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Explorations of Crystalline Effects on 4-(Benzyloxy)Benzaldehyde Properties

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Abstract: The properties of 4-(benzyloxy)benzaldehyde (BBA), as a pharmaceutically important compound, have been investigated through the density functional theory (DFT) calculations. The properties of original crystalline and optimised gaseous structures have been evaluated to recognise the crystalline effects. In addition to the structural properties, nuclear magnetic resonance (NMR) properties have also been evaluated for both investigated systems to better detect the effects in atomic levels. The results indicated that the structural shape of BBA is significantly changed in the optimised gaseous system, showing significant crystalline effects on the geometrical positions. Moreover, the magnitudes for energies and dipole moments indicate notable effects on the electronic properties. The evaluated NMR properties also show that the atoms of aromatic systems detect significant changes more than the atoms of aliphatic systems in the investigated BBA. And finally, the oxygen bridge atom plays a dominant role in combining two benzene rings of BBA.

Keywords: 4-(Benzyloxy)Benzaldehyde; Crystalline Effect; Density Functional Theory; NMR.

1 Introduction

The molecules detect several effects including intra- and intermolecular interactions in crystalline phases, in which hydrogen bond (HB) interactions are among the most important ones [1, 2]. Therefore, geometrical atomic positions are rearranged to minimise the employed effects in the crystalline phases. To detect the magnitudes of

effects on structural and electronic properties of molecules, performing computations in isolated gas phases could help to provide insightful information comparable with available X-ray crystallographic data. Within this work, the crystalline effects on geometrical positions and electronic properties of 4-(benzyloxy)benzaldehyde (BBA) (Fig. 1) are investigated through the density functional theory (DFT) calculations. The crystalline structure of BBA has been earlier reported by Kennedy et al. [3], showing the presence of weak HB interactions. In contrast with classical strong HB interactions, recent works have indicated that the weak HB interactions are important in determining the three-dimensional shapes of chemical structures [4–7]. For this purpose, nuclear magnetic resonance (NMR) spectroscopy has been introduced among the most versatile characterisation techniques to investigate the properties of the weak HB interactions in organic and biological compounds [8, 9]. The computed results are compared between the isolated gas phase and crystalline phase of BBA to investigate the magnitudes of crystalline effects on the properties of original structure. BBA and its derivatives have been viewed as important compounds with inhibitory activities in pharmaceutical applications [10–12]. Chang et al. [13] have earlier studied the inhibitory activity of BBA derivatives against formation of neutrophil superoxide species. In another work, the inhibitory activity of BBA derivatives has been studied in cancer therapy applications by Lin et al. [14]. Reports on the applications of BBA derivatives in treatments of HIV are also available [15]. Since the properties are defined by chemical structures, investigating the details of employed effects on the structures is important to determine their properties for desired applications. Moreover, detecting the magnitudes of effects employed by the weak HB interactions on the properties of crystalline structures is crucial for better understanding the nature of intermolecular interactions [16].

2 Computational Details

All DFT calculations of this work have been performed using the B3LYP exchange-correlation functional and

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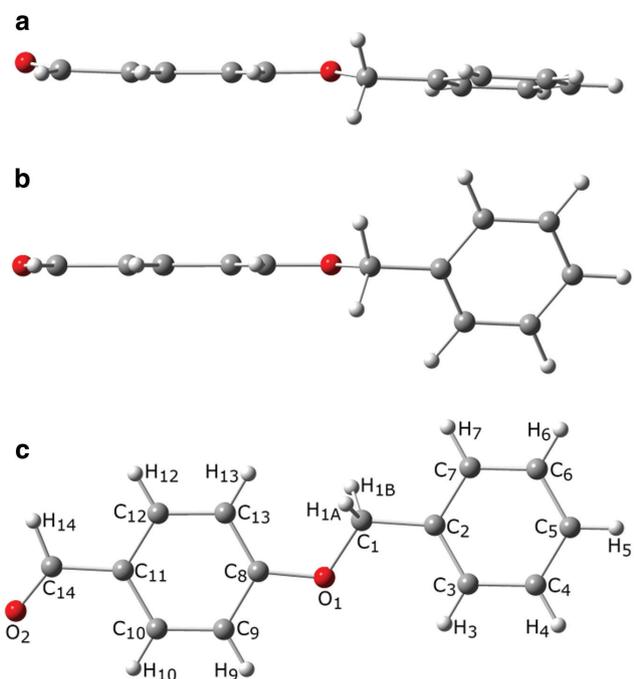


