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Ab Initio Study and Its Comparison with X-ray Crystal Structure of 4-[1-(4-Chloro-phenylamino)-ethyl]-5-methyl-2-*p*-tolyl-2,4-dihydro-pyrazol-3-one

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The ab initio calculation of the title compound was carried out at HF as well as DFT level of theory. The full geometry optimization of the ligand was carried out using 6-31G(d) basis set. The results obtained were correlated with the single crystal X-ray data, also reported in this paper, shows close resemblance between these two. The influence of electron correlation effects also was studied by carrying out geometry optimization at the MP2 level. The attempts were also made to ascertain the most stable tautomer of the said compound.

KEY WORDS: acyl pyrazolone; ab initio claculation; X-ray structure; AM1; DFT.

INTRODUCTION

Acyl pyrazolone and their derivatives are important class of chelating compounds called heterocyclic β-diketones. Coordination chemists have taken keen interest in these moieties because of its selectivity and versatility in the solvent extraction of different metal ions. There are number of reports in which these classes of reagents are being used in solvent extraction of different metal ions [1–12]. Moreover, it is possible to design ligands by having different substituent, with either electron withdrawal or electron donor groups, into the different positions of the pyrazolone, particularly fourth position, to obtain better reagent for solvent extraction. Theoretical techniques can be useful in predicting the efficiency of the designed ligand in the solvent extraction. Therefore, the theoretical investigations on azoles derivatives are the area of interest for many researchers, in which the geometry was optimized at either semi-emperical level or using ab initio level of theory [13–23]. However there is no systematic studies deal with the correlation on the theoretical data with those obtained from X-ray crystal structure. The present communication describes the full geometry optimization of 4-[1-(4-chloro-phenylamino)-ethyl]-5-methyl-2-*p*-tolyl-2,4-dihydro-pyrazol-3-one (**I**) using 6-31G(d) basis set at HF level of theory as well as using DFT and AM1 semi empirical Hamiltonian. The obtained theoretical results were correlated with the experimental results derived from single crystal X-ray analysis. There is close resemblance between the theoretical calculations and solid state structural investigations indicate the accuracy of the method used for computation. The attempt is also made to ascertain the most stable tautomer of the compound using theory as well as experimental techniques.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

The synthesis and characterization of the compound using various physico-chemical techniques such as, m.p., microanalytical analysis, IR, ^{1}H and ^{13}C NMR data of the title compound has been reported by us recently [24]. Single crystals suitable for X-ray diffraction study of this compound were grown from acetonitrile solution by slow evaporation. Data collection was carried out on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at

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293 K. An absorption correction based on SADABS [25] was also applied. The structures was solved by direct methods (SHELXTL) and refined by least squares methods with atomic anisotropic thermal parameters for all non-hydrogen atoms [26, 27]. Except the hydrogen atom attached to the N1 nitrogen which is located from the Fourier difference map, all other hydrogen atoms were generated by using SHELXTL and refined as riding with the parent atom to which it is attached.

The full geometry optimization of **I** has been carried out in Cartesian coordinates by quasi-Newton-Raphson gradient method using the restricted Hartree-Fock (RHF) approximation with help of Gaussian 98 program package [28]. Symmetry restrictions were not applied. The standard basis set of Gauss functions 6-31G(d) [29, 30] was used. The choice of basis set was optimal taking into account the computational time required and a reasonable accuracy of the results. The influence of electron correlation effects also was studied by carrying out optimization at MP2/6-31G(d) level. The molecular geometry of **I** was also fully optimized at B3LYP/6-31G(d) level of theory. The 6-31G(d) basis set used Cartesian d functions.

In addition the equilibrium geometry of **I** has also been obtained by the semi-empirical AM1 [31] level of theory at the Restricted Hartree-Fock levels (RHF). The calculations were performed using MOPAC 7.0 [32].

