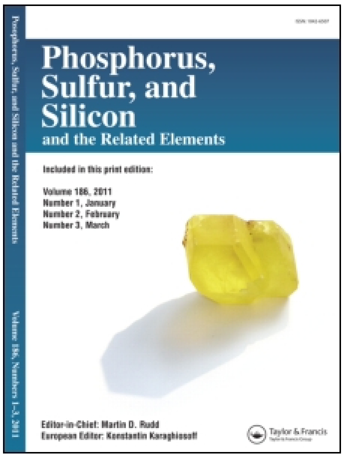

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Ali, Hussein M. and El-Qurashi, Mohamed A. M.(1998) 'Synthesis and Application of Some Dianilinosilanes, Bis (Trimethylsilyl) Phenylenediamines and Dialkyl Benzo-1,3,2-Diazasilolines as Antioxidants', Phosphorus, Sulfur, and Silicon and the Related Elements, 134: 1, 521 — 529

To link to this Article: DOI: 10.1080/10426509808545493

URL: http://dx.doi.org/10.1080/10426509808545493

Phosphorus, Sulfur and Silicon, 1998, Vol. 134/135, pp. 521-529
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SYNTHESIS AND APPLICATION OF SOME DIANILINOSILANES, BIS (TRIMETHYLSILYL) PHENYLENEDIAMINES AND DIALKYL BENZO-1,3,2-DIAZASILOLINES AS ANTIOXIDANTS

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(Received 1 February, 1998; In final form 5 May, 1998)

A number of dialkyl or diphenyl dianilinosilanes, bis (trimethylsilyl) phenylenediamines and dialkyl benzo-1,3,2-diazasilolines were synthesized and used as antioxidants for lubricating base oils. Thermal analysis methods (DSC, TG and DTG) and IR technique were used to follow the oil oxidation. The first peak in the DSC thermograms of oil with the additive antioxidants is the sum of the endothermic oil evaporation process and the exothermic oxidation process. The onset temperature of this peak was used as a sensitive measure of the thermo-oxidation stability of the oil. Results showed that the prepared antioxidants increased the oil thermo-oxidation stability from 218°C up to 270°C which is close to the temperature of the oil evaporation as indicated by the TG thermograms. The antioxidation effect of the anilinosilane derivatives was attributed to the extra stability of the amine radical by both the silyl and phenyl groups. This radical is formed after binding the peroxy radical responsible for the oil deterioration.

Keywords: anilinosilanes; diazasilolines; antioxidants; thermal analysis

INTRODUCTION

Oxidation is one of the major sources of chemical breakdown of lubricating base oils under processing conditions. Most oil components react with atmospheric oxygen to give undesirable products. Antioxidant additives are used to delay oxidation and increase the temperature at which the oxidation occurs. Examples of antioxidants used are butylmethylphenol[1], carbamodithioate[1], zinc alkyl

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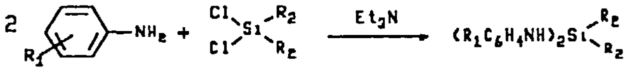
dithiophosphates[2], zinc salt and dialkyl ester of phosphorodithioic acid[3], phenylnaphthylamines and sulfides and their copper salts[4] and polyisobutenylsuccinic acid amides[5].

Silicon has shown deoxidizing ability in liquid iron[6] while some silicones (polysiloxanes) are used as antioxidants[7], antifoam agents[8] and high performance synthetic lubricants[9]. We have shown that anilinosilanes, in addition to being thermally stable, have good antioxidation effect. The silyl groups also increased the solubility of the amines in the lubricating base oil[10]. This article describes the synthesis of some more hindered dianilinosilanes, bis (trimethylsilyl) phenylenediamines and dialkyl benzo-1,3,2-diazasilolines and their application as antioxidants in lubricating base oil.

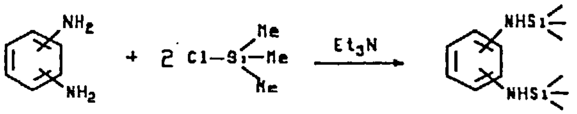
RESULTS AND DISCUSSIONS

Chlorosilanes react with anilines in the presence of triethylamine at low temperature with the omission of other solvents[11]. The following equations represent the employed reactions.

