Br(30)-C(24)	C(16)-C(28)	2.574	2.906	2.082
18	C(5)-C(24)	C(13)-C(24)	C(11)-C(28)	2.472	2.331	2.589
19	C(10)-C(23)	C(12)-C(24)	C(3)-C(28)	2.589	2.082	2.402
20	C(6)-C(23)	C(11)-C(24)	C(13)-C(24)	2.589	2.589	2.331
21	C(5)-C(23)	C(3)-C(24)	C(12)-C(24)	2.143	2.402	2.082
22	C(2)-C(23)	C(17)-C(20)	C(11)-C(24)	2.461	2.790	2.589
23	C(19)-C(22)	C(10)-C(19)	C(3)-C(24)	2.790	2.790	2.402
24	C(10)-C(22)	C(21)-C(18)	C(17)-C(20)	2.772	2.790	2.790
25	C(5)-C(22)	N(9)-C(21)	C(10)-C(19)	2.786	2.760	2.790
26	C(2)-C(22)	C(22)-C(17)	C(21)-C(18)	2.848	2.800	2.790
27	C(18)-C(21)	N(1)-C(17)	N(9)-C(21)	2.790	2.533	2.760
28	C(17)-C(20)	C(12)-C(15)	C(22)-C(17)	2.790	2.790	2.800
29	C(5)-C(17)	C(11)-C(14)	N(1)-C(17)	2.461	2.790	2.533
30	C(13)-C(16)	N(9)-Br(30)	C(12)-C(15)	2.790	3.014	2.790
31	N(3)-C(16)	C(16)-C(13)	C(11)-C(14)	2.771	2.790	2.790
32	C(12)-C(15)	C(23)-C(16)	C(16)-C(13)	2.790	2.472	2.790
33	C(11)-C(14)	C(23)-C(12)	C(23)-C(16)	2.790	2.472	2.472
34	N(4)-C(12)	C(23)-C(11)	C(23)-C(12)	2.759	2.143	2.472
35	C(2)-C(12)	C(22)-C(11)	C(23)-C(11)	2.847	2.461	2.143
36	N(4)-C(11)	N(1)-C(10)	C(22)-C(11)	2.636	2.636	2.461
37	C(7)-C(10)	C(23)-N(9)	N(1)-C(10)	2.790	2.636	2.636
38	C(6)-C(9)	C(3)-C(23)	C(23)-N(9)	2.790	2.007	2.636
39	C(5)-C(8)	C(2)-C(23)	C(3)-C(23)	2.790	2.461	2.007
40	N(3)-C(5)	C(3)-C(22)	C(2)-C(23)	2.636	2.491	2.461
41		N(1)-Br(29)	C(3)-C(22)		3.014	2.491
42		C(3)-C(6)	C(3)-C(6)		2.790	2.790
43		C(2)-C(5)	C(2)-C(5)		2.790	2.790
44		C(7)-C(4)	C(7)-C(4)		2.790	2.790

Table (5) presented the close contact of selected atoms in ligand (1) and their derivatives (2) and (3). The three compounds have different results and this indicated the effect of substitution in the structure properties, also the conjugation effect with four benzene rings can affect the results. The selected C(25)-C(28), C(24)-C(27), C(23)-C(26), C(19)-C(22), C(18)-C(21), C(17)-C(20), C(13)-C(16), C(12)-C(15), C(11)-C(14), C(6)-C(9) and C(5)-C(8) atoms in (1) were gave 2.790 in each because the net of carbon was C-C=C-C, but in C(7)-C(28) and C(9)-C(24) were 2.574 related to -C=C-C-C=N-C- in each. However, the N(3)-C(16) and N(4)-C(12) were gave 2.771 and 2.759 related to N-C-C=C and N=C-C-C-C respectively. But, N(3)-C(5) and N(4)-C(11) were gave 2.636 related to N=C-C-C in each, all net for the three compounds were presented in figure 1. The effect of position of substituted group was also studied in table 5 and the example were Br(30)-C(24), N(9)-C(21), N(1)-C(17), N(9)-Br(30), N(1)-C(10), C(23)-N(9), N(1)-Br(29) which equal to 2.906, 2.760, 2.533, 3.014, 2.636, 2.636 and 3.014 respectively in (2), but the Br(30)-C(27), Br(30)-C(26), Br(30)-C(25), N(9)-C(21), N(1)-C(17), N(1)-C(10) and C(23)-N(9) were equal to 3.227, 2.457, 3.227, 2.760, 2.533, 2.636 and 2.636 respectively in (3). Further, the internal coordinate for (1), (2) and (3) were calculated as seen in table (6-8) respectively.

