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RESEARCH ARTICLE

Quantum chemical research of the molecular structure of 3,4-dicyanofuroxan

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Abstract

Objectives. *The study set out to determine the equilibrium parameters of the 3,4-dicyanofuroxan molecule by means of molecule geometry optimization by quantum chemistry methods, verify the adequacy of the methods used, and compare the obtained results with X-ray diffraction analysis (XRD) and gas electron diffraction (GED) data.*

Methods. *Quantum chemical calculations were carried out using B3LYP, MP2, and CCSD(T) methods with 6-31G(d,p), cc-pVTZ, and aug-cc-pVTZ basis sets.*

Results. *The equilibrium molecular structure of 3,4-dicyanofuroxan was refined by means of quantum chemical calculations using the Gaussian09 program. The geometrical parameters were compared with the structure of this compound in the solid phase and a number of related compounds in gas and solid phases. It was theoretically established that the planar equilibrium structure of the dicyanofuroxan molecule has C_s symmetry. The structure of the free dicyanofuroxan molecule was found to differ depending on the phase. The B3LYP and CCSD(T) methods describe the molecular structure of dicyanofuroxan more accurately than the MP2 method. A regularity was revealed, according to which an increase in the basis, as a rule, leads to a better agreement of the geometry, regardless of the functional.*

Conclusions. *The calculations performed are in good agreement with the literature data and results of joint analysis by GED and XRD. The effect of cyano substituents on the ring geometry is observed in comparison with the literature data for the dicyanofuroxan molecule. For the molecule in question, it is better to use the B3LYP/aug-cc-pVTZ method. The values of geometric parameters obtained by this method are in better agreement with the structure in the gas phase. The discrepancies with the experimental XRD results may be due to interactions in the crystal structure. Differences in the geometric parameters obtained on the basis of different functionals and bases make this molecule interesting for experimental structural studies using GED or microwave spectroscopy, which will permit the identification of optimal methods and bases for obtaining the geometric parameters of furoxan class molecules.*

Keywords: *equilibrium structure, molecular structure, oxadiazoles, furoxans, quantum chemical studies*

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НАУЧНАЯ СТАТЬЯ

Исследование равновесной структуры молекулы 3,4-дицианофуроксана

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Аннотация

Цели. *Определение равновесных параметров молекулы 3,4-дицианофуроксана посредством оптимизации геометрии молекулы методами квантовой химии, проверка адекватности используемых методов, а также сопоставление полученных результатов с данными рентгенодифракционного анализа (РСА) и газовой электронографии (ГЭ) родственных соединений.*
Методы. *Квантовохимические расчеты методами B3LYP, MP2 и CCSD(T) с базисными наборами 6-31G(d,p), cc-pVTZ и aug-cc-pVTZ.*
Результаты. *Уточнена равновесная молекулярная структура 3,4-дицианофуроксана с помощью квантово-химических расчетов в программе Gaussian09. Проведено сравнение геометрических параметров со структурой данного соединения в твердой фазе и с рядом родственных соединений в газовой и твердой фазе. Теоретически установлено, что равновесная структура молекулы дицианофурокса-*

на является плоской и имеет симметрию C_S. Установлено, что структура свободной молекулы дицианофуроксана в зависимости от фазы различается. Методы CCSD(T) и B3LYP точнее описывает молекулярную структуру дицианофуроксана по сравнению с методом MP2. Выявлена закономерность, согласно которой увеличение базиса, как правило, приводит к лучшему согласованию геометрии независимо от функционала.