Figure 1: (a) The original crystalline structure, (b) the optimised gaseous structure, and (c) the atomic positions in the investigated structures.

the 6-311++G** standard basis set as implemented in the Gaussian 98 package [17]. The models of the study are singular crystalline and gaseous molecules (Fig. 1) and also a target molecule in the real crystalline cluster (Fig. 2). To see the crystalline effects on the geometrical properties of the investigated BBA (Fig. 1), all atomic geometries have been allowed to fully relax during the optimisation process in the isolate gas phase. The properties including

total energy, energy levels for the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, respectively), dipole moment, bond lengths, angles, and dihedral angles have been evaluated for optimised gaseous BBA (Tables 1 and 2). Moreover, the properties including total energy, energy levels for the HOMO and LUMO, and dipole moment are computed for crystalline BBA through single-point calculations (Tables 1 and 2). The values of bond lengths, angles, and dihedral angles for crystalline BBA are used from the report by Kennedy et al. [3]. Subsequently, the NMR parameters including isotropic chemical shifts (δ /ppm) and quadrupole coupling constants (C_Q /kHz) are computed for both of the crystalline and gaseous BBA structures (Table 3). The NMR parameters for a target molecule in original crystalline phase (Fig. 2) have also been calculated for a better comparison of the properties in different structural situations. The magnitudes of δ show the chemical environment properties for each atom, and the magnitudes of C_Q show the interaction energies between the electric field gradient tensors and nuclear electric quadrupole moments [18]. To evaluate δ properties, isotropic chemical shieldings (σ_{ii}) have been calculated for each atom using the gauge-included atomic

Table 1: The computed properties of crystalline and gaseous BBA.^a

Phase	Total energy (keV)	HOMO (eV)	LUMO (eV)	Dipole moment (Debye)
Crystalline	-18.808	-6.768	-1.826	5.247
Gaseous	-18.813	-6.726	-1.820	5.474

^aSee Figure 1 for the models.

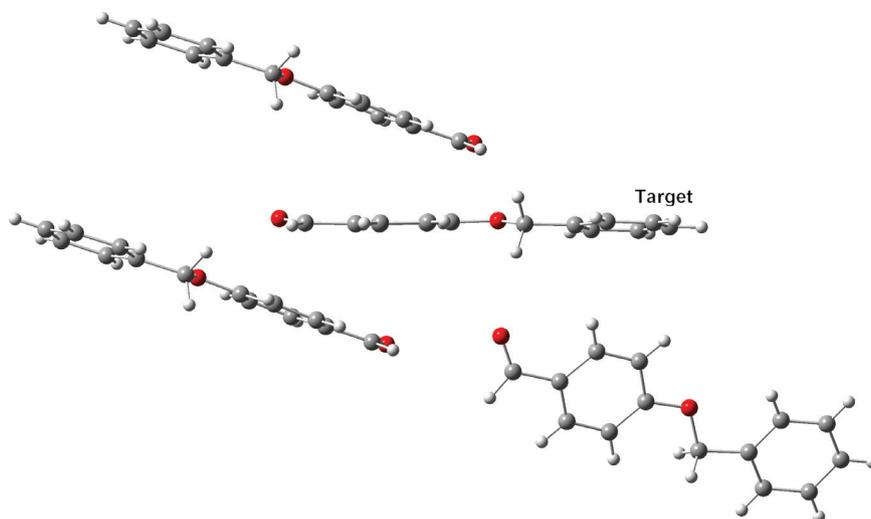


Figure 2: The original crystalline structure (target) in the real system. The atomic positions of target molecule are the same as shown in Figure 1c.

