

Research Article

Synthesis, Crystal Structure, and DFT Study of N' -(2,4-Dinitrophenyl)-2-Fluorobenzohydrazide

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A new hydrazide derivative N' -(2,4-dinitrophenyl)-2-fluorobenzohydrazide was synthesized and characterized by NMR and IR spectroscopy. The molecular structure was also studied by X-ray diffraction, and the results of the optimized molecular structure are presented and compared with density functional methods with 631-G basis set. The calculated results show that the optimized geometry can well reproduce the crystal structural parameters, for example, bond lengths and angles show good agreement with the experimental data.

1. Introduction

Hydrazides are an important class of biologically active compounds exhibiting a variety of biological activities notably, antituberculosis [1], antibacterial [2], antifungal [3], antimalarial [4], antiproliferative and antitumour [5, 6]. Several clinical drugs like the antituberculosis drug, isoniazid, antihypertensive and peripheral vasodilator drug hydralazine, and benserazide used for treatment of restless legs syndrome are hydrazides in nature. Furthermore, metallic complexes of hydrazides show potent fungicidal and antibacterial activities [7].

In addition, benzohydrazides are also used for the construction of heterocyclic rings due to the presence of carbonyl functionality as well as two nitrogens which can behave like nucleophiles in a number of reactions [8]. Examples of heterocycles include indoles, carbazoles, pyrazoles, triazines, indazolones, and indazoles [9–15].

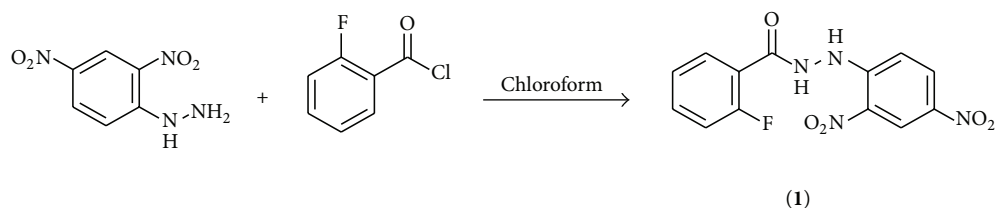
We have already reported on the synthesis and crystal structure of (2,4-dinitrophenyl) benzohydrazide [16]. Herein, we wish to report the synthesis of N' -(2,4-dinitrophenyl)-2-fluorobenzohydrazide (Scheme 1). The chemical structure of compound was confirmed by FT-IR, ¹H NMR, ¹³C NMR, elementary analysis, and X-ray single-crystal determination.

Density functional theory (DFT) has been very popular for calculations in theoretical modelling since the 1970s. DFT

predicts a great variety of molecular properties like molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, and reaction paths. The molecular structure parameters of the title compound have been calculated by density functional theory (B3LYP) with 6-31G basis set. The calculated molecular structure parameters have been analyzed and compared with obtained experimental data.

2. Results and Discussion

2.1. Crystal Structure. The PhC(O)NNPh core moiety (Figure 1) is similar to that of *N*-anilino-4-nitrobenzamide [17] and *N*-(3,5-dinitrobenzoyl)- N' -phenylhydrazine [18] with different ring substitution patterns. The molecular conformation is determined by the intramolecular N1–H···O5 and N4–H···F hydrogen bonds with H···O5 2.02 and H···F 2.10 Å. Associated torsion angles are N4–C1–C2–C7 = 9.9(3)° and N4–N1–C8–C13 = –170.9(2)°. The two aromatic ring planes make a dihedral angle of 88.65(5)°. Intermolecular hydrogen bond interactions N1–H···O1 ($x + 1, y, z$) with H···O 2.25(3) Å and N–H···O 139(2)° as well as C5–H···O4 ($x - 1, y + 1, z$) with H···O 2.44 Å and C–H···O 132° link molecules into zigzag chains extended along the *b*-axis (Figure 2).



SCHEME 1: Synthesis of title compound.