Table 6: The internal coordinates for ligand (1)

No	Atom	Bond Atom	Bond Length (Å)	Angle Atom	Angle (°)	2nd Angle Atom	2nd Angle (°)	2nd Angle Type
1	C(1)							
2	C(2)	C(1)	1.337					
3	N(3)	C(1)	1.26	C(2)	120			
4	C(11)	C(1)	1.337	C(2)	120	N(3)	120	Pro-R
5	C(23)	N(3)	1.26	C(1)	115	C(2)	0	Dihedral
6	N(4)	C(2)	1.26	C(1)	120	N(3)	180	Dihedral
7	C(5)	C(2)	1.337	C(1)	120	N(4)	120	Pro-R
8	C(17)	N(4)	1.26	C(2)	115	C(1)	-180	Dihedral
9	C(6)	C(5)	1.395	C(2)	119.998	C(1)	-90	Dihedral
10	C(10)	C(5)	1.395	C(2)	119.999	C(6)	120.003	Pro-R
11	C(7)	C(6)	1.395	C(5)	119.997	C(2)	-179.994	Dihedral
12	C(33)	C(6)	1.497	C(5)	120.002	C(7)	120.001	Pro-R
13	C(8)	C(7)	1.395	C(6)	120	C(5)	-0.006	Dihedral
14	H(29)	C(7)	1.1	C(6)	120	C(8)	120	Pro-S
15	C(9)	C(10)	1.395	C(5)	120	C(2)	179.999	Dihedral
16	H(30)	C(8)	1.1	C(7)	119.998	C(9)	119.998	Pro-R
17	H(31)	C(9)	1.1	C(8)	120.001	C(10)	120.001	Pro-R
18	H(32)	C(10)	1.1	C(5)	120	C(9)	120	Pro-R
19	C(12)	C(11)	1.395	C(1)	113.762	C(2)	60.444	Dihedral
20	C(16)	C(11)	1.395	C(1)	120.941	C(12)	120.003	Pro-S
21	C(13)	C(12)	1.395	C(11)	119.997	C(1)	154.551	Dihedral
22	H(38)	C(12)	1.1	C(11)	120.002	C(13)	120.002	Pro-S
23	C(14)	C(13)	1.395	C(12)	120	C(11)	-0.005	Dihedral
24	H(37)	C(13)	1.1	C(12)	120	C(14)	119.999	Pro-S
25	C(15)	C(16)	1.395	C(11)	119.999	C(1)	-152.703	Dihedral
26	H(34)	C(16)	1.1	C(11)	120.001	C(15)	120	Pro-R
27	H(35)	C(15)	1.1	C(14)	120.002	C(16)	120.001	Pro-R
28	H(36)	C(14)	1.1	C(13)	119.998	C(15)	119.999	Pro-R
29	C(18)	C(17)	1.395	N(4)	119.998	C(2)	-108	Dihedral
30	C(22)	C(17)	1.395	N(4)	119.999	C(18)	120.003	Pro-R
31	C(19)	C(18)	1.395	C(17)	119.997	N(4)	-179.994	Dihedral
32	H(43)	C(18)	1.1	C(17)	120.001	C(19)	120.002	Pro-R
33	C(20)	C(19)	1.395	C(18)	120	C(17)	-0.006	Dihedral
34	H(42)	C(19)	1.1	C(18)	120	C(20)	120	Pro-R
35	C(21)	C(22)	1.395	C(17)	120	N(4)	179.999	Dihedral
36	H(39)	C(22)	1.1	C(17)	120	C(21)	120	Pro-R
37	H(40)	C(21)	1.1	C(20)	120.001	C(22)	120.002	Pro-S
38	H(41)	C(20)	1.1	C(19)	119.998	C(21)	119.998	Pro-R
39	C(24)	C(23)	1.395	N(3)	119.998	C(1)	-90	Dihedral
40	C(28)	C(23)	1.395	N(3)	119.999	C(24)	120.003	Pro-R
41	C(25)	C(24)	1.395	C(23)	119.997	N(3)	-179.994	Dihedral
42	H(48)	C(24)	1.1	C(23)	120.001	C(25)	120.002	Pro-S
43	C(26)	C(25)	1.395	C(24)	120	C(23)	-0.006	Dihedral
44	H(47)	C(25)	1.1	C(24)	120	C(26)	120	Pro-R
45	C(27)	C(28)	1.395	C(23)	120	N(3)	179.998	Dihedral
46	H(44)	C(28)	1.1	C(23)	120	C(27)	120.001	Pro-R
47	H(45)	C(27)	1.1	C(26)	120.002	C(28)	120.001	Pro-R
48	H(46)	C(26)	1.1	C(25)	119.998	C(27)	119.998	Pro-S
49	H(49)	C(33)	1.113	C(6)	109.5	C(5)	0	Dihedral
50	H(50)	C(33)	1.113	C(6)	109.442	H(49)	109.442	Pro-S
51	H(51)	C(33)	1.113	C(6)	109.462	H(49)	109.462	Pro-R