Table 2: The geometries of crystalline and gaseous BBA.^a

Bonding	Crystalline	Gaseous	Bonding	Crystalline	Gaseous
Bonds (Å)					
O ₁ -C ₈	1.366	1.356	C ₆ -C ₇	1.382	1.394
O ₁ -C ₁	1.437	1.437	C ₆ -H ₆	0.950	1.084
O ₂ -C ₁₄	1.212	1.211	C ₇ -H ₇	0.950	1.085
C ₁ -C ₂	1.506	1.505	C ₈ -C ₁₃	1.392	1.400
C ₁ -H _{1A}	0.990	1.097	C ₈ -C ₉	1.400	1.407
C ₁ -H _{1B}	0.100	1.095	C ₉ -C ₁₀	1.375	1.378
C ₂ -C ₃	1.391	1.399	C ₉ -H ₉	0.950	1.038
C ₂ -C ₇	1.395	1.395	C ₁₀ -C ₁₁	1.399	1.406
C ₃ -C ₄	1.393	1.390	C ₁₀ -H ₁₀	0.950	1.084
C ₃ -H ₃	0.950	1.084	C ₁₁ -C ₁₂	1.387	1.395
C ₄ -C ₅	1.385	1.395	C ₁₁ -C ₁₄	1.471	1.473
C ₄ -H ₄	0.950	1.084	C ₁₂ -C ₁₃	1.378	1.392
C ₅ -C ₆	1.378	1.392	C ₁₂ -H ₁₂	0.950	1.086
C ₅ -H ₅	0.950	1.084	C ₁₃ -H ₁₃	0.950	1.081
			C ₁₄ -H ₁₄	1.030	1.113
Angles (°)					
C ₈ -O ₁ -C ₁	117.2	119.1	C ₅ -C ₆ -H ₆	119.7	120.2
O ₁ -C ₁ -C ₂	109.2	108.4	C ₇ -C ₆ -H ₆	119.7	119.9
O ₁ -C ₁ -H _{1A}	109.8	109.0	C ₆ -C ₇ -C ₂	120.4	120.6
C ₆ -C ₇ -H ₇	119.8	119.8	O ₁ -C ₈ -C ₉	115.2	115.3
C ₂ -C ₇ -H ₇	119.8	119.6	C ₁₃ -C ₈ -C ₉	120.4	119.9
O ₁ -C ₈ -C ₁₃	124.4	124.7	C ₁₀ -C ₉ -C ₈	120.0	120.1
C ₂ -C ₁ -H _{1A}	109.8	110.7	C ₁₀ -C ₉ -H ₉	120.0	121.7
O ₁ -C ₁ -H _{1B}	109.8	109.8	C ₈ -C ₉ -H ₉	120.0	118.1
C ₂ -C ₁ -H _{1B}	109.8	110.5	C ₉ -C ₁₀ -C ₁₁	120.1	120.5
H _{1A} -C ₁ -H _{1B}	108.3	108.4	C ₉ -C ₁₀ -H ₁₀	120.0	121.0
C ₃ -C ₂ -C ₇	119.0	119.1	C ₁₁ -C ₁₀ -H ₁₀	120.0	118.4
C ₃ -C ₂ -C ₁	123.2	120.2	C ₁₂ -C ₁₁ -C ₁₀	119.1	119.0
C ₇ -C ₂ -C ₁	117.8	120.7	C ₁₂ -C ₁₁ -C ₁₄	118.7	120.3
C ₂ -C ₃ -C ₄	120.2	120.4	C ₁₀ -C ₁₁ -C ₁₄	122.2	120.7
C ₂ -C ₃ -H ₃	119.9	119.5	C ₁₃ -C ₁₂ -C ₁₁	121.6	121.2
C ₄ -C ₃ -H ₃	119.9	120.0	C ₁₃ -C ₁₂ -H ₁₂	119.2	119.3
C ₅ -C ₄ -C ₃	120.2	120.1	C ₁₁ -C ₁₂ -H ₁₂	119.2	119.4
C ₅ -C ₄ -H ₄	119.9	120.0	C ₁₂ -C ₁₃ -C ₈	118.8	119.2
C ₃ -C ₄ -H ₄	119.9	120.1	C ₁₂ -C ₁₃ -H ₁₃	120.6	119.6
C ₆ -C ₅ -C ₄	119.8	119.8	C ₈ -C ₁₃ -H ₁₃	120.6	121.1
C ₆ -C ₅ -H ₅	120.1	120.1	O ₂ -C ₁₄ -C ₁₁	125.5	125.1
C ₄ -C ₅ -H ₅	120.1	120.1	O ₂ -C ₁₄ -H ₁₄	120.9	120.6
C ₅ -C ₆ -C ₇	120.5	120.0	C ₁₁ -C ₁₄ -H ₁₄	113.5	114.3
Dihedral angles (°)					
C ₈ -O ₁ -C ₁ -C ₂	176.5	177.4	O ₁ -C ₈ -C ₉ -C ₁₀	-179.3	179.5
O ₁ -C ₁ -C ₂ -C ₃	-9.8	-62.5	C ₁₃ -C ₈ -C ₉ -C ₁₀	0.5	-0.1
O ₁ -C ₁ -C ₂ -C ₇	171.1	117.8	C ₈ -C ₉ -C ₁₀ -C ₁₁	0.0	0.0
C ₇ -C ₂ -C ₃ -C ₄	-0.7	0.1	C ₉ -C ₁₀ -C ₁₁ -C ₁₂	-0.5	0.1
C ₁ -C ₂ -C ₃ -C ₄	-179.8	-179.6	C ₉ -C ₁₀ -C ₁₁ -C ₁₄	177.7	-179.9
C ₂ -C ₃ -C ₄ -C ₅	0.6	0.3	C ₁₀ -C ₁₁ -C ₁₂ -C ₁₃	0.5	-0.1
C ₃ -C ₄ -C ₅ -C ₆	0.3	-0.3	C ₁₄ -C ₁₁ -C ₁₂ -C ₁₃	-177.7	179.9
C ₄ -C ₅ -C ₆ -C ₇	-1.0	-0.1	C ₁₁ -C ₁₂ -C ₁₃ -C ₈	-0.1	-0.1
C ₅ -C ₆ -C ₇ -C ₂	0.9	0.4	O ₁ -C ₈ -C ₁₃ -C ₁₂	179.4	-179.9
C ₃ -C ₂ -C ₇ -C ₆	-0.1	-0.4	C ₉ -C ₈ -C ₁₃ -C ₁₂	-0.4	0.2
C ₁ -C ₂ -C ₇ -C ₆	179.1	179.3	C ₁₂ -C ₁₁ -C ₁₄ -O ₂	171.8	179.9
C ₁ -O ₁ -C ₈ -C ₁₃	6.0	1.8	C ₁₀ -C ₁₁ -C ₁₄ -O ₂	-6.3	0.0
C ₁ -O ₁ -C ₈ -C ₉	-174.2	-178.3			