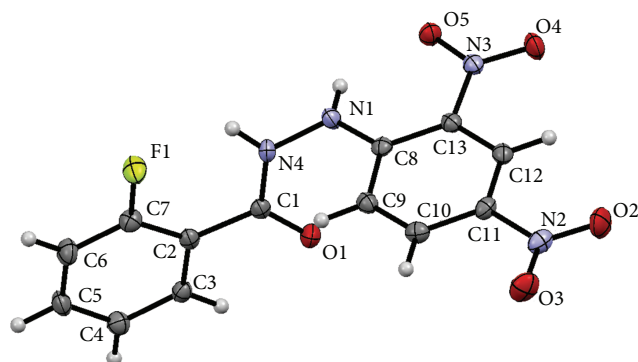


FIGURE 1: The molecular structure of the title molecule (1), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as small spheres of arbitrary radii.

2.2. Molecular Geometry and Optimized Structures. The optimized geometrical parameters, namely, bond lengths and angles experimental and calculated by B3LYP/6-31G level listed in Table 2. From the theoretical results, expected fluctuations of the calculated values against the experimental ones were observed. Comparing experimental bond lengths and angles with theoretical bond lengths and bond angles it is of notice that the bond lengths calculated are always higher than experimental values. Optimized structures yields identical bond lengths for the C–C bonds on the Aryl rings and calculated values by 631G basis set are finest closed to experimental. The calculated bond lengths of the C–C bond in benzene ring is between 1.365 and 1.509 Å, while experimentally, it ranges 1.365–1.500 Å which is much shorter than the typical C–C single bond (1.54 Å) and longer than the C=C double bond (1.34 Å) [19, 20].

By comparison of the results obtained by DFT calculations by 63-1G basis set and the experimental data in Table 2, several observations can be made. The experimental C9–C10 bond length is 1.366 Å; this value was calculated as 1.379. The N2–C11 and N3–C13 bond lengths are 1.454 and 1.449 Å, respectively, which are in good agreement with the experimental values 1.453 and 1.449 and smaller than the normal C–N single bond length of about 1.47 Å [21]. From the calculation results of bond angles which are analyzed in the present work, it can be obtained that the calculated bond angles are very close to their experimental data except F1–C7–C6 and C7–C2–C1; both were underestimated, and C12–C13–N3 is the only one which is overestimated. While most of the calculated angles for 1 at 631-G basis set differ only in the decimal

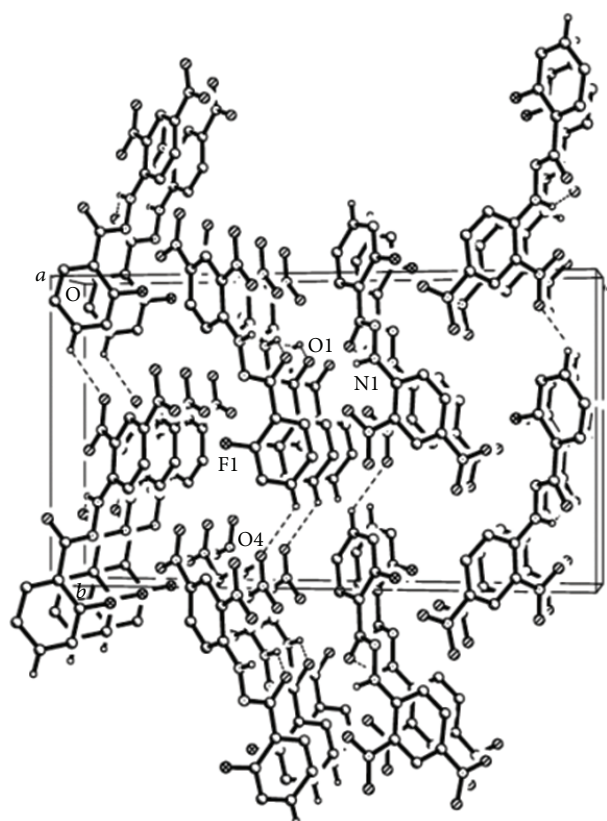


FIGURE 2: Crystal packing is viewed approximately along *a*-axis with H-bonding as dashed lines. H atoms not involved are omitted.

with the experimental values. These results indicate that the calculated angles are very similar to the crystal structure of titled compound 1. When the X-ray structure of the title compound is compared with its optimised counterparts (see Figure 3), minor conformational discrepancies are observed between them. A logical method for globally comparing the structures obtained with the theoretical calculations is by superimposing the molecular skeleton with that obtained from X-ray diffraction.

