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Synthesis, characterization, crystal structure and DFT studies on 1-acetyl-3-(2,4-dichloro-5-fluoro-phenyl)-5-phenyl-pyrazoline

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Abstract

The title compound, 1-acetyl-3-(2,4-dichloro-5-fluoro-phenyl)-5-phenyl-pyrazoline, has been synthesized and characterized by elemental analysis, IR, UV–vis and X-ray single crystal diffraction. Density functional (DFT) calculations have been carried out for the title compound by using B3LYP method at 6-31G* basis set. The calculated results show that the predicted geometry can well reproduce the structural parameters. Predicted vibrational frequencies have been assigned and compared with experimental IR spectra and they are supported each other. The theoretical electronic absorption spectra have been calculated by using TD-DFT method. Molecular orbital coefficients analyses suggest that the above electronic transitions are mainly assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions. On the basis of vibrational analyses, the thermodynamic properties of the title compound at different temperatures have been calculated, revealing the correlations between $C_{p,m}^0$, S_m^0 , H_m^0 and temperatures. © 2007 Elsevier B.V. All rights reserved.

Keywords: Synthesis; Crystal structure; Vibrational frequency; Electronic absorption spectra; DFT

1. Introduction

Fluorescent probes are powerful tools in cell biology for the non-invasive measurement of intracellular ion concentrations [1]. They have found widespread applications, e.g., to gauge intracellular calcium concentrations [2], to visualize labile zinc [3,4] and iron pools [5], or as pH sensors [6]. Among various possible fluorescent probes, pyrazoline-based fluorophores stand out since their simple structure and favorable photophysical properties such as large extinction coefficient and quantum yields $(\Phi_{\rm f} \approx 0.6-0.8)$ [7]. Their attractive properties, including cationor pH-sensitive probes, have been described [8-10], and the suitability of pyrazoline fluorophores as probes in a biological environment is also explored [11]. Because of its modular nature, the synthesis of 1,3,5-trisubstituted pyrazoline fluorophores provides a high degree of structural flexibility [7,12]. On the other hand, density functional theory (DFT) has long been recognized as a better alternative tool in the study of organic chemical systems than the *ab initio* methods used in the past [13],

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since it is computationally less demanding for inclusion of electron correlation. Detailed analyses [14–17] on the performance of different DFT methods have been carried out particularly for equilibrium structure properties of molecular systems, such as geometry, dipole moment, vibrational frequency, etc. The general conclusion from these studies is that DFT methods, particularly with the use of nonlocal exchange-correlation function, can predict accurate equilibrium structure properties. With these in mind, after the title compound of 1-acetyl-3-(2,4-dichloro-5-fluoro-phenyl)-5-phenyl-pyrazoline was synthesized, we performed DFT calculations on it. In this paper, we wish to report the experimental values as well as the calculated results.

2. Experimental and theoretical methods

2.1. General method

Elemental analyses for carbon, hydrogen and nitrogen were performed by a Perkin-Elmer 240C elemental instrument. The melting points were determined on a Yanaco MP-500 melting point apparatus. IR spectra ($4000-400 \text{ cm}^{-1}$), as KBr pellets, were recorded on a Nicolet FT-IR spectro-

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photometer. Electronic absorption spectra in EtOH solution were measured on a Shimadzu UV3100 spectrophotometer.

2.2. Synthesis

All chemicals were obtained from a commercial source and used without further purification.

The reaction path is shown in Scheme 1.

1-2,4-Dichloro-5-fluoro-phenyl-3-phenyl-2-propenyl-1ketone (0.01 mol) and hydrazine hydrate (0.015 mol) were mixed in acetic acid (40 mL) and stirred in refluxing for 6 h, then, the mixture was poured into ice-water to afford lightyellow solids. The solids were filtrated and washed with water until the pH of solution is about to 7. Finally, the light-yellow solid crystals were dry under room temperature. Yield 87%, mp 149–150 °C. Found: C, 58.01; H, 3.58; N, 7.88%. Calcd. for C₁₇H₁₃Cl₂FN₂O: C, 58.14; H, 3.73; N, 7.98%. Electronic absorption spectra in hexahydrobenzene (nm, log ε): $\lambda_{max} = 210$ (1.70), $\lambda = 236$ (0.81), $\lambda = 312$ (1.19).