Выводы. *Проведенные расчеты хорошо согласуются с литературными данными, а также результатами совместного анализа методами ГЭ и РСА. Влияние циано-заместителей на геометрию кольца наблюдается в сравнении с литературными данными для молекулы дицианофуроксана. Для рассматриваемой молекулы лучше использовать метод B3LYP/aug-cc-pVTZ. Значения геометрических параметров, полученные этим методом, лучше согласуются со структурой в газовой фазе. Расхождения с экспериментальными результатами РСА могут быть обусловлены взаимодействиями в кристаллической структуре. Различия в геометрических параметрах, полученных на основе разных функционалов и базисов, делают эту молекулу интересной для проведения экспериментального структурного исследования методами ГЭ или микроволновой спектроскопии, что позволит в будущем найти оптимальные методы и базисы для получения геометрических параметров молекул класса фуроксанов.*

Ключевые слова: *равновесная структура, молекулярная структура, оксодиазолы, фуроксаны, квантово-химические исследования*

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INTRODUCTION

The class of oxadiazoles, representing one of the most promising in the creation of energy-intensive compounds, became the focus of research attention in the first decades of the 21st century [1] due to the combination of unusual thermochemical characteristics: high enthalpy of formation and thermal stability. The presence of active oxygen in oxadiazole and oxadiazole N-oxide also increases the energy capacity of the molecule [2]. In addition, the chemical properties of oxadiazoles make it easy to introduce groups containing high-energy bonds that increase the total energy of the molecule.

The 3,4-dicyano-1,2,5-oxadiazole-2-oxide (3,4-dicyano-furoxan, DCFO) substance is used in the solution of many urgent problems. Representing an intermediate in the organic synthesis of high-energy materials [3], the substance is used in chemical ignition systems (it spontaneously ignites upon contact with rocket fuel components [4]), as well as showing pharmacological and biological activity (vasodilator) [5]. In addition, DCFO derivatives have antimalarial properties [6] and potential for application as coagulants and enzymes.

DCFO was synthesized for the first time in 1925 [7]. Subsequently, several more options for DCFO obtaining were proposed in 1962, 1975, 2001, and 2019 [3–5, 8]. For a long time, the 1962 synthesis [8] was the most reliable. However, in 2019 a group of scientists from Maryland developed a reproducible, economical, safe, and highly efficient method for DCFO obtaining, obtaining a crystal of the substance for the first time and confirming the result using X-ray diffraction on a single crystal [5].

At that time, the structure of nitro-containing derivatives of furoxans in the gas phase, such as 3-methyl-4-nitro- and 4-methyl-3-nitrofuroxan,

had already been studied by gas electron diffraction (GED) and quantum chemical calculations [9]. A number of pyridines containing a cyano group were also studied using the same methods [10–12].

In 1996, the first attempt was made to optimize the geometry of the DCFO molecule by means of the Gaussian-92 software package using the Hartree–Fock (HF) method, involving exchange-correlation 3-parametric Becke–Lie–Yang–Parr (B3LYP) density functional and density functional based on the second-order Möller–Plesset perturbation theory (MP2) with basis sets 6-31G(d,p) (HF/6-31G(d,p), B3LYP/6-31G (d,p), and MP2/6-31G(d,p)) [13]. A year later, the obtained calculation data for this substance were compared with the results of ultraviolet and infrared spectroscopy [14].

In 2012, a study was conducted using the Gaussian 09 software package [15]. However, the authors limited themselves to the level of the B3LYP/cc-pVTZ theory. Calculations based on the same methods using different bases are also of interest.

The aim of the present work is to determine the equilibrium structure of the DCFO molecule by optimizing the molecule geometry using B3LYP and MP2 quantum chemistry methods with the 6-31G(d,p)[1], cc-pVTZ[2], and aug-cc-pVTZ[3] bases in the Gaussian 09 program; to carry out a calculation at the theoretical level CCSD(T)[4] with the basis 6-31G(d,p); to check the adequacy of the methods used; and to compare the results with the data of X-ray diffraction analysis (XRD) and GED for related compounds.

EXPERIMENTAL

Quantum chemical calculations were carried out with by means of the Gaussian 09 software package [16] using the density functional theory method with the B3LYP functional [17, 18] and MP2 perturbation theory [19] with correlationally consistent basis sets 6-31G(d,p) [20], cc-pVTZ [21], and aug-cc-pVTZ [22]. A calculation using the CCSD(T) method [23] was additionally carried out with basis sets 6-31G(d,p). To determine the equilibrium structure of DCFO, complete optimization of the geometry and calculation of the oscillation frequencies were performed. The atom numbering for the DCFO molecule are shown in the figure.