3. Experimental and Computational Details

3.1. Materials and Analyses. All chemicals were of reagent grade and used as commercially purchased without additional purification. All solvents were dried and distilled before use. For TLC analysis, precoated plates of silica gel 60 F254

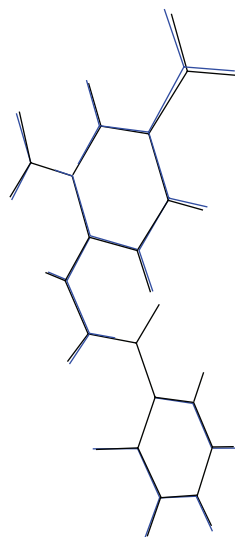


FIGURE 3: Atom-by-atom superimposition of the structures calculated (blue) by B3LYP/6-31G on the X-ray structure (black) of the title compound.

were used. The ^1H NMR spectra were recorded on a Bruker AM_300 instrument, and chemical shifts are reported in parts per million (ppm). The melting point was determined on Staurt SMP3 apparatus and is uncorrected. The FT-IR spectrum was recorded using a Shimadzu IR 460 instrument by attenuated total reflectance (ATR) method. The CHN elemental analysis was performed on LECO CHNS-932 analyser.

3.2. Synthesis. 2,4-Dinitrophenyl hydrazine (2.8 mmol) in dry CHCl_3 (10 mL) was treated with 2-fluorobenzoyl chloride (2.8 mmol), and the mixture was refluxed for 2 hours. On completion of reaction, the mixture was allowed to cool, and the solvent was evaporated under reduced pressure. Yellow prisms of the title compound were recrystallized from ethanol by slow evaporation at room temperature (m.p 190–192°C). IR: 3418 ((C=O)NH), 3293 (NH), 1675 (C=O), 3101 ($\text{C}_{\text{sp}^2}\text{-H}$), cm^{-1} . $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.23–7.39 (m, 3H, Ar-H), 7.59 (m, 1H, Ar-H), 8.07 (ddd, 1H, Ar-H), 8.32 (dd, 1H, Ar-H), 8.94 (d, 1H, Ar-H), 9.71 (s, 1H, CONH), 11.24 (s, 1H, NH); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 164.5, 154.6, 148.1, 137.1, 133.5, 133.1, 130.3, 129.8, 129.5, 127.0, 126.6, 119.3, 116.0, 115.8.

3.3. X-Ray Structure Determination. Data were collected at 130(2) K on a Bruker [22] AXS SMART APEX CCD diffractometer using $\text{MoK}\alpha$ radiation. The structure was solved by direct methods [18] and refined on F^2 by full-matrix least-squares [23] with 215 parameters and 1806 unique intensities. All nonhydrogen atoms were refined anisotropically. All H atom positions were clearly derived from difference Fourier maps and refined on idealized positions with $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{C/N})$, C–H distances of 0.95 Å. H(N) positions were refined freely. The title compound crystallizes in the noncentrosymmetric space group $P 2_1 2_1 2_1$; however, in the absence

TABLE 1: Parameter for data collection and structure refinement of 1.

Empirical formula	$\text{C}_{13} \text{H}_9 \text{F} \text{N}_4 \text{O}_5$
Formula weight	320.24
Temperature	130(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P 2_1 2_1 2_1$
Unit cell dimensions	$a = 4.8195(11)$ Å
$b = 12.314(3)$ Å	
$c = 21.582(5)$ Å	
Volume	$1280.8(5)$ Å ³
Z	4
Density (calculated)	1.661 Mg/m^3
Absorption coefficient	0.140 mm^{-1}
$F(000)$	656
Crystal size	$0.35 \times 0.18 \times 0.10 \text{ mm}^3$
Theta range for data collection	1.89 to 27.87°
Index ranges	$-6 \leq h \leq 6$, $-14 \leq k \leq 16$, $-28 \leq l \leq 27$
Reflections collected	10321
Independent reflections	1806 [$R(\text{int}) = 0.0295$]
Completeness to $\theta = 27.87^\circ$	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9862 and 0.9527
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1806/0/215
Goodness-of-fit on F^2	1.049
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0313$, $wR2 = 0.0758$
R indices (all data)	$R1 = 0.0361$, $wR2 = 0.0789$
Absolute structure parameter	2.0(10)
Largest diff. peak and hole	0.269 and $-0.184 \text{ e} \cdot \text{Å}^{-3}$

of significant anomalous scattering effects, the Flack parameter is essentially meaningless. Accordingly, Friedel pairs were merged. Experimental data are listed in Table 1.