^aSee Figure 1 for the atomic positions. The crystalline geometries are from [3], and the gaseous geometries are obtained through optimisation.

Table 3: The computed isotropic chemical shifts (δ , ppm) and quadrupole coupling constants (C_Q , kHz) for atoms of target, crystalline, and gaseous BBA.^a

Atom	δ (ppm)	C_Q (kHz)	Atom	δ (ppm)	C_Q (kHz)
	Targ.; Cryst.; Gas.	Targ.; Cryst.; Gas.		Targ.; Cryst.; Gas.	Targ.; Cryst.; Gas.
C ₁	63; 62; 75	4311; 4080; 3526	O ₁	133; 124; 151	10,835; 10,944; 11,016
C ₂	148; 144; 144	2541; 2327; 2095	O ₂	53; 21; 34	11,490; 11,850; 11,520
C ₃	126; 125; 137	2945; 2943; 2490	H _{1A}	4; 3; 5	345; 352; 192
C ₄	129; 129; 135	3093; 3107; 2554	H _{1B}	4; 3; 5	343; 350; 193
C ₅	124; 125; 135	2931; 3018; 2576	H ₃	6; 6; 8	446; 445; 212
C ₆	126; 126; 134	3068; 3083; 2516	H ₄	6; 6; 8	448; 449; 214
C ₇	123; 122; 135	2709; 2671; 2428	H ₅	6; 6; 8	450; 450; 214
C ₈	175; 173; 172	3409; 3393; 3192	H ₆	6; 6; 8	451; 449; 214
C ₉	119; 119; 125	2453; 2440; 1953	H ₇	6; 5; 8	447; 448; 212
C ₁₀	128; 130; 136	3445; 3530; 3069	H ₉	5; 5; 7	446; 447; 214
C ₁₁	136; 137; 137	1834; 1977; 1781	H ₁₀	6; 6; 8	443; 443; 210
C ₁₂	134; 134; 142	3319; 3343; 2862	H ₁₂	6; 6; 8	446; 445; 210
C ₁₃	112; 106; 113	2169; 1988; 1510	H ₁₃	5; 5; 7	445; 448; 217
C ₁₄	173; 174; 174	4336; 4280; 4075	H ₁₄	10; 9; 10	279; 279; 178

