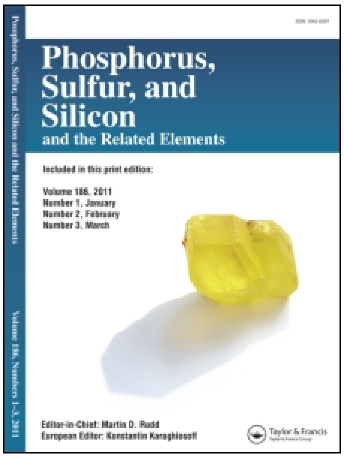

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New Heterocyclic Phosphorus Ylides: Synthesis, Crystal Structure, and Theoretical Calculation of Alkyl Substituted 3-(4-Benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrazol-3-yl)-3-oxo-2-(triphenylphosphoranylidene) Propanoates

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To cite this Article Üngören, Ş. Hakan , Saçmacı, Mustafa , Arıcı, Cengiz , Şahin, Ertan , Arslan, Taner and Kandemirli, Fatma(2009) 'New Heterocyclic Phosphorus Ylides: Synthesis, Crystal Structure, and Theoretical Calculation of Alkyl Substituted 3-(4-Benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrazol-3-yl)-3-oxo-2-(triphenylphosphoranylidene) Propanoates', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 11, 2877 — 2890

To link to this Article: DOI: 10.1080/10426500802591481

URL: http://dx.doi.org/10.1080/10426500802591481

Phosphorus, Sulfur, and Silicon, 184:2877–2890, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802591481

New Heterocyclic Phosphorus Ylides: Synthesis, Crystal Structure, and Theoretical Calculation of Alkyl Substituted 3-(4-Benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrazol-3-yl)-3-oxo-2-(triphenylphosphoranylidene) Propanoates

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*Novel alkyl substituted 3-(4-benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrazol-3-yl)-3-oxo-2-(triphenylphosphoranylidene) propanoates* ***(3)*** *were synthesized from 4-benzoyl-1,5-diphenyl-1H-pyrazole-3-carbonylchloride (1) and alkyl (triphenylphosphoranylidene) acetates* ***(2a–b)****. The synthesized compounds were characterized by elemental analysis, spectroscopic studies* ***(3a–b)****, and single crystal X-ray diffraction (3a). The mechanism of the reaction between* ***(1)*** *and* ***(2a)*** *was studied by AM1, and the geometrical parameters of the studied molecules were also carried out in B3LYP methods with the standard 6–31G (d,p) basis set. NBO analysis were studied for* ***1*** *and* ***2a*** *B3LYP methods with the standard 6–31G (d,p) basis set.*

Keywords AM1; B3LYP; 2,3-dihydro-1*H*-pyrazol; phosphorus ylides; reaction mechanism; X-rays

Received 20 July 2008; accepted 14 October 2008.

This study was financially supported by the Research Center of Bozok University. We thank Eskisehir Osmangazi Univ. Rectorate for the Gaussian03W program. We also thank Dr. O. Zafer Yesilel for his constructive suggestions throughout this work.

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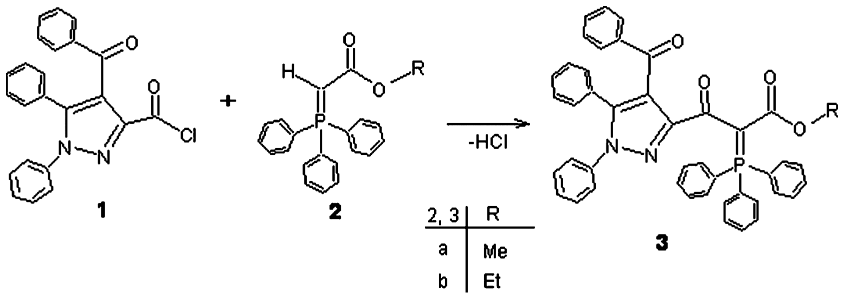
INTRODUCTION

Phosphorus ylides are reactive compounds that take part in many reactions of value in the synthesis of organic products. Phosphorus ylides are synthetic targets of interest, not least because of their value for a variety of industrial, biological, and chemical synthetic uses.[1–4]

Several methods have been developed for the preparation of phosphorus ylides. These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually obtained from the phosphine and an alkyl halide.[4–9]

Furthermore, it is well known that methylenephosphoranes including at least one proton attached to the methylene portion with acid chlorides lead to phosphorus ylides by losing halogen acid as in Scheme 1. We have reported an efficient synthetic route to heterocyclic phosphorus ylide (**3**) (Scheme 1) using 4-benzoyl-1,5-diphenyl-1H-pyrazole-3-carbonylchloride (**1**) and alkyl (triphenylphosphoranylidene) acetates (**2a–b**). The electronic structures of reagents, products, and transition and intermediate states were calculated to use in the mechanisms of the reaction discussion (Scheme 2).



