Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 2 (1)
Science and Research Campus
ISSN: 1735-2126

The evaluation of basis set, method and initial geometry on structural properties of a cyclic phosphor amidate compound by SPSS

Majid Monajjemi [a*], Anita Abedi [b]

[a] Science and Research Campus, Islamic Azad University, P.O. Box 14515-775, Tehran,Iran
[b] Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

ABSTRACT

The structural properties of a new cyclic phosphor amide have been investigated in three methods and four basis sets and results have been compared with experimental data by spss. The best level for this type compound is HF/6-31++G** and with considering to this result, at this level, hyper chem input as initial geometry have been evaluated.

INTRODUCTION

The molecular structure of phosphoramidates is of considerable interest because phosphoramidate derivatization markedly increases the anti-HIV activity of 2',3'-didehydro-2',3'-dideoxythymidine (d4T) in both wild-type and thymidine kinase-deficient CEM cells at this reason, this compound explores as a prodrug [1] In last work, we syntheses and determined structural properties of a new cyclic phosphor amidates, 5,5-dimethyl-2-(p-methylanilino)-2-oxo-1,3,2-diaza-phosphorinane by X-Ray spectrometry, [2]. The aim of this work is the determining of the best calculated level that its results would be similar to the experimental data. This is necessary about phosphoramidates because of their extended exploring in the agriculture, pharmacy, metalogy, industry and so on. The crystallization of these compounds is diffidult, so some reports published about crystallized phosphoramidates. In the other view, cytotoxicity of these drugs depends on geometric and electronic properties, so the structural determine of them is very important.

Biomedical computing is the application and development of computer methods for biomedical research. The ultimate goal of biomedical computing is to advance the bio medical sciences by simulating life at all applicable levels of detail: the biochemical, physiological, cell, organ, organism, and population levels. The results promise to include better diagnoses, better drugs and other therapies that are developed faster, perhaps through mass customization, better surgical procedures, better prostheses, better recognition and repair of public health problems, and thus a healthier population, perhaps with lower medical costs[4].

For small and medium sized molecules, quantum theory can be used to determine structures, often very accurately. Many times experimental structures are not known and theoretical means are the only choice [5,6].

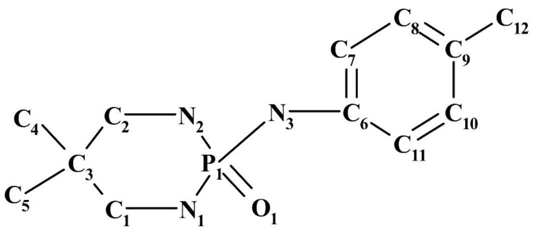


Fig. 1. Molecular structure of a cyclic phosphor amidate

---

[*] Corresponding author

There is a large amount of bibliography showing that DFT methods can be an effective approach to calculating molecular structures properties [7-9]. However, it is not possible to predict in advance the particular combination of exchange and correlation functional that will lead to the best results for a given system. As a consequence, there is a need for doing evaluations and comparisons of different density functional procedures. it is the objective of this work to test the influence and effectiveness of different model chemistries, for the calculation of structural properties, including with atomic distances atomic angles and torsion angles of a cyclic phosphorus amidate [fig.1].

These model chemistries are represented by traditional Hartree-Fock (HF) and two Density Functional Theory, hybrid B3LYP and gradient corrected BLYP together with four basis sets with and without d polarization functions.

METHODOLOGY

Geometry optimization and structural properties calculations (atomic distances, atomic angles and torsion angles) were performed in GUSSIAN 98 [10]. All computational calculation was done by using the crystalline forms [1] as initial geometries. Structural molecular properties obtaining with HF, B3LYP and BLYP on different basis sets including 6-31G**, 6-31+G**, 6-31++G** and 6-311++G** were compared with experimental data [1].

Critical limit for geometry optimization and SCF-convergence were 10^{-7} hartree/bohr and 10^{-9} hartree, respectively. The force constants and vibrational frequencies were determined by the FREQ calculations on the stationary points obtained after the optimization to check if there were true minima.

The low level basis sets e. g. STO-3G, STO-3G*,3-21G*, 3-21G** 3-21++G** and 6-31G** are calculated for compound but aren't brought because of high volume of data and high error of these methods.

In tables for abbreviation, B3LYP and BLYP are replaced with B3 and B, and also 6- 31+G**, 6-31++G** and 6-311++G** are replaced +, ++, 311 respectively.

In all calculating cases, the structures are optimized and it isn't used of single point in any where.

Statistical calculations were performed using the SPSS 12.0 for Windows (Statistical Package for the Social Sciences).

RESULTS AND DISCUSSION

Internuclear distances

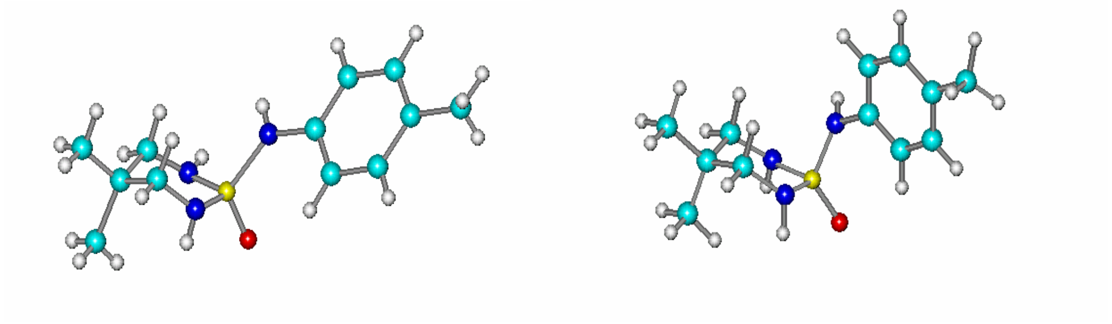
atomic distances for crystallography data along with optimized structures in three level HF, B3LYP and BLYP at three basis set 6-31+G**, 6-31++G** and 6-311++G** are summarized in table 1. More data obtaining with B3LYP and BLYP levels for atomic distances are bigger than their related experimental distance.