2.3. Crystal structure determination

The diffraction data were collected on a Enraf-Nonius CAD-4 diffractometer with graphite-monchromated Mo Kα radiation ($\lambda = 0.71073$ Å, T = 293 K). The technique used was ω -2 θ scan mode with limits 1.41-25.00°. The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using the SHELXTL [18] software package. All non-hydrogen atoms were anisotropically refined. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final conventional R = 0.0826 and $R_w = 0.1466$ for 2509 reflections with $I > 2\sigma(I)$ using the weighting scheme, $w = 1/[\sigma(F_o^2 + (0.0467P)^2 + 1.6334P])$, where $P = (F_o^2 + 2F_c^2)/3$. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [19]. A summary of the key crystallographic information is given in Table 1. Further details on the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 626447 for this paper. These data can be obtained free of charge via http://www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK [Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk]).

Table 1
Crystal data and structure refinement

Empirical formula	C ₁₇ H ₁₃ Cl ₂ FN ₂ O
Formula weight	351.19
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Tetragonal, P-421c
Unit cell dimensions	a = 20.460(3) Å, $b = 20.460(3)$ Å,
	c = 7.7246(15) Å
Volume	3233.8(9) Å ³
Z, Calculated density	8, 1.443 Mg/m ³
Absorption coefficient	0.416
<i>F</i> (000)	1440
θ range for data collection	$1.41-25.00^{\circ}$
Limiting indices	$-24 \le h \le 22, -21 \le k \le 24, -9 \le l \le 6$
Reflections collected/unique	13068/2837 [$R_{\text{in t}} = 0.0561$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2837/0/208
Goodness-of-fit on F^2	1.289
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0826, wR_2 = 0.1466$
R indices (all data)	$R_1 = 0.0930, wR_2 = 0.1511$
Largest diff. peak and hole	$0.263 \text{ and } -0.172 \text{ e} \text{ Å}^{-3}$

2.4. Theoretical methods

DFT calculations with a hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) at basis set 6-31G* by the Berny method [20] were performed with the Gaussian 03 software package [21]. Vibrational frequencies calculated ascertain the structure was stable (no imaginary frequencies). The thermodynamic properties of the title compound at different temperatures were calculated on the basis of vibrational analyses. Natural bond orbital (NBO) analyses and the time-dependent density functional theory (TD-DFT) [22–25] calculations of electronic absorption spectra were also performed on the optimized structure.

All calculations were performed on a DELL PE 2850 server and a Pentium IV computer using the default convergence criteria.

3. Results and discussions

3.1. Description of the crystal structure

For the title compound, the displacement ellipsoid plot with the numbering scheme is shown in Fig. 1 and a perspective view of the crystal packing in the unit cell is shown in Fig. 2. Selected bond lengths and bond angles by X-ray diffraction are listed in Table 2 along with the calculated bond parameters.



Scheme 1.



Fig. 1. Molecular structure with the atomic numbering scheme for the title compound.

The molecular structure of the title compound consists of discrete [PhFCl₂C₃H₃N₂PhC₂H₃O] entities. All of the bond lengths and bond angles in the phenyl rings are in the normal range. In the pyrazolinyl ring, the C=N and C–N bond lengths are all shorter than those found in similar structures[C=N 1.291(2)–1.300(10) Å, C–N 1.482(2)–1.515(9) Å] [11]. On the contrary, the N–N bond length is longer than those found in the above-cited structures [N–N 1.373(2)–1.380(8) Å] [11]. The dihedral angles between the pyrazolinyl ring with the phenyl rings at positions 3 and 5 of the pyrazoline are 3.87(2)° and 79.98(3)°, respectively.

