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Review Article

Synthesis and Properties of N-Bromosuccinimide Derivatives of Ammonium Dialkyl/Alkylene Dithiophosphates

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Reaction of N-bromosuccinimide with ammonium salt of alkylene (dialkyl) dithiophosphates, [$OGOPS_2NH_4$; G=–CMe_2CMe_2–$CH_2CMe_2CH_2$–, $CMe_2CH_2CHMe_2$–, $CH_2CH_2CHMe_2$–; $(RO)_2PS_2NH_4$; R=C_2H_5, n–C_3H_7, i–C_3H_7], in 1 : 1 molor ratio in refluxing benzene solution yields red/brown-colored sticky liquids. These newly synthesized complexes have been characterised by physicochemical and spectroscopic techniques (MW, IR, NMR [^{1}H and ^{31}P]). The computational semiempirical calculations (MOPAC6P/c) have also been studied for these complexes. On the basis of the above studies, the formation of P–S–N chemical linkage has been established.

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1. INTRODUCTION

A lot of work had been reported on organic, metal, and organometal derivatives of O, O′ alkylene/dialkyl dithiophosphates from our laboratories [1–10] during the last decade. In continuation to our earlier investigations on synthesis and properties of phenyl acetyl, p-methyl benzoyl [11], 2-alkylene dialkyl dithiophosphato-2-oxo-1,3,2-dioxa phosphorinane [12], phosphorus trichloride [13], and thio phosphoryl chloride [14] derivatives of alkylene dithiophosphates, it was considered of interest to extend the investigations on the derivatives of the above ligands with N-bromosuccinimide.

2. RESULTS AND DISCUSSION

Reaction of N-bromosuccinimide with ammonium dialkyl (alkylene) dithiophosphates has been carried out in the presence of anhydrous acetonitrile which proceeds to completion within in 6-7 h (refluxing) with the precipitation of ammonium bromide as shown in Scheme 1.

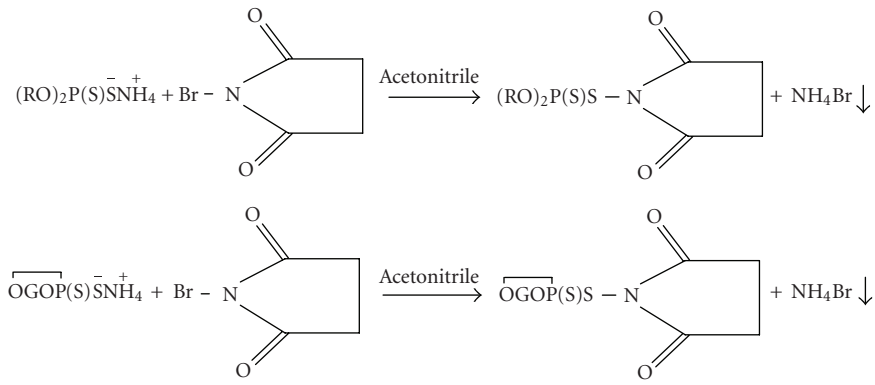
The derivatives shown in Scheme 1 are reddish- or brown-colored sticky liquids. They are nonvolatile even under reduced pressure and are miscible with common organic solvents. On heating, these compounds tend to decompose. Besides, for these compounds are reddish-colored sticky liquids, it could not be possible to have a single crystal X-ray data for correlation. The computational semiempirical calculations (Mopac6p/c) for one representative complex {1-[(diethoxy phosphorothioyl)thio] pyrrolidine-2,5-dione} have been studied and the data regarding the structure of molecule has been tabulated, (see Table 1 and Figure 1). The molecular weight data corresponds with the results obtained. The molecular data indicates a large deviation in the tetrahedral-bond angle values for almost all the atoms. It also indicates a good stability of the molecule ($\Delta H_f = -178.8\,K\cdot Cal$). The five membered ring at nitrogen atom seems to be puckered. A distorted tetrahedral structure around phosphorus atom has been proposed. These computer-based calculations/data are also in good agreement with the analytical and spectroscopic (IR, PMR, ^{31}P NMR) data obtained for these compounds.

