Rotational Energy Surfaces of 3-methyl-2-benzothiazolylidenaminodichlorophosphine: A Semi-empirical Study

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Abstract- Semi-empirical PM3 calculations have been performed with MOPAC 6.0 programme to study conformational analysis of different stereoisomer of 3-methyl-2-benzothiazolylidenaminodichlorophosphine (I) and their rotational energy surfaces to find the most stable conformation. The geometry optimization of four possible conformers of I gives rise to two minimum energy structures of IA and IB having syn orientation of lone pair of electrons on nitrogen and phosphorus. These structures were confirmed to be global minima by the force calculations. In terms of heat of formation, the geometrical isomer IA is more stable than IB by ~0.6 kcal/mol. Force calculation were carried out to locate transition state and global minima. The minimum energy structure on potential energy surface represents rotamer IA, (Planar orientation of lone pair of electrons on N_{10} & P_{11}) confirms this to be most stable conformer. The maxima on the graph correspond to the stereoisomer IB; which is least least stable conformer. The rotational barrier is found to be 1.5 kcal/mol. The increased stability of the rotamer IA, representing minima can be attributed to the presence of negative hyperconjugation effect.

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1 INTRODUCTION

Stereochemical properties of amines and phosphines have attracted the attention of theoretical chemists due to the possibility of various conformational isomers resulting from different relative orientations of the lone of electrons on pyramidal nitrogen and phosphorus [1-4].

A number of theoretical studies have been carried out on the simplest aminophosphine to establish the ground state geometry, torsional barriers and pyramidal inversion.

Similarly, rotational energy surfaces of a number of other phosphorus and nitrogen derivatives like alkylphosphines [5-6], pyridiniumdichlorophosphines [7], azabutadiene and phosphabutadiene [8], diphosphines and hydrazines have also been investigated [4].

3-alkyl-2-benzothiazolylidenaminodichlorophosphine (1), the precursors of various amidothiophosphates and trisamidothiophosphates [9-10], also comprise the category of aminophosphines incorporating trigonal planar nitrogen bonded to pyramidal phosphorus. Relative orientation of lone pair of electrons on nitrogen and phosphorus gives rise to the possibility of a number of conformational

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isomers ranging from the one having syn orientation of the lone pair of electrons to that having their anti-orientation.

It was considered worthwhile to carryout the theoretical calculations to identify the most stable conformer of 1 and compare the relative stabilities of different conformers. For this purpose, PM3 semi empirical calculations of 3-alkyl-2-benzothiazolylidenaminodichlorophosphine have been carried out and the rotational energy hyper surface has been investigated.

2 COMPUTATIONAL METHODS

The calculations were carried out with MOPAC 6.0 programme using semi empirical methods [11-12]. The geometries of four stereoisomers A, B, C, D of 1 were optimized at the SCF level of computation by energy minimization algorithm with respect to all geometrical variables. The force calculations were carried out to characterize the global minima (1A and 1C) with zero number of imaginary frequencies (NIMAG). The rotational potential energy surface was generated by complete geometry optimization with the dihedral angle ω (C2-N10-P11-Cl12), about the single bond between nitrogen (N10) and phosphorus (P11) repeatedly incremented by intervals of 10°. The highest energy structure on the rotational energy potential surface was refined by gradient minimization to locate transition state structure, which is found to be corresponding to stereoisomer 1B was verified by the presence of one and only one imaginary frequency (NIMAG) in the force constant calculations.

3 RESULTS AND DISCUSSION

3.1 Geometry Optimization of Stereoisomers Representing Possible Minima

The presence of C2=N10 bond in 1 gives rise to two types of geometrical isomers; those (1A and 1B) having anti orientation of the phosphorus with the ring nitrogen and the others (1C and 1D) incorporating syn orientated phosphorus with respect to the ring nitrogen. The geometry optimization in both cases reveals the minimum energy structures 1A and 1B to be having syn orientation of the lone pairs on N and P in each case. These geometries are confirmed to be real minima by force calculations when no imaginary frequency was obtained.

