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RESEARCH ARTICLE

Synthesis, thermal properties, spectroscopic characterization and DFT computations of 1,3-propanediylbis (triphenylphosphonium) peroxydisulfate as a new oxidative agent

Faezeh Makari[1†] Mostafa Gholizadeh[1†*] Seyed Reza Nokhbeh[1†]

Abstract: Thermal properties and spectroscopic characterization of new synthesized 1,3-propanediylbis (triphenylphosphonium) peroxydisulfate as a member of phosphonium persulfates were studied. ^{1}H, ^{13}C, ^{31}P NMR and FT-IR were used for structural characterization of the title salt. To study the thermal behavior of the salt DSC, TG and DTA methods were used. Self-accelerating decomposition temperature of anion determined 200-205°C and decomposition point for organic moiety was recorded 340°C by DSC method. The specific heat capacity of the salt was determined 1.32 to 1.96 j/g °C in comparison of sapphire disk between 30 to 160°C. Theoretical DFT computations such as structural optimization, energy, charge distribution, HOMO-LUMO energy levels and thermochemical parameters were performed with the Gaussian 09 package software using B3LYP/6-31+G* level of theory. Theoretical calculations show HOMO-LUMO energy gap is 3.73 eV. Oxidation of several benzylic alcohols was performed by the persulfate salt in the water as a mild oxidative agent under reflux condition.

Keywords: thermal properties, phosphonium peroxydisulfate, specific heat capacity, oxidizing agent, Density Function Theory computations

1 Introduction

Nowadays, the use of quaternary ammonium, phosphonium and pyridinium salts is a growing trend in various fields of organic synthesis, medicine and industries[1–12]. There are many reports on the synthesis of various types of the salts[1, 13]. Negligible vapor pressure, high thermal stability, appropriate environmental aspects, miscibility with water and polar organic solvents, high viscosity, reusability, their versatility and non-toxicity are some of the interesting properties of these salts. Because of their distinctive properties, these organic salts gained increased interest in the last decade in many fields specifically in organic chemistry as a phase transfer catalyst[14–18], halogenating[19, 20], oxidative[21, 24], reductive[25] reagents in some organic transformations and as radical initiators in polymerizations[26].

Many reagents such as chromium trioxide in acetic acid[27, 28], ceric ammonium nitrate in aqueous acetic acid[29], permanganate ion[30]selenium dioxide[31], silver (II) oxide[32], chlorochromate[23] and dichromate ion[21, 22] have been used to oxidation of organic substrates. However the above reagents either were used in aqueous acidic solution or in the presence of a metal ion as catalyst. Persulfates are known as oxidizing agents in the preparation of aldehydes, ketones, carboxylic acids, Quinone's and a variety of other compounds. The pharmaceutical industries use sodium persulfate as a reagent in the preparation of antibiotics. Examples of oxidation of organic functional groups with this oxidant ion are: oxidation decarboxylation of acids[32], aromatic hydroxylation[33, 34], oxidation of carbon-nitrogen double bonds[35], alkenes[36] and alcohols[37]. The reaction of peroxydisulfate ions at ambient temperature is considerably slow therefore, the reaction is accelerated in the presence of Ag(I)[34] Cu(I)[34] and Ni(II)[38, 39] under reflux condition. For reactions of alcohols, the oxidation reaction carried out at acidic media and is accompanied by fragmentation[40]. Therefore, introduction of a new peroxydisulfate oxidizing agent which works under neutral and aprotic condition for the selective oxidation of alcohols is an important process in organic synthesis[37, 41].

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[*] **Correspondence to**: Mostafa Gholizadeh, Department of chemistry, Faculty of science, Ferdowsi University of Mashhad, Mashhad, I.R., Iran; Email: m_gholizadeh@um.ac.ir

[†] These authors contributed equally to this work and share first authorship

[1] Department of chemistry, Faculty of science, Ferdowsi University of Mashhad, Mashhad, I.R., Iran.

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These reagents are comparatively less hazardous, stable, solid, environmentally benign reagents and can be synthesized very easily by precipitating of peroxydisulfate ion with phosphonium, ammonium and pyridinium cations. These salts are sometimes used as a conveniently weighable, green, non-toxic source of oxidizing agents in organic synthesis. Therefore, several oxidizing salts have been synthesized. The most frequently used quaternary phosphonium and ammonium oxidizing reagents are 1,4-bis(triphenylphosphonium) butane peroxydisulfate[42], 1,4-tetrabutylammonium peroxydisulfate[43,45], methyl triphenyl phosphonium peroxydisulfate[46,47], 3,6 bis(triphenylphosphonium)-cyclohexene peroxydisulfate[48].

Sulfate radical anion $SO_4{}^{\bullet-}$ is one of the most important and powerful oxidant in organic synthesis[49]. The first step of oxidation of organic functional groups by peroxydisulfate anion is the decomposition of the anion which has a relatively high oxidation potential and an activation energy of approximately 30 Kcal/mol[44].

$$S_2O_8^{2-}{}_{(aq)} + 2e \rightarrow 2SO_4^{2-}{}_{(aq)} \quad E_O = 2.01\ V \tag{1}$$

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-} \quad E_{act} = 30\ Kcal/mol \tag{2}$$

Also, decomposition of the anion is accelerated by strong mineral acids or by trace metal ions[50]. The readily available peroxydisulfate salt is an excellent and versatile oxidant for most of organic compounds.

Thus, in this article we report the synthesis, thermal properties, structural characterization (^1H, ^{13}C, ^{31}P NMR, FT-IR, and DSC/TG/DTA) and DFT calculations of 1,3-propanediylbis (triphenylphosphonium) peroxydisulfate as a mild, inexpensive and efficient oxidizing agent. Furthermore, we obtained specific heat capacity of the new salt and related bromide salt by DSC method. We also report the use of new salt to oxidation of benzylic alcohols in water as an environmental protections, clean and green solvent with excellent yields.

2 Results and discussion

1,3-Propanediylbis(triphenylphosphonium) dibromide **I**, prepared initially as white powder by the reaction of triphenyl phosphine with 1,3-dibromopropane (m.p.: 349-354°C by DSC method, 95% yield)[51] and then treated with an aqueous solution of ammonium peroxydisulfate in the ratio 1:1, white precipitate **II** was filtered and dried under a stream of air (Figure 1) (self-accelerating decomposition temperature SADT 200-205°C by DSC method, 97% yield) Figure 2.

2.1 Thermal properties of salt II

DSC thermogram shows a sharp and strong exothermic peak at the 200-205°C as a decomposition point of persulfate ion (self-accelerating decomposition temperature SADT) according to following reaction and a weak endothermic broad peak at the 320-360°C as a decomposition range for the organic moiety of compound **II**. Figure 2. DSC and TG/DTG/DTA thermograms for compound **I** are reported in our previous work[51].