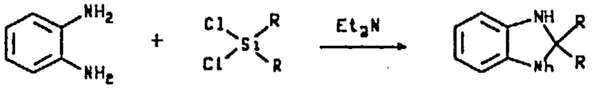


dianilinosilanes

$R_1 = H$ $R_2 = Me$ **1**
$R_1 = p\text{-}Me$ $R_2 = Me$ **2**
$R_1 = m\text{-}Me$ $R_2 = Me$ **3**
$R_1 = p\text{-}OMe$ $R_2 = Me$ **4**
$R_1 = m\text{-}Br$ $R_2 = Me$ **5**
$R_1 = m\text{-}Cl$ $R_2 = Me$ **6**
$R_1 = H$ $R_2 = Et$ **7**
$R_1 = H$ $R_2 = Ph$ **8**



Bis (trimethylsilyl) *o*- (**9**)
or *p*-(**10**) phenylenediamine



dialkyl-benzo-1,3,2-diazasilolines
R = Me **11**
R = Et **12**

IR spectra of these compounds are characterized by the presence of Si-N band at $\sim$ 1040 cm^{-1}and Si-C band at $\sim$ 1270 cm^{-1} for aliphatic carbon or $\sim$ 1135 cm^{-1} for aromatic carbon (compound 8). Other important absorption bands are summarized in table I. ^{1}H NMR spectra showed the upfield absorption of protons on α-carbon to silicon at chemical shift < 1.3 ppm. Interestingly, the ethyl methylene protons of 7 gave a quartet at 1.25 ppm downfield of the methyl proton triplet (1.0 ppm) while the same protons of **12** gave a quartet at 0.7 ppm upfield of the methyl proton triplet (1.0 ppm). This could be attributed to the deshielding effect of the two phenyl groups in **7**. Similarly, the $SiMe_2$ protons of compound **1** were deshielded by the two phenyl groups at 0.6 ppm compared to the same $SiMe_2$ protons of compound **11** which appear at 0.45 ppm. The four aromatic hydrogen of o-phenylenediamine and its derivatives are usually similarly affected by the two amino groups and give a singlet between 6.4–6.8 ppm. Analyses of other peaks are presented in table II. The pure compounds showed only one endothermic peak for evaporation in their DSC thermograms and one weight-loss step in their TG thermograms indicating the purity of these compounds and their thermal stability up to their complete evaporation except for diphenyl dianilinosilane **8** which decomposed and gave exothermic peak. The onset temperatures of the DSC peaks and the peak temperatures (temperatures at the maximum weigh-loss rates) of the DTG peaks are listed in table III. Examples of the DSC and TG thermograms of are presented in figure 1.

TABLE I The characteristics IR bands of the prepared compounds

Compound	*N-H*[1]	*Aromatic C-H sir.*	*Aliphatic C-H str.*	*C=C str.*	*C-N str.*	*Si-C str.*	*Si-N*	*Others*
1	3390	3050	2975	1605,1505	1280	1270	1040	
2	3340	3040	2975	1625, 1520	1295	1270	1035	
3	3350	3050	2970	1620,1500	1300	1270	1030	
4	3330	3040	2970	1620,1520	1270	1250	1050	1225 (OMe)
5	3320	3030	2980	1600,1485	1320	1280	1020	1080 (C-Br)
6	3350	3060	2970	1600,1490	1310	1280	1020	1085 (C-Cl)
7	3380	3050	2960	1600,1500	1300	1250	1035	
8	-	3040	-	1440	1230	1135	1030	
9	3350	3030	2980	1600,1480	1305	1260	1050	
10	3300	3050	2980	1600,1470	1310	1250	1040	
11	3270	3020	2950	1600,1480	1300	1260	1020	
12	3300	3020	2950	1600,1480	1280	1260	1030	

[1] All samples were neat except compounds 4 and 8 which were dissolved in $CDCl_3$.

TABLE II ^{1}H NMR data of the prepared compounds

compound	*SiR*	*NH*	*ArN*[1]	*Others*
1	0.6s(6H)	3.10	6.7m(3H*o,p*),7.0m(2H*m*)	
2	0.34s(6H)	3.50	6.6d(2H*o*),6,9d(2H*m*)	2.19s(6H,Me)
3	0.1s(6H)	3.65	6.4m(6H*o,p*),6.96m(2H*m*)	2.21s(6H, Me)
4	0.5s(6H)	3.55	6.7m(8H)	3.75s(6H,Me)
5	0.1s(6H)	3.85	6.85m(6H*o,p*),7.0m(2H*m*)	
6	0.1s(6H)	3.60	6.62m(6H*o,p*),7.05m(2H*m*)	
7	1.25q(4H), 1.0t(6H)	3.68	6.7m(6H*o,p*),7.1m(4H*m*)	
8	7.48m(6H*o,p*),7.7m(4H*m*)	4.25	6.75m(6H*o,p*),7.27m(4H*m*)	
9	0.4s(18H)	3.30	6.4m(4H)	
10	0.26s(18H)	3.20	6.55s(4H)	
11	0.45s(6H)	3.72	6.7s(4H)	
12	0.7q(4H), 1.0t(6H)	3.42	6.79s(4H)	

[1] positions of aromatic protons relative to amine.