An attempt was also made to optimize the geometries of conformer 1B & 1D having N & P lone pairs in anti orientation. In the case of 1B, the optimized geometry with anti orientation of lone pair is of higher energy & corresponds to the T.S. (obtained from rotational energy surface and characterized by one imaginary higher value) however, the attempt to optimize the geometry conformer 1D was not successful & resulted in the optimized structure corresponding to the conformer 1C (having N10 & P11 lone pairs in syn orientation).

In the optimized minimum energy structures of the two geometrical isomers i.e. 1A (with P11 anti to ring N; ω (N1-C2-N10-P11) = 176.9° and 1C (P11 syn to ring N; ω (N1-C2-N10-P11) = 5.4° the lone pairs on N10 & P11 are in syn orientation; which is evident from almost equal dihedral angles ω (C2-N10-P11-Cl12) and ω (C2-N10-P11-Cl13). The phosphorus is pyramidal in each case with the two N10-P11-Cl angles in the range 101-104°. The bond length C2-N10 (~ 129.53 pm) in 1A & 1C is comparable to PM3 calculated C=N bond lengths (130 pm) in CH2=NH thus indicating an equally effective double bond between C2 & N10. In addition N1-C2 bond length in 1A & 1C is shorter by about 5pm than that in trimethylamine (calculated by PM3 method), indicating delocalization of lone pairs of electrons in the present case. This is further supported by the +Cl of a net +ve charge 0.136 ± 0.009 e.s.u. and total positive π charge of 0.348 ± 0.007 e.s.u. The exocyclic N is having net negative charge (-0.517 ± 0.002), while the phosphorus is having a net +ve charge of ~ 1 electron, the latter is compensated by the net –ve charges on the two chlorine atoms. In terms of heat of formation the geometrical isomer 1A is more stable than 1C by ~ 0.6 kcal/mol.

## 3.2 Determination of Rotational Energy Surface

The potential energy hyper surface from the analysis of rotational process and N10 – P11 bond of 1A has been obtained from the plot of heat of formation of different rotamers as a junction of the dihedral angle ω (C2-N10-P11-Cl12) which is repeatedly in cremented by 10° to complete one full rotation and N10-P11.

The minimum energy structures on the potential energy hyper surface corresponds to the structures 1A with the synperiplanar orientation of lone pairs on P11 & N10,

while maxima corresponds to structure 1B with antiperiplanar orientation of lone pairs on N10 & P11 as indicated by the dihedral angles ω (C2-N10-P11-Cl12) = -132.6° & ω (C2-N10-P11-Cl13) = 126.4°. The refinement of geometry of the maxima 1B by gradient minimization and the force calculation confirmed its transition nature. The value of rotational barrier in the present case is 1.5 kcal/mol.
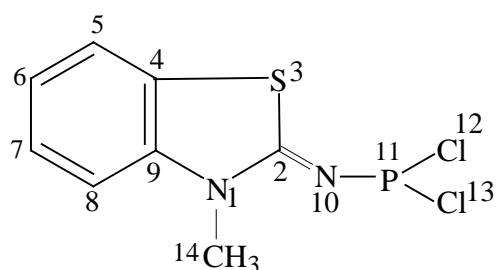
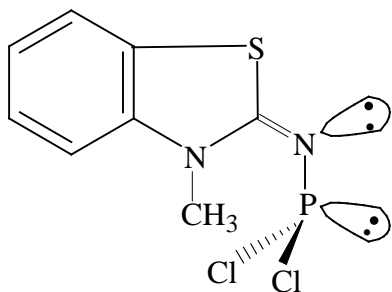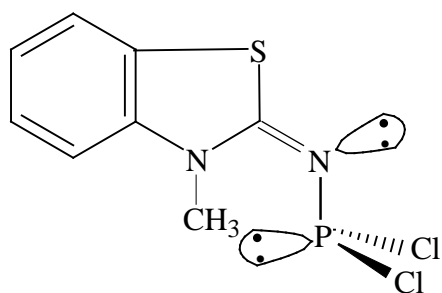**I** (3-alkyl-2-benzothiazolylidenaminodichlorophosphine)