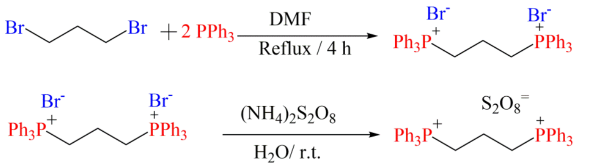


Figure 1. Schematic reactions for preparation of 1,3-propanediylbis (triphenylphosphonium) bromide **I** and peroxydisulfate **II**

$$S_2O_8^{2-} \; + \; heat \rightarrow 2SO_4^{\bullet-} \tag{3}$$

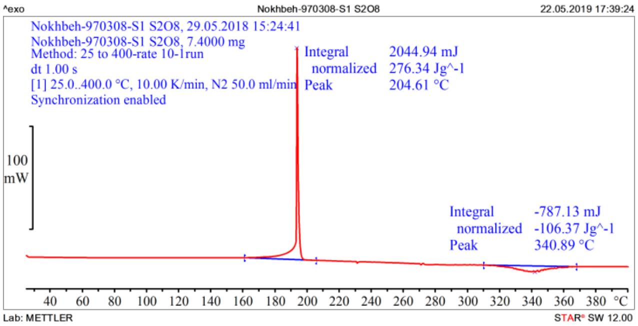


Figure 2. DSC thermogram of compound **II**

In the TG/DTG/DTA thermogram of **II** we can see an exothermic strong and sharp peak at about 204°C in DTA (blue) curve and a small decrease in TG (red) curve (4.1 %) for decomposition of peroxydisulfate anion. The small broad endothermic peak in the range of 310-350°C in the DTA curve and strong, broad peak in DTG (brown) curve with a significant sharp decrease in TG (red) curve (90.2 %) for the complete decomposition of compound **II** and about 5.6 % at 800°C for ash was observable which are completely matched with DSC thermograms (Figure 3). Comparison of DSC and TG/DTG/DTA thermograms shows that compound **I** is more thermally stable than compound **II**. Because the structure of the cation is the same in both compounds, **I** and **II**, so the thermal instability of the **II** can be attributed to the difference in anions. For compound **II**, before it reaches the melting point suffer from accelerating decomposition phenomenon. In addition, the auto oxidation of **II** by anion can be considered. Anyway, both salts are very stable on the bench-top in the form of powder or in the organic solvent and in contact with air without any destruction over 9 months. In comparison with potassium, ammonium and sodium peroxydisulfate as common inorganic persulfates (decomposition point <

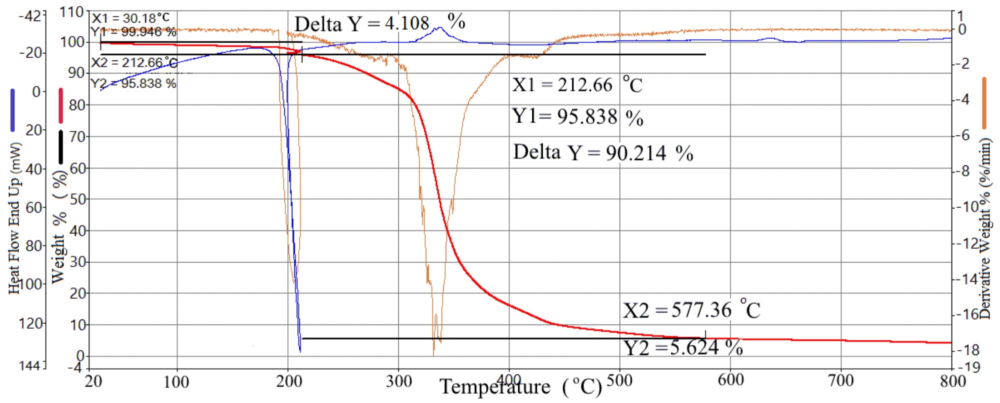


Figure 3. TG/ DTG/ DTA thermogram of compound **II**

100, 120, 180°C, respectively) that are used as oxidative reagents, compound **II** has a higher decomposition point and more thermal stability.

Heat capacity is one of the most important physical and thermal properties of materials. To understand the properties of materials and their reactions, it is significant to have deep knowledge of thermodynamic functions such as enthalpy, entropy, and Gibbs free energy. These functions can be directly determined from the specific heat capacity. It is a key property for designing of chemical processes such as injection molding, crystallization, spray drying, the safety analysis of chemical processes and the design of chemical reactors (process engineering) that can be measured by DSC method. In literature, it is defined as the amount of thermal energy required to raise the temperature of an amount of a substance per unit of mass. It is an extensive property since its value is directly proportional to the mass of the substance. The heat capacity of an object, defined by C is:

$$C = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} \tag{4}$$

Where ΔQ is the amount of heat that must be given to the mater (of mass M) to raise its temperature by ΔT. The value of this parameter usually depending on the starting temperature T of the object and the pressure P applied to it. Therefore, it should be considered as a function of those two variables C (P, T). The SI unit for heat capacity of an object is a joule per Kelvin (J/K, or J K^{-1}).

A more meaningful material property is the specific heat capacity, c_p, with a small c and the subscript p. The specific heat capacity is the amount of heat energy that required to raising the temperature of 1 kg of the substance by 1°C or 1 K. The SI unit for specific heat is joules per Kelvin per kilogram (J/K/kg, J/ (kg K), J K^{-1} kg^{-1}, *etc.*) For specific heat capacity, we can write:

$$C_P = \frac{dQ}{dT} \cdot \frac{1}{m} \tag{5}$$

These definitions were only valid in the absence of chemical reactions and/or phase transitions. Nowadays, this concept has been expanded. In the absence of phase transitions and chemical reactions, c_p is referred to as the baseline c_p. The deviation caused by phase transitions and chemical reactions is valid the excess c_p and the sum of both is known as the total specific heat capacity. If we divide the heat capacity by the mole number, we get the molar heat capacity in units of Joules per mole Kelvin.