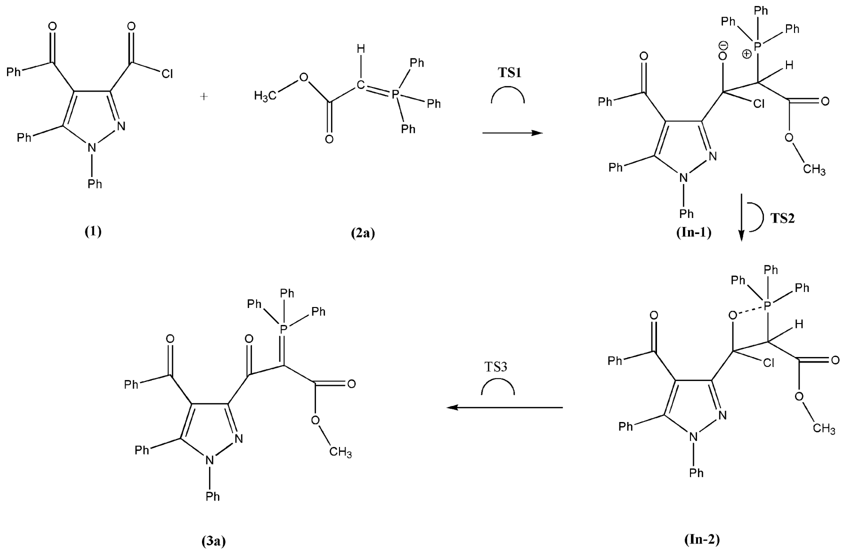
2, 3	R
a	Me
b	Et

SCHEME 1 Representative scheme of the studied reaction.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were acquired from a Gemini-Varian 200 MHz spectrometer (using $SiMe_4$ as an internal standard). Infrared absorption spectra were obtained from 4000 to 400 cm^{-1} in KBr pellet using a Jasco Plus Model 460 FT IR spectrometer. Elemental analyses were carried out using LECO-932 CHN-S analyzer. Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected.

Compound **1** was prepared according to published literature.[10] The compounds **3a–b** were obtained in good yields from the reaction of **1** and **2a–b**.



SCHEME 2 Schematic representation of the reaction of (**3a**).

For the crystal structure determination, the single crystal of the compound **3a** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The cylindrically shaped imaging plate covers the two-theta angular range between −60 and 140° with a crystal-film distance of 127.4 mm. The graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and oscillation scans technique with $\Delta\omega = 5^\circ$ for one image were used for data collection. Images for 3a were taken successfully by varying ω with three sets of different χ and ϕ values. For each compound, 216 images for six different runs covering about 99.7% of the Ewald spheres were performed. The lattice parameters were determined by the least-squares method on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects, and cell refinement was performed using Crystal Clear (Rigaku/MSC Inc., 2005) software.[11] The structures were solved by the direct method using SHELXS.[12] The positional and atomic displacement parameters (ADPs) were refined by the full-matrix least-squares method using SHELXL[12] and SIR2002.[13] An ORTEP drawing of structure with atomic numbering is shown in Figure 1. Details of crystal data, data collection, and refinement are given in Table I. Selected geometric parameters are given in Table II.

