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# A Combined Experimental and Theoretical Study on the Reaction Mechanism and Molecular Structure of 4-(Diphenylamino)-3-iodo-2(5*H*)-furanone

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The simultaneous  $\alpha$ -iodination and N<sup>β</sup>-arylation mechanism of 5-alkyloxy-4-phenylamino-2(5*H*)-furanone by (diacetoxyiodo)benzene was investigated by means of density functional theory (DFT) with B3LYP/6-31G\*//LANL2DZ, selecting 4-(diphenylamino)-5-methyloxy-3-iodo-2(5*H*)-furanone as the calculation model. In addition, the effect of solvent on the reaction pathway was investigated using the Polarisable Continuum Model (PCM). Good agreement was found between the computational and the experimental results. Furthermore, single crystals of 4-(diphenylamino)-5-ethoxy-3-iodo-2 (5*H*)-furanone were grown by slow evaporation technique. The molecular structure analysis was performed by single crystal X-ray analysis and theoretical calculations using a semi-empirical quantum chemical method and DFT/B3LYP methods with a LANL2DZ as basis set.

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#### Introduction

2(5H)-Furanones have been widely explored since they are frequently found in many natural products and have recently emerged as significant synthetic intermediates.<sup>[1-7]</sup> Among the studies on 2(5H)-furanone chemistry, <sup>[8–15]</sup> much attention has also been focussed on the efficient synthesis of iodo-2 (5H)-furanones for their diverse value.<sup>[16–20]</sup> In our previous work,<sup>[21]</sup> a series of novel 4-diarylamino-3-iodo-2(5H)furanones were synthesised accidentally via the simultaneous  $\alpha$ -iodination and N<sup> $\beta$ </sup>-arylation by an efficient difunctionalizable transfer reagent PhI(OAc)<sub>2</sub> ((diacetoxyiodo)benzene, DIB), during our study on the intramolecular cyclization of 4-arylamino-2(5H)-furanones. A possible mechanism of the simultaneous  $\alpha$ -iodination and N<sup> $\beta$ </sup>-arylation was also proposed. As part of the ongoing studies, further investigation on the simultaneous  $\alpha$ -iodination and N<sup> $\beta$ </sup>-arylation mechanism was carried out by means of density functional theory (DFT) calculations with B3LYP/6-31G\*//LANL2DZ, and the effect of solvent on the reaction pathway using the Polarisable Continuum Model (PCM). In addition, the molecular structure analysis of the product 4-(diphenylamino)-5ethoxy-3-iodo-2(5H)-furanone was performed by single crystal X-ray and quantum chemical calculations. The geometrical parameters (bond lengths, bond angles, and torsion angles) were calculated by a semi-empirical quantum

chemical method (AM1) and DFT/B3LYP methods with a LANL2DZ basis set.

### Experimental

Synthesis of 4-Diarylamino-3-iodo-2(5H)-furanones

The 4-diarylamino-3-iodo-2(5*H*)-furanones were synthesized in our previous study (Scheme 1).<sup>[21]</sup>

## X-Ray Crystallographic Studies

The single crystals of 4-(diphenylamino)-5-ethoxy-3-iodo-2 (5H)-furanone used for data collection were obtained by slow evaporation of a petroleum ether–dichloromethane solvent mixture with a temperature variation of 25°C. A yellow block



single crystal of the compound with dimensions of 0.24 mm  $\times$  $0.21 \text{ mm} \times 0.18 \text{ mm}$  was chosen. The crystal data collections were made using a Bruker SMART 1000 CCD area detector equipped with graphite used for data collection, cell refinement, and data reduction. The structure was solved by direct methods using the *SHELXS* program of the *SHELXL*-97 package and refined with the *SHELXL* program.<sup>[22,23]</sup> The final refinement was performed by a full-matrix least-squares method with anisotropic thermal parameters on  $F^2$  for the non-hydrogen atoms. The hydrogen atoms were determined by theoretical calculations. The details of the X-ray data collection, structure solution, and structure refinement are given in Table 1. Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre. CCDC No: 1038867 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK. Fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk.