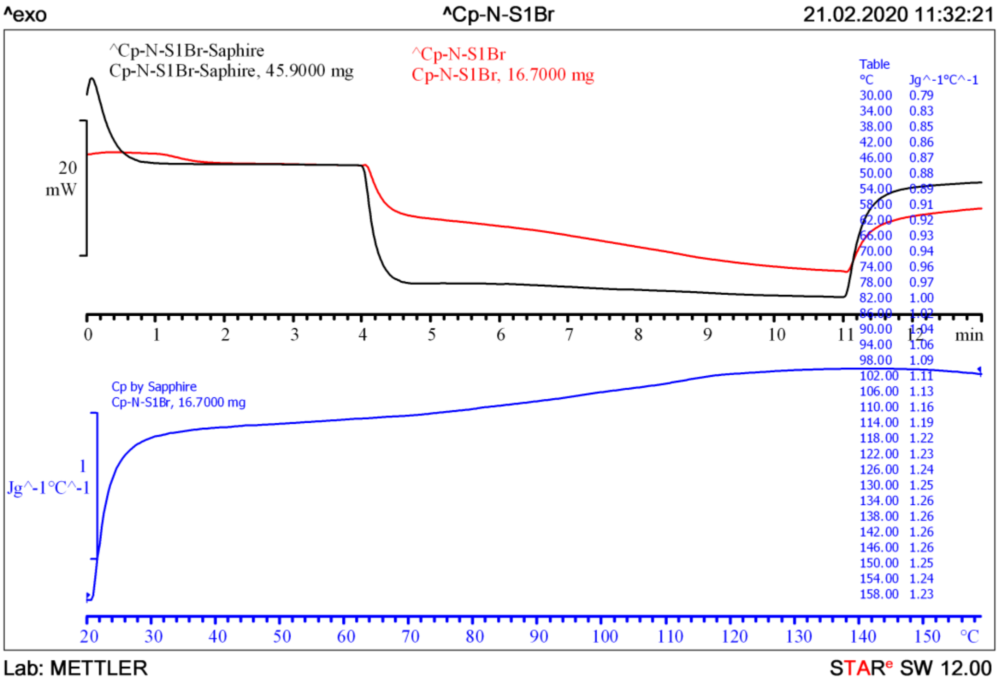
Thus, we determined and reported specific heat capacity of **I** and **II** by DSC method in the range of 30 to 160°C in comparison of sapphire disk and with automatic blank curve subtraction (Figure 4 and Figure 5). A comparative measurement was frequently used which involved measuring a reference material (sapphire, single crystal alumina α-Al_2O_3) under the same conditions as the sample. A simple calculation, then allowed the unknown specific heat capacity of the sample to be obtained from the known specific heat capacity of c_{ps} of α-Al_2O_3. Numerical data are tabulated in Table 1.

$$C_p = \frac{\Phi}{\Phi_S} \cdot \frac{m_S}{m} C_{ps} \tag{6}$$

Comparison of plots for two compounds shows that the specific heat capacity is between 0.79 to 1.26 j/g °C for I and in the range of 1.32 to 1.96 j/g °C for II and that the specific heat capacity of **II** is higher than **I** in a whole range (Figure 6, Table 1).

2.2 Theoretical DFT computation

Over the recent year's computational calculation based on the DFT theory has been developed to investigate and predict the structure, vibrational, magnetic and electrical, thermal and spectroscopic properties of substances[52–59]. The Gaussian 09 software package was used to perform the DFT calculations at the B3LYP (Becke-3- Lee-Yang-Par) level and with 6-311+G* basis sets for compound **I** and **II**. The DFT computations were done by using the



Table

°C	Jg^-1°C^-1
30.00	0.79
34.00	0.83
38.00	0.85
42.00	0.86
46.00	0.87
50.00	0.88
54.00	0.89
58.00	0.91
62.00	0.92
66.00	0.93
70.00	0.94
74.00	0.96
78.00	0.97
82.00	1.00
86.00	1.02
90.00	1.04
94.00	1.06
98.00	1.09
102.00	1.11
106.00	1.13
110.00	1.16
114.00	1.19
118.00	1.22
122.00	1.23
126.00	1.24
130.00	1.25
134.00	1.26
138.00	1.26
142.00	1.26
146.00	1.26
150.00	1.25
154.00	1.24
158.00	1.23

Figure 4. Plot of specific heat capacity for **I**

Gaussian 09 software package at the B3LYP/6-31+G* basis sets for title compound **II**. The structural parameters such as bond lengths, bond angles and dihedral (torsion) angles thermochemical parameters and were computed after optimization of structure (Table 2 and Table 3). The DFT calculation predicted energy and dipole moment for **I**, E (RB3LYP) -7334.05720641 Hartrees, Dipole moment = 16.9062 Debye[51], while for **II**, E (RB3LYP) = -3589.09159282 Hartrees, Dipole moment 25.0194 Debye.

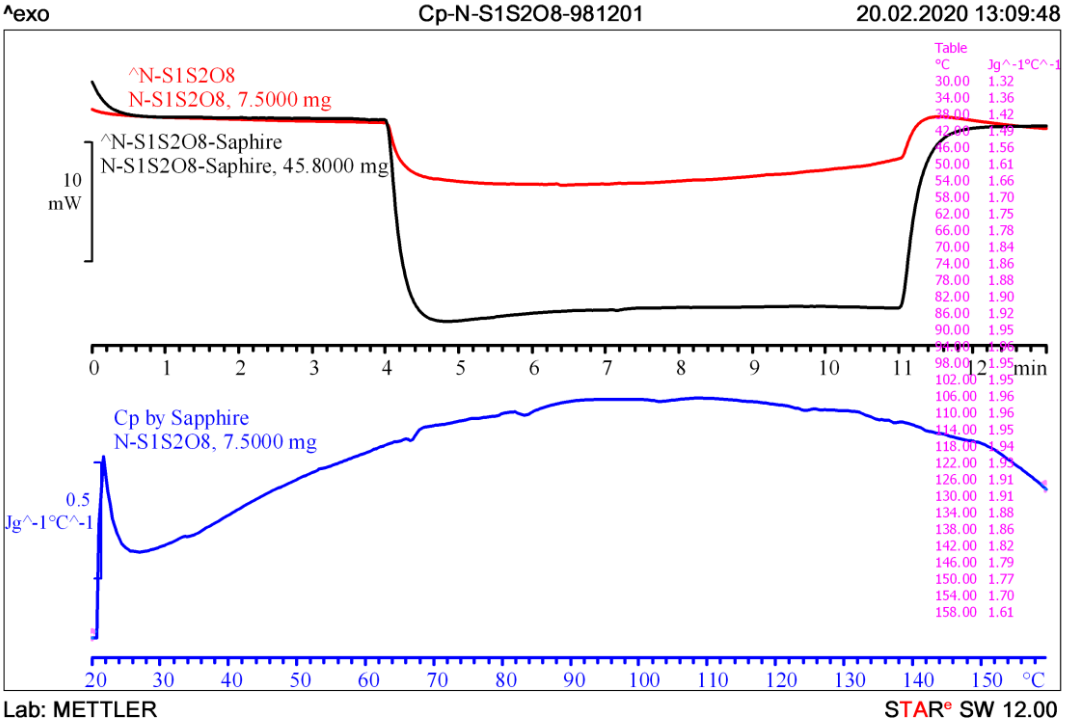
B3LYP/6-31+G* method was used to calculate 255 vibrational frequencies for compound II. Highest predicted frequencies are 3147.96 cm^{-1} for the stretching vibration of C-H in aromatic rings, 3048.66 cm^{-1} for the in plane symmetric stretching of aliphatic H-C-H, 2987.09 cm^{-1} for the stretching vibration of aliphatic C-H, 1441.19 cm^{-1} for the stretching vibration of S=O, 1357.74 cm^{-1} for the asymmetric stretching of O=S=O and 772.81 cm^{-1} for the stretching of S-O in anion (Table 4).