TABLE I Crystal Data and Structure Refinement Parameters for 3a

	3a
Empirical formula	C_{44} H_{33} N_2 O_4 P
Formula weight	684.69
Temperature (K)	293 (2)
Wavelength (Å)	0.71073 MoK_α
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.6181(12)
b (Å)	20.5319(14)
c (Å)	18.4961(13)
β (°)	92.7360(10)
V (Å^3)	3648.4(6)
Z	4
Absorption coefficient (mm^{-1})	0.121
D_{calc} (Mg m^{-3})	1.25
Theta range for data collection (å)	2.3–30.6
Number of reflection	10790
Number of reflection used	5049 ($I>2\sigma(I)$)
Parameters	461
Absorption correction type	Multi Scan
R	0.079
Rw	0.217
Goodness-of-fit	1.12
$[(\Delta\rho)_{\min}, (\Delta\rho)_{\max}]$ (eÅ^{-3})	0.20, −0.21

Methyl 3-(4-Benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrazol-3-yl)-3-oxo-2-(triphenyl phosphoranylidene) Propanoate (3a)

Compound **1** (0.38 g, 1 mmol) and compound **2a** (0.33 g, 1 mmol) were boiled in distilled toluene for 24 h. The toluene was extracted from the evaporator, and the oily residue was triturated with dry ether. The colorless crude product was filtered and recrystallized from acetonitrile and left to dry over P_2O_5.

Mp 148°C, yield; 0.49 g (72%). IR (KBr, cm^{-1}): $\gamma = 3058$, 2943 (C-H, arom. and aliph.); 1672, 1654, 1648 (C=O); 1437 (P-Ph). ^{1}H NMR (DMSO, ppm): $\delta = 3.42$ (s, 3H, OCH_3); 7.23–7.99 (m, 30H, Ph-H). ^{13}C NMR (DMSO, ppm): $\delta = 51.54$ (CH_3); 71.62 (P=C); 121.78 (C24-C25); 145.31 (C23-N1); 125.64–145.31 (C=C, arom.); 168.58 (C20-O1); 185.29 (C22-O3); 1971.67 (C26-O4). Found: C, 77.18; H, 4.86; N, 4.09%. Anal. Calc. for $C_{44}H_{33}N_2O_4P$: C, 77.11; H, 4.89; N, 4.00%.

TABLE II NBO Calculation Results of C—O Bond for (1) and (2a) Molecules

Bond	**1**	Bond	**2a**
$(\mathrm{C{-}O})_{\sigma\mathrm{bond}}$	$(0.581sp^{1.96})_C + (0.814sp^{1.26})_O$	$(\mathrm{C{-}P})_{\sigma\mathrm{bond}}$	$(0.766sp^{2.09})_C + (0.642sp^{2.24})_p$
$(\mathrm{C{-}O})_{\sigma\mathrm{anti\text{-}bond}}$	$(0.814sp^{1.96})_C - (0.581sp^{1.26})_O$	$(\mathrm{C{-}P})_{\sigma\mathrm{anti\text{-}bond}}$	$(0.642sp^{2.09})_C + (0.766sp^{2.24})_p$
$(\mathrm{C{-}O})_{\pi\mathrm{bond}}$	$(0.580p)_C + (0.815p)_O$	$(\mathrm{C{-}P})_{\pi\mathrm{bond}}$	$(0.950p)_C + (0.310pd)_P$
$(\mathrm{C{-}O})_{\pi\mathrm{anti\text{-}bond}}$	$(0.815p) - (0.580p)_O$	$(\mathrm{C{-}P})_{\pi\mathrm{anti\text{-}bond}}$	$(0.950p)_C - (0.310pd)_P$

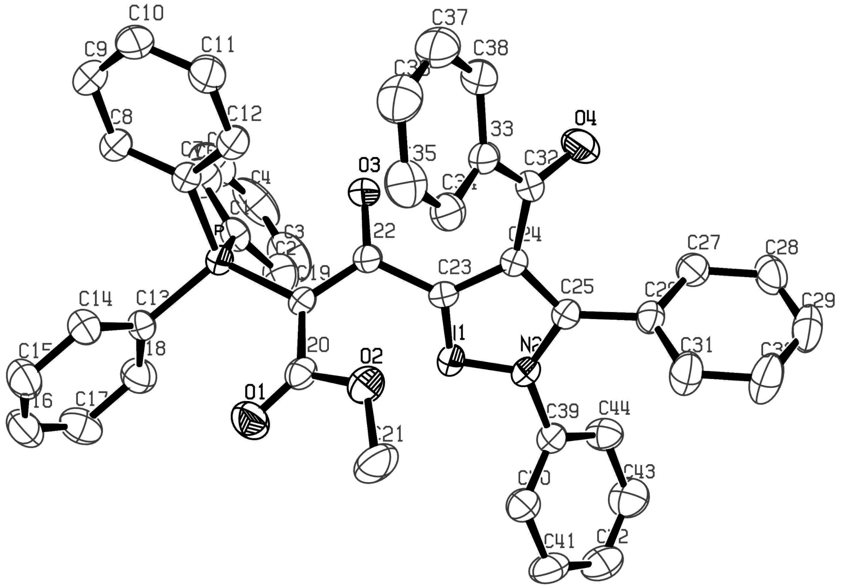


FIGURE 1 Molecular structure of **3a** showing the atom labelling scheme.