In the crystal lattice, there are two potentially weak intermolecular interactions (C–H···Y, Y = O) [26,27]. The distances and angles between donor and acceptor are 3.3730(2) Å and 141.93(2)° for C(4)–H(4A)···O(1) [symmetry code: x, y, 1+z], and 3.3664(2) Å and 163.72(2)° for C(11)–H(11A)···O(1) [symmetry code: y, -x, -z], respectively. In the solid state, above supramolecular interactions stabilize the crystal structures.



Fig. 2. A view of the crystal packing down the c axis for the title compound.

Table 2
Selected structural parameters by X-ray and theoretical calculations

	Experimental	Calculated
Bond lengths (Å)		
Cl(1)-C(15)	1.730(5)	1.750
Cl(2)-C(13)	1.739(6)	1.741
F(1)-C(12)	1.339(6)	1.341
O(1)-C(16)	1.217(6)	1.222
N(1)-C(16)	1.340(6)	1.364
N(1)-N(2)	1.383(5)	1.387
N(1)-C(7)	1.457(6)	1.485
N(2)-C(9)	1.282(6)	1.294
C(14)-C(15)	1.379(7)	1.395
C(1)-C(2)	1.366(10)	1.395
C(4)-C(5)	1.376(9)	1.394
C(6)-C(7)	1.494(7)	1.518
C(7)–C(8)	1.540(7)	1.553
C(8)-C(9)	1.516(6)	1.525
C(9)–C(10)	1.457(7)	1.466
C(10)-C(15)	1.394(6)	1.417
C(12)-C(13)	1.361(8)	1.394
C(16)-C(17)	1.502(7)	1.514
Bond lengths (°)		
N(2)-N(1)-C(7)	113.1(4)	114.1
C(2)-C(1)-C(6)	121.5(7)	120.6
C(3) - C(4) - C(5)	120.6(7)	120.1
N(1)-C(7)-C(8)	101.3(3)	100.7
N(2)-C(9)-C(8)	112.6(4)	112.7
C(12)-C(11)-C(10)	122.0(5)	122.1
C(14) - C(13) - C(12)	119.8(5)	119.7
O(1)-C(16)-C(17)	123.1(5)	124.3
C(9) - N(2) - N(1)	109.0(4)	109.4
C(5) - C(6) - C(1)	117.3(6)	119.0
C(4) - C(5) - C(6)	120.5(6)	120.5
C(9)-C(8)-C(7)	102.3(4)	102.8
C(15)-C(10)-C(11)	115.9(5)	116.4
C(14) - C(15) - C(10)	121.4(5)	121.3
O(1) - C(16) - N(1)	119.6(5)	119.4
N(1)-C(16)-C(17)	117.2(5)	116.2

3.2. Optimized geometry

DFT calculations were performed on the title compound at B3LYP/6-31G* level of theory. Some optimized geometric parameters are also listed in Table 2. Comparing the theoretical values with the experimental ones indicates that all of the optimized bond lengths are slightly larger than the experimental values, as the theoretical calculations are performed for isolated a molecule in gaseous phase and the experimental results are for a molecule in a solid state. The geometry of the solidstate structure is subject to intermolecular forces, such as van der Waals interactions and crystal packing forces. The biggest differences of bond lengths and bond angles between the experimental and the predicted values are -0.033 Å for C(12)–C(13) bond distance and -1.7° for C(5)–C(6)–C(1) bond angle, which suggests that the calculational precision is satisfactory [28] and the B3LYP/6-31G* level of theory is suitable for the system studied here. Based on the optimized geometries, electronic spectra and thermodynamic properties of the title compound are discussed as follows.



Fig. 3. Experimental IR spectra and predicted spectrum at B3LYP/6-31G* level for the title compound.