The results extracted from NBO calculations have provided deeper insight into the nature of electronic structure of molecule **II**[60]. Since atomic charges affect some properties of molecular systems, including electronic structure, dipole moment, molecular polarizability; atomic charges calculation has an important role in the quantum chemical calculation of molecular systems. NBO method was used to calculate natural charge distribution on the whole molecule of **II**. Calculation show the amount of charge distribution on atoms and indicated that C and O atoms have negative character; while P, S and H atoms have positive ones (Table 5).

HOMO and LUMO orbitals are referred to frontier orbitals and the difference in energy between these orbitals is termed HOMO-LUMO gap that can be used to predict chemical stability and reactivity of organic compounds[61,62]. The energy level of frontier orbitals shows a tendency to giving an electron as a donor or to take an electron as an acceptor in chemical reactions. HOMO-LUMO energies were calculated by B3LYP/6-31+G* presented in Figure 7. In comparison with **I**; although the HOMO and LUMO energy levels have been reduced, but the HOMO level is dropped significantly and as a result the energy gap increased from 2.38 eV (for **I**) to 3.73 eV (for **II**). This means that although the compound II has become more stable than **I** with anion exchange, in the red-ox reactions it plays the role of an electron acceptor.

3 Materials and methods

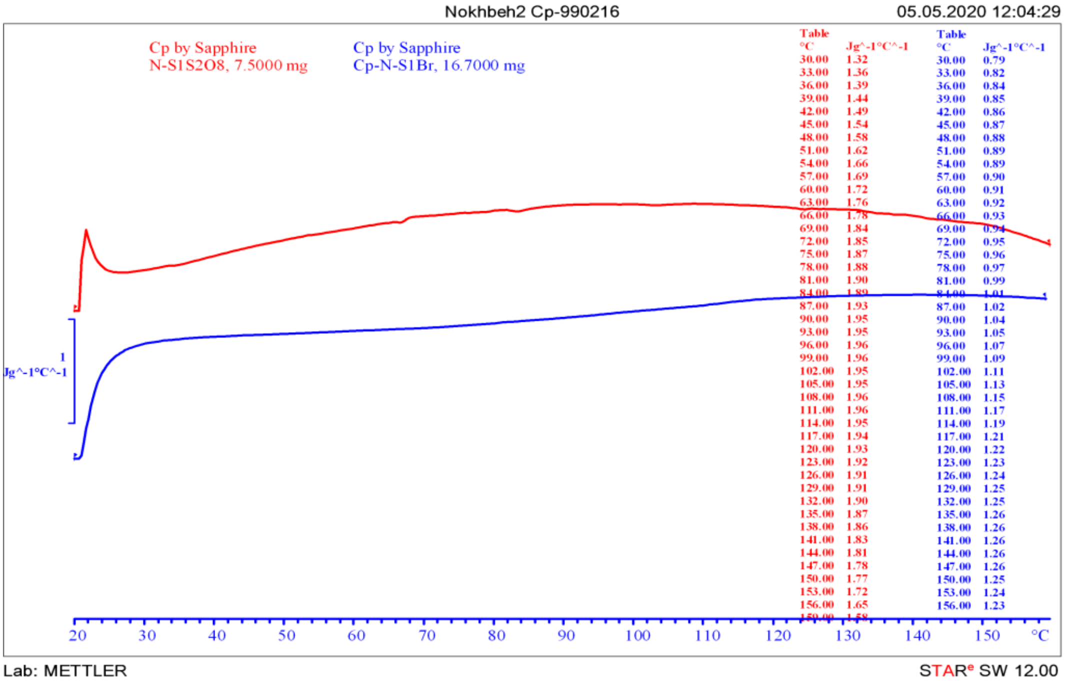
All chemicals, including raw materials, reagents and solvents were purchased from Merck Co. 1,3-dibromopropane was purified and checked by Gas Chromatograph to give purity not less than 99%. The progresses of reactions were monitored by TLC and GC. ^1H, ^{13}C and ^{31}P NMR spectra were recorded by the Bruker AC 300 and 500 MHz spectrometer with D_2O, $CDCl_3$ and DMSO-d_6 as solvents. c_p and DSC thermograms were recorded by DSC-822e METTLER -TOLEDO thermal



Table

°C	Jg^-1°C^-1
30.00	1.32
34.00	1.36
38.00	1.42
42.00	1.49
46.00	1.56
50.00	1.61
54.00	1.66
58.00	1.70
62.00	1.75
66.00	1.78
70.00	1.84
74.00	1.86
78.00	1.88
82.00	1.90
86.00	1.92
90.00	1.95
94.00	1.96
98.00	1.95
102.00	1.95
106.00	1.96
110.00	1.96
114.00	1.95
118.00	1.94
122.00	1.93
126.00	1.91
130.00	1.91
134.00	1.88
138.00	1.86
142.00	1.82
146.00	1.79
150.00	1.77
154.00	1.70
158.00	1.61

Figure 5. Plot of specific heat capacity for **II**



Table

°C	Jg^-1°C^-1
30.00	1.32
33.00	1.36
36.00	1.39
39.00	1.44
42.00	1.49
45.00	1.54
48.00	1.58
51.00	1.62
54.00	1.66
57.00	1.69
60.00	1.72
63.00	1.76
66.00	1.78
69.00	1.84
72.00	1.85
75.00	1.87
78.00	1.88
81.00	1.90
84.00	1.89
87.00	1.93
90.00	1.95
93.00	1.95
96.00	1.96
99.00	1.96
102.00	1.95
105.00	1.95
108.00	1.96
111.00	1.96
114.00	1.95
117.00	1.94
120.00	1.93
123.00	1.92
126.00	1.91
129.00	1.91
132.00	1.90
135.00	1.87
138.00	1.86
141.00	1.83
144.00	1.81
147.00	1.78
150.00	1.77
153.00	1.72
156.00	1.65
159.00	1.58

Table

°C	Jg^-1°C^-1
30.00	0.79
33.00	0.82
36.00	0.84
39.00	0.85
42.00	0.86
45.00	0.87
48.00	0.88
51.00	0.89
54.00	0.89
57.00	0.90
60.00	0.91
63.00	0.92
66.00	0.93
69.00	0.94
72.00	0.95
75.00	0.96
78.00	0.97
81.00	0.99
84.00	1.01
87.00	1.02
90.00	1.04
93.00	1.05
96.00	1.07
99.00	1.09
102.00	1.11
105.00	1.13
108.00	1.15
111.00	1.17
114.00	1.19
117.00	1.21
120.00	1.22
123.00	1.23
126.00	1.24
129.00	1.25
132.00	1.25
135.00	1.26
138.00	1.26
141.00	1.26
144.00	1.26
147.00	1.26
150.00	1.25
153.00	1.24
156.00	1.23