^aSee Figures 1 and 2 for the models and atomic positions.

orbital (GIAO) approach [19], and they have been placed in equation: $\delta = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$. To evaluate the C_Q properties, electric field gradients (q_{ii} : $|q_{zz}| > |q_{yy}| > |q_{xx}|$) have been calculated for each atom and they have been placed in equation: $C_Q = e^2 Q q_{zz} / h$. The standard values of nuclear electric quadrupole moment (Q) have been used for the C_Q evaluations [20]. Since the NMR parameters are initially originated from the electronic sites of atoms, they could reveal helpful information about the electronic properties of matters [18]. Fortunately, high-level quantum chemical computations could yield reliable NMR parameters, which are comparable to experiments as an advantage of computational chemistry studies [21].

3 Results and Discussion

3.1 Optimised Properties

The results of optimisation processes for the investigated structures (Fig. 1) including energies and geometries are summarised in Tables 1 and 2. As shown in Figure 1, the planarity of single molecule in the crystalline phase is reoriented in the gaseous phase, which shows the effects of existence of neighbourhood molecules in the crystalline phase. The main goal of this work is to show the effects of neighbourhood molecules on a central molecule (target) in the crystalline structure (Fig. 2), which is investigated by comparison of results for gaseous and

crystalline phases. The results of total energies for two structures of gaseous and crystalline phases show that the former structure is more stable than the latter one. The trend could be followed by the changes of geometries for the gaseous molecule in comparison with the crystalline molecule as seen by the parameters of Table 2. The changes of geometries from the original crystal to optimised gaseous structure are obvious, and they show that the molecule undergoes a relaxation in the absence of neighbourhood molecules. The changes of geometries are seen for all bond lengths, angles, and dihedrals. Since the positions of hydrogen atoms are not correctly detected by the X-ray crystallography technique, the geometries of hydrogen atoms positions in the gaseous structure show significant differences in comparison with the crystalline structure. The geometries of other atoms also detect the effects of being in gaseous and crystalline structures as could be seen by the change of molecular shape from planar form in the crystalline structures to non-planar form in the gaseous structure. The dihedral angles are important in determining the three-dimensional shapes of the structures, in which their changes yielded different molecular shapes in the two phases. The neighbourhood molecules have direct and indirect effects on the central molecule of crystalline phase; therefore, the real properties of molecules could be better defined by their existence in the investigated models. It is known that the final properties and applications of chemical compounds are mainly dependent on the three-dimensional shapes of the structures; therefore, detections of correct structures

and their changes are important tasks for these purposes. The values of energy level for the HOMO and the LUMO show significant effects for the HOMO levels regarding the changes of LUMO levels. Another observation is that the distance between HOMO and LUMO levels is increased in the gaseous form in comparison with the crystalline form, which means that the electric conductivities are changed in two crystalline and gaseous phases. Since the dipole moments are dependent on the structural orientations, it could be seen that the polarity is increased in the gaseous phase as a result of structural changes during optimisation (Fig. 1). It is noted that the geometries of original crystalline structure are directly reported from [3] and their properties are obtained by performing single-point energy calculations for the original structure as is. The geometries and properties of the gaseous structure are all obtained by the optimisation process.