3.3. Vibrational frequency

The experimental IR spectra and the simulated IR spectra are shown in Fig. 3, where the calculated intensity is plotted against the harmonic vibrational frequencies. Vibrational frequencies calculated at B3LYP/6-31G* level were scaled by 0.96 [29]. Some primary calculated harmonic frequencies are listed in Table 3 and compared with the experimental data. The descriptions concerning the assignment have also been indicated in the Table 3. Gauss-view program [30] was used to assign the calculated harmonic frequencies. In Fig. 3, the predicted harmonic vibration frequencies and the experimental data are very similar to each other except for the peak at 3293 cm^{-1} in experimental IR spectra, which is attributed to the ν_{O-H} of water molecules. Our present experimental conditions cannot avoid this v_{O-H} peak of water. On the other hand, there is a bigger difference on the C=O stretch vibration frequency. The experimental $v_{C=O}$ stretch is at 1660 cm^{-1} , while the predicted value is at 1708 cm^{-1} . The reason may be that in the solid state, there are two potentially weak

molecular interactions occurring on O(1) atoms, which finally influence the C=O stretch vibration frequency, while in the calculations, the studied molecule is isolated in gas state and there is no other interaction to be considered. In a word, the scaled frequencies of the DFT calculation are close to the corresponding FTIR vibration data and the DFT-B3LYP/6-31G* level can predict the vibrational frequencies for the system studied here on the whole.

3.4. Electronic absorption spectra

Experimental electronic spectra measured in hexahydrobenzene solution along with the theoretical electronic absorption spectra calculated on the B3LYP/6-31G* level optimized structure are listed in Table 4.

Seen from Table 4, both the experimental electronic spectra and predicted electronic spectra have three absorption peaks, with the latter having some blue shifts compared with the former. In addition, the theoretical electronic spectra have a broad band

Table 3 Comparison of the observed and calculated vibrational spectra of the title compound

Assignments	Experimental IR (with KBr)	Calculated (B3LYP/6-31G*) 3112–3111	
Phenyl ring C-H str.	3098		
Methyl group C-H str.	3053	3053	
Methyl group C-H str.	3027	3012	
Pyrazolinyl ring C-H str.	2965	2986-2975	
Pyrazolinyl ring C-H bend	2919	2939	
C=O str.	1660	1708	
Phenyl ring C=C str. + C=N str.	1590	1587–1582	
Phenyl ring C=C str. + C=N str.	1579	1570	
Phenyl ring C-H bend	1496	1485	
Methyl group C-H bend	1441	1445–1443	
Methyl group C-H bend	1417	1435	
Pyrazolinyl ring C-H bend	1353	1350	
Phenyl ring C-H bend	1316	1313	
Phenyl ring C=C str. + pyrazolinyl ring C-H bend	1290	1293	
Pyrazolinyl ring C-H bend	1260	1265	
Phenyl ring C-H bend	1212	1228	
Pyrazolinyl ring C-H bend + N-Nstr.	1153	1154	
All C-H bend	1095	1073	
Phenyl ring C=C str. + pyrazolinyl ring C-N str.	1064	1064	
Methyl group C-H bend	1022	1022	
Phenyl ring C=C str.	968	978	
Phenyl ring C-H twist.	899	890	
Phenyl ring C-H twist.	873	857	
Phenyl ring str. + pyrazolinyl ring str.	764	762	
Phenyl ring C-H twist. + pyrazolinyl ring C-H twist	733	745	
Phenyl ring C=C str.	700	711	
Phenyl ring C-H twist.	684	684	
Skeleton deformation	625	618	

from 304 to 308 nm, which is different from the experimental peak at 312 nm. Molecular orbital coefficients analyses based on the optimized geometry indicate that the frontier molecular orbitals are mainly composed of p atomic orbitals, so electronic transitions corresponding to above electronic spectra are mainly assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions. Fig. 4 shows the surfaces of the HOMO-1, HOMO, LUMO and LUMO+1 for the title compound. As seen from Fig. 4, in the HOMO-1, electrons are mainly delocalized on the acetyl group, pyrazolinyl ring and 5-position phenyl ring, while in the LUMO+1, electrons are all delocalized on 3-position phenyl ring. So, the electronic spectra are corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions.