Absolute different of experimental data and calculation results is shown in table *.With considering to table * the high different atomic distances between crystal and optimized structure is related to P-N and P-O distances, that the best level for P-N distances are resulted by HF and for P-O is obtained by B3LYP.

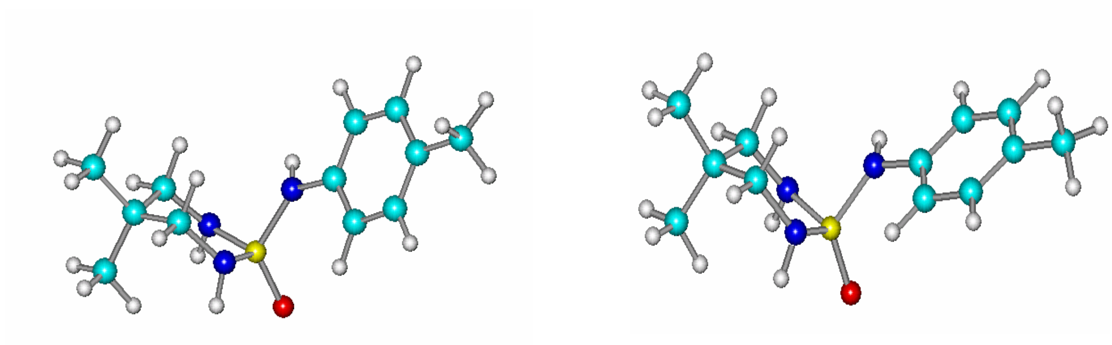
Totally, in toluene ring the resulted amounts of optimized structure is near to experiment but this matter exists for phosphor diamide ring lowly (fig.1).

Table 1. Internuclear distances (°A) of crystal form and optimized structures

Group	Exp	HF/+	HF/++	HF/311	B3/+	B3/++	B3/311	B/+	B/++	B/311
P1-O1	1.485	1.463	1.463	1.458	1.490	1.491	1.486	1.507	1.508	1.502
P1-N1	1.650	1.666	1.659	1.657	1.686	1.686	1.683	1.711	1.711	1.708
P1-N2	1.640	1.659	1.666	1.664	1.693	1.694	1.689	1.718	1.718	1.714
P1-N3	1.650	1.663	1.663	1.659	1.688	1.688	1.686	1.715	1.714	1.712
N1-C1	1.478	1.465	1.461	1.461	1.472	1.473	1.472	1.490	1.491	1.49
C1-C2	1.536	1.545	1.545	1.545	1.553	1.554	1.553	1.568	1.568	1.567
N2-C3	1.476	1.461	1.465	1.466	1.472	1.478	1.477	1.494	1.495	1.492
C2-C3	1.529	1.545	1.545	1.544	1.553	1.553	1.552	1.568	1.567	1.566
C2-C4	1.525	1.534	1.534	1.534	1.538	1.537	1.538	1551	1.551	1.549
C2-C5	1.526	1.535	1.535	1.534	1.539	1.539	1.538	1.551	1.551	1.549
N3-C6	1.407	1.423	1.423	1.423	1.415	1.416	1.414	1.429	1.429	1.428
C6-C7	1.399	1.389	1.388	1.388	1.403	1.403	1.400	1.415	1.415	1.411
C6-C11	1.393	1.388	1.388	1.386	1.402	1.402	1.399	1.412	1.412	1.410
C7-C8	1.385	1.385	1.385	1.384	1.394	1.395	1.391	1.404	1.404	1.401
C8-C9	1.393	1.391	1.391	1.389	1.401	1.401	1.398	1.412	1.412	1.409
C9-C10	1.385	1.390	1.390	1.388	1.402	1.402	1.398	1.412	1.412	1.408
C9-C12	1.507	1.512	1.512	1.512	1.511	1.512	1.510	1.521	1.521	1.519
C10-C11	1.390	1.387	1.387	1.386	1.395	1.395	1.393	1.405	1.405	1.402



Exp HF



B3LYP BLYP

Fig. 2. Crystalline and optimized structures

Also number, minimum, maximum, sum, mean and standard deviation of distances different are calculated by SPSS (table 2). This program helps us with evaluating of results and calculation methods.

As shown in Table 2, the better results are obtained by HF method with 6-31+G** basis set (in less Standard deviation: .0063) . It is important notice, in HF method, exploring of 311 (triplet-ξ) in valance shell instead of 31(doublet- ξ) and also ++ instead of + not only doesn't modify results but also increases standard deviation (std. deviation: .0063, .0069 and .0071 for 6-31+G**, 6-31++G** and 6-311++G** respectively). In table 1, the distance parameters producing with 6-31G** basis set aren't displayed (for abbreviation) but in table 2 this basis set is evaluated.