2.1. Spectral studies

2.1.1. IR spectra

The IR spectra of these derivatives show the following characteristic changes, (see Table 2).

(1) The νC=O absorption band is present in the region 1700–1680 cm^{-1}. No change in its position has been observed.
(2) The νP−S−N absorption band present in the region 1270–1250 cm^{-1} has been shifted towards lower-wave



Scheme 1

Table 1

SUMMARY OF PM3 CALCULATION

MOPAC 6/PC VERSION 6.12

C8 H14 N O4 P S2

: 4/23/2005

PM3 PRECISE VECTORS
neelam4.dat
neelam41.dat

GRADIENT TEST NOT PASSED, BUT FURTHER WORK NOT JUSTIFIED
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION	= -178.839248 KCAL
ELECTRONIC ENERGY	= -18094.654202 EV
CORE-CORE REPULSION	= 15099.004585 EV
GRADIENT NORM	= 7.570623
DIPOLE	= 6.88535 DEBYE
NO. OF FILLED LEVELS	= 46
IONIZATION POTENTIAL	= 9.152115 EV
MOLECULAR WEIGHT	= 283.297
SCF CALCULATIONS	= 89
COMPUTATION TIME = 21.000 SECONDS	

FINAL GEOMETRY OBTAINED

PM3 PRECISE VECTORS
neelam4.dat
neelam41.dat

O	.0000000	0	.000000	0	.000000	0	0	0	0	CHARGE	-.56
P	1.7056025	1	.000000	0	.000000	0	1	0	0		1.62
O	1.6906302	1	102.206224	1	.000000	0	2	1	0		-.55
C	1.4061362	1	126.316331	1	-13.324730	1	3	2	1		.11
C	1.5201295	1	107.663182	1	177.148478	1	4	3	2		-.12
C	1.4045791	1	121.029119	1	-96.825282	1	1	2	3		.11
S	2.1389991	1	112.178880	1	114.192661	1	2	3	1		-.24
C	1.5206367	1	110.815755	1	116.984887	1	6	1	2		-.14
N	1.7683873	1	128.380442	1	-59.101570	1	7	2	3		-.17
C	1.4382558	1	130.132877	1	-5.382537	1	9	7	2		.28
C	1.4594594	1	120.768531	1	176.947733	1	9	7	2		.28
C	1.5155913	1	109.897524	1	-176.444344	1	10	9	7		-.12
C	1.5256314	1	105.802822	1	-1.728400	1	12	10	9		-.13
S	1.9255849	1	115.324140	1	-133.749203	1	2	3	1		-.57
H	1.1137994	1	109.362401	1	56.530709	1	4	3	2		.03
H	1.1059833	1	109.680043	1	-61.763119	1	4	3	2		.05
H	1.0975300	1	109.859604	1	179.686236	1	5	4	3		.04
H	1.0978338	1	112.037534	1	60.132012	1	5	4	3		.05
H	1.0977353	1	112.231063	1	-60.548861	1	5	4	3		.04
H	1.1057936	1	104.739309	1	-123.194668	1	6	1	2		.05
H	1.1092348	1	110.488197	1	-7.304802	1	6	1	2		.03
H	1.0968382	1	110.316742	1	-175.783629	1	8	6	1		.05
H	1.0977545	1	111.795131	1	64.446898	1	8	6	1		.05
H	1.1032792	1	112.091376	1	-55.584005	1	8	6	1		.05
O	1.2145088	1	122.496721	1	4.145734	1	10	9	7		-.34
H	1.1064842	1	110.442470	1	-123.610378	1	12	10	9		.08
H	1.1065725	1	110.156894	1	119.861032	1	12	10	9		.09
H	1.1064205	1	112.242629	1	121.749969	1	13	12	10		.09
H	1.1067406	1	112.199850	1	-119.233112	1	13	12	10		.09
O	1.2076848	1	123.508593	1	-2.661777	1	11	9	7		-.28