Ethyl 3-(4-Benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrazol-3-yl)-3-oxo-2-(triphenyl phosphoranylidene) Propanoate (3b)

Compound **1** (0.38 g, 1 mmol) and compound **2b** (0.35 g, 1 mmol) were refluxed in distilled toluene for 24 h. The toluene was extracted from the evaporator, and the oily residue was triturated with dry ether. The colorless crude product was filtered, recrystallized from acetonitrile, and left to dry over P_2O_5.

Mp 238 °C, yield; 0.47g (70%). IR (KBr, cm^{-1}): γ = 1671, 1668, 1653, (C=O), 1440 (P-Ph). ^1H NMR (DMSO, ppm): δ = 0.73, 0.77, 0.80 (t, 3H, CH_3), 3.43, 3.67, 3.71, 3.74 (q, 2H, OCH_2), 7.22–8.02 (m, 30H, Ph-H). ^{13}C NMR (DMSO, ppm): δ = 15.39 (CH_3), 60.08 (CH_2), 71.50 (P=C), 121.81 (C=C-Ph), 145.33 (C=N), 125.70–156.37 (Ar-C=C), 168.49, 185.27, 191.62 (C=O). Found: C, 77.35; H, 5.05; N, 4.01%. Anal. Calc. for $C_{45}H_{35}N_2O_4P$: C, 77.41; H, 5.12; N, 3.97%.

Computational Methodology

The calculations were performed by using GAUSSIAN 03W program package (Version 6.1, Rev D.01)[14] by means of AM1 and

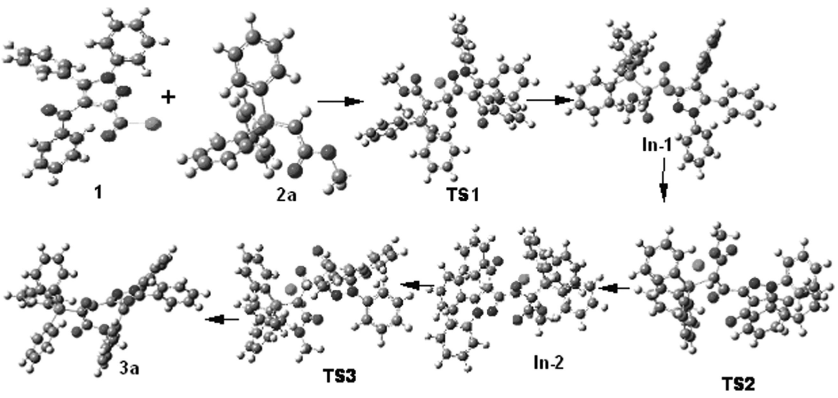


FIGURE 2 Structures of **1, 2a, TS1, TS2, TS3, In-1, In-2, 3a**.

B3LYP/6–31G(d,p) methods. Reactants, intermediates, and final products were carried out to study the mechanism of the reaction using AM1 method. Reactants and products were optimized at the B3LYP/6–31G(d,p) level of theory, and frequency calculations were carried out to check that no imaginary frequence exists also. Natural bond analysis (NBO) was carried out at B3LYP/6–31G(d,p) for reactants and products. Negative imaginary frequencies being found for transitional states (TS) means that their structures are true transition states, but does not guarantee that the TS have been found. One way to determine what reactants and products the transition structure connects is to perform an intrinsic reaction coordinate (IRC) calculation to follow the reaction path and thereby determine the reactants and products explicitly. Transition states were found using the AM1 semi-empirical level. All calculations were applied for the X-ray diffraction solved (**3a**) molecule, its reactants, and transitions states. These calculations will be a model for (**3b**) molecule also.