Table 2 The statistical data for internuclear distances differenent between experimental and calculation data

Group	N	Minimum	Maximum	Sum	Mean	Std. Deviation
|Exp. -HF/6-31G**|	18	.001	.026	.193	.01072	.007061
| Exp. -HF/6-31+G**|	18	.000	.022	.187	.01039	.006251
| Exp. -HF/6-31++G**|	18	.000	.026	.188	.01044	.006947
| Exp. -HF/6-311++G**|	18	.001	.027	.186	.01033	.007054
| Exp. –B3LYP/6-31G**|	18	.053	.001	.259	.01439	.014825
| Exp. –B3LYP/6-31+G**|	18	.053	.004	.273	.01517	.013984
| Exp. –B3LYP/6-31++G**|	18	.054	.002	.275	.01528	.014170
| Exp. –B3LYP/6-311++G**|	18	.049	.001	.235	.01306	.013765
| Exp. –BLYP/6-31G**|	18	.078	.011	.505	.02806	.019597
| Exp. –BLYP/6-31+G**|	18	.078	.012	.529	.02939	.019181
| Exp. –BLYP/6-31++G**|	18	.078	.013	.530	.02944	.018937
| Exp. –BLYP/6-311++G**|	18	.074	.011	.482	.02678	.018913
Valid N (listwise)	18					

Internal angles

The amounts of internal angles are shown in table 3 that contains with angles of crystal (exp.) and calculated structures including HF/6-31+G** (HF/+), HF/6-31++G** (HF/++) , HF/6-311G** (HF/311), B3LYP/6-31+G** (B3/+), B3LYP/6-31++G** (B3/++), B3LYP/6-311++G** (B3/311), BLYP/6-31+G** (B/+), BLYP/6-31++G** (B/++), BLYP/6-311++G** (B/311).

Table 3. Internal angles (°) of crystalline form and calculated structures

Group	**Exp.**	**HF/+**	**HF/++**	**HF/311**	**B3/+**	**B3/++**	**B3/311**	**B/+**	**B/++**	**B/311**
O1-P1-N2	115.2	113.3	113.3	113.3	114.0	114.0	114.0	113.9	113.9	114.1
O1-P1-N3	111.5	119.4	119.4	119.3	120.2	120.1	120.0	120.7	120.7	120.5
N2-P1-N3	104.3	100.1	100.1	100.1	98.5	98.5	98.6	97.6	97.6	97.8
O1-P1-N1	109.4	113.3	112.2	112.2	112.2	112.2	112.2	112.3	112.3	112.4
N2-P1-N1	105.5	107.0	107.0	107.0	107.4	107.4	107.4	107.7	107.7	107.4
N3-P1-N1	110.8	103.5	103.5	103.5	103.0	103.0	103.2	102.9	102.9	103.0
C1-N1-P1	118.1	118.7	118.7	118.8	118.0	118.0	118.1	117.5	117.6	117.9
N1-C1-C2	113.0	114.4	114.4	114.4	115.0	115.0	115.0	115.6	115.5	115.4
C3-N2-P1	123.0	118.8	118.8	118.9	118.4	118.4	118.6	118.0	117.9	118.5
C5-C2-C4	110.1	109.5	109.5	109.5	109.7	109.8	109.9	109.7	109.7	109.7
C5-C2-C3	111.2	110.6	110.6	110.6	110.6	110.6	110.6	110.8	110.9	110.9
C4-C2-C3	107.5	108.4	108.4	108.3	108.3	108.4	108.3	108.2	108.3	108.2
C5-C2-C1	110.7	110.7	110.7	110.7	110.8	110.6	110.7	110.8	110.9	110.9
C4-C2-C1	108.8	108.5	108.5	108.5	108.4	108.3	108.4	108.3	108.3	108.3
C3-C2-C1	108.5	109.2	109.2	109.1	108.9	108.9	108.9	108.8	108.9	108.9
C6-N3-P1	128.0	125.8	125.8	125.9	128.6	128.6	128.9	128.7	128.7	128.9
N2-C3-C2	113.0	115.0	115.0	115.0	115.6	115.6	115.5	116.0	116.0	115.9
C11-C6-C7	118.6	119.0	119.0	118.9	118.6	118.6	118.6	118.5	118.5	118.5
C11-C6-N3	122.7	122.0	122.0	122.2	122.7	122.6	122.6	123.0	122.9	122.9
C7-C6-N3	118.7	118.8	118.8	118.9	118.8	118.8	118.8	118.5	118.5	118.6
C8-C7-C6	120.3	120.5	120.5	120.5	120.7	120.7	120.7	120.6	120.6	120.7
C7-C8-C9	121.6	121.2	121.2	121.2	121.4	121.4	121.4	121.5	121.5	121.4
C10-C9-C8	117.5	117.6	117.6	117.7	117.3	117.3	117.3	117.2	117.2	117.2
C10-C9-C12	121.2	121.2	121.2	121.2	121.3	121.3	121.3	121.4	121.4	121.4
C8-C9-C12	121.3	121.2	121.2	121.2	121.5	121.4	121.4	121.4	121.4	121.4
C9-C10-C11	121.9	121.7	121.7	121.6	122.0	122.0	122.0	122.2	122.2	122.1
C10-C11-C5	120.1	120.0	120.0	120.0	120.0	120.0	120.1	120.0	120.0	120.0

Absolute angles different of experimental data and calculation results is shown in table **. The high difference of atomic angles between experimental data and optimized structures is related to P atom angles (especially in N3-P1-N1 and N3-P1-O1, it means, the most far between experiment and calculation exists in angles of N3 with two rings. however the better method for these angles is HF.

Also number, minimum, maximum, sum, mean and standard deviation for amounts of table** for every level are calculated by SPSS (table 4). Table 4 shows that HF method results better data. The less Standard deviation (2.0886) is related to HF/6-311++G**. Notice that difference of standard deviation for this level in compared with HF/6-31++G** (2.1102) is no considerable.