3.2 NMR Properties

The NMR properties including chemical shifts (δ) and quadrupole coupling constants (C_Q), which are both generated from the electronic sites of atoms, could reveal insightful information about the investigated structures [18]. Within this work, both NMR parameters have been obtained to achieve information about the crystalline effects on the electronic and structural properties of the investigated BBA structure (Table 3). The NMR properties have been calculated for the original crystalline structure as is, and they have been calculated for the optimised gaseous structure to make a comparison between the results. The main purpose of this work is to investigate the properties of singular molecules in different crystalline and gaseous phases (Fig. 1). However, we also calculated the properties for a target molecule in the real crystalline cluster (Fig. 2) to make possible a better comparison of properties for an interested reader. The obtained results show that the atomic properties detect the effects of crystalline and gaseous phases, in which the magnitudes of effects are different for different atoms. There are three sets of atoms including carbon, oxygen, and hydrogen with initial different chemical characteristics. As shown in Figure 1, the atoms C_2 – C_7 and C_8 – C_{13} belong to two benzene rings and the atoms C_1 and C_{14} are placed outside the rings. The atom C_1 , as a typical aliphatic carbon with sp^3 hybridisation, plays as a connection point between the two benzene rings through the atom O_1 bridge. Comparing the NMR properties of the atom C_1 and the other carbon atoms shows significant changes between their chemical environments as expected due to different hybridisations.

As shown in Figure 1, the planarity of molecule in the crystalline phase is changed to non-planar form in the gaseous phase by twisting around the C_1 – O_1 bond. As a result, significant changes for δ and C_Q properties of the atom C_1 could be seen from the crystalline phase to gaseous structure. Examining the magnitudes of δ parameters shows that the chemical environment of the atom C_1 has been shifted to higher fields in the gaseous structure in comparison with the crystalline structure, which yields the lower magnitude of C_Q for this condition.

For the atoms C_2 – C_7 of the first benzene ring, the properties of atoms are almost similar with notable changes from the crystalline to gaseous structure. Among which, the significant properties are seen for the addition point of benzene ring, the atom C_2 . For the atoms C_8 – C_{13} of the second benzene ring, the changes are also seen between the atoms of crystalline and gaseous structures. The most notable properties are also seen for the atom C_8 , which is the addition point of the second benzene ring, and it is directly connected to the atom O_1 . It is worth noting that the prediction of three-dimensional structures is very important in determining their properties as could be seen by different evaluated properties of the investigated crystalline and gaseous structures. The atom C_{14} , which is placed outside the second benzene ring as an aldehyde carbon atom, reasonably shows different properties in comparison with the other carbon atoms. Interestingly, the fact that the magnitudes of δ for the atoms C_8 and C_{14} are similar may be due to similarities in hybridisations and connecting oxygen atoms. The atoms O_1 and O_2 make the second set of atoms of the investigated structures, in which different chemical environments are seen for them. The atom O_2 is placed outside the benzene ring, in which its chemical environment is less changed than the atom O_1 as the bridge of two connected benzene rings. The hydrogen atoms are the third sets of existing atoms in the investigated structures. The atoms H_{1A} and H_{1B} are the hydrogens of the aliphatic C_1 atom; therefore, their properties are different from the other hydrogen atoms. The electronic sites of hydrogen atoms are not electron rich; therefore, their shifts of chemical environments are not notable in comparison with heavier atoms. However, from crystalline to gaseous structure, the magnitudes of C_Q properties are significantly changed due to the improper localisation of hydrogen atomic positions by the X-ray technique. The aldehyde atom H_{14} also shows different properties in comparison with the other hydrogen atoms. As a concluding remark, removal of crystalline limitations could make the structures to detect new properties, which is important especially in the low-concentration studies with molecules far from each other. Finally, the

intermolecular interactions dictate the molecules to be arranged, in which the molecules are differently relaxed in the absence of these interactions as could be seen by the investigated gaseous structure.

4 Conclusions

Our DFT calculations indicated that the properties of BBA detect the crystalline effects as could be easily seen by different shapes of gaseous and crystalline phases. Moreover, the atomic properties indicated that the crystalline effects could also influence on electronic properties of atoms as could be seen by the evaluated magnitude of δ and C_q properties for both gaseous and crystalline structures. However, the magnitudes of effects are different for different atomic positions, in which the effects for atoms in aromatic ring are more significant than the atoms outside the rings. The linker oxygen atom of the two benzene rings also plays an important role in determinations of the properties of BBA.

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