3.5. Thermodynamic properties

On the basis of vibrational analyses and statistical thermodynamics, the standard thermodynamic functions: heat capacity

 Table 4

 Experimental and theoretical electronic absorption spectra values

Experimental		Calculated	
Wave length (nm)	$\log \varepsilon$	Wave length (nm)	Oscillator strength
210	1.70	204.87	0.3307
236	0.81	226.80	0.0655
312	1.19	304.82	0.2645
		308.61	0.3700

 $(C_{p,m}^{0})$, entropy (S_{m}^{0}) and enthalpy (H_{m}^{0}) were obtained and listed in Table 5. The scale factor for frequencies is still 0.96.

As observed from Table 5, all the values of $C_{p,m}^0$, S_m^0 and H_m^0 increase with the increase of temperature from 100.0 to 700.0 K, which is attributed to the enhancement of the molecular vibration while the temperature increases.

The correlations between these thermodynamic properties and temperatures T are shown in Fig. 5. The correlation equations are as follows:

$C_{p,m}^{0} = 28.54 + 1.214T - 5.484 \times 10^{-4} T^{2} (R^{2} = 0.9995);$
$S_{\rm m}^0 = 290.68 + 1.389T - 3.861 \times 10^{-4} T^2 (R^2 = 0.99995);$
$H_{\rm m}^{0} = -5.30 + 9.847 \times 10^{-2} T + 3.942 \times 10^{-4} T^2 (R^2 = 0.9998)$

These equations could be used for the further studies on the title compound. For instance, when we investigate the interaction

Table 5	
Thermodynamic properties at different temperatures at B3LYP/6-31G* la	evel

$T(\mathbf{K})$	$C_{p,m}^0 (\mathrm{J}\mathrm{mol}^{-1}\mathrm{K}^{-1})$	$S_{\rm m}^0 ({\rm J} {\rm mol}^{-1} {\rm K}^{-1})$	$H_{\rm m}^0$ (kJ mol ⁻¹)
100.0	149.04	423.73	9.59
200.0	243.76	556.01	29.22
300.0	340.36	673.15	58.44
400.0	429.05	783.53	97.02
500.0	502.55	887.46	143.73
600.0	561.13	984.47	197.03
700.0	607.82	1074.60	255.56



Fig. 4. Surfaces of HOMO-1, HOMO, LUMO and LUMO + 1 for the title compound.



Fig. 5. Correlation graphics of thermodynamic properties and temperatures for the title compound.

between the title compound and another compound, thermodynamic properties $C_{p,m}^0$, H_m^0 and S_m^0 could be obtained from these equations and then used to calculate the change of Gibbs free energy of the reaction, which will assist us to judge the spontaneity of the reaction.

4. Conclusions

1-Acetyl-3-(2,4-dichloro-5-fluoro-phenyl)-5-phenyl-

pyrazoline has been synthesized and characterized by elemental analysis, IR, UV–vis and X-ray single crystal diffraction. DFT calculations at B3LYP/6-31G* level for the title compound show that the optimized geometry closely resemble the crystal structure. The comparisons between the calculated vibrational frequencies and the experimental IR spectra indicate they are supported each other. The predicted electronic absorption spectra have some blue shifts compared with the experimental data and molecular orbital coefficients analyses suggest that the electronic spectra are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions. The correlations between the thermodynamic properties $C_{p,m}^0$, S_m^0 and H_m^0 and temperatures *T* are also obtained.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2007.05.016.