In table 3, the distance parameters producing with 6-31G** basis set aren't brought (for abbreviation) but in table 4 this basis set is evaluated.

Dihedral angles

The Torsion angles for crystallography data along with optimized structures in three level HF, B3LYP and BLYP at three basis set 6-31+G**, 6-31++G** and 6-311++G** are shown in table 5.

The selected torsion angles which the difference of experimental and calculating torsion angles is high relatively are summarized in table ***. the more difference between experiment and calculations data are seen in torsion angles between two ring and inside of phosphor diamide ring .

Table 4. The statistical data for internal angles difference between experimental and calculation data

Group	N	Minimum	Maximum	Sum	Mean	Std. Deviation
|Exp. –HF/6-31G**|	27	.0	8.3	42.2	1.563	2.2183
|Exp. –HF/6-31+G**|	27	.0	7.9	42.3	1.567	2.1460
|Exp. –HF/6-31++G**|	27	.0	7.9	41.2	1.526	2.1102
|Exp. –HF/6-311++G**|	27	.0	7.8	41.0	1.519	2.0886
|Exp. –B3LYP/6-31G**|	27	.0	9.4	48.3	1.789	2.5863
|Exp. –B3LYP/6-31+G**|	27	.0	8.7	42.2	1.563	2.4115
|Exp. –B3LYP/6-31++G**|	27	.0	8.6	42.2	1.563	2.3991
|Exp. –B3LYP/6-311++G**|	26	.0	8.5	41.2	1.585	2.3847
|Exp. –BLYP/6-31G**|	27	.0	9.7	49.1	1.819	2.7230
|Exp. –BLYP/6-31+G**|	27	.1	9.2	46.5	1.722	2.5574
|Exp. –BLYP/6-31++G**|	27	.1	9.2	46.5	1.722	2.5613
|Exp. –BLYP/6-311++G**|	27	.1	9.0	44.6	1.652	2.4896
Valid N (listwise)	26					

Table 5. Torsion angles (°) of crystalline form and optimized structures

Group	Exp.	HF/+	HF/++	HF/311	B3/+	B3/++	B3/311	B/+	B/++	B/311
O1-P1-N1-C1	156.8-	158.2-	158.2-	157.8-	157.8-	157.8-	157.5-	157.6-	157.6-	157.2
N2-P1-N1-C1	32.3-	33.4-	33.4-	33.0-	31.8-	31.8-	31.5-	31.3-	31.4-	30.9-
N3-P1-N1-C1	79.9	71.8	71.8	72.3	71.6	71.6	72.0	71.1	71.1	71.7
P1-N1-C1-C2	53.4	49.1	49.1	48.9	49.0	48.9	48.8	48.6	48.6	48.6
O1-P1-N2-C3	148.5	156.1	156.1	155.8	155.0	155.0	154.8	155.1	155.1	154.4
N3-P1-N2-C3	89.0-	75.5-	75.5-	76.0-	76.5-	76.5-	77.0-	76.4-	76.4-	77.2-
N1-P1-N2-C3	27.7	32.0	32.0	31.6	30.0	30.1	29.8	29.9	29.9	29.1
N1-C1-C2-C5	59.4	64.7	64.7	64.7	63.4	63.3	63.3	63.7	63.8	63.7
N1-C1-C2-C4	179.5-	175.3-	175.3-	175.2-	176.2-	176.2-	176.2-	175.9-	175.8-	175.9-
N1-C1-C2-C3	62.8-	57.3-	57.3-	57.3-	58.5-	58.5-	58.5-	58.4-	58.4-	58.4-
O1-P1-N3-C6	39.0-	65.3-	65.3-	65.4-	64.4-	64.5-	65.3-	58.5-	58.5-	58.0
N2-P1-N3-C6	163.8-	170.6	170.6	170.5	171.3	171.4	170.5	177.8	177.9	178.1
N1-P1-N3-C6	83.1	60.2	0.2	60.1	61.2	61.2	60.3	67.6	67.6	68.1
P1-N2-C3-C2	42.3-	46.6-	46.6-	46.3-	45.4-	45.5-	45.3-	45.5-	45.5-	44.8-
C5-C2-C3-N2	66.0-	65.8-	65.8-	65.9-	65.3-	65.2-	65.2-	65.4-	65.4-	65.8-
C4-C2-C3-N2	173.4	174.2	174.2	174.1	174.4	174.4	174.3	174.3	174.3	173.9
C1-C2-C3-N2	55.9	56.2	56.2	56.1	56.7	56.8	56.6	56.8	56.8	56.4
P1-N3-C6-C11	6.3-	31.9	31.9	33.6	4.5	4.5	5.0	26.8-	26.9-	27.2-
P1-N3-C6-C7	172.7	148.8-	148.8-	147.1-	175.5-	175.5-	175.0-	154.6	154.6	154.4
C11-C6-C7-C8	6.-	5.	5.	4.	1.-	1.-	2.-	3.-	3.-	2.-
N3-C6-C7-C8	179.6-	178.8-	178.8-	178.9-	179.8	179.8	179.8	178.3	178.3	178.3
C6-C7-C8-C9	1.	1.4-	1.4-	1.4-	8.-	8.-	8.-	3.	3.	2.
C7-C8-C9-C10	5.	1.0	1.0	1.0	9.	9.	9.	0.	0.	0.
C7-C8-C9-C12	178.0-	178.0-	178.0-	178.0-	178.2-	178.2-	178.2-	178.8-	178.8-	178.9-
C8-C9-C10-C11	4.-	3.	3.	3.	1.-	1.-	1.-	3.-	4.-	4.-
C12-C9-C10-C11	178.0	179.3	179.3	179.3	179.0	179.0	179.0	178.5	178.4	178.6
C9-C10-C11-C6	1.-	1.2-	1.2-	1.2-	8.-	8.-	9.-	4.	5.	5.
C7-C6-C11-C10	6.	8.	8.	9.	9.	9.	1.0	0.	1.-	1.-
N3-C6-C11-C10	179.6	179.9-	179.9-	179.9-	179.0-	179.0-	179.0-	178.6-	178.6-	178.5-