The atoms' spatial arrangements in reactants, intermediate (In), transition states (TS), and products are shown in Figure 2.

RESULT AND DISCUSSION

The mechanism for the reaction of alkyl substitute 3-(4-benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrazol-3-yl)-3-oxo-2-(triphenylphosphoranylidene) propanoates involves three steps. Two distinct intermediates are formed. The carbonyl group is an important functional group in organic chemistry. It undergoes both nucleophilic and electrophilic additions and has a profound influence on the properties of neighboring groups. 4-Benzoyl-1,5-diphenyl-1H-pyrazole-3-carbonylchloride **(1)** is the electrophilic group for this reaction.

NBO analysis gives the hybridization of the atoms and the weight of each atom in each localized electron pair bond. NBO calculation results for the C-O bond for (**1**) and (**2a**) molecules are as follows:

The results of NBO calculation (see Table II), which yields $(0.580p)_C + (0.815p)_O$, shows that the π bonding orbital of carbonyl group for **1** is polarized towards the oxygen atom. The NBO calculation for π^* antibonding orbital of carbonyl group for **1** yields $(0.815p)_C - (0.580p)_O$, and this shows polarization is towards the carbon atom, thus the larger coefficient of the carbon 2p orbital means that the carbon atom will interact with the nucleophilic groups.

According to the NBO analysis, π bonding consisting of $(0.950p)_C - (0.310pd)_P$ orbital for methyl (triphenylphosphoranylidene) acetates means that polarization is towards the carbon atom, and so in the reaction, the C(19) atom of methyl (triphenylphosphoranylidene) acetates plays important role as nucleophile.

The C(22) atom of the carbonyl group on benzoyl-1,5-diphenyl-1H-pyrazole-3-carbonylchloride, that is the electrophilic group, will approach the C(19) atom of methyl (triphenylphosphoranylidene) acetates during the reaction.

The charge of the C(22) atom of **1** number molecule 0.322 ē and the charge of the C(19) atom of **2a** number molecule is −1.514 ē. Therefore, charge control plays an essential role in this interaction and in the compounds' chemical reactivity.

Conformational and electron characteristic of the reactants, intermediates, and TS are given in Table III.

At first, the C(22) atom of (**1**) and the C(19) atom of (**2a**) are far away enough, though as the reaction progresses, the bond between the C(19) atom of (**2a**) and the C(22) atom of (**1**) becomes 1.593Å and the bond between the C(22), and the leaving group, Cl atom becomes 1.891 Å (Table III). In the transition state **TS1**, the distances between C(19)–C(22) and C(22)–Cl are 1.923 Å and 1.804, respectively (Table II). In the **TS1** structure, the π bond is formally broken. The atoms C(22) atom and C(19) are in a tetrahedral state, as seen from the angles given in Table III; for example, the bond angle C(23)–C(22)-Cl that is 113.8° in **(1)** becomes 103.3° in **In-1**.

Mulliken charges of C(19) and C(22) atoms being −1.514 ē and 0.322 ē in the molecules that are far away becomes −1.273 ē, 0.430 ē in the **TS1** and −1.011 ē, 0.381 ē in the **In-1** (Table III). The changing of Mulliken population values on atoms is due to the electronic density

TABLE III The AM1 Calculated Geometric and Electronic Parameters for 1, 2 TS1, TS2, TS3, In-1, In-2, and 3a and X-ray Data of 3a