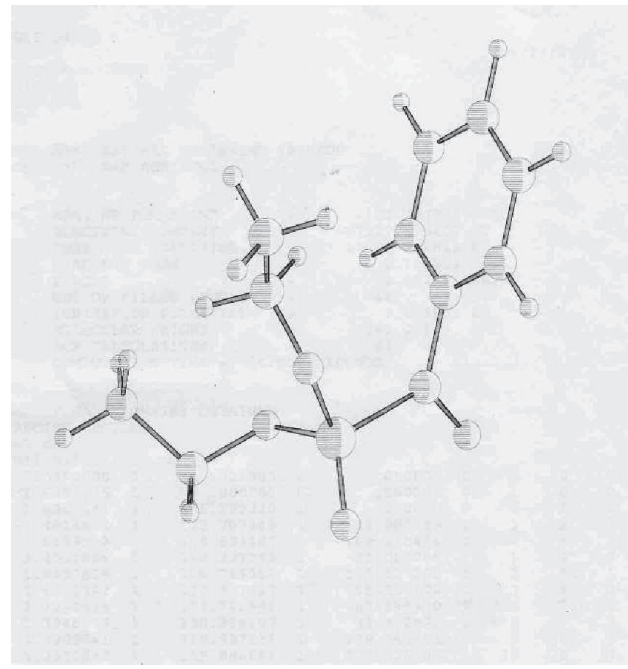


Figure 1: 1-[(diethoxy phosphorothioyl)thio] pyrrolidine-2,5-dione.

number (20–30 cm^{-1}) for six membered (dioxaphosphorinane) ring derivatives.

(3) A strong absorption band present in the regions 1125–1020 cm^{-1} and 905–865 cm^{-1} has been observed for ν(P)−OC and νP−O(C) stretching vibrations, respectively.

(4) The νN−Br absorption band present in the region 912–866 cm^{-1} has been disappeared, which supports the formation of >P−S−N chemical linkage.

(5) The absorption band around 640–670 cm^{-1} has been observed for νP=S vibrations and absorption band present in the region 550–580 cm^{-1} is due to νP−S vibrations. Ring vibrations have been observed in the region 964–950 cm^{-1}.

2.1.2. ^{1}H NMR spectra

^{1}H NMR spectra of these derivatives are listed in Table 3. The spectra show the characteristic resonance for alkyl and glycoxy groups present on phosphorus. A multiplet at δ 4.7–4.9 ppm is assigned for glycoxy protons, which is due to

Table 2: IR spectral data of N-bromosuccinimide derivatives of ammonium dialkyl/alkylene dithiophosphate.

S. No.	Compounds	ν(P)O−C	νP−O(C)	Ring vibrations	νP=S	νP−S	νC=O	νS−N
1	$\overline{OCH_2CH_2CHMeOP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}}$	1120	900	950	660	580	1685	1240
2	$\overline{OCH_2C(Me)_2CH_2OP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}}$	1115	905	960	670	575	1680	1240
3	$\overline{OC(Me)_2CH_2CHMeOP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}}$	1115	905	950	670	575	1685	1235
4	$\overline{OC(Me)_2C(Me)_2OP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}}$	1125	900	964	670	580	1690	1250
5	$(i-C_3H_7O)_2P(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	1020	875	—	650	560	1700	1230
6	$(C_2H_5O)_2P(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	1050	865	—	640	555	1682	1235
7	$(n-C_3H_7O)_2P(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	1025	885	—	650	550	1700	1230

long-range coupling of these protons with magnetically active phosphorus atom. A singlet appears for CH_2 proton of succinimide ring at δ 1.1–1.5 ppm.