Table I. Summary of Crystallographic Data for I

Chemical formula	$C_{19}H_{18}N_3O_1Cl_1$
Formula weight	339.81
Crystal system	Orthorhombic
Space group	*Aba*2
a (Å)	37.107(4)
b (Å)	12.1423(12)
c (Å)	7.3646(7)
Z	8
V (Å^3)	3318.2(6)
Radiation used λ (Å)	0.71073
ρ_{calcd} (g cm^{-3})	1.360
Abs. coeff., μ (cm^{-1})	2.41
θ_{max} (°)	28.27
h_{min}, h_{max}	−42, +47
k_{min}, k_{max}	−16, +15
l_{min}, l_{max}	−6, +9
completeness of data (%)	48.1
F (0 0 0)	1424
Total no. of recorded reflections	9815
Total no. of observed reflections	2128
R_{int}	0.0248
Number of parameter refined	224
Largest difference of peak and hole (−eÅ^{-3})	0.294 and −0.244
Minimum and maximum transmission	0.866 and 0.987
GOF on F^2	1.070
R_1^a/wR_2^b ($[I > 2\sigma(I)]$	0.0458/0.1183
R_1/wR_2 (all data)	0.0539/0.1320

$R_1^a = \sum||F_o| - |F_c||/\sum|F_o|.R_w^b = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)]^{1/2}$.

RESULTS AND DISCUSSION

X-ray Crystal Structure

ORTEP [33] diagram of compound **I** with atom numbering scheme is shown in Fig. 1. Summary of crystallographic data and selected bond lengths and angles are given in Tables I, II, and III, respectively. This compound can exist in two tautomeric forms such as enol and keto form in solid state (Fig. 2). The single crystal X-ray diffraction study on this compound clearly indicates that the present compound exists in keto from without any ambiguity. Structural data shows that the C(10)—O(1) distances in the pyrazole moiety of this compounds is 1.248(3) Å, which are significantly shorter than the distance found for >C—OH in some pyrazolone derivatives, 1.341, 1.346 Å [34] and 1.331 Å [35]; but well in the range of >C═O distances found in similar compounds and 1.254 Å [36]. Significantly longer C(7)—N(1) distances of the imine moiety 1.337(3) Å, compared to the C═N in pyrazolone compound, 1.298 Å [37] and 1.292 Å [36], and comparable to >C—N (1.339 Å) distance observed in similar compounds [38], further supports the keto from in the present case. The C═O and C—N distances observed in this compound is comparable and well within the range reported by Allen *et al*. [39] in compilation of CSD data base, which summarizes many bond distances for various types of bonds including required one. In addition to the above observation, the location of the hydrogen atom attached to the N1 atom from the difference Fourier map and the geometry around the atom C8 carbon shows the total values of the angle involving the C8 carbon (C(7)—C(8)—C(9) = 132.2(2)°, C(7)—C(8)—C(10) = 122.6(2)°, C(9)—C(8)—C(10) = 105.1 (2))° is 359.9°,

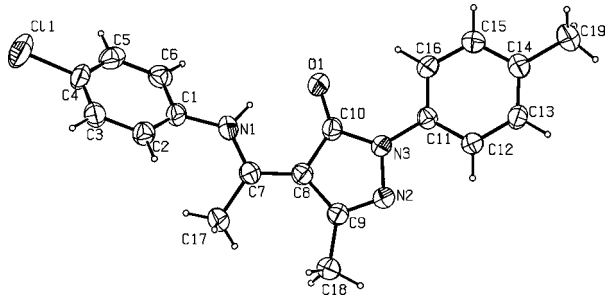


Fig. 1. ORTEP diagram (50% probability factor for thermal ellipsoid) with atom numbering scheme for compound **I**.

Table II. Theoretically Calculated (B3LYP/6-31G(d) level) and Experimentally Obtained Values of Selected Bond Lengths (in angstrom) for the Title Compound

	Calculated	Experimental[a]
C(1)—C(2)	1.403	1.387(4)
C(1)—C(6)	1.404	1.399(4)
C(1)—N(1)	1.411	1.419(4)
C(10)—C(8)	1.464	1.443(4)
C(10)—N(3)	1.385	1.38(3)
C(10)—O(1)	1.250	1.248(3)
C(11)—C(12)	1.402	1.391(4)
C(11)—C(16)	1.403	1.388(4)
C(11)—N(3)	1.418	1.428(3)
C(12)—C(13)	1.392	1.39(4)
C(13)—C(14)	1.401	1.385(4)
C(14)—C(15)	1.400	1.38(4)
C(14)—C(19)	1.511	1.514(4)
C(15)—C(16)	1.394	1.384(4)
C(2)—C(3)	1.394	1.388(4)
C(3)—C(4)	1.394	1.368(4)
C(4)—C(5)	1.396	1.387(5)
C(4)—Cl(1)	1.757	1.739(3)
C(5)—C(6)	1.392	1.375(4)
C(7)—C(17)	1.506	1.499(4)
C(7)—C(8)	1.392	1.39(4)
C(7)—N(1)	1.355	1.335(4)
C(9)—C(18)	1.500	1.496(4)
C(9)—C(8)	1.447	1.44(4)
C(9)—N(2)	1.308	1.295(4)
N(2)—N(3)	1.393	1.399(3)

[a]Figures in parentheses are Estimated Standard Deviations (ESDs).