Table 7: The internal coordinates for ligand (2)

No	Atom	Bond Atom	Bond Length (A)	Angle Atom	Angle (°)	2nd Angle Atom	2nd Angle (°)	2nd Angle Type
1	N(1)							
2	C(2)	N(1)	1.26					
3	C(3)	C(2)	1.395	N(1)	119.998			
4	C(7)	C(2)	1.395	N(1)	119.999	C(3)	120.003	Pro-R
5	C(4)	C(3)	1.395	C(2)	119.997	N(1)	-179.994	Dihedral
6	H(41)	C(3)	1.1	C(2)	120.001	C(4)	120.002	Pro-R
7	C(5)	C(4)	1.395	C(3)	120	C(2)	-0.006	Dihedral
8	H(42)	C(4)	1.1	C(3)	119.999	C(5)	120	Pro-R
9	C(6)	C(7)	1.395	C(2)	120	N(1)	179.999	Dihedral
10	Br(29)	C(7)	1.881	C(2)	120	C(6)	120	Pro-S
11	H(43)	C(5)	1.1	C(4)	119.998	C(6)	119.998	Pro-R
12	H(44)	C(6)	1.1	C(5)	120.001	C(7)	120.001	Pro-S
13	C(22)	N(1)	1.26	C(2)	115	C(3)	0	Dihedral
14	C(8)	C(22)	1.337	N(1)	120	C(2)	-180	Dihedral
15	C(23)	C(22)	1.337	N(1)	120	C(8)	120	Pro-S
16	N(9)	C(8)	1.26	C(22)	120	N(1)	180	Dihedral
17	C(10)	C(8)	1.337	N(9)	120	C(22)	120	Pro-S
18	C(11)	N(9)	1.26	C(8)	115	C(10)	-180	Dihedral
19	C(12)	C(11)	1.395	N(9)	119.999	C(8)	-90	Dihedral
20	C(16)	C(11)	1.395	N(9)	119.999	C(12)	120.003	Pro-R
21	C(13)	C(12)	1.395	C(11)	119.997	N(9)	-179.994	Dihedral
22	Br(30)	C(12)	1.881	C(11)	120.002	C(13)	120.002	Pro-R
23	C(14)	C(13)	1.395	C(12)	120	C(11)	-0.005	Dihedral
24	H(48)	C(13)	1.1	C(12)	120	C(14)	120	Pro-S
25	C(15)	C(16)	1.395	C(11)	120	N(9)	179.999	Dihedral
26	H(45)	C(15)	1.1	C(14)	120.001	C(16)	120.002	Pro-S
27	H(46)	C(16)	1.1	C(11)	120	C(15)	120	Pro-S
28	H(47)	C(14)	1.1	C(13)	119.998	C(15)	119.998	Pro-R
29	C(17)	C(10)	1.395	C(8)	119.998	N(9)	-144	Dihedral
30	C(21)	C(10)	1.395	C(8)	119.999	C(17)	120.003	Pro-R
31	C(18)	C(17)	1.395	C(10)	119.997	C(8)	-179.994	Dihedral
32	H(35)	C(17)	1.1	C(10)	120.002	C(18)	120.001	Pro-R
33	C(19)	C(18)	1.395	C(17)	120	C(10)	-0.006	Dihedral
34	H(34)	C(18)	1.1	C(17)	120	C(19)	120	Pro-R
35	C(20)	C(21)	1.395	C(10)	120	C(8)	179.999	Dihedral
36	H(31)	C(21)	1.1	C(10)	120	C(20)	120	Pro-S
37	H(32)	C(20)	1.1	C(19)	120.002	C(21)	120.001	Pro-S
38	H(33)	C(19)	1.1	C(18)	119.998	C(20)	119.998	Pro-S
39	C(24)	C(23)	1.395	C(22)	119.999	N(1)	-90	Dihedral
40	C(28)	C(23)	1.395	C(22)	119.999	C(24)	120.003	Pro-R
41	C(25)	C(24)	1.395	C(23)	119.997	C(22)	-179.994	Dihedral
42	H(36)	C(24)	1.1	C(23)	120.002	C(25)	120.001	Pro-R
43	C(26)	C(25)	1.395	C(24)	120	C(23)	-0.006	Dihedral
44	H(37)	C(25)	1.1	C(24)	120	C(26)	120	Pro-R
45	C(27)	C(28)	1.395	C(23)	120	C(22)	179.999	Dihedral
46	H(38)	C(26)	1.1	C(25)	119.998	C(27)	119.998	Pro-S
47	H(39)	C(27)	1.1	C(26)	120.002	C(28)	120.002	Pro-R
48	H(40)	C(28)	1.1	C(23)	120	C(27)	120	Pro-S

