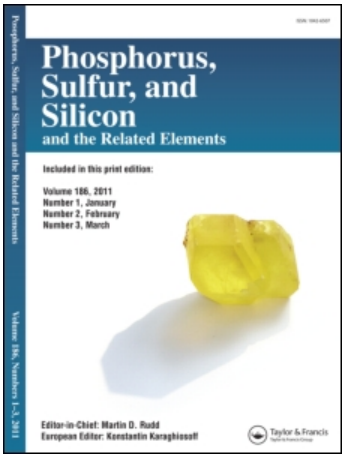

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ESR STUDY OF THE STABLE PHOSPHORANYL-IDENEAMINO(DICYANO)METHYL RADICALS, RESULTING FROM REVERSIBLE THERMAL HOMOLYSIS OF 1,2-BIS(PHOSPHORANYLIDENE-AMINO)TETRACYANOETHANES

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To cite this Article Kadirov, M. K. , Morozov, V. I. , Kamalov, R. M. , Stepanov, G. S. , Il'yasov, A. V. and Pudovik, M. A.(1992) 'ESR STUDY OF THE STABLE PHOSPHORANYL-IDENEAMINO(DICYANO)METHYL RADICALS, RESULTING FROM REVERSIBLE THERMAL HOMOLYSIS OF 1,2-BIS(PHOSPHORANYLIDENE-AMINO)TETRACYANOETHANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 68: 1, 247 — 252
To link to this Article: DOI: 10.1080/10426509208038391
URL: http://dx.doi.org/10.1080/10426509208038391

Phosphorus, Sulfur, and Silicon, 1992, Vol. 68, pp. 247–252
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ESR STUDY OF THE STABLE PHOSPHORANYLIDENEAMINO(DICYANO)METHYL RADICALS, RESULTING FROM REVERSIBLE THERMAL HOMOLYSIS OF 1,2-BIS(PHOSPHORANYLIDENEAMINO)TETRACYANOETHANES

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(Received June 6, 1991; in final form October 28, 1991)

Thermally-induced equilibrium homolytic dissociation of 1,2-bis(phosphoranylideneamino)tetracyanoethanes, resulting in the formation of the stable phosphoranylideneamino(dicyano)methyl radicals has been studied by ESR spectroscopy. Enthalpies and entropies of the dissociation have been estimated. Magnetic resonance parameters, found from ESR spectra, are characteristic of π-radicals. Temperature-dependent phosphorus hyperfine splittings have been studied.

Key words: Thermally-induced reversible homolysis; stable phosphorus-containing radicals; ESR spectra.

INTRODUCTION

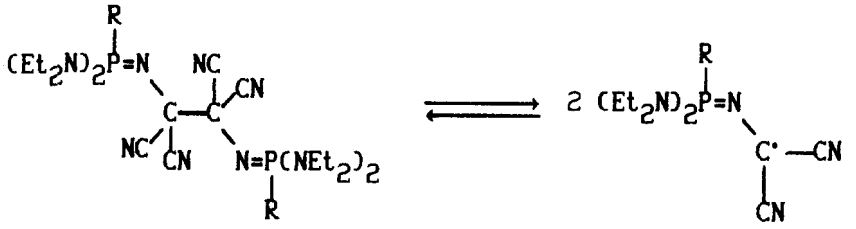
1,2-Bis(phosphoranylideneamino)tetracyanoethanes **1** are the minor products of the interaction between aminophosphines $(Et_2N)_2PR$ [where R = Et_2N (a) and Ph (b)] and alkyl thiocyanates. By monitoring the reaction of ethyl thiocyanate and hexaethyltriaminophosphine by means of ^{31}P NMR spectroscopy ^{31}P chemically induced dynamic nuclear polarization (^{31}P CIDNP) has been observed, and free radicals have been detected in the reaction mixture by ESR spectra. These data have provided grounds for assuming that the formation of products **1** can proceed by pathways, including homolytic stages.[1]

Essential lengthening of the $(CN)_2C—C(CN)_2$ bond has been found [1.609(6)Å] by X-Ray study of compound **1a**, and the fragments with m/z, corresponding to a half of molecular masses of initial compounds have been detected in electron impact mass spectra of **1a, b**. These data made it possible to assume easy cleavage of the central C—C bond in **1a, b**, which gives rise to radicals **2**. The dissociation of a similar type has been studied rather well on 1,2-diarylethanes[2,3] and 1,5-hexadienes,[4] bearing donor-acceptor substituents. In order to investigate the possibility of such a process, ESR study of compounds **1** has been carried out.

RESULTS AND DISCUSSION

The ESR investigation of solutions of compounds **1a, b** in toluene and hexamethyltriamidophosphate (HMP) in the 300–400 K temperature range has demonstrated

the existence of an equilibrium homolytic dissociation, resulting in the formation of radicals **2a, b**.