Also number, minimum, maximum, sum, mean and standard deviation of absolute torsion different are calculated by SPSS (table 6). This program helps us to evaluate results and calculation methods. In table 6, it is looked, the best level of calculation for dihedral angle is B3LYP/6-31+G** (with 6.1941 standard deviation) although the less mean of difference is related to B3LYP/6-311++G** (with 3.989 mean).

Table 6. The statistical data for dihedral angles differenent between experimental and calculation data

Group	N	Minimum	Maximum	Sum	Mean	Std. Deviation
|Exp. –HF/6-31G**|	29	.1	27.7	173.6	5.986	8.1915
|Exp. –HF/6-31+G**|	29	.0	26.3	172.1	5.933	8.2708
|Exp. –HF/6-31++G**|	29	.0	26.3	172.1	5.933	8.2708
|Exp. –HF/6-311++G**|	29	.0	27.3	172.9	5.963	8.5717
|Exp. –B3LYP/6-31G**|	28	.0	29.5	125.4	4.479	7.2777
|Exp. –B3LYP/6-31+G**|	29	.2	25.4	117.0	4.035	6.1941
|Exp. –B3LYP/6-31++G**|	29	.2	25.5	117.6	4.056	6.2035
|Exp. –B3LYP/6-311++G**|	29	.2	26.3	115.7	3.989	6.3636
|Exp. –BLYP/6-31G**|	29	.0	22.2	156.5	5.397	6.8883
|Exp. –BLYP/6-31+G**|	29	.1	20.5	147.9	5.101	6.5119
|Exp. –BLYP/6-31++G**|	29	.0	20.6	148.0	5.104	6.5315
|Exp. –BLYP/6-311++G**|	29	.0	20.9	143.2	4.939	6.5097
Valid N (listwise)	28					

Result. it is looked, in totally, the best calculation method for optimization of structural properties in cyclic phosphor amidates is HF/6-31++G**.

Comparing of two conformers

In section 3-1 to 3-3, gaussian calculation was done by using the crystalline forms [4] as initial geometries and after optimization by three methods we received figure 2. Hereafter, the optimized calculation is done by using of hyper chem. model built on structure of figure 1 as initial geometry. We want to know: does this form of input give us proper optimized structures? (many phosphoramidates dosen't display crystalline form.)

With the exploring of Model built of hyper chem program on noticed structure (fig. 1) and optimization of it, structures in fig. 3 are resulted.

Table 7. Calculating distances (°A) by using of crystal and hyper chem as initial geometry

Distances	Exp.	HF/+	HF/++	HF/+M	HF/++M
1	1.485	1.463	1.463	1.466	1.466
2	1.650	1.666	1.659	1.664	1.664
3	1.640	1.659	1.666	1.674	1.674
4	1.650	1.663	1.663	1.663	1.663
5	1.478	1.465	1.461	1.466	1.466
6	1.536	1.545	1.545	1.538	1.538
7	1.476	1.461	1.465	1.466	1.468
8	1.529	1.545	1.545	1.538	1.538
9	1.525	1.534	1.534	1.536	1.534
10	1.526	1.535	1.535	1.535	1.535
11	1.407	1.423	1.423	1.417	1.417
12	1.399	1.389	1.388	1.387	1.388
13	1.393	1.388	1.388	1.394	1.394
14	1.385	1.385	1.385	1.390	1.390
15	1.393	1.391	1.391	1.386	1.386
16	1.385	1.390	1.390	1.394	1.394
17	1.507	1.512	1.512	1.512	1.510
18	1.390	1.387	1.387	1.383	1.383

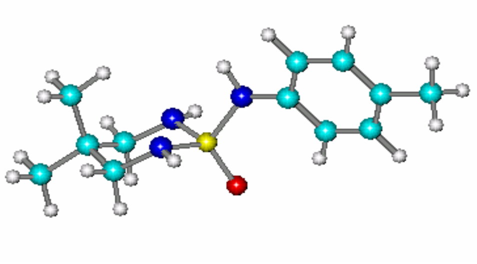
Table 8. Calculating atomic angles(°) by using of crystal and hyper chem as initial geometry

Angles	Exp.	HF/+	HF/++	HF/+M	HF/++M
1	115.2	113.3	113.3	115.7	118.4
2	111.5	119.4	119.4	112.3	112.3
3	104.3	100.1	100.1	107.7	102.0
4	109.4	113.3	112.2	118.4	115.8
5	105.5	107.0	107.0	99.10	99.01
6	110.8	103.5	103.5	102.0	107.6
7	118.1	118.7	118.7	118.7	117.9
8	113.0	114.4	114.4	112.0	111.7
9	123.0	118.8	118.8	118.0	118.6
10	110.1	109.5	109.5	109.5	109.5
11	111.2	110.6	110.6	108.5	108.4
12	107.5	108.4	108.4	110.7	110.7
13	110.7	110.7	110.7	108.4	108.4
14	108.8	108.5	108.5	110.7	110.8
15	108.5	109.2	109.2	109.1	109.0
16	128.0	125.8	125.8	127.9	127.8
17	113.0	115.0	115.0	111.8	112.0
18	118.6	119.0	119.0	118.8	118.8
19	122.7	122.2	122.2	122.2	122.3
20	118.7	118.8	118.8	118.9	118.9
21	120.3	120.5	120.5	120.7	120.6
22	121.6	121.2	121.2	121.3	121.3
23	117.5	117.6	117.6	117.3	117.3
24	121.2	121.2	121.2	120.9	120.9
25	121.3	121.2	121.2	121.8	121.8
26	121.9	121.7	121.7	122.2	122.2
27	120.1	120.0	120.0	119.8	119.8