#### Computational Details

#### Quantum Chemical Calculations

All the calculations were performed by using the *Gaussian 03* package and *Gauss-View* molecular visualization software on a personal computer without restricting any symmetry for the title. For modelling, the initial guess of the compound was first obtained from the X-ray coordinates and the structure was optimized by a semi-empirical quantum chemical method (AM1) and density functional theory (DFT)/B3LYP methods with LANL2DZ as the basis set. Geometric parameters for optimized molecular structures and electric charge densities were calculated by the B3LYP method with LANL2DZ basis sets.

### Reaction Mechanism Study

In our previous work,<sup>[21]</sup> a possible simultaneous  $\alpha$ -iodination and N<sup>β</sup>-arylation mechanism of 5-alkyoxy-4-phenylamino-2 (5*H*)-furanone in the presence of DIB was proposed (Scheme 2).

In the proposed mechanism, as the transition structures are unstable and it is difficult to detect them experimentally, theoretical studies seemed to be more appropriate. To determine the conformational stability of the transition structures and products, we carried out molecular geometry optimization calculations for all conformations using the 6-31G\* or LANL2DZ basis set with the B3LYP method. Energy, frequency calculations, and zero-point energy (ZPE) corrections were performed at the same level of theory. As for the transition structures calculation, the B3LYP method was applied with the LANL2DZ basis set. In order to lower the computational cost, 4-(diphenylamino)-5-methoxy-3-iodo-2(5H)-furanone was selected as the calculation model. The computed stationary points were characterized as minima or transition states by diagonalizing the Hessian matrix and analyzing the vibrational normal modes. In this way, the stationary points can be classified as minima if no imaginary frequencies are shown, or as transition structures if only one imaginary frequency is obtained.<sup>[24]</sup> Furthermore, the intrinsic reaction coordinate (IRC) calculations were performed to confirm that the optimized transition states correctly connect two relevant minima.<sup>[25]</sup> The particular nature of the transition structures has been determined by analyzing the motion described by the eigenvector associated with the imaginary frequency. The solvation energies for the reactants, transition structures, and products were computed using the solvation model PCM

Empirical formula	C <sub>18</sub> H <sub>16</sub> INO <sub>3</sub>
Formula weight	421.22
Temperature [K]	298(2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
a [Å]	10.7597(19)
<i>b</i> [Å]	9.8460(18)
c [Å]	18.725(3)
$\beta$ [°]	114.829(8)
Volume [Å <sup>3</sup> ]	1800.4(5)
Ζ	4
$D_{\rm c} [{\rm g m}^3]$	1.554
$\mu [\mathrm{mm}^{-1}]$	1.792
F(000)	832
$2\theta$ range for data collection	$2.09^{\circ} < \theta < 25.25^{\circ}$
Index ranges	$-12 \le h \le 12, -11 \le k \le 11,$
	$-22 \le l \le 21$
Reflections measured	9001
Unique reflections	3260
Observed reflections $(I > 2\sigma(I))$	2554
Goodness-of-fit on $F^2$	1.040
Final <i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.0483, wR_2 = 0.1333$
Final R indexes [all data]	$R_1 = 0.0609, wR_2 = 0.1453$
Largest diff. peak/hole [e Å <sup>-3</sup> ]	1.075/-1.163

 Table 1.
 Crystal data and structure refinement for 4-(diphenylamino) 

 5-ethoxy-3-iodo-2(5H)-furanone

with permittivities of 46.826, 35.688, 10.125, 8.930, and 2.374, for DMSO, CH<sub>3</sub>CN, CH<sub>2</sub>ClCH<sub>2</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, and toluene, respectively.