Table III. Theoretically Calculated (B3LYP/6-31G(d) level) and Experimentally Obtained Values of Selected Bond Angles for the Title Compound

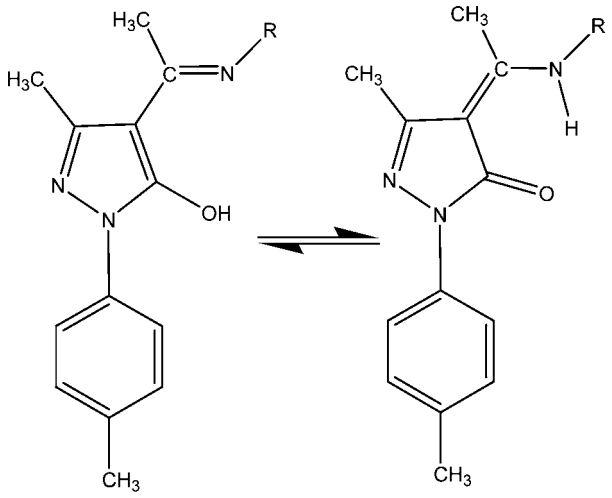
Angle (°)	Calculated	Experimental[a]
C(1)—C(2)—C(3)	120.5	119.4(3)
C(10)—N(3)—C(11)	129.3	129.5(2)
C(10)—N(3)—N(2)	111.7	112(2)
C(11)—C(12)—C(13)	119.9	119.6(3)
C(12)—C(11)—C(16)	119.4	119.5(3)
C(12)—C(11)—N(3)	119.2	118.9(2)
C(13)—C(14)—C(19)	121.3	121.3(3)
C(14)—C(13)—C(12)	121.8	121.7(3)
C(14)—C(15)—C(16)	122.1	122.6(3)
C(15)—C(14)—C(13)	117.4	117.3(3)
C(15)—C(14)—C(19)	121.4	121.3(3)
C(15)—C(16)—C(11)	119.5	119.2(3)
C(16)—C(11)—N(3)	121.3	121.6(2)
C(2)—C(1)—C(6)	119.0	119.6(3)
C(2)—C(1)—N(1)	123.3	122.9(3)
C(3)—C(4)—C(5)	120.7	121.6(3)
C(3)—C(4)—Cl(1)	119.6	119.4(2)
C(4)—C(3)—C(2)	119.7	120.0(3)
C(5)—C(4)—Cl(1)	119.7	118.9(2)
C(5)—C(6)—C(1)	120.8	120.9(3)
C(6)—C(1)—N(1)	117.6	117.2(3)
C(6)—C(5)—C(4)	119.4	118.4(3)
C(7)—C(8)—C(10)	122.2	122.6(3)
C(7)—C(8)—C(9)	133.1	132.3(3)
C(7)—N(1)—C(1)	130.6	129.9(3)
C(8)—C(7)—C(17)	122.8	122.9(3)
C(8)—C(9)—C(18)	130.5	129.5(3)
C(9)—C(8)—C(10)	104.7	105.0(2)
C(9)—N(2)—N(3)	107.7	106.6(2)
N(1)—C(7)—C(17)	119.8	120.3(3)
N(1)—C(7)—C(8)	117.4	116.9(3)
N(2)—C(9)—C(18)	118.3	118.6(2)
N(2)—C(9)—C(8)	111.2	111.8(3)
N(2)—N(3)—C(11)	119.0	118.4(2)
N(3)—C(10)—C(8)	104.7	104.4(2)
O(1)—C(10)—C(8)	128.2	129.4(3)
O(1)—C(10)—N(3)	127.1	126.2(3)

[a]Figures in parentheses are ESDs.

which is very close to 360°, rules out the possibility of enol form with the attachment of hydrogen with C(8). Thus it is clear from the X-ray studies establishing the keto form in the present compound in accordance with the series of similar compounds reported by us recently [24].