2.1.3. ^{31}P NMR spectra

In the proton decoupled ^{31}P NMR spectra only one ^{31}P NMR signal has been observed for each compound (see Table 3). Only one sharp resonance signal at δ 58–62 ppm shows purity of these compounds. An upfield shift (δ 19–22 ppm) is observed for these derivatives in comparison to parent dialkyl (alkylene) dithiophosphates, suggesting the covalent nature of newly formed sulfur-nitrogen linkage as well as the absence of any coordinating tendencies in the above derivatives. Thereby appears a unidentate nature of dithiophosphate moiety.

On basis of the above spectral [IR, NMR (^1H, ^{31}P)] and other physicochemical evidences, the formation of [P−S−N] chemical bond has been established and the structures in Figures 2 and 3 have been tentatively assigned for the above derivatives.

2.1.4. Experimental

Solvents were dried by standard methods. Ammonium salt of dialkyl/alkylene dithiophosphate was prepared by the methods reported in the literature [14]. Sulphur was estimated gravimetrically as barium sulphate (messenger method) [15]. Molecular weights were determined by the "Knaur Vapor pressure Osmometer" using a chloroform solution at 45°C. IR spectra were recorded in Nujol mull (4000–200 cm^{-1}) on an FT IR spectrophotometer model Megna-IR-550 MICOLAC-USA. Carbon and hydrogen analyses were performed on a Perkin Elmer CHN/O analyzer. ^1H NMR spectra were recorded in $CDCl_3$ solution on a 90 MHz JEOL FX 90 spectrometer using TMS as an internal reference. ^{31}P NMR was recorded in C_6H_6 using H_3PO_4 as an external reference (CDRI Lucknow). The experimental details of representative compounds are described below. Analytical results are summarized in Table 4.

2.1.5. Preparation of $\overline{OC(Me)_2CH_2CHMeOP(S)\text{-}SNC(O)CH_2CH_2C(O)}$

An anhydrous acetonitrile solution (50 mL) of N-bromosuccinimide (0.98 g) was added into the suspension of ammonium salt of hexylene dithiophosphate (1.33 g) and refluxed for 6-7 h. Ammonium bromide precipitated within the course of reaction was filtered off and the solvent was removed under reduced pressure. A red/brown-colored sticky liquid product (1.8 g, 82.21%) was isolated. Synthetic and analytical data are given in Table 4.

Table 3: NMR ^{1}H and ^{31}P spectral data of N-bromosuccinimide derivative of ammonium dialkyl/alkylene dithiophosphate.

S. No.	Compounds	^{1}H (δppm)	^{31}P (δppm)
1	$OCH_2CH_2CHMeOP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	1.40, d, 3H(CH_3); 2.7–3.1, m, 2H(CH_2) 4.7–4.9, m, 3H(OCH_2, OCH); 1.5, s, 4H(CH_2)	59.12
2	$OCH_2C(Me)_2CH_2OP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	1.5, S, 6H(CH_3); 4.2, d, 4H(CH_2O) 1.1–1.5, s, 4H(CH_2)	59.71
3	$OC(Me)_2CH_2CHMeOP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	2.1–2.5, m, 11H(CH_3, CH_2); 5.2–5.4, m, 1H(CHO), 1.7, s, 4H(CH_2)	60.32
4	$OC(Me)_2C(Me)_2OP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	1.7, S, 12H(CH_3); 1.6, s, 4H(CH_2)	62.51
5	$(i-C_3H_7O)_2P(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	1.42–1.53, d, 12H(CH_3); 1.6, s, 4H(CH_2)	55.61
6	$(C_2H_5O)_2P(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	1.45–1.72, t, 6H(CH_3); 4.9–5.3, m, 4H(OCH_2); 1.7, s, 4H(CH_2)	58.71
7	$(n-C_3H_7O)_2P(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$	1.4–1.52, t, 6H(CH_3); 2.01–3.1, m, 4H(CH_2); 4.8–5.5, m, 4H(OCH_2); 1.6, s, 4H(CH_2)	57.32