3.4. Computational Method. Optimized molecular structure of the title compound (1) in the ground state (S_0) was computed with PC GAMESS/Firefly version 7.1.G [24] (based in part on the codes of the GAMESS program (USA)) [25] together with the Gabedit [26] graphical interface by using density functional theory (DFT) Becke-3-Lee-Yang-Parr (B3LYP) functional [27, 28]. Furthermore, experimental molecular geometry was used as the initial guess for optimization.

4. Conclusion

In this study, we have synthesized a novel compound N' -(2,4-dinitrophenyl)-2-fluorobenzohydrazide, $\text{C}_{13}\text{H}_9\text{FN}_4\text{O}_5$, characterized by spectroscopic (FT-IR, NMR) and structural (XRD) techniques. Theoretical geometrical parameters by DFT were compared with experimental data results and

TABLE 2: The bond lengths (Å) and bond angles [°] for title compound (1) determined by X-ray diffraction and DFT calculations using 63-1G basis set.

	X-ray	DFT
Bond lengths		
F(1)–C(7)	1.360(2)	1.409
O(1)–C(1)	1.217(2)	1.246
O(2)–N(2)	1.235(2)	1.265
O(3)–N(2)	1.229(2)	1.267
O(4)–N(3)	1.234(2)	1.262
O(5)–N(3)	1.232(2)	1.280
N(1)–C(8)	1.352(2)	1.368
N(1)–N(4)	1.391(2)	1.388
N(2)–C(11)	1.453(2)	1.454
N(3)–C(13)	1.449(2)	1.449
N(4)–C(1)	1.368(2)	1.387
C(1)–C(2)	1.500(3)	1.497
C(2)–C(7)	1.391(3)	1.399
C(2)–C(3)	1.400(3)	1.409
C(3)–C(4)	1.389(3)	1.394
C(4)–C(5)	1.387(3)	1.402
C(5)–C(6)	1.383(3)	1.398
C(6)–C(7)	1.376(3)	1.388
C(8)–C(13)	1.421(3)	1.431
C(8)–C(9)	1.423(3)	1.422
C(9)–C(10)	1.366(3)	1.379
C(10)–C(11)	1.404(3)	1.407
C(11)–C(12)	1.365(3)	1.384
C(12)–C(13)	1.391(3)	1.398
Bond angles		
C(8)–N(1)–N(4)	119.93(16)	121.77
O(3)–N(2)–O(2)	123.32(18)	123.98
O(3)–N(2)–C(11)	118.40(17)	117.73
O(2)–N(2)–C(11)	118.28(17)	118.28
O(5)–N(3)–O(4)	122.54(16)	122.22
O(5)–N(3)–C(13)	118.73(15)	118.85
O(4)–N(3)–C(13)	118.72(16)	118.91
C(1)–N(4)–N(1)	118.71(16)	120.13
O(1)–C(1)–N(4)	121.42(17)	121.30
O(1)–C(1)–C(2)	121.33(17)	121.45
N(4)–C(1)–C(2)	117.22(16)	117.24
C(7)–C(2)–C(3)	116.71(16)	116.58
C(7)–C(2)–C(1)	127.07(17)	126.76
C(3)–C(2)–C(1)	116.22(16)	116.65
C(4)–C(3)–C(2)	121.19(17)	121.29
C(5)–C(4)–C(3)	119.81(18)	120.09
C(6)–C(5)–C(4)	120.37(18)	119.96
C(7)–C(6)–C(5)	118.63(18)	118.46
F(1)–C(7)–C(6)	117.32(17)	116.65
F(1)–C(7)–C(2)	119.41(17)	119.74
C(6)–C(7)–C(2)	123.26(18)	123.59
N(1)–C(8)–C(13)	123.14(17)	122.34
N(1)–C(8)–C(9)	120.72(17)	120.59
C(13)–C(8)–C(9)	116.14(17)	117.04
C(10)–C(9)–C(8)	121.85(18)	121.60
C(9)–C(10)–C(11)	119.48(18)	119.64

TABLE 2: Continued.