The Cartesian coordinates of the DCFO optimized using the CCSD(T)/6-31G(d,p), B3LYP/6-31G(d,p), and MP2/cc-pVTZ functionals are presented in the appendix (Tables S1, S2, and S3).

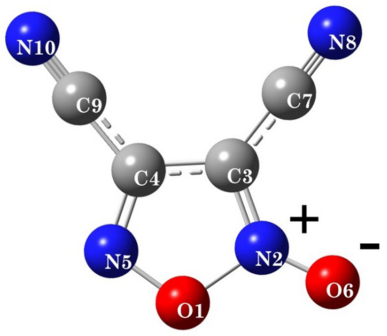

Fig. Atom numbering in the DCFO molecule.

RESULTS AND DISCUSSION

It follows from Table 1 that B3LYP/aug-cc-pVTZ calculations reproduce the C–N and C=O DCFO bond lengths better than MP2 calculations with the same basis set (especially when compared with the latest experimental data for the crystal [4]). This statement is also true for some bond angles. Quantum chemistry calculations show that the planar DCFO molecule has C_S symmetry. XRD revealed that there are 2 forms in the solid phase, the parameters of which differ in the case of bond lengths.

The equilibrium structure calculated by the B3LYP/aug-cc-pVTZ method is in good agreement with the solid phase determined by XRD. The discrepancies between the data are no more than 0.01 Å for the bond lengths, while the values of the bond angles differ by no more than 1°. In contrast to the gas phase, two molecules of the crystalline phase are nonplanar; however, the deviation from the plane does not exceed 4° (Table 1). A comparison of the equilibrium structure of DCFO with the structure in the crystalline phase demonstrates the similarity of the bond lengths of the oxadiazole rings with a maximum deviation not exceeding 0.02 Å and 2° in the bond lengths and bond angles, respectively. This indicates that the B3LYP method is likely to better predict the structure of DCFO in the gas phase. However, due to the different state of aggregation of these structures, their differences can be associated with the effects of intermolecular interactions in the crystal.

[1] 6-31G(d,p) is a valence-split basis set with addition of d-type polarization functions for each atom from Li to Ca and p-type polarization functions for each light atom (H, He).

[2] cc-pVTZ is a triple-zeta correlation consistent basis set.

[3] aug-cc-pVTZ is an augmented version of the previous basis set with added diffuse features.

[4] CCSD(T) is a coupled cluster single-double and perturbative triple method.