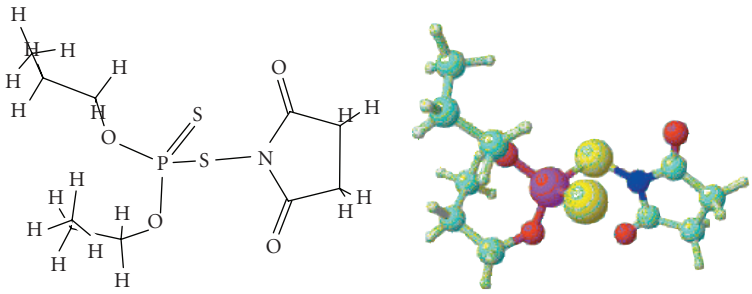


Figure 2: 1-[(dipropoxyphosphorothioyl)thio]pyrrolidine-2,5-dione.

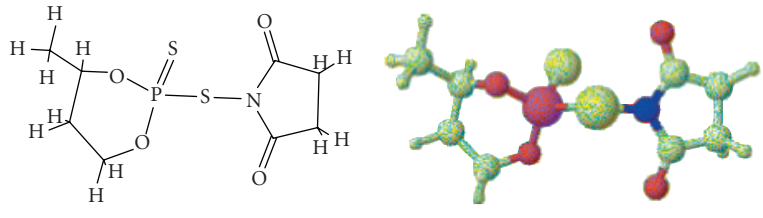


Figure 3: 1-[(4-methyl-2-sulfido-1,3,2-dioxaphosphinan-2-yl)thio]pyrrolidine-2,5-dione.

Table 4: Synthetic and analytical data of N-bromosuccinimide derivatives of ammonium dialkyl/alkylene dithiophosphate.

S. No.	Reactant g(mM)		Product	Found/(calculated) (age (%))			M. wt found (calculated)
	$\overline{OGOP(S)SNH_4}$/$(RO)_2P(S)SNH_4$ G= R=	$BrN<^{C(O)-CH_2}_{C(O)-CH_2}$	– – – g, – – – %	C	H	S	
1	$-CH_2CH_2CHMe-$ 1.37 (6.81)	1.15 (6.46)	$\overline{OCH_2CH_2CHMeOP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}}$ 1.35, 70.41	33.21 (34.16)	3.81 (4.27)	21.92 (22.77)	277 (281)
2	$-CH_2C(Me)_2CH_2-$ 1.34 (6.23)	1.05 (5.89)	$\overline{OCH_2C(Me)_2CH_2OP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}}$ 1.84, 88.51	37.01 (36.61)	5.12 (4.74)	22.10 (21.69)	— (295)
3	$-C(Me)_2CH_2CHMe-$ 1.33 (5.80)	0.98 (5.50)	$\overline{OC(Me)_2CH_2CHMeOP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}}$ 1.80, 82.21	39.01 (38.83)	4.83 (5.38)	21.11 (20.71)	— (309)
4	$-C(Me)_2C(Me)_2-$ 1.70 (7.42)	1.25 (7.02)	$\overline{OC(Me)_2C(Me)_2OP(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}}$ 1.75, 76.66	37.91 (38.83)	4.52 (5.38)	21.11 (20.71)	305 (309)
5	$i-C_3H_7-$ 1.80 (7.79)	1.31 (7.35)	$(i-C_3H_7O)_2P(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$ 1.75, 72.61	39.01 (38.58)	6.11 (5.78)	21.11 (20.57)	— (311)
6	C_2H_5- 1.22 (8.86)	1.01 (5.67)	$(C_2H_5O)_2P(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$ 1.36, 80.28	34.15 (33.92)	5.16 (4.91)	23.03 (22.61)	279 (283)
7	$n-C_3H_7-$ 1.71 (7.40)	1.25 (7.02)	$(n\text{-}C_3H_7O)_2P(S)SN<^{C(O)-CH_2}_{C(O)-CH_2}$ 2.04, 87.61	39.15 (38.58)	6.81 (5.78)	21.37 (20.57)	— (311)