TABLE III DSC and DTG data of lubricating base oil and the prepared compounds

Compound	*Pure compounds*		*Oil + Compound*			
	DSC[1,2]	*TG*[3]	*TG*		*DSC*[1]	
			Starts of evaporation	*Peak*[3]	*1st*	*2nd*
1	179	220	265	310	256 endo	400 exo
2	175	184	275	316	260 endo	490 exo
3	170	176	270	309	265 exo	450 exo
4	250	268	270	306	261 endo	-
5	212	245	260	288	225 exo	400 exo
6	190	194	270	322	260 endo	398 exo
7	178	230	260	307	230 exo	465 exo
8	245	297	260	329	245 exo	-
9	181	184	275	335	225 exo	363 exo
10	205	232	275	324	225 exo	348 exo
11	198	265	275	358	222 exo	361 exo
12	194	235	275	345	270 exo	495 exo

[1] The onset temperatures.

[2] All are endothermic for evaporation except compound 8 is exothermic for decomposition.

[3] Peak temperatures (the temperatures at the maximum weight-loss rates).

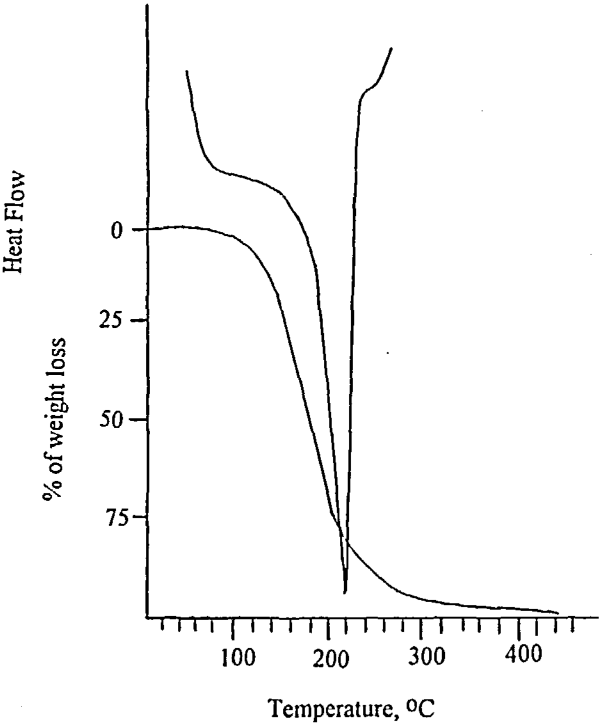
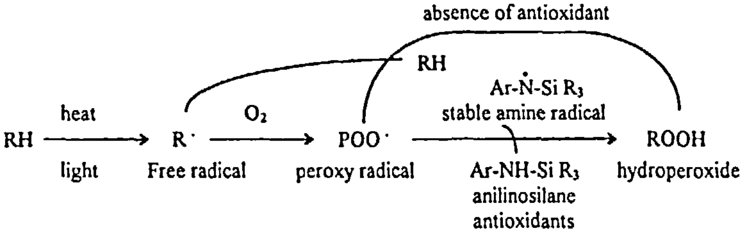


FIGURE 1 DSC and TG thermogrames of compound **2**

The onset temperature of the oil oxidation peak in a DSC thermogram showed to be a sensitive way to measure the oil thermo-oxidation stability. Thermogravimetry (TG) was also used[10,12]. The base oil 300 SN used in this study was obtained before the addition of the manufacturer antioxidant (named MOX). The physical properties of the oil were reported previously[12]. The oil before and after the manufacturer antioxidant addition started oxidation at 218 and 265°C respectivily[10]. The prepared compounds were dissolved in the oil in percentage not more than 2%, according to their solubility, by stirring overnight. Although amines are used as antioxidants[4], their solubility is usually difficult; however, silylation enhanced the solubility of the starting anilines in oil. Analyses of the DSC and DTG thermograms of oil with each compound were tabulated in table III. Most samples showed two peaks in their DSC curves. The onset temperature of the first peak was taken as the start of oil deterioration and reflects the temperature under which the oil is stable. Table III also shows the temperatures at the maximum weight-loss rates taken from differential thermogravimerty