# **Results and Discussion**

## Reaction Mechanism

The DFT calculations suggest a possible simultaneous  $\alpha$ -iodination and N<sup>β</sup>-arylation mechanism of 5-alkyoxy-4phenylamino-2(5*H*)-furanone via DIB. The possible reaction path is that of reaction via TS1, TS2, and TS3 leading to the reaction product. The optimized stationary structures (the reactant, the transition structures, and the product) on the potential energy surfaces of the reactions are depicted schematically in Figs 1–5. Geometry optimization of the transition structures involved was carried out at the B3LYP level of theory with the LANL2DZ basis set. Normal mode analysis clearly indicates the structures have only one imaginary frequency of 17.725i, 174.7878i, and 28.1065i cm<sup>-1</sup>, which were confirmed to be the first-order saddle point connecting the corresponding reactants and products by IRC calculations.

The transition structure TS1 was formed from substrate 1 and PhI(OAc)<sub>2</sub> in the first step. In the transition structure TS1, the new bond produced between Ph-I<sub>7</sub> and C<sub>1</sub> has a bond distance of 2.10 Å. The distance between O<sub>23</sub> and I<sub>7</sub> is 2.54 Å, and the distance between O<sub>26</sub> and I<sub>7</sub> is 3.61 Å (the atom numbering is given in Fig. 2). The distances between the oxygen atom in acetate and I<sub>7</sub> are all longer than a normal bond distance. So **A** is not actually produced in the reaction and the bond of O<sub>23</sub> and I<sub>7</sub> or the bond of O<sub>26</sub> and I<sub>7</sub> is automatically broken to give the transition structure TS1. Furthermore, the distance between N and H (1.01 Å), before the reaction, increases to 1.07 Å after the reaction. Due to the increase of distance, the N–H bond disconnects. TS1 in then converted into TS2 in the second step.



Scheme 2. Plausible mechanism for DIB-promoted difunctionalization.



Fig. 1. DFT-optimized structures of 1 and  $PhI(OAc)_2$ , distances are in Å.



Fig. 2. DFT-optimized structures of TS1, distances are in Å.



Fig. 3. DFT-optimized structures of TS2, distances are in Å.



Fig. 4. DFT-optimized structures of TS3, distances are in Å.

In the second step, the bond length between  $I_7$  and  $C_{17}$  (the atom numbering is given in Fig. 2) which is  $I_7$  and  $C_{11}$  in Fig. 3, increased slowly from 2.19 to 2.22 Å. The distance between  $N_6$ and  $C_{17}$  (the atom numbering is given in Fig. 2) which is  $N_6$  and  $C_{11}$  in Fig. 3, decreased slowly from 4.75 to 4.20 Å. These changes are beneficial for  $N_6$ ,  $C_{11}$ ,  $I_7$ ,  $C_1$ , and  $C_2$  to form a fivemembered cycle (the atom numbering is given in Fig. 3). In the third step, the TS2 is converted into TS3 (Fig. 4) through a fivemembered cycle. In the process, the phenyl bonded to  $I_7$ transfers to  $N_6$ . Finally, the TS3 transforms into the product (Fig. 5) by bond length changes of the compound.

By means of the interrelationship of reactants, products, and transition states, as well as their relative energies, the potential energy surface profiles of the pathways corresponding to the



Fig. 5. DFT-optimized structures of product ( $R^1 = CH_3$ ,  $R^2 = H$ ), distances are in Å.

reaction are depicted in Table 2. From Table 2, we can see that the activation energy for the formation of TS2 is 400.766 kcal mol<sup>-1</sup>, which is in good agreement with the experimental observations. The  $\Delta H_{\text{gas}}$  of the reaction is 342.724 kcal mol<sup>-1</sup>, so the reaction is endothermic, which indicates a higher temperature can promote the reaction, but the temperature should not exceed a certain range. The calculated results were verified by experiments on temperature (Table 2).<sup>[21]</sup>

The effect of solvent on the reaction pathway was investigated using the PCM model. As shown in Table 3, the solvation energy (negative value) decreases with the increasing polarity of the solvent. This clearly indicates that reactants, transition structures, and products become more stable when the polarity of the solvent increases. Thus, the reactants, transition structures, and products in CH<sub>3</sub>CN are more stable compared with those in other organic solvents, even if CH<sub>3</sub>CN is not the most polar of the five solvents. This can be rationalized in that solvents play a crucial role in the reaction by stabilizing transition structures and providing an alternative lower energy pathway by which the reaction may proceed. Furthermore, the calculated results indicate CH<sub>3</sub>CN is the best solvent for the reaction, which were verified by experiments on the solvent effect (Table 4) in our previous study.<sup>[21]</sup>