Table 8: The internal coordinates for ligand (3)

No	Atom	Bond Atom	Bond Length (A)	Angle Atom	Angle (°)	2nd Angle Atom	2nd Angle (°)	2nd Angle Type
1	N(1)							
2	C(2)	N(1)	1.26					
3	C(3)	C(2)	1.395	N(1)	119.998			
4	C(7)	C(2)	1.395	N(1)	119.999	C(3)	120.003	Pro-S
5	C(4)	C(3)	1.395	C(2)	119.997	N(1)	-179.994	Dihedral
6	H(45)	C(3)	1.1	C(2)	120.002	C(4)	120.001	Pro-S
7	C(5)	C(4)	1.395	C(3)	120	C(2)	-0.006	Dihedral
8	H(46)	C(4)	1.1	C(3)	120	C(5)	120	Pro-S
9	C(6)	C(7)	1.395	C(2)	120	N(1)	179.999	Dihedral
10	Br(29)	C(5)	1.881	C(4)	119.998	C(6)	119.998	Pro-S
11	H(47)	C(6)	1.1	C(5)	120.001	C(7)	120.001	Pro-S
12	H(48)	C(7)	1.1	C(2)	120	C(6)	120	Pro-R
13	C(22)	N(1)	1.26	C(2)	115	C(3)	0	Dihedral
14	C(8)	C(22)	1.337	N(1)	120	C(2)	-180	Dihedral
15	C(23)	C(22)	1.337	N(1)	120	C(8)	120	Pro-R
16	N(9)	C(8)	1.26	C(22)	119.999	N(1)	-180	Dihedral
17	C(10)	C(8)	1.337	N(9)	120	C(22)	120	Pro-R
18	C(11)	N(9)	1.26	C(8)	115	C(10)	-180	Dihedral
19	C(12)	C(11)	1.395	N(9)	119.999	C(8)	-90	Dihedral
20	C(16)	C(11)	1.395	N(9)	119.999	C(12)	120.003	Pro-R
21	C(13)	C(12)	1.395	C(11)	119.997	N(9)	-179.994	Dihedral
22	H(34)	C(12)	1.1	C(11)	120.002	C(13)	120.002	Pro-R
23	C(14)	C(13)	1.395	C(12)	120.001	C(11)	-0.005	Dihedral
24	H(31)	C(13)	1.1	C(12)	120	C(14)	120	Pro-S
25	C(15)	C(16)	1.395	C(11)	119.999	N(9)	179.999	Dihedral
26	Br(30)	C(14)	1.881	C(13)	119.999	C(15)	119.999	Pro-R
27	H(32)	C(15)	1.1	C(14)	120.001	C(16)	120.001	Pro-S
28	H(33)	C(16)	1.1	C(11)	120	C(15)	120	Pro-S
29	C(17)	C(10)	1.395	C(8)	119.998	N(9)	-144	Dihedral
30	C(21)	C(10)	1.395	C(8)	119.999	C(17)	120.003	Pro-R
31	C(18)	C(17)	1.395	C(10)	119.997	C(8)	-179.994	Dihedral
32	H(39)	C(17)	1.1	C(10)	120.001	C(18)	120.002	Pro-R
33	C(19)	C(18)	1.395	C(17)	120	C(10)	-0.006	Dihedral
34	H(38)	C(18)	1.1	C(17)	120	C(19)	120	Pro-R
35	C(20)	C(21)	1.395	C(10)	120	C(8)	179.999	Dihedral
36	H(35)	C(21)	1.1	C(10)	120	C(20)	120	Pro-S
37	H(36)	C(20)	1.1	C(19)	120.001	C(21)	120.001	Pro-S
38	H(37)	C(19)	1.1	C(18)	119.998	C(20)	119.998	Pro-S
39	C(24)	C(23)	1.395	C(22)	119.999	N(1)	-90	Dihedral
40	C(28)	C(23)	1.395	C(22)	119.999	C(24)	120.003	Pro-R
41	C(25)	C(24)	1.395	C(23)	119.997	C(22)	-179.994	Dihedral
42	H(40)	C(24)	1.1	C(23)	120.002	C(25)	120.001	Pro-S
43	C(26)	C(25)	1.395	C(24)	120	C(23)	-0.006	Dihedral
44	H(41)	C(25)	1.1	C(24)	120	C(26)	120	Pro-R
45	C(27)	C(28)	1.395	C(23)	120	C(22)	179.999	Dihedral
46	H(42)	C(26)	1.1	C(25)	119.999	C(27)	119.998	Pro-S
47	H(43)	C(27)	1.1	C(26)	120.001	C(28)	120.001	Pro-R
48	H(44)	C(28)	1.1	C(23)	120	C(27)	120	Pro-S