Atoms	**1**	**2a**	**TS1**	**In-1**	**TS2**	**In-2**	**TS3**	**3a**	(**3a**)*
				Bond Lengths (Å)					
P–C(1)	—	1.618	1.634	1.630	1.631	1.612	1.593	1.622	1.800 (4)
P–C(19)	—	1.522	1.584	1.643	2.322	1.747	1.691	1.556	1.747 (3)
O(2)–C(21)	—	1.420	1.425	1.428	1.422	1.431	1.427	1.423	1.436 (5)
N(1)–N(2)	1.336	—	1.340	1.344	1.331	1.338	1.343	1.342	1.365 (4)
N(2)–C(39)	1.432	—	1.429	1.427	1.434	1.430	1.429	1.428	1.430 (5)
O(3)–C(22)	1.225	—	1.262	1.295	1.270	1.225	1.236	1.239	1.242 (4)
N(1)–C(23)	1.367	—	1.363	1.361	1.367	1.364	1.364	1.363	1.323 (4)
P–C(7)	—	1.617	1.606	1.613	1.635	1.669	1.598	1.615	1.804 (4)
O(1)–C(20)	—	1.251	1.240	1.226	1.235	1.225	1.221	1.239	1.199 (5)
C19–C20	—	1.411		1.593		1.491		1.441	1.445 (5)
N(2)–C(25)	1.415	—	1.414	1.413	1.415	1.410	1.417	1.414	1.364 (5)
O(2)–C(20)	—	1.392	1.384	1.377	1.387	1.382	1.386	1.385	1.356 (5)
P–C(13)	—	1.617	1.620	1.613	1.631	1.634	1.634	1.622	1.811 (4)
C(19)–C(22)	—	—	1.923	1.593	1.451	1.524	1.534	1.435	1.417 (5)
C(2)2–Cl	1.734	—	1.804	1.891	2.868	2.681	2.548	—	—
P–O(3)	—	3.367	2.588	2.496	2.059	3.411	3.296	2.660	—
C(22)–C(23)	1.467	—	1.486	1.501	1.457	1.486	1.485	1.476	1.500 (5)
O(4)–C(32)	1.238	—	1.240	1.240	1.241	1.242	1.234	1.238	1.215 (5)

(Continued on next page)

TABLE III The AM1 Calculated Geometric and Electronic Parameters for 1, 2 TS1, TS2, TS3, In-1, In-2, and 3a and X-ray Data of 3a *(Continued)*

Atoms	**1**	**2a**	**TS1**	**In-1**	**TS2**	**In-2**	**TS3**	**3a**	**(3a)***
				Bond Angles (°)					
C(2)3–C(22)–Cl	113.8	—	108.8	103.3	131.3	85.7	101.0	—	
O(3)–C(22)–Cl	121.3		117.0	111.8	64.7	134.9	104.0	—	
O(3)–C(22)–C(23)	124.9		121.6	117.5	121.4	118.4	117.9	120.8	116.3 (4)
C(1)–P–C(7)	–	105.5	107.4	109.7	108.2	108.3	110.2	107.2	108.7 (2)
C(1)–P–C(19)	–	108.1	107.0	110.2	121.4	112.6	118.3	110.4	109.2 (2)
C(7)–P–C(19)	–	115.5	111.1	114.6	95.2	110.7	102.4	112.3	114.0 (18)
C(13)–P–C(19)	–	113.1	120.5	113.5	153.7	113.6	118.3	112.3	112.0 (18)
O(3)–C(22)–C(23)	–	—	121.6	115.4	121.4	117.0	117.9	117.9	116.3 (4)
O(1)–C(20)–O(2)	–	113.6	117.2	117.5	116.0	120.7	116.9	114.8	119.8 (4)
C(19)–C(22)–C(23)	–	—	102.8	125.5	126.8	123.2	116.0	121.3	121.0 (3)
P–C(19)–C(20)	–	135.0	119.2	124.6	131.4	116.4	123.1	129.12	121.3 (3)
				Mulliken Charges (ē)					
O(1)	–	−0.476	−0.337	−0.300	−0.381	−0.299	−0.251	−0.392	
O(2)	–	−0.295	−0.342	−0.331	−0.304	−0.359	−0.359	−0.290	
O(3)	−0.220	—	−0.528	−0.636	−0.480	−0.254	−0.286	−0.417	
O(4)	−0.280	—	−0.315	−0.324	−0.028	−0.319	−0.258	−0.291	
N(1)	−0.009	—	0.004	−0.025	−0.001	−0.038	−0.001	−0.034	
N(2)	−0.059	—	−0.068	−0.075	−0.056	−0.067	−0.076	−0.072	
P	–	3.404	3.394	3.379	3.283	3.350	3.362	3.414	
C(19)	–	−1.514	−1.273	−1.011	−0.777	−0.848	−0.882	−1.374	
C(22)	0.322	—	0.430	0.381	0.384	0.382	0.422	−0.403	
Cl	−0.071	–	−0.198	−0.317	−0.685	−0.821	−0.823	—	
				Dipole Moment(μ)					
	6.0816	6.9820	3.4522	6.9945	5.3045	3.9691	11.4403	4.3147	

*X-ray results.