Figure 6. Comparison of specific heat capacity of **I** and **II**

Table 1. Numerical data for specific heat capacity C_p of **I** & **II**

Temp °C	I J/g/°C	II J/g/°C	Temp °C	I J/g/°C	II J/g/°C
30	0.79	1.32	96	1.07	1.96
32	0.81	1.34	98	1.09	1.95
34	0.83	1.36	100	1.1	1.96
36	0.84	1.39	102	1.11	1.95
38	0.85	1.42	104	1.12	1.95
40	0.86	1.46	106	1.13	1.96
42	0.86	1.49	108	1.15	1.96
44	0.87	1.52	110	1.16	1.96
46	0.87	1.56	112	1.17	1.96
48	0.88	1.58	114	1.19	1.95
50	0.88	1.61	116	1.2	1.95
52	0.89	1.64	118	1.22	1.94
54	0.89	1.66	120	1.22	1.93
56	0.9	1.68	122	1.23	1.93
58	0.91	1.7	124	1.23	1.91
60	0.91	1.72	126	1.24	1.91
62	0.92	1.75	128	1.25	1.91
64	0.92	1.77	130	1.25	1.91
66	0.93	1.78	132	1.25	1.9
68	0.93	1.83	134	1.26	1.88
70	0.94	1.84	136	1.26	1.87
72	0.95	1.85	138	1.26	1.86
74	0.96	1.86	140	1.26	1.85
76	0.97	1.87	142	1.26	1.82
78	0.97	1.88	144	1.26	1.81
80	0.98	1.89	146	1.26	1.79
82	1	1.9	148	1.26	1.78
84	1.01	1.89	150	1.25	1.77
86	1.02	1.92	152	1.25	1.74
88	1.03	1.94	154	1.24	1.7
90	1.04	1.95	156	1.23	1.65
92	1.05	1.95	158	1.23	1.61
94	1.06	1.96			

analyzer. TG/DTG/DTA thermograms were recorded by Perkin Elmer Diamond TG/DTA Instrument. Infrared spectra were recorded on a Perkin Elmer-Spectrum 65-FT-IR and Bruker vortex 80 spectrometers as a KBr disk (400 - 4000 cm^{-1} region).

3.1 Preparation of 1,3-propanediylbis bromide ($C_{39}H_{36}P_2Br_2$) I

Triphenylphosphine (6.55 g, 25 mmol, excess) was dissolved in DMF (30 mL) in a 50 mL roundbottom flask and magnetically stirred under reflux condition. 1,3-Dibromopropane (2.01 g, 1.01 mL, 10 mmol, d = 1.989 g/cm^3) was added dropwise with a 1 mL syringe. The mixture was refluxed for over 4 h. The white precipitate was cooled, filtered and washed with DMF (3 × 10 mL). The product was air dried overnight (6.9 g, 95% yield, purity after recrystallization in hot water 99.7%), m.p. 349-353°C (by DSC and DTA)[51].

3.2 Preparation of 1,3-propanediylbis peroxydisulfate ($C_{39}H_{36}-P_2S_2O_8$) II

2.38 g, (20 mmol) of compound **I** was dissolved in H_2O (30 mL) at 70°C in a 50 mL beaker, an aqueous solution of ammonium peroxydisulfate (1.03 g, 20 mmol in 50 mL

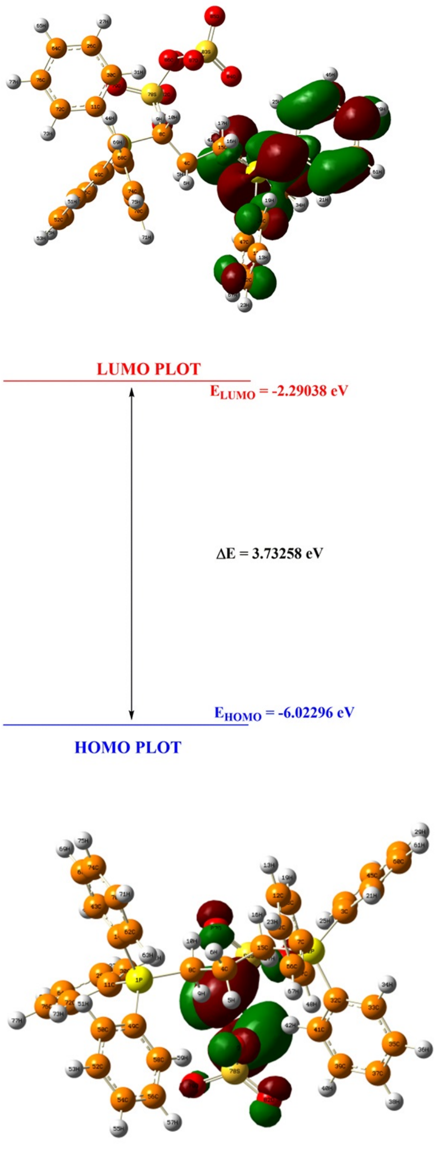


Figure 7. HOMO-LUMO diagram and energy levels for **II**

water) was added dropwise with continuous magnetically stirring for 30 min. Solution was mixed for over 20 min. The white precipitate was filtered and washed with cooled water (3 × 10 mL). The product was air dried overnight and crystallized in H_2O / EtOH 50% V/V (97% yield, purity after recrystallization 99.5%), decomposition point 340°C (by DSC and DTA). ^{1}H NMR (300 MHz, DMSO-d_6, δ; ppm): 1.80 ppm (s, 2H, center CH_2), 3.88 (s, 4H, terminal CH_2's), 7.76-7.91 (m, 30H, aromatic hydrogens). $_{31}$P NMR (200MHz, DMSO-d6, ; ppm): 34.74 ppm (1 s, for P atom). ^{13}C NMR (75 MHz, DMSO-d_6, δ; ppm): 16.6 (C_20), 20.72 (C21, C19), 117.81, 118.96, 130.80, 134.15 and 135.56 (5 × s, C_6H_5). FT-IR: $\overline{\nu}$ = 509, 539 (m), 686,723 (m), 996 (w), 1040 (s), 1112 (s), 1249, 1267 (s), 1439 (m), 1486, 1589 (w), 2904, 2938 (w), 3060 (w)