A

B

C

D

A, B, C and D are stereoisomers of 3-alkyl-2-benzothiazolylidenaminodichlorophosphine
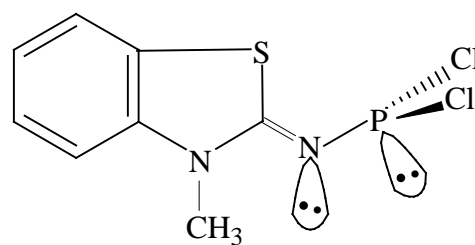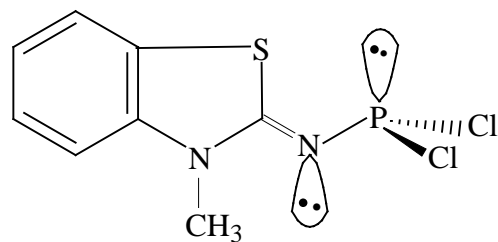
OPTIMIZES PHYSICAL AND GEOMETRICAL
PARAMETERS OF DIFFERENT ROTAMERS OF
3-alkyl-2-benzothiazolylidenaminodichlorophosphine

Dihedral angle (°) C_2-N_{10}-P_{11}-Cl_{12}	Heat of Formation H_f (Kcal/mol)	Bond Length (pm)		
		P_{11} - Cl_{12}	P_{11} - Cl_{13}	N_{11} - P_{11}
180	-21.52	207.6	207.9	174.2
170	-21.64	207.7	208.0	173.8
160	-21.71	207.7	208.1	173.5
150	-21.78	207.6	208.0	173.2
140	-21.84	207.7	208.0	172.8
130	-21.92	207.7	208.1	172.6
120	-21.99	207.7	208.1	173.4
110	-22.04	207.8	208.1	172.4
100	-22.12	207.8	208.1	172.4
90	-22.29	207.9	208.1	172.1
80	-22.38	208.0	208.0	172.1
70	-22.47	208.0	208.1	172.2
60	-22.54	208.1	208.1	172.2
50	-22.55	208.1	208.1	172.1
40	-22.58	208.1	208.1	172.1
30	-22.53	208.1	208.1	172.2
20	-22.45	208.1	208.1	171.9
10	-22.42	208.1	208.0	172.2
0	-22.35	208.1	207.9	172.3
-10	-22.02	208.1	207.9	172.4
-20	-22.16	208.1	207.8	172.4
-30	-22.08	208.1	207.7	172.6
-40	-22.00	208.0	207.7	172.8
-50	-21.88	207.9	207.7	173.0
-60	-21.88	208.0	207.6	173.4
-70	-21.79	208.0	207.6	173.8
-80	-21.66	207.9	207.6	174.1
-90	-21.43	207.9	207.6	174.5
-100	-21.21	207.8	207.6	174.7
-110	-21.17	207.8	207.6	174.9
-120	-21.07	207.8	207.6	175.0
-130	-21.02	207.7	207.6	175.2
-140	-21.04	207.7	207.7	175.1
-150	-21.11	207.6	207.8	174.9
-160	-21.23	207.6	207.8	174.7
-170	-21.38	207.6	207.9	174.5
-180	-21.52	207.6	207.9	174.2

TABLE 1

Fig. 1 Bond length for rotatmers of 3-alkyl-2-benzothiazolylidenaminodichlorophosphine at different dihedral angle.