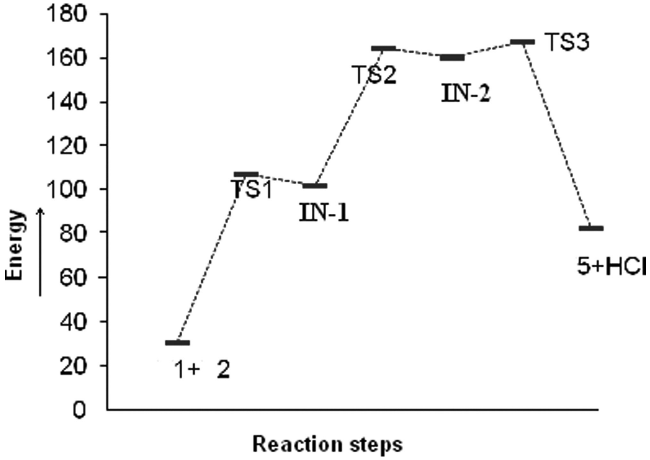


FIGURE 3 The reaction energy graphic of the studied molecules.

redistribution because of different orbitals overlapping. In the second mechanism **In-2** intermediate occurs via **TS2**, as the phosphorus atom is in the approximately tetrahedral state in **In-1**, and is in the trigonal pyramid in **TS2** and **In-2** (see Table III). In the last step, full breakage of Cl occurs, and **3a** is formed. Energy characteristics are given in Figure 2. The reaction coordinate is the quantity that measures the progress of the reaction. We can see that an energy barrier exists between the reactants and the products. The first step in this reaction is very slow, as seen from the Figure 3.

The AM1 and B3LYP/6–31G(d,p) calculated geometrical parameters of the studied molecules were given in Tables III and IV with X-ray results respectively. Phosphorus-containing bond lengths are approximately 0.2 Å smaller at the AM1 level and approximately 0.02 Å bigger at the B3LYP/6–31G(d,p) level than the experimental values for the **3a** molecule. For example, bond lengths of P–C(1), O(2)–C(21), N(1)–C(23), C(19)–C(20) are 1.800(4) Å, 1.436(5) Å, 1.323(4) Å, and 1.445(5) Å for experimental results; 1.827 Å, 1.432 Å, 1.328 Å, and 1.444 Å for the B3LYP/6–31G(d,p) results; and 1.622 Å, 1.423 Å, 1.363 Å, and 1.441 Å for AM1 results.

However, in Table III (AM1) and Table IV (DFT), phosphorus-containing bond angles are most near to experimental values at AM1 level than B3LYP/6–31G(d,p) level for **3a** molecule. The biggest differences for the bond lengths without phosphorus were observed for N(2)–C(25) (1.414 calculated–1.364 X-ray) at AM1 level; O(1)–C(20) (1.233 calculated–1.199 X-ray) at DFT level in selected bond lengths.

TABLE IV The B3LYP/6–31G(d,p) Calculated Geometric and Electronic Parameters of 1, 2a, In-1, In-2, and 3a and X-ray Data of 3a