(DTG) curves. These curves showed that the oil samples evaporated completely in this step. The evaporation process starts between 260 and 275°C while the temperatures at the maximum weight-loss rates ranged from 306 to 358°C which could be affected by the sample weight. The first peak in the DSC thermograms is the sum of the evaporation process (endothermic) and the oxidation process (exothermic). This explains why this peak is either exothermic in some cases or endothermic in others. The onset temperature of the first peak reached 256, 260, 265, 261, 260 and 270°C in compounds **1**, **2**, **3**, **4**, **6** and **12** respectively. These temperatures are close to those of the starts of oil evaporation as indicated by TG curves. This means that the oil was stable in these cases against oxidation almost up to its evaporation. In addition, the first peak in some cases (compounds **2**, **3**, **7** and **12**) was weak compared to the strong exothermic peak of the base oil 300 SN antioxidant additive which indicates that oxidation is retorted by the effect of the used compounds. Examples of the first peak in the DSC curves of oil without or with some antioxidants are presented in figure 2.

Oxidation of oils under service is initiated at processing temperatures by forming free radical (R) which reacts with atmospheric oxygen to form the peroxyradical (ROO). In the absence of antioxidant the peroxyradical absorbs a hydrogen atom from another hydrocarbon molecule to form again a free radical to complete the cycle and hydroperoxide (ROOH). The later decomposes further by the effect of heat and light to give the undesirable carbonyl compounds[13]. In the presence of anilinosilane antioxidants, the amine hydrogen binds the peroxyradical to terminate the cycle. The silyl and phenyl groups stabilize the left out amine radical as indicated below.



The inhibitor radicals of aromatic amines formed after quenching the peroxy radicals react through radical combination or electron transfer to give quinone-imines, or gives complexes that do not maintain the radical chain mechanism of the autoxidation reaction[13b]. This point is being now under further investigation.

The antioxidation effect on oils can also be followed by IR spectroscopy[14]. Therefore, The oil alone or with antioxidant **1** was heated in the TG crucible to 260°C then the IR spectrum was recorded. As shown in figure 3, spectrum of oil without antioxidant showed a band at 3420 cm^{-1} for the hydroperoxide OH

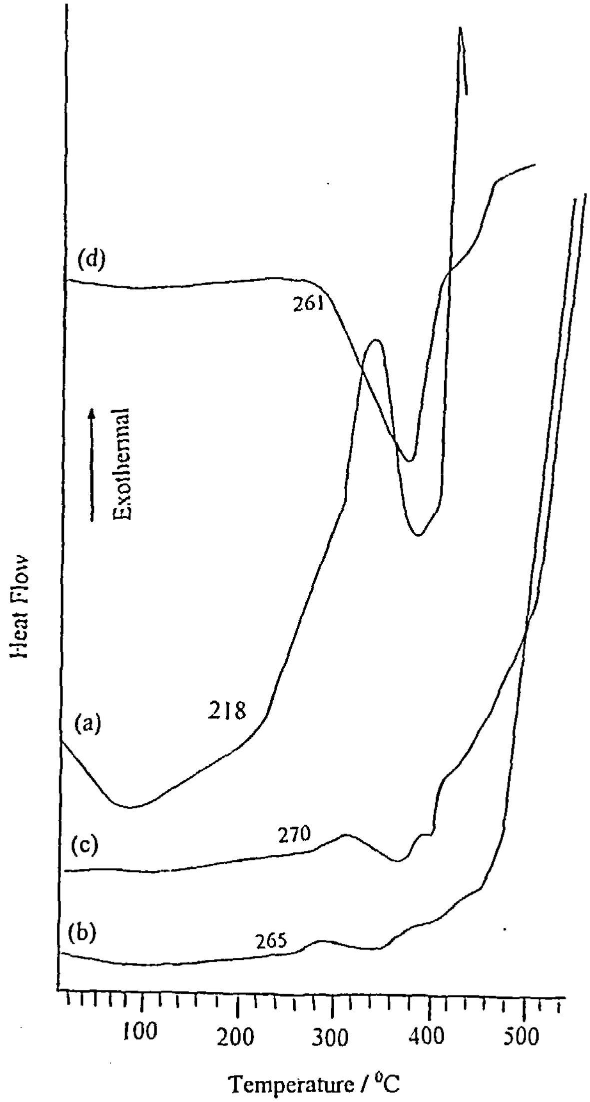


FIGURE 2 DSC thermogrames showing the onset temperatures of (a) oil, (b) oil + **3**, (c) oil + **12** and (d) oil + **4**