Table 1. Molecular parameters of DCFO

Parameter	B3LYP			MP2			CCSD(T)	XRD[4]	
	/6-31G(d,p)	/cc-pVTZ	/aug-cc-pVTZ	/6-31G(d,p)	/cc-pVTZ	/aug-cc-pVTZ	/6-31G(d,p)	1	1A
r_e(O1–N2)	1.475	1.472	1.470	1.651	1.552	1.567	1.479	1.458(2)	1.453(3)
r_e(N2–C3)	1.345	1.340	1.339	1.357	1.354	1.353	1.346	1.336(3)	1.346(3)
r_e(C3–C4)	1.430	1.425	1.426	1.408	1.403	1.403	1.426	1.404(3)	1.396(3)
r_e(C4–N5)	1.314	1.306	1.306	1.345	1.337	1.338	1.320	1.301(3)	1.296(3)
r_e(O1–N5)	1.351	1.346	1.347	1.311	1.314	1.312	1.369	1.366(3)	1.356(3)
r_e(N2–O6)	1.205	1.195	1.196	1.201	1.194	1.194	1.215	1.204(2)	1.205(3)
r_e(C3–C7)	1.410	1.405	1.406	1.414	1.408	1.409	1.420	1.418(3)	1.427(3)
r_e(C4–C9)	1.425	1.420	1.421	1.422	1.417	1.417	1.434	1.430(3)	1.422(4)
r_e(C7–N8)	1.163	1.152	1.152	1.185	1.174	1.175	1.174	1.135(3)	1.133(3)
r_e(C9–N10)	1.161	1.150	1.150	1.185	1.174	1.174	1.173	1.136(3)	1.127(4)
A(O1–N2–C3)	105.2	105.2	105.2	100.2	102.1	101.8	105.5	105.4(2)	105.0(2)
A(N2–C3–C4)	106.9	106.9	106.9	110.5	109.0	109.4	107.0	107.2(2)	107.2(2)
A(C3–C4–N5)	111.5	111.4	111.4	112.5	111.6	111.6	112.1	112.2(2)	111.9(2)
A(O1–N5–C4)	107.3	107.6	107.6	109.2	108.2	108.4	106.8	106.7(2)	107.4(2)
A(N2–O1–N5)	109.1	108.9	108.9	107.6	109.0	108.8	108.7	108.5(2)	108.5(2)
A(O1–N2–O6)	119.1	119.0	119.0	120.8	119.9	120.0	119.0	118.4(2)	118.0(2)
A(C3–N2–O6)	135.7	135.8	135.8	138.9	138.0	138.2	135.5	136.2(2)	137.0(2)
A(N2–C3–C7)	122.2	122.2	122.3	119.6	120.3	120.2	121.6	121.8(2)	121.6(2)
A(C4–C3–C7)	131.0	130.9	130.8	129.9	130.6	130.3	131.4	131.0(2)	131.0(2)
A(C3–C4–C9)	126.5	126.7	126.7	126.1	126.6	126.5	126.5	126.3(2)	127.4(2)
A(C3–C7–N8)	179.1	179.0	179.0	179.8	179.7	179.7	179.1	178.8	178.9
A(C4–C9–N10)	178.6	178.3	178.2	178.5	178.4	178.1	178.4	177.9	178.0

Table 1. Continued

Parameter	B3LYP			MP2			CCSD(T)	XRD[4]	
	/6-31G(d,p)	/cc-pVTZ	/aug-cc-pVTZ	/6-31G(d,p)	/cc-pVTZ	/aug-cc-pVTZ	/6-31G(d,p)	1	1A
A(N5–C4–C9)	121.9	121.9	121.9	121.3	121.8	121.8	121.4	121.4(2)	120.7(2)
D(O1–N2–C3–C4)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.3
D(N2–O1–N5–C4)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.6
D(C3–C4–N5–O1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–0.6	–0.4
D(O1–N2–C3–C7)	180.0	180.0	180.0	180.0	180.0	180.0	180.0	177.5	175.9
D(C7–C3–C4–C9)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	–1.5	–3.8

Note: The DCFO crystal cell consists of two independent molecules 1 and 1A. r_e(O1–N2) is the equilibrium bond length between the corresponding atoms. A(O1–N2–C3) is the value of the angle between the corresponding atoms. D(O1–N2–C3–C4) is the value of the dihedral angle between the corresponding atoms. Bond lengths are given in angstroms. The angles are given in degrees.

The molecular structure of DCFO is relatively well described by the B3LYP/aug-cc-pVTZ method: the functional gives the best fit for most bond lengths as compared to the MP2/cc-pVTZ method. The largest differences are observed for the O1–N2 bond: its length of 1.458(4) Å refined according to XRD data correlates with the length determined by the B3LYP/aug-cc-pVTZ method (1.470 Å) and does not coincide when using the MP2/cc-pVTZ method (1.552 Å). The same situation is observed with the O1–N5 bond length: according to XRD, its value is 1.366(5)Å, which is close to the value determined by B3LYP/aug-cc-pVTZ (1.347 Å); moreover, it noticeably differs from the results of MP2/cc-pVTZ (1.314 Å). The worst matches are given by MP2/6-31G(d,p): in this case, the difference for bond lengths reaches 0.1 Å.

The CCSD(T)/6-31G(d,p) method adequately describes the molecule structure, with most of the bond lengths correlating with the experimental data: the calculated O1–N2 bond length is 1.480 Å, while the bond length refined by XRD is 1.458(4) Å. The O1–N5 bond length as calculated by the CCSD(T)/6-31G(d,p) method and obtained by XRD coincides with high precision (1.369 and 1.366(5) Å, respectively).