Table 2. Cartesian coordinates for compound **II**

Center Number	Atomic Number	Atomic Type	Coordinates			Center Number	Atomic Number	Atomic Type	Coordinates		
			X	Y	Z				X	Y	Z
1	15	0	-2.7286	0.981156	-0.16078	45	6	0	4.890518	-1.21773	-3.15419
2	15	0	3.030109	0.615363	-0.01612	46	1	0	4.697306	-2.08425	-3.7801
3	6	0	4.206602	0.248681	-1.35562	47	6	0	3.205255	2.767115	1.790462
4	6	0	0.14858	0.904342	0.077057	48	1	0	3.213644	2.018086	2.576188
5	1	0	0.213581	0.706817	1.151151	49	6	0	-2.99729	1.305632	1.605887
6	1	0	0.124786	1.991171	-0.06464	50	6	0	-3.75463	2.409437	2.037789
7	6	0	3.171342	2.37552	0.443582	51	1	0	-4.13546	3.134108	1.323974
8	6	0	-1.10948	0.20963	-0.48208	52	6	0	-4.02083	2.578929	3.396994
9	1	0	-1.15225	-0.80736	-0.07095	53	1	0	-4.60683	3.432279	3.727942
10	1	0	-1.04819	0.101192	-1.57197	54	6	0	-3.53827	1.650883	4.325807
11	6	0	-4.01951	-0.13459	-0.77788	55	1	0	-3.75064	1.783255	5.383634
12	6	0	3.176151	4.709933	-0.22412	56	6	0	-2.7907	0.552307	3.895181
13	1	0	3.16739	5.46158	-1.00879	57	1	0	-2.42168	-0.17801	4.609606
14	6	0	-2.82318	2.560787	-1.07405	58	6	0	-2.51697	0.368387	2.537424
15	6	0	1.354425	0.309036	-0.67802	59	1	0	-1.93821	-0.4999	2.222479
16	1	0	1.381619	0.69992	-1.70291	60	6	0	6.297311	0.647303	-2.51474
17	1	0	1.2575	-0.78353	-0.78693	61	1	0	7.201489	1.235675	-2.64607
18	6	0	3.150363	3.357044	-0.56379	62	6	0	-2.16932	3.708807	-0.59198
19	1	0	3.122681	3.069301	-1.61172	63	1	0	-1.66115	3.690454	0.367898
20	6	0	5.378702	1.004166	-1.52619	64	6	0	-6.04334	-1.82773	-1.6906
21	1	0	5.576307	1.869479	-0.89997	65	1	0	-6.82824	-2.4957	-2.03549
22	6	0	3.218171	5.094898	1.12022	66	6	0	3.230166	4.124214	2.124115
23	1	0	3.242393	6.149267	1.38261	67	1	0	3.259991	4.418496	3.169588
24	6	0	3.962179	-0.87389	-2.1688	68	6	0	-3.49695	3.796156	-3.05176
25	1	0	3.071822	-1.48897	-2.04263	69	1	0	-4.01444	3.825612	-4.00657
26	6	0	-4.7268	-2.02552	-2.10724	70	6	0	-2.18575	4.889203	-1.33659
27	1	0	-4.47282	-2.84825	-2.76882	71	1	0	-1.68461	5.773706	-0.95251
28	6	0	6.052868	-0.46232	-3.32935	72	6	0	-5.3461	0.061085	-0.35118
29	1	0	6.769834	-0.73889	-4.09796	73	1	0	-5.59112	0.853252	0.351174
30	6	0	-3.70559	-1.1824	-1.65895	74	6	0	-2.8491	4.934497	-2.56675
31	1	0	-2.68975	-1.3783	-1.99157	75	1	0	-2.86255	5.855575	-3.14338
32	6	0	3.418109	-0.43254	1.406814	76	6	0	-6.35393	-0.782	-0.81317
33	6	0	4.685758	-0.32293	2.01421	77	1	0	-7.37601	-0.63487	-0.47493
34	1	0	5.40586	0.416744	1.672298	78	16	0	-0.94904	-3.30374	1.712134
35	6	0	5.025161	-1.18188	3.055894	79	8	0	-2.40948	-3.41396	1.850896
36	1	0	6.002564	-1.09922	3.523958	80	8	0	-0.49414	-1.87697	1.597608
37	6	0	4.115009	-2.15816	3.487303	81	8	0	-0.53492	-4.02264	0.206166
38	1	0	4.391183	-2.83375	4.292849	82	8	0	-0.11116	-4.13245	2.594182
39	6	0	2.865024	-2.27311	2.88009	83	16	0	0.018614	-3.02652	-2.15104
40	1	0	2.147213	-3.03074	3.184406	84	8	0	1.295823	-2.59459	-1.51769
41	6	0	2.510723	-1.41008	1.83626	85	8	0	0.07646	-4.31195	-2.8482
42	1	0	1.525991	-1.53199	1.395143	86	8	0	-1.1109	-3.19881	-0.85476
43	6	0	-3.48663	2.61239	-2.31005	87	8	0	-0.70521	-1.92634	-2.84779
44	1	0	-3.9951	1.73256	-2.69248						

Note: Total energy of optimized structure II = -3589.0915928 Hartree

Table 3. Thermochemical parameters calculated by for compound **II**

Zero-point correction=	0.679505 (Hartree/Particle)
Thermal correction to Energy=	0.722073
Thermal correction to Enthalpy=	0.723018
Thermal correction to Gibbs Free Energy=	0.599403
Sum of electronic and zero-point Energies=	-3586.69
Sum of electronic and thermal Energies=	-3586.64
Sum of electronic and thermal Enthalpies=	-3586.64
Sum of electronic and Thermal Free Energies=	-3586.77

Table 4. Calculated frequency and intensity of some selected vibrations for compounds **II**

	Frequency of vibration cm^{-1}	Intensity D (10^{-40} esu^2 cm^2)
1	3147.96	208.6
2	3048.66	163.2
3	2987.09	330.9
4	1441.19	762.5
5	1357.74	855.7
6	772.81	1490.6

cm^{-1} (Figure 8).

3.3 General experimental procedure for oxidation of benzylic alcohols in water

In a typical reaction, the alcohol as substrate (3 mmol) was dissolved thoroughly in DM water (5 mL) at 40 °C and stirred well. 1,3-propanediylbis (triphenylphosphonium) peroxydisulfate **II**, as oxidant (3 mmol) dissolved in water (5 mL) at 50°C and was added to an aqueous solution of substrate dropwise with constant stirring under reflux condition. The progress of the reaction was monitored by TLC. n-hexane/ethyl acetate (8:2) was used as mobile phase. After completion of the reaction, the mixture was cooled down, products extracted with chloroform (3 × 5 mL). The crude product, thus obtained