## Molecular Structure

As one of the 4-diarylamino-3-iodo-2(5*H*)-furanone products, the structure of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5*H*)furanone was confirmed by the result of a single crystal X-ray structure determination. The molecular structure with atom numbering of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5*H*)-furanone is shown in Fig. 6. Experimental details for data collection and structure refinement are summarized in Table 1. The selected bond lengths and angles are presented in Tables 5 and 6.

The compound 4-(diphenylamino)-5-ethoxy-3-iodo-2(5*H*)furanone is a 2(5*H*)-furanone derivative in which the structure shows two phenyl rings and a butenolide ring linked by an N atom. The two phenyl rings and butenolide ring are near to planarity, the angles between each phenyl ring and the butenolide ring being 122.8(4)° (C15–N1–C12) and 121.1(4)° (C15–N1–C6), respectively. The C14–C15–N1–C12 torsion angle is 16.6(10)°. The five-membered butenolide ring containing the atoms O2, C13,

Species	$\Delta E_{\rm gas}$ [Hartree mol <sup>-1</sup> ]	$\Delta H_{\rm gas}$ [Hartree mol <sup>-1</sup> ]	$\Delta G_{\rm gas}$ [Hartree mol <sup>-1</sup> ]	
1	-705.980148	-705.979204	-706.033555	
PhI(OAc) <sub>2</sub>	-699.590636	-699.589691	-699.658400	
TS1	-1176.496972	-1176.496028	-1176.580906	
TS2	-947.471747	-947.470803	-947.544385	
TS3	-947.557964	-947.557019	-947.626276	
Product	-947.565188	-947.564244	-947.636682	
Acetic acid	-229.015190	-229.014246	-229.047024	
Acetate	-228.445176	-228.444231	-228.477200	

Table 2. B3LYP/6-31G\* //LANL2DZ calculated thermodynamic properties (total energy with zero-point energy, free energy) of the reactants, transition states, and products

 Table 3. The solvation energies (kcal mol<sup>-1</sup>) of the reactants, transition structures, and products in seven distinct solvents

Species	DMSO	CH <sub>3</sub> CN	CH <sub>2</sub> ClCH <sub>2</sub> Cl	$\mathrm{CH}_2\mathrm{Cl}_2$	Toluene
1	-14.70	-15.38	-14.20	-13.92	-7.53
PhI(OAc)	-19.69	-21.57	-20.48	-20.10	-10.50
TS1	-26.49	-28.06	-26.24	-25.75	-13.93
TS2	-32.92	-34.03	-31.22	-30.59	-16.63
TS3	-18.31	-19.11	-17.79	-17.46	-9.78
Product	-20.64	-21.64	-20.09	-19.71	-10.84
Acetic acid	-4.43	-5.29	-5.24	-5.15	-3.15
Acetate	-57.00	-59.42	-56.19	-55.34	-34.31

 

 Table 4.
 Comparison of the 4-(diphenylamino)-5-methoxy-3-iodo-2 (5H)-furanone isolated yields in different solvents

Entry <sup>A</sup>	Solvent	Yield <sup>B</sup> [%]	
1	CH <sub>3</sub> CN	86	
2	ClCH <sub>2</sub> CH <sub>2</sub> Cl	73	
3	Toluene	65	
4	$CH_2Cl_2$	45	
5	DMSO	Trace	

<sup>A</sup>Reaction conditions: 5-methoxy-4-phenylamino-2(*5H*)-furanone 0.2 mmol, DIB 0.3 mmol, solvent 10 mL, reaction temperature 60°C, reaction time 40 h. <sup>B</sup>Isolated yield.