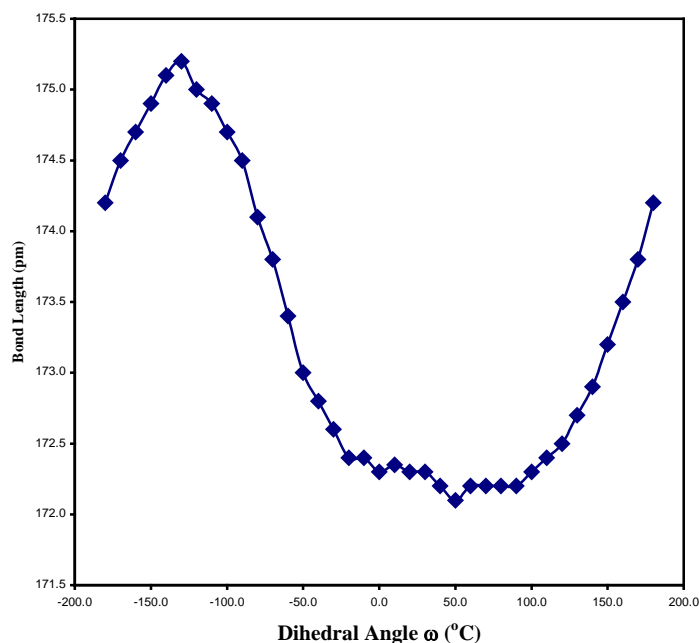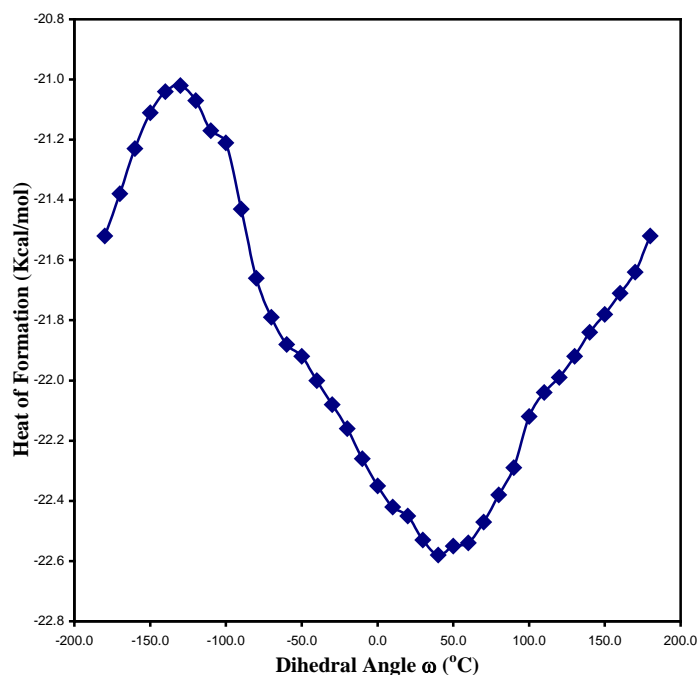Fig. 2 Bond length of two geometrical isomers of 3-alkyl-2-benzothiazolylidenaminodichlorophosphine at different dihedral angle

Fig. 3 Heat of formation for 3-alkyl-2-benzothiazolylidenaminodichlorophosphine at different dihedral angle
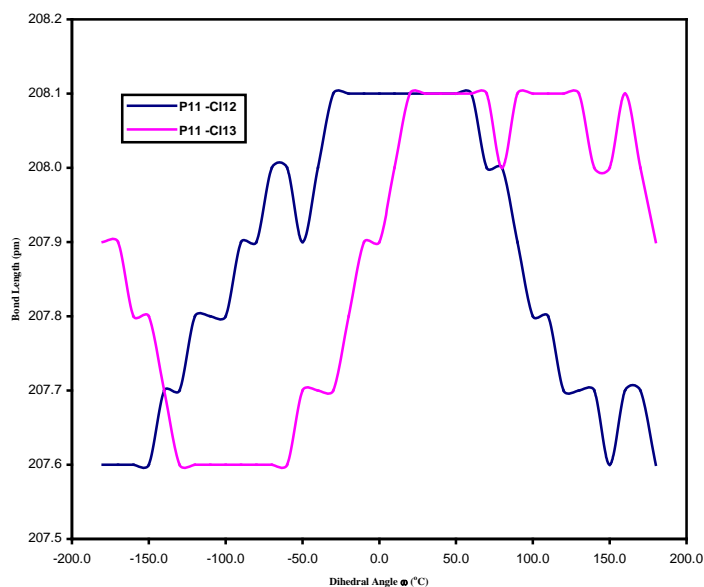
4 CONCLUSION

From semiemperical studies of 3-alkyl-2-benzothiazolylidenaminodichlorophosphine rotamers, it is found that that negative hyperconjugation play important role in the stability of the compounds. Heat of formation and bond length of 3-alkyl-2-benzothiazolylidenaminodichlorophosphine gives mixed trends with different dihedral angles because of hyperconjugation.

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