The tables displayed the effect of the substitution and their position in the phenyl ring in the internal coordinate of the three compounds. The tables also showed that the bond length of C=N, C-C, C=C, C-H and C-Br were equal to 1.260 Ǻ, 1.337 Ǻ, 1.395 Ǻ, 1.100 Ǻ and 1.881 Ǻ respectively which indicated the previous results. Table (6) was showed that the C(11) bond to C(1) and the bond length was equal to 1.337 Ǻ and the bond angle of C(11)-C(1)-C(2) and C(11)-C(1)-N(3) were equal to 120° and the atoms around the double bond was in R configuration. The C(23) bond to N(3) and the bond length was equal to 1.26 Ǻ and the bond angle of C(23)-N(3)-C(1) and C(23)-N(3)-C(1)-C(2) were equal to 115° and 0° respectively and the angle type was dihedral, but the C(16) bond to C(11) and the bond length was equal to 1.395 Ǻ and the bond angle of C(16)-C(11)-C(1) and C(16)-C(11)-C(12) were equal to 120.941° and 120.003° respectively and the atoms around the double bond was in S configuration. All data calculated in same way in tables (6-8) with respect the structure presented in figure (1).

The MMFF94 energy and gradient for (1), (2) and (3) were also calculated. The results showed that the total energy for this frame were (746.902, 1223.418 and 1235.345) kcal/mol respectively and the RMS gradients were 80.761, 175.979 and 178.38 respectively. The MMFF94 minimization iteration was also calculated which equal to 455, 500 and 500 respectively for each ligand, this minimization terminated normally because the gradient norm is less than the minimum gradient norm and the final energy were equal to (120.525, 153.35 and 117.306) kcal/mol respectively and the best minimization was observed in compound (3). Molecular mechanics[3] is a method for calculating the E of a molecule, and for the program to try to optimize the structure such as minimize E by stretching or contracting bond lengths, opening and closing of angles, and twisting around single bonds. Molecular mechanics treats bonds as springs which can be stretched, bend or twisted. Therefore, MM2 minimization for (1), (2) and (3) were calculated, (Stretch: 3.7997, 4.0145 and 3.4901; Bend: 14.7696, 16.5822 and 14.3095; Stretch-Bend: 0.3756, 0.4999 and 0.4207; Torsion: 19.5219, 21.2435 and 15.2067; Non-1,4 Van der Waals: 7.0861, 5.6320 and 6.5217; 1,4 Van der Waals: 32.8090, 34.8408 and 34.0070; Dipole/Dipole: 0.1184, 2.5464 and 0.7568 and the total energy: 78.4465, 85.3592 and 74.7126 kcal/mol), these results showed the difference between the three compounds and the effect of substitution. The compound (2) was gave high total energy higher than (1) and (3) because the bulky substituted Br in ortho position which near to the nitrogen of imine group can effective by steric effect and this can explain the high value of E. High dipole/dipole value also in compound (2) higher than (1) and (3) and the later was higher than (1) which explain the effect of substituted group and their position in the structure properties. The best minimization either use MMFF94 or MM2 were observed in compound (3) which gave lower total energy than (1) and (2). The MMFF94 minimization and MM2 minimization were indicated the steric effect of o-Br in compound (2).