	X-ray	DFT
C(12)–C(11)–C(10)	121.36(18)	121.03
C(12)–C(11)–N(2)	118.42(17)	119.42
C(10)–C(11)–N(2)	120.21(18)	119.54
C(11)–C(12)–C(13)	119.11(18)	119.43
C(12)–C(13)–C(8)	122.00(18)	121.20
C(12)–C(13)–N(3)	115.61(17)	116.50
C(8)–C(13)–N(3)	122.39(17)	122.29

seemed to be in a good agreement with experimental ones. The X-ray structure is found to be very slightly different from it optimized counterpart, and the crystal structure is stabilized by N–H...O and N–H...F type hydrogen bonds. It is noted here that the experimental results are for the solid phase and the theoretical calculations are for the gaseous phase. The geometry of the solid state structure is subject to intermolecular forces, such as van der Waals interactions and crystal packing forces.

References

- [1] B. Koçyiğit-Kaymakçioğlu, E. Oruç, S. Unsalan et al., "Synthesis and characterization of novel hydrazide-hydrazones and the study of their structure-antituberculosis activity," *European Journal of Medicinal Chemistry*, vol. 41, no. 11, pp. 1253–1261, 2006.
- [2] M. V. Angelusiu, S.-F. Barbuceanu, C. Draghici, and G. L. Almajan, "New Cu(II), Co(II), Ni(II) complexes with aroyl-hydrazone based ligand. Synthesis, spectroscopic characterization and in vitro antibacterial evaluation," *European Journal of Medicinal Chemistry*, vol. 45, no. 5, pp. 2055–2062, 2010.
- [3] C. Loncle, J. M. Brunel, N. Vidal, M. Dherbomez, and Y. Letourneux, "Synthesis and antifungal activity of cholesterol-hydrazone derivatives," *European Journal of Medicinal Chemistry*, vol. 39, no. 12, pp. 1067–1071, 2004.
- [4] P. Melnyk, V. Leroux, C. Sergheraert, and P. Grellier, "Design, synthesis and in vitro antimalarial activity of an acylhydrazone library," *Bioorganic and Medicinal Chemistry Letters*, vol. 16, no. 1, pp. 31–35, 2006.
- [5] K. K. Vijaya Raj, B. Narayana, B. V. Ashalatha, N. Suchetha Kumari, and B. K. Sarojini, "Synthesis of some bioactive 2-bromo-5-methoxy- N^1 -[4-(aryl)-1,3-thiazol-2-yl]benzohydrazide derivatives," *European Journal of Medicinal Chemistry*, vol. 42, no. 3, pp. 425–429, 2007.
- [6] K. K. Narang and V. P. Singh, "Synthesis, characterization, thermal studies and biological activity of Iron(III) complexes with some acylhydrazines," *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, vol. 23, pp. 971–989, 2007.
- [7] Z. Muhi-Eldeen, K. Al-Obaidi, M. Nadir, and V. F. Roche, "Synthesis and antimicrobial activity of Ni(II), Co(II), Zn(II) and Cd(II) complexes of 4-substituted-3-mercapto-5-phenyl-4H-1,2,4-triazoles," *European Journal of Medicinal Chemistry*, vol. 27, no. 2, pp. 101–106, 1992.
- [8] R. W. Leiby and N. D. Heindel, "Synthesis of 3,4-dihydro- and 1,4-dihydro-5H-1,3,4-benzotriazepin-5-ones," *Journal of Organic Chemistry*, vol. 41, no. 16, pp. 2736–2739, 1976.