group and a weak peak at 1720 cm^{-1} for the carbonyl group. These peaks were either absent (carbonyl) or very weak (hydroperoxide OH) in the spectrum of oil with antioxidant additive. This shows the efficient of anilinosilane derivatives to retard oxidation by binding up the peroxy radical.

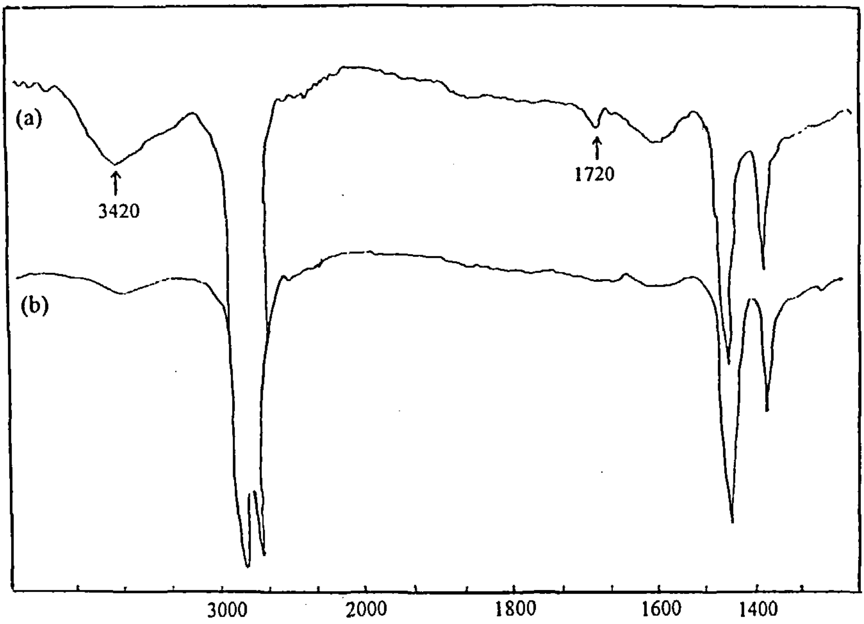


FIGURE 3 IR spectra of (a) oil and (b) oil + **1** after heating to 260°C in TG crucible

EXPERIMENTAL

The lubricating base oil used in this study is designated 300 SN and was obtained from Petrolube company, Jeddah, Kingdom of Saudi Arabia. Chemical used were of reagent grade. Triethylamine was dried over KOH and distilled. Chlorosilanes were manipulated under dry nitrogen atmosphere.

^{1}H NMR spectra were recorded by using Varian EM 390 NMR spectrometer and $CDCl_3$ as a solvent. IR spectra were obtained by use of Pye Unican SP3–100 grating IR spectrometer. Differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermogravimetry (DTG) analyses were performed by using TA 3000 Mettler system. Measurements were conducted under atmospheric air (static condition). The operation condition was: initial temperature, 50°C; final temperature, 550°C and heating rate, 10°C/min. The onset temperatures were taken from DSC curves at the intersection of the extrapolated base line before transition with a tangent to the deflected peak. Synthesis of dialkyl or diaryl dianilinosilanes:

A 0.05 mol. of the appropriate substituted aniline was dissolved in dried triethylamine. The solution was stirred and cooled to –5°C under dry nitrogen; then

0.025 mol. of the appropriate dichlorosilane (dimethyl, diethyl or diphenyl chlorosilane) was added slowly via syringe. The reaction mixture was stirred for three more hours then filtered and washed with ether. The solvents were evaporated and the product was distilled under reduced pressure.

Synthesis of bis (trimethylsilyl) *o* or *p* phenylenediamines:

The previous procedure was followed except a 2 molar ratio of trimethyl chlorosilane was used.

Synthesis of dimethyl or diethyl benzo-1,3,2-diazasilolines.

The same general procedure was adopted except a 1 molar ratio of the appropriate dialkyl dichlorosilane was used.

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