Experimental

Synthesis of *N*^{1},*N*^{2},1,2-tetraphenylethane-1,2-diimine (1)

The Aniline (20 mmol, 1.86 g) and Benzil (10 mmol, 2.1 g) in mixture of ethanol (1 mL) and acetic acid (16 ml) were vigorously stirred for 48 hrs. at 110 ^{o}C with open stoppers bottom flask. Then, the mixture was evaporated and dissolved in chloroform followed by the addition of $NaHCO_3$ solution with constant stirring for half of hour. The aqueous layer was extracted and the combined organic layer was dried and evaporated. The crude product was purified by recrystallization from chloroform/petroleum ether to give a yellow solid, the title compound (3.43 g, 95.3%). {Found [M+Na]$^+$: 383.1524, $C_{26}H_{20}NaN_2$ requires: 383.1525}. This showed δ_H: (400 MHz, $CDCl_3$): δ 7.8 (2H, d, *J* 7.7 Hz), 7.7 (2H, d, *J* 7.6 Hz), 7.4 (4H, t, J 7.5,), 7.2 (4H, t, *J* 8.5, Hz) and 7.1 (4H, t, *J* 7.5, Hz); δ_C (125 MHz, $CDCl_3$): 153.2, 151.7, 133.1,131.0, 130.0, 129.2, 128.8, 127.2, 118.8.

Synthesis of *N*^{1},*N*^{2}-*bis*(2-bromophenyl)-1,2-diphenylethane-1,2-di imine (2)

The 2-BromAniline (20 mmol, 3.44 g) and Benzil (10 mmol, 2.1 g) in mixture of ethanol (1 ml) and acetic acid (16 mL) were vigorously stirred for 48 hrs. at 110 ^{o}C with open stoppers bottom flask. Then, the mixture was evaporated and dissolved in chloroform followed by the addition of $NaHCO_3$ solution with constant stirring for half of hour. The aqueous layer was extracted and the combined organic layer was dried and evaporated. The crude product was purified by recrystallization from diethyl ether/petroleum ether to give a green to yellow solid, the title compound (4.73 g, 90%). {Found [M+Na]$^+$: 538.9733, $C_{26}H_{18}NaBr_2N_2$ requires: 538.9734}. This showed δ_H: 8.4 (3H, d, *J* 7.95 Hz), 7.9 (3H, d, *J* 7.75 Hz), 7.6 (3H, d, *J* 7.42 Hz), 7.4 (4H, t, *J* 8.0 Hz),7.4 (4H, t, *J* 8.0 Hz), 7.3 (4H, t, *J* 6.0 Hz) and 6.9 (4H, t, *J* 7.523 Hz); δ_C (125 MHz, $CDCl_3$): 151.0, 133.1,132.9, 130.0, 128.8, 126.6, 119.7.

Synthesis of *N*^{1},*N*^{2}-bis(4-bromophenyl)-1,2-diphenylethane-1,2-diimine (3)

The 4-BromAniline (20 mmol, 3.44 g) and Benzil (10 mmol, 2.1 g) in mixture of ethanol (1 ml) and acetic acid (16 mL) were vigorously stirred for 48 hrs. at 110 ^{o}C with open stoppers bottom flask. Then, the mixture was evaporated and dissolved in chloroform followed by the addition of $NaHCO_3$ solution with constant stirring for half of hour. The aqueous layer was extracted and the combined organic layer was dried and evaporated. The crude product was purified by recrystallization from dichloromethane/ethyl acetate/petroleum to give a green solid, the title compound (4.8 g, 93%). {Found [M+Na]$^+$: 538.9733, $C_{26}H_{18}NaBr_2N_2$ requires: 538.9734}. This showed δ_H: (400 MHz, $CDCl_3$): δ 7.8 (3H, d, *J* 7.2 Hz), 7.4 (3H, d, *J* 7.2 Hz), 7.4 (3H, d, *J* 7.2 Hz), 7.1 (2H, t, *J* 8.0) and 7.1 (2H, t, *J* 8.0); δ_C (125 MHz, $CDCl_3$): 152.2, 133.1, 132.9, 121.6, 119.9. Theoretical studies were done using the molecular mechanics force field (MMFF94) and the molecular mechanics (MM2) minimization

Summary

The area of molecular mechanics is to study the detailed structure and physical properties of molecules. Molecular mechanics calculates the energy of a molecule and then adjusts the energy through changes in the bond lengths and angles to obtain the minimum energy structure. Internal coordinate also have some advantages for suggesting a new derivatives.

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