In this work, we also compared the structural parameters of DCFO with the geometry of related compounds (3-methyl-4-nitrofuroxan and 4-methyl-3-nitrofuroxan) determined by the GED method in [12].

From Table 2, it can be seen that DCFO is similar in parameters to 3-methyl-4-nitrofuroxan: for most bond lengths, the difference is no more than 0.08 Å, while the angles differ by no more than 2°–3°. The most noticeable deviations are in the C3–C7 (0.082 Å), N2–O6 (0.019 Å), and C3–C4 (0.012 Å) bonds. Among the angles, N2–C3–C4 (2.3°) and C3–C4–N5 (2.5°) show the largest discrepancy. The situation changes with the transition to 4-methyl-3-nitrofuroxan. The angles mostly do not coincide, while the lengths of only two bonds (C3–C4 and N2–O6) are close in their values (the difference is less than 0.009 Å). Such significant differences (0.03–0.10 Å) may be due to the effect of substituents.

In general, it can be argued that when comparing the results of calculations by the B3LYP and MP2 methods with the basis sets 6-31G(d,p), cc-pVTZ, and aug-cc-pVTZ, there is a tendency for a better agreement between the calculated molecular parameters and the experimental values. It can be seen that an increase in the basis, as a rule, leads to better geometry matching, regardless of the chosen functional (Table 3).

Table 2. Comparison of structural parameters of DCFO, 3-methyl-4-nitrofuroxan, and 4-methyl-3-nitrofuroxan

Parameter	DCFO B3LYP/aug-cc-pVTZ	3-methyl-4-nitrofuroxan GED [12]	4-methyl-3-nitrofuroxan GED [12]
r_e(O1–N2)	1.470	1.462(9)	1.382(6)
r_e(N2–C3)	1.339	1.333(9)	1.307(6)
r_e(C3–C4)	1.426	1.414(9)	1.422(6)
r_e(C4–N5)	1.306	1.304(9)	1.340(6)
r_e(O1–N5)	1.347	1.354(9)	1.429(6)
r_e(N2–O6)	1.196	1.215(9)	1.205(6)
r_e(C3–C7)	1.406	1.488(9)	1.488(6)
A(O1–N2–C3)	105.2	107.2(5)	107.5(3)
A(N2–C3–C4)	106.9	104.6(5)	109.2(3)
A(C3–C4–N5)	111.4	113.9(5)	109.2(3)
A(O1–N5–C4)	107.6	106.1(10)	104.7(4)
A(N2–O1–N5)	108.9	108.1(10)	109.4(5)
A(O1–N2–O6)	119.0	118.1(6)	118.6(3)
A(N2–C3–C7)	122.3	121.2(5)	121.1(3)

Note: bond lengths are given in Å; angles are in degrees.

We also compared the C–N bond lengths in DCFO with a number of cyanopyridines, the data for which were obtained by two independent methods (Table 4).

The C–N bond length of DCPO is very similar to that in the corresponding cyanopyridines. The spread of values does not exceed 1%, which can be considered a good indicator, demonstrating

Table 3. Comparison of DCFO selected parameters during various quantum chemical calculations

Method	r_e(O1–N2), Å	r_e(O1–N5), Å
XRD [4]	1.458(2)	1.366(3)
B3LYP/6-31G(d,p)	1.475	1.351
B3LYP/cc-pVTZ	1.472	1.346
B3LYP/aug-cc-pVTZ	1.470	1.347
MP2/6-31G(d,p)	1.651	1.311
MP2/cc-pVTZ	1.552	1.314
MP2/aug-cc-pVTZ	1.567	1.312
CCSD(T)/6-31G(d,p)	1.480	1.369

Table 4. Comparison of bond lengths C–N in DCFO – 2-cyanopiridine – 3-cyanopiridine – 4-cyanopiridine series