C14, C15, and C16 and is defined by a plane with the least square plane equation: 0.6254x - 0.7387y + 0.2513z = -0.7004. Furthermore, the atoms O1, N1, and I1 attached to the butenolide ring are nearly coplanar with the butenolide ring, with deviations from the plane of 0.1220, 0.0347, and 0.0599 Å, respectively. Both the C14–C15 (1.348(7) Å) and C13–O1 (1.207(7) Å) bonds show typical double bond characteristics. The C15–N1 bond length (1.358(6) Å) is significantly shorter than for C6–N1 (1.449(7) Å) and C12–N1 (1.433(7) Å). The shortening of C15–N1, and atoms N1 and O1 being nearly coplanar with the butenolide ring, indicates that extensive conjugation take places among lone pair electrons of N1, the C14–15 double bond, and the C13–O1 carbonyl bond.

The structural parameters of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5*H*)-furanone were also calculated theoretically and the optimized molecular structure is shown in Fig. 7. Some selected optimized parameters (bond lengths, bond angles, and torsion angles) theoretically calculated by AM1 and B3LYP/



**Fig. 6.** Molecular structure of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5*H*)-furanone, showing 30% probability displacement ellipsoids and atom labelling scheme.

LANL2DZ methods are listed in Tables 5 and 6. These selected parameters are compared with their experimental values. It is well known that DFT-optimized bond lengths are usually longer and more accurate than AM1, due to the inclusion of electron correlation. Conversely, according to correlations values, the AM1 method correlates well with the bond lengths compared with the B3LYP method. While the B3LYP method gave more accurate results for the bond angles compared with the AM1 method, the AM1 method gave more accurate results for the torsion angles compared with the B3LYP method. From Table 5 it is seen that most bond lengths are found to be greater than the experiment results. These differences are probably due to the experimental results corresponding to the solid phase while the theoretical calculations correspond to the gaseous phase. In the solid state, the existence of the crystal field along with the intermolecular interactions has connected the molecules together, which results in the differences of bond parameters between the calculated and experimental values.

The electric charge distribution for 4-(diphenylamino)-5ethoxy-3-iodo-2(5*H*)-furanone by B3LYP/LANL2DZ is shown in Table 7. The electric charge densities for atoms N1, C15, C14, C13, and O1 are -0.500, 0.201, -0.450, 0.785, and -0.565 e, respectively, which supports the observation that the essential part of the electron delocalization is concentrated in the N1, C15, C14, C13, and O1 region, forming the

Bond AM1	Bond length [Å]		Bond	Bond length [Å]			
	B3LYP	Experimental		AM1	B3LYP	Experimental	
C(14)–C(15)	1.381	1.373	1.348(7)	C(5)–C(6)	1.408	1.408	1.374(9)
C(15)-C(16)	1.558	1.552	1.511(8)	C(6) - C(1)	1.411	1.409	1.385(8)
C(15)–N(1)	1.361	1.382	1.358(6)	C(4)–C(5)	1.393	1.405	1.395(9)
C(13)–C(14)	1.470	1.478	1.434(8)	C(3)–C(4)	1.393	1.410	1.373(10)
C(14)–I(1)	1.988	2.097	2.070(6)	C(2)–C(3)	1.394	1.408	1.378(11)
C(16)–O(2)	1.427	1.461	1.411(8)	C(1) - C(2)	1.392	1.407	1.377(9)
C(16)–O(3)	1.399	1.434	1.369(9)	C(11)–C(12)	1.409	1.410	1.369(8)
C(13)–O(2)	1.406	1.433	1.375(8)	C(12)–C(7)	1.409	1.410	1.395(8)
C(13)–O(1)	1.222	1.229	1.207(7)	C(10)–C(11)	1.393	1.405	1.384(9)
C(17)-C(18)	1.511	1.534	1.497(2)	C(9) - C(10)	1.394	1.408	1.372(10)
O(3)-C(17)	1.431	1.480	1.435(11)	C(8)–C(9)	1.394	1.409	1.359(11)
N(1)-C(6)	1.433	1.454	1.449(7)	C(7)–C(8)	1.393	1.405	1.390(10)
N(1)-C(12)	1.431	1.447	1.433(7)				