1 2

The relationship between ln K_{eq} and the reverse temperature ($1/T$) is linear:

$$\ln K_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S_0}{R}, \qquad \text{where } K_{eq} = \frac{[2]^2}{[1] - \frac{[2]}{2}}$$

The values of the dissociation enthalpy and entropy for **1a, b** have been estimated from the above relationship by the least-squares method refinement and are listed in Table I. The value of dissociation enthalpy is in good correlation with the —C—C— bond distances.[3] Slight destabilization in polar solvent (HMP) is due to the solvation, which is especially obvious in the changes of dissociation entropy observed when passing from toluene to HMP.

ESR spectra of solutions of radicals **2a, b** have a well split hyperfine structure (Figure 1). Magnetic resonance parameters, summarized in Table II, have been estimated by simulating the ESR spectra on a computer. General extension and view of the spectra are temperature-dependent (Figure 2).

It has been shown,[5] that hydrogen abstraction from trialkoxyphosphoranylidene-aminomethanes of type **3** results in the formation of trialkoxyphosphoranylidene-

TABLE I

Thermodynamic parameters of the dissociation **1** ⇄ **2**

Precursor	Radical	Solvent	ΔH^0, kcal/mol	ΔS^0, cal/mol·K
1a	2a	HMP	-18.0±04	34±1
1a	2a	toluene	-19.3±0.4	28.2±1
1b	2b	HMP	-18.3±0.4	30.2±1

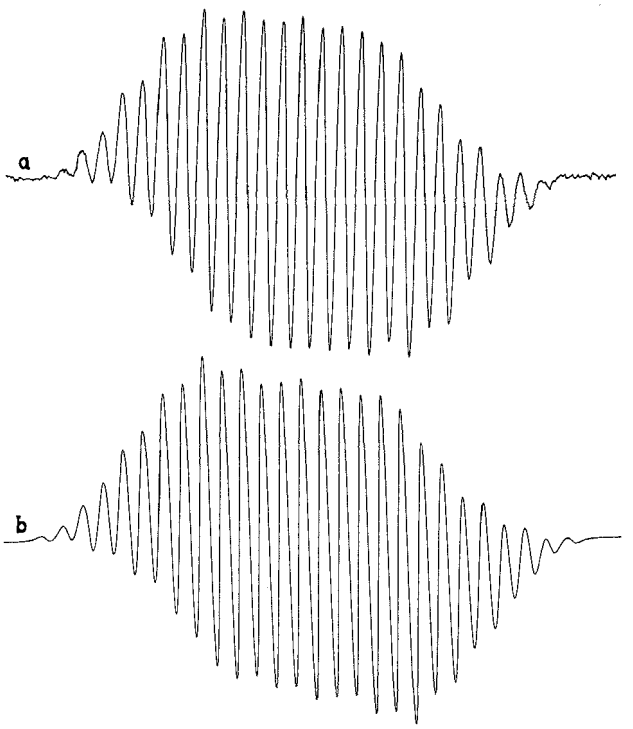


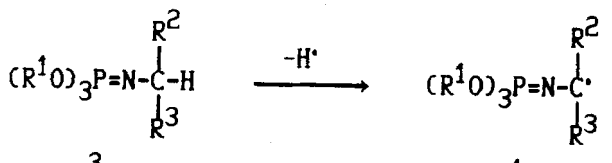
FIGURE 1 Observed (a) and computer-simulated (b) ESR spectra of free radical **2a** at 333 k in HMP.

TABLE II

Experimental values of magnetic resonance parameters for **2a, b** and reference data for free radical **4** ($R^1 = R^2 = R^3 = Me$)[5]

Radical	Solvent	T,K	Hyperfine splittings/mT				g-factor
			a^P	$a^N_{P=N-C_\alpha}$	$a^N_{Et_2N}$	a^N_{CN}	
2a	HMP	313	0.236	0.458	0.102	0.184	2.003
2b	HMP	318	0.146	0.418	0.134	0.200	2.003
4	cyclo-propane	188	1.620	0.130	-	$a^H_{CH_3}$=1.94	2.0028

aminomethyl radicals **4**. Similar to the latter an unpaired electron is located predominantly on the carbon atom of free radicals **2a, b**.



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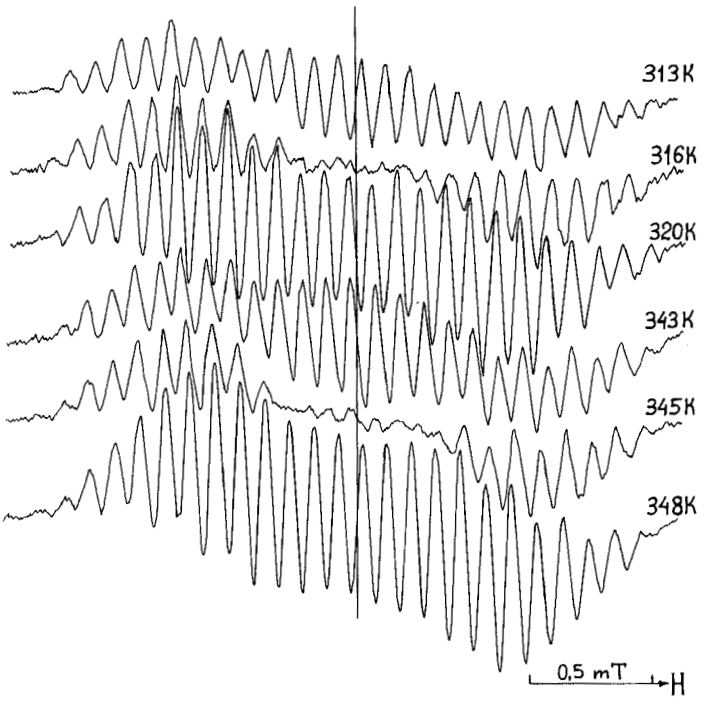
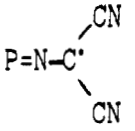