Table 5. Summary of Natural Population Analysis for compound **II**

Atom	No	Natural Charge	Core	Valence	Rydberg	Total	Atom	No	Natural Charge	Core	Valence	Rydberg	Total
P	1	1.59568	9.99741	3.34228	0.06464	13.40432	C	45	-0.17826	1.99916	4.16122	0.01788	6.17826
P	2	1.59859	9.99741	3.34363	0.06037	13.40141	H	46	0.22346	0	0.77592	0.00063	0.77654
C	3	-0.39104	1.99893	4.36491	0.0272	6.39104	C	47	-0.17145	1.99906	4.15464	0.01775	6.17145
C	4	-0.38086	1.99925	4.36303	0.01857	6.38086	H	48	0.23008	0	0.7693	0.00062	0.76992
H	5	0.22569	0	0.77296	0.00135	0.77431	C	49	-0.40046	1.99892	4.37423	0.02731	6.40046
H	6	0.19629	0	0.80239	0.00132	0.80371	C	50	-0.18977	1.99906	4.17303	0.01768	6.18977
C	7	-0.38503	1.99893	4.35693	0.02917	6.38503	H	51	0.21438	0	0.78494	0.00068	0.78562
C	8	-0.76273	1.99918	4.73785	0.02569	6.76273	C	52	-0.20117	1.99915	4.18428	0.01773	6.20117
H	9	0.32818	0	0.66959	0.00223	0.67182	H	53	0.21033	0	0.78906	0.0006	0.78967
H	10	0.27586	0	0.72304	0.0011	0.72414	C	54	-0.16769	1.99916	4.1512	0.01733	6.16769
C	11	-0.40454	1.99892	4.37644	0.02917	6.40454	H	55	0.21036	0	0.78904	0.00059	0.78964
C	12	-0.19309	1.99916	4.176	0.01794	6.19309	C	56	-0.1795	1.99915	4.16244	0.0179	6.1795
H	13	0.21442	0	0.78494	0.00064	0.78558	H	57	0.22305	0	0.77627	0.00068	0.77695
C	14	-0.38286	1.99892	4.3553	0.02863	6.38286	C	58	-0.16798	1.99905	4.14961	0.01933	6.16798
C	15	-0.74161	1.99918	4.72012	0.02231	6.74161	H	59	0.2748	0	0.72308	0.00212	0.7252
H	16	0.24465	0	0.75473	0.00063	0.75535	C	60	-0.19753	1.99915	4.18052	0.01785	6.19753
H	17	0.32692	0	0.67094	0.00215	0.67308	H	61	0.21055	0	0.78878	0.00067	0.78945
C	18	-0.179	1.99907	4.16221	0.01772	6.179	C	62	-0.18476	1.99906	4.16798	0.01771	6.18476
H	19	0.21942	0	0.7799	0.00069	0.78058	H	63	0.21742	0	0.78186	0.00072	0.78258
C	20	-0.18841	1.99906	4.17177	0.01759	6.18841	C	64	-0.16111	1.99916	4.14473	0.01722	6.16111
H	21	0.21114	0	0.78746	0.0014	0.78886	H	65	0.21081	0	0.7886	0.00059	0.78919
C	22	-0.1727	1.99916	4.15598	0.01756	6.1727	C	66	-0.18914	1.99916	4.17231	0.01767	6.18914
H	23	0.21277	0	0.78668	0.00055	0.78723	H	67	0.21588	0	0.78346	0.00065	0.78412
C	24	-0.17263	1.99905	4.15468	0.0189	6.17263	C	68	-0.18667	1.99916	4.16993	0.01759	6.18667
H	25	0.26999	0	0.72877	0.00123	0.73001	H	69	0.21624	0	0.78314	0.00062	0.78376
C	26	-0.17349	1.99915	4.15597	0.01836	6.17349	C	70	-0.19501	1.99915	4.17799	0.01787	6.19501
H	27	0.22619	0	0.77313	0.00068	0.77381	H	71	0.21172	0	0.78764	0.00063	0.78828
C	28	-0.16841	1.99916	4.15169	0.01755	6.16841	C	72	-0.17487	1.99906	4.15863	0.01719	6.17487
H	29	0.21139	0	0.78803	0.00058	0.78861	H	73	0.20957	0	0.78899	0.00143	0.79043
C	30	-0.16171	1.99904	4.14344	0.01922	6.16171	C	74	-0.17217	1.99916	4.15558	0.01743	6.17217
H	31	0.26479	0	0.73299	0.00222	0.73521	H	75	0.21213	0	0.78732	0.00055	0.78787
C	32	-0.41758	1.99891	4.39124	0.02743	6.41758	C	76	-0.19571	1.99915	4.1789	0.01765	6.19571
C	33	-0.18849	1.99907	4.17188	0.01755	6.18849	H	77	0.21021	0	0.78914	0.00064	0.78979
H	34	0.2055	0	0.79295	0.00155	0.7945	S	78	2.42965	9.99914	3.34681	0.2244	13.57035
C	35	-0.2007	1.99916	4.18371	0.01784	6.2007	O	79	-0.92853	1.9998	6.91788	0.01085	8.92853
H	36	0.20923	0	0.79011	0.00066	0.79077	O	80	-1.03875	1.9998	7.0216	0.01734	9.03875
C	37	-0.16295	1.99916	4.14666	0.01712	6.16295	O	81	-0.45072	1.99989	6.43386	0.01697	8.45072
H	38	0.21133	0	0.78808	0.0006	0.78867	O	82	-0.93045	1.9998	6.91892	0.01173	8.93045
C	39	-0.17602	1.99914	4.15777	0.01911	6.17602	S	83	2.43369	9.99913	3.34531	0.22187	13.56631
H	40	0.25438	0	0.74456	0.00106	0.74562	O	84	-0.99208	1.99979	6.97734	0.01495	8.99208
C	41	-0.15874	1.99904	4.14025	0.01945	6.15874	O	85	-0.89976	1.9998	6.88951	0.01045	8.89976
H	42	0.27064	0	0.72713	0.00224	0.72936	O	86	-0.49887	1.9999	6.47636	0.0226	8.49887
C	43	-0.16663	1.99906	4.14992	0.01764	6.16663	O	87	-0.98616	1.99981	6.9741	0.01225	8.98616
H	44	0.23038	0	0.76899	0.00064	0.76962							
Total	*	0	133.95632	260.54648	1.4972	396							

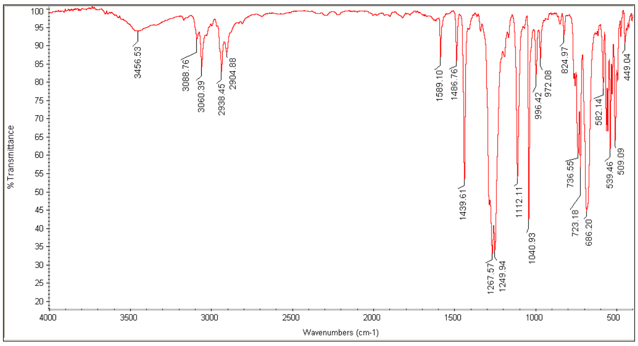


Figure 8. FT-IR spectrum of 1,3-propanediylbis (triphenylphosphonium) peroxydisulfate **II** (as KBr disk)

and then subjected to the short column of silica gel (pore size 60$\mathring{A}$, 200-400 mesh particle size) using a mixture of n-hexane and ethyl acetate (8:2) as the eluent. All of isolated products are known and physical data have been reported in literature. The main products, reaction times and isolated yields are tabulated in Table 6. Identification of products were made by comparison with their FT-IR, mass, ^{1}H, ^{13}C NMR spectra and physical data with those of authentic samples. We have reported some spectra of products as sample (see supplementary file):