Table 5. Comparison of the selected bond lengths (Å) of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5H)-furanone by using AM1 and B3LYP/LANL2DZ

Table 6. Comparison of the selected bond angles (°) of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5H)-furanone by using AM1 and B3LYP/ LANL2DZ

Angle	Size of angle [deg.]			Angle	Size of angle [deg.]		
	AM1	B3LYP	Experimental		AM1	B3LYP	Experimental
C(14)-C(15)-C(16)	107.514	108.298	106.9(5)	C(4)–C(3)–C(2)	119.750	119.734	120.5(6)
C(14)-C(15)-N(1)	131.627	132.630	133.8(5)	C(2)–C(1)–C(6)	120.516	120.112	119.5(6)
C(16)-C(15)-N(1)	120.836	119.069	119.2(5)	C(6)-C(1)-C(2)	119.972	119.857	119.5(6)
C(15)-C(14)-C(13)	108.138	109.946	109.6(5)	N(1)-C(12)-C(11)	119.584	120.469	120.8(5)
C(15)–C(14)–I(1)	131.549	131.089	133.4(4)	N(1)-C(12)-C(7)	120.924	119.662	119.1(5)
C(13)–C(14)–I(1)	120.311	118.762	116.9(4)	C(11)-C(12)-C(7)	119.441	119.819	120.0(5)
C(15)-C(16)-O(2)	105.176	104.376	105.4(5)	C(12)-C(11)-C(10)	119.839	119.905	120.6(6)
C(15)-C(16)-O(3)	115.277	114.080	108.5(5)	C(11)-C(10)-C(9)	120.515	120.474	119.4(7)
O(2)-C(16)-O(3)	106.879	112.637	112.0(6)	C(10)–C(9)–C(8)	119.849	119.446	120.7(7)
C(16)-O(2)-C(13)	109.275	109.698	109.3(5)	C(9)–C(8)–C(7)	120.526	120.434	120.7(6)
C(14)-C(13)-O(2)	109.638	107.650	108.5(5)	C(12)-C(7)-C(8)	119.830	119.920	118.6(6)
C(14)-C(13)-O(1)	135.593	131.203	131.3(7)	C(6)–N(1)–C(12)	115.590	117.322	116.1(4)
O(2)-C(13)-O(1)	114.759	121.129	120.1(6)	N(1)-C(6)-C(5)	120.857	120.145	120.9(5)
C(16)-O(3)-C(17)	118.159	119.732	106.4(7)	N(1)-C(6)-C(1)	119.863	119.608	118.5(5)
O(3)-C(17)-C(18)	110.089	114.090	107.1(9)	C(5)-C(6)-C(1)	119.253	120.233	120.6(5)
C(15)–N(1)–C(6)	121.186	119.174	121.1(4)	C(6)-C(5)-C(4)	119.925	119.685	119.6(6)
C(15)–N(1)–C(12)	123.015	123.502	122.8(4)	C(5)–C(4)–C(3)	120.583	120.370	119.6(7)
Torsion angle	Size of torsion angle [deg.]			Torsion angle	Size of torsion angle [deg.]		le [deg.]
	AM1	B3LYP	Experimental		AM1	B3LYP	Experimental
C(14)-C(15)-N(1)-C(12)	7.818	28.466	16.6(10)	C(15)-C(14)-C(13)-O(1)	-178.969	-179.716	-172.3(7)
C(14)-C(15)-N(1)-C(6)	-166.701	-150.977	-164.0(6)	C(15)-C(16)-O(2)-C(13)	-4.978	-1.672	-2.0(8)
C(14)-C(15)-C(16)-O(2)	4.879	0.867	4.5(7)	O(3)-C(16)-O(2)-C(13)	118.022	122.609	115.8(6)
N(1)-C(15)-C(16)-O(3)	68.992	56.896	61.2(8)	C(16)-O(2)-C(13)-O(1)	177.473	179.524	175.8(7)
C(12)-N(1)-C(6)-C(5)	-92.826	-135.525	-121.3(6)	C(12)-N(1)-C(6)-C(1)	84.568	41.901	56.6(7)
N(1)-C(12)-C(11)-C(10)	179.604	178.903	177.5(5)	N(1)-C(12)-C(7)-C(8)	-178.167	-179.612	-178.2(5)
N(1)-C(6)-C(5)-C(4)	177.541	178.094	179.5(7)	N(1)-C(6)-C(1)-C(2)	-177.384	-177.761	-178.5(6)