FIGURE 2 Temperature-dependent changes of ESR spectra of free radical **2a** in HMP.

Planarity of the P=N—C—C—N=P fragment in **1a** was established by X-Ray.[1] Probably, the most stable conformation of free radicals **2a, b** is defined by a flat arrangement of the phosphazene group, two cyano groups and the λ^3-carbon atom. In this case the P=N—C fragment is bent as in the precursors 1[1] (cf.[5]). The planar character of the



fragment in radicals **2a, b** is evidenced by small values of constant by hyperfine splitting of phosphorus, which is in β-position towards the radical center.

The value of phosphorus hyperfine splitting constant is due to the competition of the principal mechanisms of spin density transfer. On the one hand, spin polarization of the P—N σ-bond by positive π-spin density on the nitrogen atom gives rise to negative spin density on the P-3s orbital. On the other hand, delocalization, involving π-orbitals, and hyper-conjugation provide a positive contribution.

Similar to **4** the free radicals **2a, b** are characterized by the temperature-dependence of the hyperfine splitting. In case of the radical **2a** in HMP the reduction of the phosphorus hyperfine splitting constant has been detected in the 300–360 K range. The change of the ESR spectrum general extension is directly proportional to variation of the a^P constant. The selection of theoretical spectra for a description of experimental ones (Figure 2) has confirmed that main changes are due to the

a^P variation. The angular coefficient of other splitting temperature dependences is essentially smaller. The temperature behavior of the spectra may be described without taking into consideration the dependence of the line width on the projection of nuclear spin, which is a characteristic of the radical dynamic processes. The decrease of the a^P constant with its subsequent increase has been observed for **2a** in toluene as well as for **2b** in HMP in the 300–360 K range:

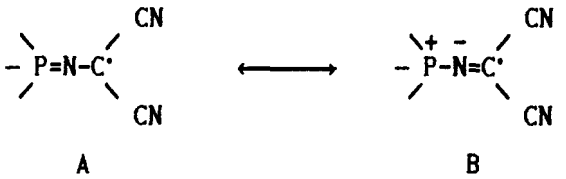
$$\frac{da^P}{dT} \simeq \pm 3.0 \cdot 10^{-3} \text{ mT/K}$$

for **2a,b** as compared with

$$\frac{da}{dT} = 9.0 \cdot 10^{-3} \text{ mT/K}$$

for **4** ($R^1 = R^2 = R^3 = Me$).[5]

The value of a^P becomes 0 at temperature (T_c) – 398 K for **2a** in HMP, at −338 K for **2a** in toluene and at − 363 K for **2b** in HMP. The difference between the values of T_c in HMP and toluene for **2a** can be due to the increase of the contribution of the spin polarization mechanism for ionic structure B, stabilized with polar solvent.



The temperature rise brings out the defrosting of torsional motions around the P—N bonds and to the enlargement of positive spin density on phosphorus atom by the hyper-conjugation mechanism.

Solvation of polar fragments as well as high viscosity of HMP restrain motions, in particular, torsional motions.[6] This results in the restrictions both as regards the dimerization process and bringing the phosphorus atom out of the plane, which contributes to hyper-conjugation.

SUMMARY

Phosphoranylideneamino(dicyano)methyl radicals **2a, b**, resulting from the thermally-induced equilibrium homolytic dissociation of 1,2-bis(phosphoranylideneamino)tetracyanoethanes **1a, b**, are characterized by higher stability as compared with known trialkoxyphosphoranylideneaminomethyl radicals **4**. This is likely due to the conjugation between the radical center and the π-electron system of two cyano groups and a phosphazene substituent.

EXPERIMENTAL

ESR spectra were recorded on an ESR spectrometer Bruker ER 200D, supplied with a temperature variator B-VT-1000. ESR spectra simulations were performed on an Aspect-2000 computer using a standard program. The samples were vacuated to 10^{-3} torr. Measurements of the radicals **2a, b** concentrations were conducted using a double rectangular resonator TE_{104}. A stable nitroxide radical (1-oxy-2,2,6,6-tetramethylpiperidine) with a certain paramagnetic centers concentration was used as a standard. The accuracy of measurements of the absolute spin concentration in a double resonator equals 25–30%.

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