DCFO (B3LYP/aug-cc-pVTZ)		2-cyanopiridine [10]		3-cyanopiridine [11]		4-cyanopiridine [12]	
		GED	XRD	GED	XRD	GED	XRD
r_e(C7–N8), Å	1.152	1.158(5)	1.1452(8)	1.157(2)	1.1499(12)	1.159(3)	1.1370(8)
r_e(C9–N10), Å	1.150						
r_e(C4–C9), Å	1.421	1.445(3)	1.448(2)	1.432(2)	1.4303(12)	1.438(3)	1.439(8)
r_e(C3–C7), Å	1.406						

that the chosen method and basis describe the molecule under consideration quite well.

CONCLUSIONS

The equilibrium structure of the DCFO molecule was refined by optimizing the free geometry using quantum chemistry methods. The adequacy of the methods used was checked by comparing the obtained results with those mentioned in the literature. The obtained results are compared with the XRD data for the molecule in the crystalline phase.

Equilibrium geometric structural parameters characterizing the DCFO molecule were obtained (calculation results are given in Tables 1 and 2). The results are consistent with those of related compounds.

It should be noted that, although structural comparison of solid DCFO with modeling of the molecule properties in the gas phase between the centers of maximum electron density is somewhat difficult, the structures under study are quite similar. The data obtained by XRD correlate with the corresponding geometric parameters of the DCFO backbone calculated by the B3LYP/aug-cc-pVTZ method (r_e(O1–N2) bond length is 1.458(2) and 1.470 Å; r_e(O1–N5) bond length is 1.366(3) and 1.347 Å; r_e(N2–C3) bond length is 1.336(3) and 1.339 Å).

SUPPLEMENTARY

Table S1. Cartesian coordinates of atoms in the DCFO molecule obtained at the level of the CCSD(T)-31G(d,p) theory

No.	Symbol	X	Y	Z
1	O	1.0630	–1.6922	0.0
2	N	1.4296	–0.2798	0.0
3	C	0.2732	0.3759	0.0
4	C	–0.7800	–0.5742	0.0
5	N	–0.2976	–1.7930	0.0
6	O	2.5878	0.0245	0.0
7	C	0.2018	1.7728	0.0
8	N	0.1196	2.9355	0.0
9	C	–2.1677	–0.3032	0.0
10	N	–3.3028	–0.0472	0.0

Table S2. Cartesian coordinates of atoms in the DCFO molecule obtained at the level of the B3LYP/6-31G(d,p) theory

No.	Symbol	X	Y	Z
1	O	–1.81695	–0.83540	0.0
2	N	–1.34222	0.56103	0.0
3	C	0.0	0.47737	0.0
4	C	0.32868	–0.91407	0.0
5	N	–0.74964	–1.66405	0.0
6	O	–2.15078	1.45395	0.0
7	C	0.82413	1.62158	0.0
8	N	1.51834	2.55455	0.0
9	C	1.63809	–1.47669	0.0
10	N	2.71587	–1.90832	0.0

Table S3. Cartesian coordinates of atoms in the DCFO molecule obtained at the level of the MP2/cc-pVTZ theory

No.	Symbol	X	Y	Z
1	O	–1.81233	–0.89477	0.0
2	N	–1.34771	0.58627	0.0
3	C	0.0	0.46095	0.0
4	C	0.33496	–0.90095	0.0
5	N	–0.75514	–1.67493	0.0
6	O	–2.15711	1.46346	0.0
7	C	0.81982	1.60597	0.0
8	N	1.50816	2.55741	0.0
9	C	1.64067	–1.45056	0.0
10	N	2.73510	–1.87474	0.0

Authors' contributions

I.N. Kolesnikova – general management, setting research tasks, performing quantum-chemical calculations, and writing the text of the article;

N.V. Lobanov – analysis of literature sources, writing the text of the article, performing quantum chemical calculations, preparing bibliography and illustrative materials;

V.N. Lobanov – conceptualization of materials, consultations during the research, and editing of the article;

I.F. Shishkov – general guidance, setting research tasks, and editing the article.

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