conjugation system N1–C15–C14–C13–O1. Obviously, the electric charge transfers from N1 to O1. It is interesting to find that C6 and C12 are electropositive, accompanied by the other carbon atoms being electronegative in the two phenyl rings. The electric charge distribution result shows that excellent electron delocalization among N1, C15, C14, C13, and O1 takes place at the expense of the weakening degree of conjugation of the phenyl rings.

The compound is stabilized by an intermolecular hydrogen bond between C10–H10 as donor and the carbonyl oxygen atom O1 as acceptor, forming C10–H10…O1 ( $d_{H10...O1}$  2.5013 Å,  $d_{C10-H10}$  0.9300 Å,  $d_{C10-H10...O1}$  3.1997 Å,  $\angle$  C10–H1–O1 132.076°), as shown in Fig. 8. In addition, the extended crystal of the title compound is further stabilized by aromatic paralleddisplaced  $\pi \cdots \pi$  stacking interactions, and the centroid– centroid distance is 5.8634(8) Å, as shown in Fig. 9.



Fig. 7. Theoretical geometric structure of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5H)-furanone by (a) AM1 and (b) DFT/B3LYP methods.

Atom	Charge	Atom	Charge	Atom	Charge
C(1)	-0.222	C(9)	-0.210	C(17)	-0.057
C(2)	-0.200	C(10)	-0.199	C(18)	-0.664
C(3)	-0.217	C(11)	-0.201	N(1)	-0.500
C(4)	-0.196	C(12)	0.156	I(1)	0.257
C(5)	-0.229	C(13)	0.785	O(1)	-0.565
C(6)	0.165	C(14)	-0.450	O(2)	0.604
C(7)	-0.237	C(15)	0.201	O(3)	-0.631
C(8)	-0.202	C(16)	0.432		

Table 7. The nbo charge distribution (e) for the 4-(diphenylamino)-5ethoxy-3-iodo-2(5H)-furanone molecule by B3LYP



**Fig. 8.** Packing crystal structure of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5*H*)-furanone, the hydrogen bonds are shown as dashed lines.



**Fig. 9.**  $\pi \cdots \pi$  Stacking interaction of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5*H*)-furanones, H atoms not involved in the motif shown have been omitted.

# Conclusion

In summary, on the basis of the synthesis of 4-diarylamino-3iodo-2(5*H*)-furanones via the simultaneous  $\alpha$ -iodination and N<sup>β</sup>-arylation by an efficient difunctionalizable transfer reagent PhI(OAc)<sub>2</sub>, 4-(diphenylamino)-5-methoxy-3-iodo-2(5*H*)furanone was selected as the calculation model to further study the proposed reaction mechanism by DFT calculations. The calculations data show a good agreement with the experimental results. The effect of solvent on the reaction pathway was carried out by the PCM model, indicating that CH<sub>3</sub>CN is the best solvent for the reaction. In addition, the molecular structure analysis of 4-(diphenylamino)-5-ethoxy-3-iodo-2(5*H*)-furanone was studied experimentally (single crystal X-ray) and theoretically (AM1 and DFT/B3LYP method). The theoretical optimized geometric parameters (bond lengths, bond angles, and torsion angles) were compared with the experimental data. The calculated data are only slightly different from the experimental ones. An extensive conjugation takes places among N1, C14, C15, C13, and O1 at the expense of a weakened degree of conjugation of the phenyl rings. The crystal molecules are stabilized by an intermolecular hydrogen bond and aromatic paralled-displaced  $\pi \cdots \pi$  stacking interactions.

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