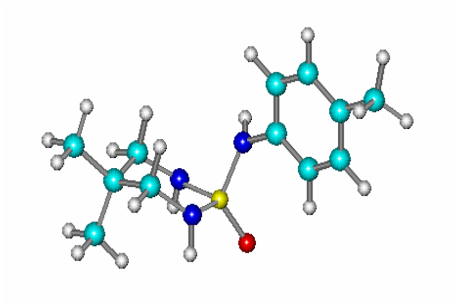
Table 9. Calculating torsion angles (°) by using of crystal and hyper chem as initial geometry

Torsions	Exp.	HF/+	HF/++	HF/+M	HF/++M
1	156.8-	158.2-	158.2-	78.2-	76.8
2	32.3-	33.4-	33.4-	49.5	49.2-
3	79.9	71.8	71.8	155.2	159.5-
4	53.4	49.1	49.1	59.3-	58.2
5	148.5	156.1	156.1	76.9	78.1-
6	89.0-	75.5-	75.5-	159.4-	155.4
7	27.7	32.0	32.0	49.0-	49.7
8	59.4	64.7	64.7	175.4	174.6-
9	179.5-	175.3-	175.3-	64.4-	65.3
10	62.8-	57.3-	57.3-	57.6	56.9-
11	39.0-	65.3-	65.3-	32.8-	32.8-
12	163.8	170.6	170.6	160.6-	95.8
13	83.1	60.2	60.2	95.8	160.6-
14	42.3-	46.6-	46.6-	58.0	59.4-
15	66.0-	65.8-	65.8-	174.7-	175.4
16	173.4	174.2	174.2	65.3	64.4-
17	55.9	56.2	56.2	56.8-	57.6
18	41.9	31.9-	31.9-	6.3-	18
19	172.7	148.8	148.8	140.5-	140.2-
20	6.-	5.-	5.-	4.	4.
21	179.6-	178.8-	178.8-	177.4-	177.4-
22	1.	1.4	1.4	9.-	9.-
23	5.	1.0	1.0	5.	5.
24	178.0-	178.0-	178.0-	179.6-	179.6-
25	4.-	3.-	3.-	4.	4.
26	178.0	179.3	179.3	179.5-	179.6-
27	1.-	1.2-	1.2-	9.-	8.-
28	6.	5.	8.	5.	5.
29	179.6-	179.9-	179.9-	178.2	178.1

Exploring methods are HF/6-31+G** and HF/6-31++G** (see result). Atomic distances (table7), internal angles (table8) and dihedral angles (table9) for crystal (exp.) and optimized structures resulted with crystalline forms (HF/+ and HF/++) and hyperchem model built (HF/+M and HF/++M) as initial geometries are brought below. The difference of experiment and calculating structures is calculated by SPSS (it isn't shown) and also minimum, maximum, sum, mean and standard deviation of different for distances (table10), angles (table 11) and torsions (table12) are calculated by SPSS.



Crystal input



Hyperchem input

Fig. 3. Optimized structures obtaining of crystal and hyperchem inputs at HF/6-31++G**

Table 10. The statistical evaluation of atomic distances difference between experimental and calculation data for crystal and hyperchem model built (M) inputs

Group	N	Minimum	Maximum	Sum	Mean	Std. Deviation
|Exp. –HF/6-31+G**|	18	.000	.022	.187	.01039	.006251
|Exp. –HF/6-31++G**|	18	.000	.026	.188	.01044	.006947
|Exp. –HF/6-31+G**|M	18	.001	.034	.189	.01050	.007286
|Exp. –HF/6-31++G**|M	18	.001	.034	.182	.01011	.007403

Table 11. The statistical evaluation of atomic angles difference between experimental and calculation data for crystal and hyperchem model built (M) inputs

Group	N	Minimum	Maximum	Sum	Mean	Std. Deviation
|Exp. –HF/6-31+G**|	27	.0	7.9	42.3	1.567	2.1460
|Exp. –HF/6-31++G**|	27	.0	7.9	41.2	1.526	2.1102
|Exp. –HF/6-31+G**|M	27	.1	9.0	51.3	1.900	2.5606
|Exp. –HF/6-31++G**|M	27	.2	6.5	43.9	1.626	1.8536

Table 12. The statistical evaluation of torsion angles difference between experimental and calculation data for crystal and hyperchem model built (M) inputs

Group	N	Minimum	Maximum	Sum	Mean	Std. Deviation
|Exp. –HF/6-31+G**|	29	.0	26.3	172.1	5.933	8.2708
|Exp. –HF/6-31++G**|	29	.0	26.3	172.1	5.933	8.2708
|Exp. –HF/6-31+G**|M	29	.0	116.0	908.5	31.327	41.0840
|Exp. –HF/6-31++G**|M	29	.0	115.2	1041.4	35.910	41.8401

Table 10 shows optimized structures obtained of hyperchem model build as initial geometry input has low dispute with experiment (std deviation: 0.0073, 0.0074) and it is similar to crystal input almost (std deviation 0.0062, 0.0069).Also table 11 shows results obtained of hyperchem input is compatible with experiment well (std deviation: 2.6, 1.9) even it is better than crystal input (std deviation: 2.1). but statistical calculation for torsion angles(table12) appears results arising with hyperchem isn't useful (std deviation: 41.1, 41,8).