	1	**2a**	**In-1**	**In-2**	**3a**	**(3a)***
Bond Lengths (Å)						
P–C(1)	—	1.842	1.831	1.842	1.827	1.800 (4)
P–C(19)	—	1.713	1.863	1.851	1.765	1.747 (3)
O(2)–C(21)	—	1.427	1.443	1.440	1.432	1.436 (5)
N(1)–N(2)	1.341	—	1.339	1.356	1.355	1.365 (4)
N(2)–C(39)	1.433	—	1.430	1.433	1.428	1.430 (5)
O(3)–C(22)	1.196	—	1.223	1.235	1.243	1.242 (4)
N(1)–C(23)	1.332	—	1.331	1.336	1.328	1.323 (4)
P–C(7)	—	1.837	1.813	1.825	1.833	1.804 (4)
O(1)–C(20)	—	1.238	1.204	1.211	1.233	1.199 (5)
C19–C20	—	1.421	1.548	1.536	1.444	1.445 (5)
N(2)–C(25)	1.385	—	1.386	1.396	1.381	1.364 (5)
O(2)–C(20)	—	1.374	1.342	1.357	1.367	1.356 (5)
P–C(13)	—	1.842	1.832	1.830	1.829	1.811 (4)
C(19)–C(22)	—		1.557	1.545	1.450	1.417 (5)
C(22)–Cl	1.811	—	3.105	3.145	—	—
P–O(3)	—	—	2.843	2.896	2.992	—
C(22)–C(23)	1.468	—	1.464	1.489	1.493	1.500 (5)
O(4)–C(26)	1.224	—	1.228	1.227	1.227	1.215 (5)
Bond Angles (°)						
C(23)–C(22)–Cl	114.6	—	90.0	87.2	—	—
O(3)–C(22)–Cl	120.4	—	99.9	133.4	—	—
O(3)–C(22)–C(23)	124.9	—	121.8	122.2	123.1	116.3 (4)
C(1)–P–C(7)	—	106.0	109.6	108.4	108.3	108.7 (2)
C(1)–P–C(19)	—	114.5	120.1	115.5	112.6	109.2 (2)
C(7)–P–C(19)	—	117.6	110.4	114.2	110.7	114.0 (18)
C(13)–P–C(19)	—	106.2	107.9	108.5	113.6	112.0 (18)
O(3)–C(22)–C(23)	—	—	106.2	109.5	117.0	116.3 (4)
O(1)–C(20)–O(2)	—	120.8026	118.2	118.9	120.6	119.8 (4)
C(19)–C(22)–C(23)	—	—	110.5	118.1	123.1	121.0 (3)
P–C(19)–C(20)	—	120.5873	106.7	112.4	116.4	121.3 (3)
Mulliken Charges (ē)						
O(1)	–	−0.568	−0.451	−0.485	−0.546	
O(2)	—	−0.499	−0.459	−0.495	−0.493	
O(3)	−0.380	—	−0.487	−0.423	−0.526	
O(4)	−0.462	—	−0.485	−0.510	−0.480	
N(1)	−0.338	—	−0.373	−0.317	−0.363	
N(2)	−0.430	—	−0.430	−0.423	−0.445	
P	—	0.664	0.803	0.464	0.765	
C(19)	—	−0.458	−0.479	−0.414	−0.391	
C(22)	0.256		0.482	0.447	0.398	
Cl	−0.038		−0.749	−0.385	—	
Dipol Moment(μ)						
	6.3178	4.7356	11.5417	3.2126	3.7938	

*X-ray results.

The biggest differences for the bond angles without phosphorus were observed for O(1)–C(20)–O(2) (114.763 calculated–119.8 X-ray) at the AM1 level and P–C(19)–C(20) (116.17 calculated–121.3 X-ray) at the DFT level in selected bond lengths. The B3LYP/6–31G(d,p) calculations yield reasonable bond lengths; errors are typically in the order of 0.02 Å. However AM1 calculations yield better bond angles for molecules including phosphorus atoms, but have almost same deviation values with the DFT method for bond angles without phosphorus.

We can easily say that for our molecule, the B3LYP/6–31G(d,p) method is better than AM1 for bond length calculations. However, the AM1 method is better for phosphorus-containing bond angles and has almost same deviation values with the DFT method for bond angles without phosphorus.

The dipole moments for **1**, **2a**, **TS1**, and **In-1** are 6.0816 D, 6.9820 D, 3.4522D, and 6.9945D. In the first step, the dipole moment of **TS1** is the smallest, but in the third step the dipole moment for **TS2** is the largest (11.4403 D). The biggest dipole moment means that there is the largest charge difference on the atoms.

The structure of methyl 3-(4-benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrazol-3-yl)-3-oxo-2-(triphenylphosphoranylidene) propanoate, [$C_{44}H_{33}N_2O_4P$] (**3a**), has been determined by X-ray diffraction. The structure derived from the NMR spectroscopy, the IR spectra, and elemental analysis is consistent with that of the X-ray diffraction. The reaction mechanism of methyl 3-(4-benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrazol-3-yl)-3-oxo-2-(triphenylphosphoranylidene) propanoate (**3a**) was studied by AM1 calculations. Electronic parameters of the reactants and products were calculated with DFT. The calculations indicate that the reaction mechanism happens in three steps. In this reaction, in the first step charges control plays an essential role.

Supplementary Material

Crystallographic data for the structure reported here has been deposited at the CCDC as supplementary data, CCDC 693637 for **3a**. Copies of the data can be obtained upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.-cam.ac.uk.

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