- [9] G. W. Gribble, "Recent developments in indole ring synthesis—methodology and applications," *Journal of the Chemical Society, Perkin Transactions 1*, vol. 1, no. 7, pp. 1045–1075, 2000.
- [10] F. D. King, "Synthesis and thermal reactions of 1,2-dihydro-1,2,4-benzotriazines," *Journal of the Chemical Society, Perkin Transactions 1*, no. 12, pp. 3381–3385, 1988.
- [11] R. B. Carlin and M. S. Moores, "The fischer reaction of cyclohexanone mesitylhydrazone. Evidence of a 1,4-methyl migration," *Journal of the American Chemical Society*, vol. 84, no. 21, pp. 4107–4112, 1962.
- [12] I. T. Barnish and M. S. Gibson, "Transitional activation phenomena: synthesis of the 4H-benzo[e][1,3,4]-thiadiazine ring," *Journal of the Chemical Society C*, no. 6, pp. 854–859, 1970.
- [13] J. J. Kulagowski, C. J. Moody, and C. W. Rees, "Generation and rearrangement of 4aH-carbazoles," *Journal of the Chemical Society, Perkin Transactions 1*, pp. 2725–2732, 1985.
- [14] A. Oliva, M. Ellis, L. Flocchi, E. Menta, and A. P. Krapcho, "N-tert-butoxycarbonyl-N-substituted hydrazines in S(N)Ar displacements. Synthetic pathways to N-1-substituted anthrapyrazoles, aza-anthrapyrazoles and aza-benzothiopyranoidazoles," *Journal of Heterocyclic Chemistry*, vol. 37, no. 1, pp. 47–55, 2000.
- [15] D. L. Hughes, "Progress in the fischer indole reaction. A review," *Organic Preparations and Procedures International*, vol. 25, no. 6, pp. 607–632, 1993.
- [16] A. Saeed, I. Arshad, and U. Florke, "*N'*-(2, 4-Dinitrophenyl)benzohydrazide," *Acta Crystallographica E*, vol. 68, pp. 2418–2426, 2012.
- [17] J. L. Wardell, J. N. Low, and C. Glidewell, "N-(4-Nitro-benzoyl)-*N'*-phenyl-hydrazine: a three-dimensional hydrogen-bonded framework," *Acta Crystallographica C*, vol. 63, no. 6, pp. 334–336, 2007.
- [18] S. M. S. V. Wardell, M. V. N. De Souza, J. L. Wardell, J. N. Low, and C. Glidewell, "N-(3,5-dinitrobenzoyl)-*N'*-phenylhydrazine: Sheets built from N–H···O and C–H···O hydrogen bonds," *Acta Crystallographica E*, vol. 62, no. 7, pp. 2589–2591, 2006.
- [19] D. R. Lide Jr., "A survey of carbon-carbon bond lengths," *Tetrahedron*, vol. 17, no. 3-4, pp. 125–134, 1962.
- [20] J.-J. Nie and D.-J. Xu, "Photosynthesis and molecular structure of 2-amino-3H-phenoxazin-3-one," *Chines Journal of Structural Chemistry*, vol. 21, no. 2, pp. 165–167, 2002.
- [21] Y. Sasada, *Molecular and Crystal Structures in Chemistry Handbook*, The Chemical Society of Japan, Maruzen, Tokyo, 3rd edition, 1984.
- [22] Bruker, *SMART (Version 5. 63)*, *S SAINT (Version 6. 02)*, Bruker AXS, Madison, Wis, USA, 2002.
- [23] G. M. Sheldrick, "A short history of SHELX," *Acta Crystallographica A*, vol. 64, no. 1, pp. 112–122, 2007.
- [24] A. A. Granovsky, Firefly version 7.1.G, <http://classic.chem.msu.su/gran/firefly/index.html>.
- [25] M. W. Schmidt, K. K. Baldridge, J. A. Boatz et al., "General atomic and molecular electronic structure system," *Journal of Computational Chemistry*, vol. 14, pp. 1347–1363, 1993.
- [26] A.-R. Allouche, "Gabedit—a graphical user interface for computational chemistry softwares," *Journal of Computational Chemistry*, vol. 32, no. 1, pp. 174–182, 2011.
- [27] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *Journal of Chemical Physics*, vol. 98, pp. 5648–5652, 1993.
- [28] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Physical Review B*, vol. 37, pp. 785–789, 1988.



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