CONCLUSION

Many times experimental structures are not known and theoretical means are the only choice. So the evaluation of calculation methods and selection of the best of them is very important. The spherical geometry helps to dissolve very problems including coupling costant dependce on atomic and angles atomic and so on. So when the crystallization is difficult, the calculation displays the basis role.

The first, with using of experimental data, the best level was determined for atomic distances, atomic angles and torsion angles that they are HF/6-31+G** with .006 °A std. deviation for atomic distances, HF/6-311++G** with 2.09° std. deviation for atomic angles that is near to HF/6-31++G** with 2.11° std. deviation and B3LYP/6-31+G** with 6.19° std. deviation for torsion (dihedral) angle. We selected HF/6-31++G** because the coupling constant depends on distance and angle more than torsion.

Then hyper chem. model build input for Gaussian as initial geometry was compared with experimental data. These calculation were done in HF/6-31+G** and HF/6-31++G**. It is shown, this input replies very well for atomic distances with .007 °A std. deviation and atomic angles with 1.9 ° std. deviation but never for torsion angle (with 41.8° std. deviation)

Acknowledgements

We thank SGS Company for its helpful support of this research.

REFERENCES

1. D. Saboulard, L. Naesens, D. Cahard and et al *Molecular Pharmacology* Vol. 56, Issue 4, 693-704, October 1999
2. K. Gholivand, M. Pourayoubi, S. Farfhidian and et al, *Analytical Sciences* (2005), Vol.21 x55-6
3. K. Gholivand, Z. Sharifinia, M. Pourayoubi and et al, *Z.Anorg. Allg. Chem*. (2005) Vol.631, 961-7
4. kay hawell, *biomedical computing requirements for HPCS*
5. K. Gholivand, Z. Sharifinia, M. Pourayoubi, *Z. Naturforsch* (2005) 60b 67-74
6. Louis D. Quin and John G. Verkade *phosphorus NMR spectral properties in compound characterization* 1994
7. R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules,* oxford university press, Newyork 1989
8. J.K. Labanowski, J.W.Aandzelm(Eds.), *Density Functional Methods in Chemistry*, Springer, Newyork, 1991
9. J.M.Seminario, (Eds), *Recent Development and Applications of Modern Density Functional Theory*, Elsevier, Amsterdam, The Netherlands 1996
10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98* (Revision A.1), Gaussian, Inc., Pittsburgh PA, 1998.

Table*. Absolute different experimental data with calculation resulted for atomic distances

Group	|Exp.- HF/+|	|Exp.- HF/++|	|Exp.- HF/311|	|Exp.- B3/+|	|Exp.- B3/++|	|Exp.- B3/311|	|Exp.- B/+|	|Exp.- B/++|	|Exp.- B/311|
P1-O1	.022	.022	.027	.005	.006	.001	.۰۲۲	.۰۲۳	.۰۱۷
P1-N1	.۰۱0	.۰۰۹	.۰۰۷	.۰۳۶	.۰۳۶	.۰۳۳	.۰۶۱	.۰۶۱	.۰۱۷
P1-N2	.019	.۰۲۶	.۰۲۴	.۰۵۳	.۰۵۴	.۰۴۹	.۰۷۸	.۰۷۸	.۰۷۴
P1-N3	.۰۱۳	.۰۱۳	.۰۰۹	.038	.۰۳۸	.۰۳۶	.۰۶۵	.۰۶۴	.۰۶۲
N1-C1	.۰۱۳	.۰۱۷	.۰۱۷	.۰۰۶	.۰۰۵	.۰۰۶	.۰۱۲	.۰۱۳	.۰۱۱
C1-C2	.009	.۰۰۹	.۰۰۹	.۰۱۷	.۰۱۸	.017	.۰۳۲	.۰۳۲	.031
N2-C3	.۰۱۵	.۰۱۱	.۰۱۰	.۰۰۴	.002	.۰۰۱	.۰۱۸	.۰۱۹	.۰۱۶
C2-C3	.۰۱۶	.۰۱۶	.۰۱۵	.024	.024	.023	.۰۳۹	.038	.۰۳۷
C2-C4	.009	.009	.009	.013	.۰۱۲	.013	.۰۲۶	.۰۲۶	.۰۲۴
C2-C5	.009	.009	.۰۰۸	.013	.013	.۰۱۲	.۰۲۵	.۰۲۵	.023
N3-C6	.۰۱۶	.۰۱۶	.۰۱۶	.۰۰۸	.۰۰۹	.007	.۰۲۲	.۰۲۲	.۰۲۱
C6-C7	.۰۱۰	.۰۱۱	.۰۱۱	.۰۰۴	.۰۰۴	.۰۰۱	.۰۱۶	.۰۱۶	.۰۱۲
C6-C11	.۰۰۵	.۰۰۵	.۰۰۷	.۰۰۹	.۰۰۹	.۰۰۶	.۰۱۹	.۰۱۹	.۰۱۷
C7-C8	.۰۰۰	.۰۰۰	.۰۰۱	.۰۰۹	.۰۱۰	.۰۰۶	.019	.019	.۰۱۶
C8-C9	.۰۰۲	.۰۰۲	.۰۰۴	.۰۰۸	.۰۰۸	.۰۰۵	.۰۱۹	.۰۱۹	.۰۱۶
C9-C10	.۰۰۵	.۰۰۵	.۰۰۳	.۰۱۷	.۰۱۷	.۰۱۳	.۰۲۷	.۰۲۷	.۰۲۳
C9-C12	.۰۰۵	.۰۰۵	.۰۰۵	.۰۰۴	.۰۰۵	.۰۰۳	.۰۱۴	.۰۱۴	.۰۱۲
C10-C11	.۰۰۳	.۰۰۳	.۰۰۴	.۰۰۵	.۰۰۵	.۰۰۳	.۰۱۵	.۰۱۵	.۰۱۲