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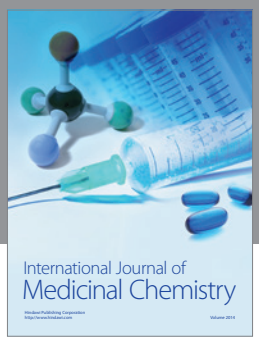

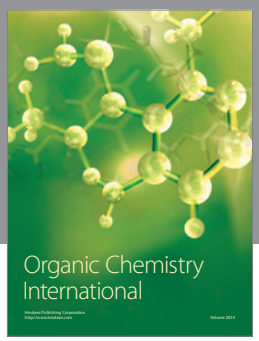

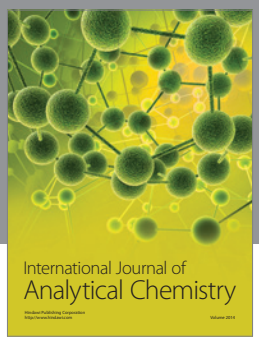

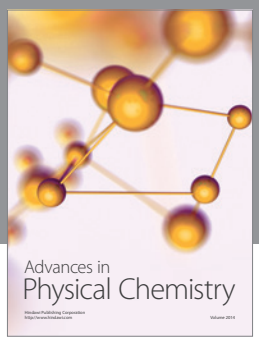

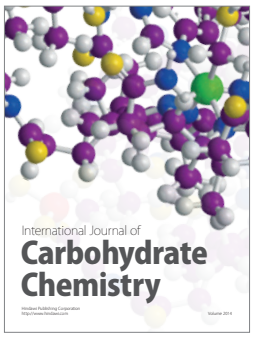

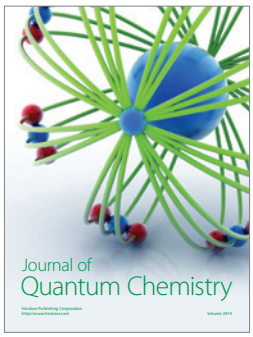

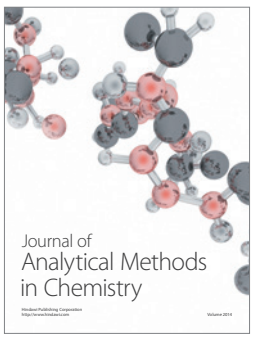

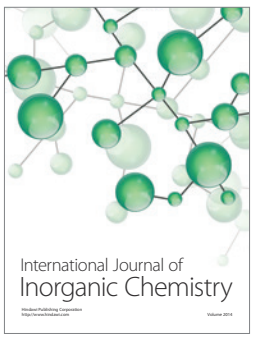

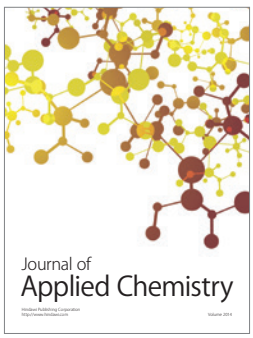

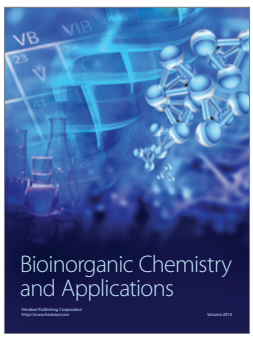

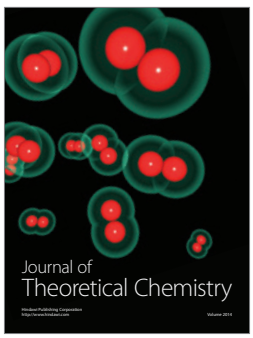

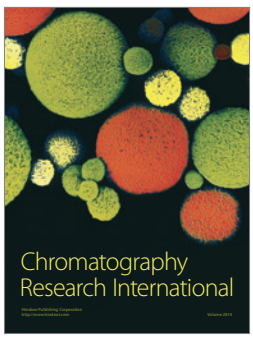

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