4-methoxy benzaldehyde: FT-IR (KBr, $\overline{\upsilon}$/cm): 833 (s, aromatic C-H, bending), 1260, 1160 (s, Ar-O-CH$_3$, stretching.), 1600, 1577 (s, C=C, stretching), 1684, 1699 (s, C=O, stretching), 2840 (s, C-H aldehyde, stretching), 2933, 2970 (C-H aliphatic, stretching), 3015, 3070 (w, C-H aromatic, stretching). Mass Spectrum: m/z (intensity,%) = 136, (MeOC$_6$H$_4$COH, 60), 107 (MeOC$_6$H$_4$, 18), 92 (OC$_6$H$_4$, 53), 77 (C$_6$H$_5$, 93), 65 (C$_5$H$_5$, 66), 51 (C$_4$H$_3$, 47), 39 (C$_3$H$_3$, 98), and 29 (CHO, 100).

4-chlorobenzaldehyde: Mass Spectrum: m/z (intensity,

%) = 140 (ClC_6H_4COH, 20), 138 (ClC_6H_3CO, 71), 110 (ClC_6H_3, 27), 75 (C_6H_3, 50), 51 (C_4H_3, 48) and 29 (CHO, 100). ^{1}H NMR (300 MHz, CDCl3, δ; ppm): 7.48, 7.50 (d, $^3J_{H-H}$ = 8.1, 2H), 7.80, 7.82 (d, $^3J_{H-H}$ = 8.1, 2H), 9.97 (s, COH, 1H),), ^{13}C NMR (75 MHz, $CDCl_3$, δ; ppm,): 190.84, (C=O), 140.88, 134.72, 130.89 and 129.43 (4 s, C_6H_5).

Benzophenone: Mass Spectrum: m/z (intensity, %) = 182 (C_6H_5CO C_6H_5, 83), 181 (C_6H_5CO C_6H_4, 92), 105 (C_6H_5CO, 100), 77 (C_6H_5, 94), 51 (C_4H_3, 51) and 29 (CHO, 57). ^{1}H NMR (300 MHz, CDCl3, δ; ppm): 7.47, 7.50, 7.53 (t, $^3J_{H-H}$ = 7.5, 2H), 7.58, 7.61, 7.63 (t, $^3J_{H-H}$ = 7.5, 1H), 7.82, 7.85 (d, $^3J_{H-H}$ = 7.5, H), ^{13}C NMR (75 MHz, $CDCl_3$, δ; ppm): 196.71, (C = O), 137.63, 132.47, 130.08 and 128.33 (4 × s, C_6H_5).

Benzil: Mass Spectrum: m/z (intensity, %) = 210 (C_6H_5COCO $_6H_5$, 4), 209 (C_6H_5COCO C_6H_4, 44), 105 (C_6H_5CO, 100), 77 (C_6H_5, 85), 51 (C_4H_3, 74) and 29 (CHO, 43). ^{1}H NMR (300 MHz, $CDCl_3$, δ; ppm): 7.52, 7.54, 7.57 (t, $^3J_{H-H}$ = 7.5, 2H), 7.66, 7.69, 7.71 (t, $^3J_{H-H}$ = 7.2, 1H), 8.00, 8.02 (d, $^3J_{H-H}$ = 7.2, 2H), ^{13}C NMR (75 MHz, CDCl3, δ; ppm,): 194.63, (C = O), 134.94, 133.01, 129.93 and 129.06 (4 × s, C_6H_5).

3.4 Computational method

The DFT calculations were performed by using the Gaussian 09 software package[63–65], the B3LYP functional[66,67] and with 6-311+G* basis set[68–70]. The population analysis has also been performed by the natural bond orbital method[71] at 6-311+G* level of theory using the NBO program under Gaussian 2009 program package.

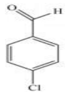
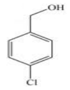
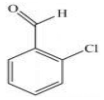
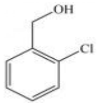
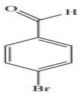
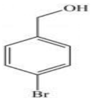
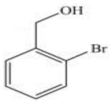
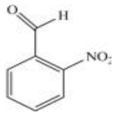
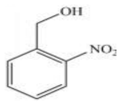
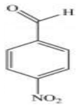
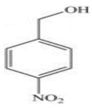
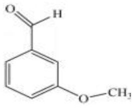
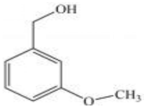
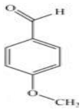
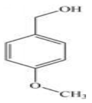
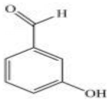
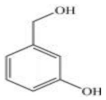
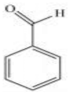
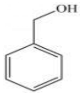
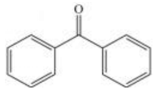
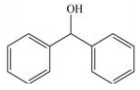
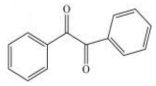
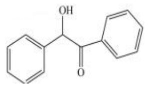
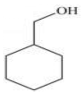
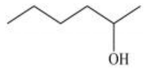
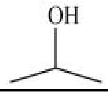
4 Conclusion

In conclusion, we describe the synthesis, thermal behavior and characterization of new quaternary phosphonium salt with oxidative anion. The specific heat capacity of the peroxydisulfate salt and related bromide salt was determined by DSC method. Furthermore, better thermal stability of title salt instead of inorganic persulfates is reported. The peroxydisulfate anion in title salt also has been used as a mild oxidizing agent for selective oxidation of benzylic alcohols in water. Ease of synthesis of **II** in aqueous solutions and oxidation of organic substrate by persulfate anion in water is another important aspect of phosphonium based oxidizing reagents. Also in the present paper the DFT computations and spectroscopic properties are reported.

Conflicts of interest

There are no conflicts to declare.

Table 6. Descriptive statistics and pearson correlations (N=233)

Entries	Substrate	Product a	Time (min)	Yield b (%)
1			5	97
2			15	96
3			5	97
4			15	97
5			135	58
6			135	60
7			135	90
8			90	93
9			60	30
10			5	98c
11			35	95
12			60	40
13		------	NR	---
14		------	NR	---
15		------	NR	---

Note: a. Products were characterized by comparison of their physical and spectra data with authentic compounds. b. Yields refer to isolated yield. c. Isolated yields as its 2,4-dinitrophenylhydrazine derivative.

Supporting Information

Copies of NMR, mass, FT-IR spectra, DSC and TG/DTA thermograms, C_p numeric data and computational study's results.

Acknowledgments

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