TABLE **. Absolute differents experimental data with calculation resulted for internal angles

Group	|Exp.- HF/+|	|Exp.- HF/++|	|Exp.- HF/311|	|Exp.- B3/+|	|Exp.- B3/++|	|Exp.- B3/311|	|Exp.- B/+|	|Exp.- B/++|	|Exp.- B/311|
P1-O1-N2	1.9	1.9	1.9	1.2	1.2	1.2	1.3	1.3	1.1
P1-N1-N3	7.9	7.9	7.8	8.7	8.6	8.5	9.2	9.2	9.0
N2-P1-N3	4.2	4.2	4.2	5.8	5.8	5.7	6.7	6.7	6.5
O1-P1-N1	3.9	2.8	2.8	2.8	2.8	2.8	2.9	2.9	3.0
N2-P1-N1	1.5	1.5	1.5	1.9	1.9	1.9	2.2	2.2	1.9
N3-P1-N1	7.3	7.3	7.3	7.8	7.8	7.6	7.9	7.9	7.8
C1-N1-P1	.6	.6	.7	.1	.1	0.	6	.5	.2
N1-C1-C2	1.4	1.4	1.4	2.0	2.0	2.0	2.6	2.5	2.4
C3-N2-P1	4.2	4.2	4.1	4.6	4.6	4.4	5.0	5.1	4.5
C5-C2-C4	.6	.6	.6	.4	.3	.2	.4	.4	.4
C5-C2-C3	.6	.6	.6	.6	.6	.6	.4	.3	.3
C4-C2-C3	.9	.9	.8	.8	.9	.8	.7	.8	.7
C5-C2-C1	0.	0.	0.	.1	.1	0.	.1	.2	.2
C4-C2-C1	.3	.3	.3	.4	.5	.4	.5	.5	.5
C3-C2-C1	.7	.7	.6	.4	.6	.4	.3	.4	.4
C6-N3-P1	2.2	2.2	2.1	.6	.6	.9	.7	.7	.9
N2-C3-C2	2.0	2.0	2.0	2.6	2.6	2.5	3.0	3.0	2.9
C11-C6-C7	.4	.4	.3	0.	0.	0.	.1	.1	.1
C11-C6-N3	.5	.5	.5	0.	.1	.1	.3	.2	.2
C7-C6-N3	.1	.1	.2	.1	.1	.1	.2	.2	.1
C8-C7-C6	.2	.2	.2	.4	.4	.4	.3	.3	.4
C7-C8-C9	.4	.4	.4	.2	.2	.2	.1	.1	.2
C10-C9-C8	.1	.1	.2	.2	.2	.2	.3	.3	.3
C10-C9-C12	0.	0.	0.	.1	.1	.1	.2	.2	.2
C8-C9-C12	.1	.1	.1	.2	.1	.1	.1	.1	.1
C9-C10-C1	.2	.2	.3	.1	.1	.1	.3	.3	.2

TABLE *.** Absolute differents experimental data with calculation resulted for torsion angles

Group	**|Exp.- HF/+|**	**|Exp.- HF/++|**	**|Exp.- HF/311|**	**|Exp.- B3/+|**	**|Exp.- B3/++|**	**|Exp.- B3/311|**	**|Exp.- B/+|**	**|Exp.- B/++|**	**|Exp.- B/311|**
N3-P1-N1-C1	8.1	8.1	7.6	8.3	8.3	7.9	8.8	8.8	8.2
P1-N1-C1-C2	4.3	4.3	4.5	4.4	4.5	4.6	4.8	4.8	4.8
O1-P1-N2-C3	7.6	7.6	7.3	6.5	6.5	6.3	6.6	6.6	5.9
N3-P1-N2-C3	13.5	13.5	13.0	12.5	12.5	12.0	12.6	12.6	11.8
N1-P1-N2-C3	4.3	4.3	3.9	2.3	2.4	2.1	2.2	2.2	1.4
N1-C1-C2-C5	5.3	5.3	5.3	4.0	3.9	3.9	4.3	4.4	4.3
N1-C1-C2-C4	4.2	4.2	4.3	3.3	3.3	3.3	3.6	3.7	3.6
N1-C1-C2-C3	5.5	5.5	5.5	4.3	4.3	4.3	4.4	4.4	4.4
O1-P1-N3-C6	26.3	26.3	26.4	25.4	25.5	26.3	19.5	19.5	19.0
N2-P1-N3-C6	6.8	6.8	6.7	7.5	7.6	6.7	14.0	14.1	14.3
N1-P1-N3-C6	22.9	22.9	23.0	21.9	21.9	22.8	15.5	15.5	15.0
P1-N2-C3-C2	4.3	4.3	4.0	3.1	3.2	3.0	3.2	3.2	2.5
P1-N3-C6-C11	25.6	25.6	27.3	1.8	1.8	1.3	20.5	20.6	20.9
P1-N3-C6-C7	23.9	23.9	25.6	2.8	2.8	2.3	18.1	18.1	18.3