References

- W.T. Mason, Fluorescent and Luminescent Probes for Biological Activity: A Practical Guide to Technology for Quantitative Real-time Analysis, Academic Press, San Diego, CA, 1999.
- [2] A. Takahashi, P. Camacho, J.D. Lechleiter, B. Herman, Physiol. Rev. 79 (1999) 1089.
- [3] S.C. Burdette, G.K. Walkup, B. Spingler, R.Y. Tsien, S.J. Lippard, J. Am. Chem. Soc. 123 (2001) 7831.
- [4] T. Hirano, K. Kikuchi, Y. Urano, T. Nagano, J. Am. Chem. Soc. 124 (2002) 6555.
- [5] B.P. Esposito, S. Epsztejn, W. Breuer, Z.I. Cabantchik, Anal. Biochem. 304 (2002) 1.
- [6] A. Takahashi, Y.P. Zhang, V.E. Centonze, B. Herman, Biotechniques 30 (2001) 804.

- [7] D.E. Rivett, J. Rosevear, J.F.K. Wilshire, Aust. J. Chem. 36 (1983) 1649.
- [8] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, M. Nieuwenhuizen, Chem. Commun. (1996) 1967.
- [9] K. Rurack, U. Resch-Genger, J.L. Bricks, M. Spieles, Chem. Commun. (2000) 2103.
- [10] K. Rurack, J.L. Bricks, B. Schulz, M. Maus, G. Reck, U. Resch-Genger, J. Phys. Chem. A 104 (2000) 6171.
- [11] C.J. Fahrni, L.C. Yang, D.G. VanDerveer, J. Am. Chem. Soc. 125 (2003) 3799.
- [12] A. Wagner, C.W. Schellhammer, S. Petersen, Angew. Chem., Int. Ed. Engl. 5 (1966) 699.
- [13] J.K. Labanowski, J. Andzelm, Density Functional Methods in Chemistry, Springer-Verlag, New York, 1991.
- [14] N. Oliphant, R.J. Bartlett, J. Chem. Phys. 100 (1994) 6550.
- [15] R.M. Dickson, A.D. Becke, J. Chem. Phys. 99 (1993) 3898.
- [16] B.G. Johnson, P.M.W. Gill, J.A. Pople, J. Chem. Phys. 98 (1993) 5612.
- [17] F. Yakuphanoglu, Y. Atalay, M. Sekerci, Spectrosc. Acta Part A 66 (2007) 438.
- [18] G.M. Sheldrick, SHELXTL, v5 Reference Manual, Siemens Analytical X-Ray Systems: Madison, WI, 1997.
- [19] A.J. Wilson, International Table for X-Ray Crystallography, vol. C, Kluwer Academic, Dordrecht, The Netherlands, 1992 (Tables 6.1.1.4 (pp. 500–502) and 4.2.6.8 (pp. 219–222), respectively).
- [20] C. Peng, P.Y. Ayala, H.B. Schlegel, M.J. Frisch, J. Comput. Chem. 49 (1996) 17.
- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Vreven, Jr., K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A.Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian Inc., Wallingford, CT, 2004.
- [22] E. Runge, E.K.U. Gross, Phys. Rev. Lett. 52 (1984) 997.
- [23] M. Petersilka, U.J. Gossmann, E.K.U. Gross, Phys. Rev. Lett. 76 (1966) 1212.
- [24] R. Bauernschmitt, R. Ahlrichs, Chem. Phys. Lett. 256 (1996) 1996.
- [25] C. Jamorski, M.E. Casida, D.R. Salahub, J. Chem. Phys. 104 (1996) 5134.
- [26] T. Steiner, Cryst. Rev. 6 (1996) 1.
- [27] G.A. Jeffrey, H. Maluszynska, J. Mitra, Int. J. Biol. Macromol. 7 (1985) 336.
- [28] F.F. Jian, P.S. Zhao, Q. Yu, Q.X. Wang, K. Jiao, J. Phys. Chem. A 108 (2004) 5258.
- [29] J.A. Pople, H.B. Schlegel, R. Krishnan, D.J. Defrees, J.S. Binkley, M.J. Frisch, R.A. Whiteside, R.F. Hout, W.J. Hehre, Int. J. Quantum Chem., Quantum Chem. Symp. 15 (1981) 269.
- [30] A. Frish, A.B. Nielsen, A.J. Holder, Gaussview Users Manual, Gaussian Inc., Pittsburgh, 2000.