Packing diagram viewed down *C*-axis is shown in Fig. 3. Each molecule is having a strong intra molecular N—H···O—H-bonding interaction between the primary amino hydrogen and exoyclic ketonic oxygen. The intra molecular H-bonding interaction with symmetry code is N1-H1N1 = 0.86 Å, H1N1···O1 = 1.92(3) Å, N1···O1 = 2.673(3) Å and >N1—H1N1···O1 =148° and symmetry code = *x*, *y*, *z*. The methyl substituted phenyl ring is in almost in plane with the central pyrazole ring (deviation between the mean plane is 2.32°) where as the chloro substituted phenyl ring is rotated by 45° from the plane of the pyrazole ring to make effective N—H···O interactions within the molecule and between the adjacent molecules along a axis to from paired molecular pairs via $\pi\cdots\pi$ stacking as shown in Fig. 3. The almost face to face $\pi\cdots\pi$ stacked chloro substituted phenyl rings of the molecular pairs are C1g···C1g = 3.72 Å and the C1g···C1g perpendicular distance is = 3.42 Å, where C1g is the center of gravity of the chloro substituted phenyl ring.

The π stacked molecular pairs further involved in C—H···π interactions involving the methyl hydrogen of substituted pyrazole ring and the methyl substituted phenyl ring from either ends along *b*-axis to from a one dimensional laired architecture as shown in the Fig. 3. The various C—H···π interactions with symmetry code is C18—H18B···Cg2: H18B···Cg2 = 2.96 Å; C18···Cg2= 3.74 Å; < C18—H18B—Cg2 =139.5° and C18—H18C···Cg2: H18C···Cg2 = 2.68 Å; C18···Cg2= 3.46 Å; < C18—H18C···Cg2 = 138.5°. The packing diagram and the various molecular interactions such as



enol form keto form

Fig. 2. Tautomers of the title compound.

C—H$\cdots\pi$ and $\pi\cdots\pi$ interactions are calculated using the program PLATON-97 [40].

Theoretical Studies

As stated earlier the present compound has potential use in solvent extraction, where it acts as a ligand

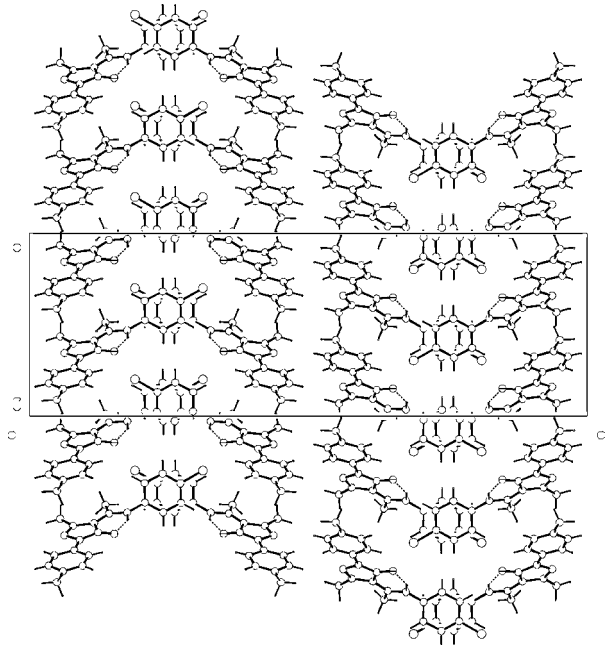


Fig. 3. Packing diagram of compound **I**.

Table IV. Rotational Potential Energy Function Correspond to Dihedral Angle N(1)—C(7)—C(8)—C(9) at Various Steps of Rotation 30°

Angle (°)	Relative energy a.u. (kcal/mol)
−180	—
180	0.0001(0.0023)
00	0.0141(0.3223)
30	0.0233(0.5326)
−30	0.0230(0.5257)
60	0.0511(1.1680)
−60	0.0488(1.1155)
90	0.0706(1.6138)
−90	0.0714(1.6321)
120	0.0485(1.1086)
−120	0.0500(1.1429)
150	0.0176(0.4023)
−150	0.0176(0.4023)

to bind various metal ions. The complex formation of I is accompanied by significant conformational changes and rotation of substituent R on fourth position. Hence the rotational potential energy function for the rotation of the substituent R around the C(7)—C(8) bonds are summarized in Table IV. The first minimum obtained, corresponds to the dihedral angle N(1)—C(7)—C(8)—C(9) of ca. 180°. This minima is consistent with the calculated equilibrium conformer resulted in full geometry optimization. It is interesting to note that in this conformer N(1)—H(1) and O(1)—C(10) are in the same direction and in the same plane, while that of aromatic ring is exactly perpendicular to the pyrazolone ring system. The driving force for this conformer to be stable may be the intra molecular hydrogen bonding between H(1) and O(1) as found in single crystal X-ray diffraction studies. The inter atomic bond distance is O$\cdots$H 1.81 Å and due to this intra molecular H-bonding a six membered stable ring is formed involving O—H$\cdots$N. The electron correlation correction does not notably influence on the position and depths of this minima as confirmed by MP2/6-31G(d) level run. The electron correlation correction at MP2 level decreases the potential barrier to 0.0000000386 a.u. only. The crystal structure obtain is quite similar to this conformer. The maximum of the rotational potential energy function corresponds to the conformation with the dihedral angel N(1)—C(7)—C(8)—C(9) of either 90 or −90. The high values of rotational barriers are caused because of strong steric interaction between two methyl groups C(17)H_3 and C(18)H_3, respectively. The selected bond lengths are listed in Table II and bond angles are listed in Table III. The data shows that there is quite resemblance in the structural parameters (such as bond length, bond angles etc.) of the title compound obtained

theoretically and experimentally obtain by X-ray crystallography. The difference between corresponding calculated and experimental bond lengths of N(3)—C(10), O(1)—C(10), C(8)—C(10) and C(7)—C(8) are 0.02 ± 0.003, 0.004 ± 0.003, 0.006 ± 0.004 and 0.01 ± 0.004, respectively. This is, probably due to involvement of these atoms into conjugation in/with pyrazolone ring. The other minima (local) also found to exist corresponds to the dihedral angle N(1)—C(7)—C(8)—C(9) ca 0°, where N(1)—H(1) and O(1)—C(10) are in opposite direction.

The full geometry optimization of **I** has also been carried out using AM1 method. The AM1 was preferred over other semi-emperical methods available in MOPAC because the present system contains many nitrogen atoms and hence AM1 is more suitable for the present system as it takes care of nitrogen atom well. The obtained minima are true minima as confirmed by Hessian calculation as well as conformational analysis. The structural parameters were also obtained from AM1 calculations. The results show that there is fairly good correlation between the structural parameters obtained from semi empirical AM1 and those obtained from either empirical one (ab initio) or experimentally (crystal structure). The maximum differences between these two are 3.47% in bond lengths and 3.08% in bond angles, respectively. This shows how even semi empirical calculation gives accurate predictions for such systems. This observation is in accordance with our previous one [24], which report the use of semi-empirical method (PM3) in predicting molecular properties such as wavelength of d—d transitions of structurally similar systems.

As mentioned earlier the present compound exhibits keto enol tautomerism, and because of this it shows interesting structural and spectroscopic properties. The studies on keto enol tautomerism of such class of compound have been the subject matter of many reports [41, 42]. However there are no systematic theoretical studies carried out so far on such systems. We have carried out full geometry optimization of both the forms of **I** by ab initio method using 6-31G(d) basis set. It is inferred from the results that keto form is stable over enol form by the relative energy of 0.0158587 a.u. (=0.3625 kcal/mol) (for keto from equilibrium energy is −1427.2590542 a.u. where as for enol form it is −1427.2431955 a.u.) by ab initio study performed on the two tautomers. Thus, the conclusion obtained from ab initio studies supports well the experimentally observed fact. i.e. the compound under investigation exists in most stable keto form in solid state at room temperature. This fact also confirmed by semi-emperical method AM1 (heat of formation of keto form 76.93467 kcal where as for enol form it is 87.982624 kcal) suggesting the existence of —NH (keto) form in the solid state at room temperature. Thus this stable form only can undergo chelation with the metal ion.

SUPPLEMENTARY MATERIALS

Crystallographic data for the compound has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 252028. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44-1233-336033, e-mail:deposit@ccdc.cam.ac.uk.

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