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Structural and Variable-Temperature NMR Studies of 9-Diisopropylphosphanylanthracenes and 9,10-Bis(diisopropylphosphanyl)anthracenes and Their Oxidation Products

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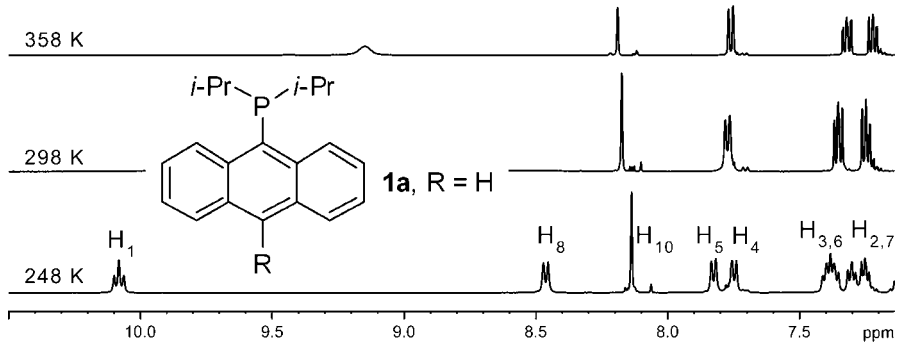

The diisopropylphosphanyl-substituted anthracenes *i*-$Pr_2P(C_{14}H_9)$ (**1a**), *i*-$Pr_2P(C_{14}H_8)Br$ (**2a**), and $(i\text{-}Pr_2P)_2(C_{14}H_8)$ (**3a**) and some of their oxidation products were prepared from 9-bromoanthracene and 9,10-dibromoanthracene, respectively. Low-temperature ^1H NMR spectra of the 9-monophosphanyl-substituted anthracenes **1a** and **2a** are in accordance with a staggered conformer, while above room temperature dynamic processes occur. The low-temperature NMR spectrum of the 9,10-diphosphanylanthracene **3a** indicates the presence of two different rotational isomers. The rotational barrier for **1a** was determined from variable-temperature ^1H NMR spectra to be 56 kJ mol^{-1} (ΔG_{298K}). The crystal structure determinations show the solid-state conformers to be consistent with the prevailing conformer at low temperature.

Introduction

Thirty-five years after the first isolation of anthracene from coal tar by Laurent and Dumas in 1832,[1] Fritzsche induced studies of its photochemical properties emphasizing the unique features of the photoreactive chromophore discovered.[2] Since then a large number of anthracene derivatives with various substituents have been synthesized, showing that substituents in positions 9 and 10 have the largest influence on the resulting characteristics, e.g., photodimerization.[3] However, the first 9-phosphorus-substituted anthracene was not synthesized before 1987 by Akasaka et al. with the objective of developing chemosensors for the determination of hydroperoxides.[4] Although the specified compound did not seem suitable for practical applications, it gave rise to the syntheses of few related derivatives starting with Schmutzler's work on fluorinated phosphanylanthracenes.[5] Additionally, some studies were published on conformational isomers that occur by temperature-dependent rotation about the $P-C_{anthracene}$ bonds, mainly observed at compounds with phenyl groups bonded to the phosphorus atom.[6]

Reports on diisopropylphosphanylanthracenes are rare and have been limited so far to 1,8-disubstituted derivatives acting

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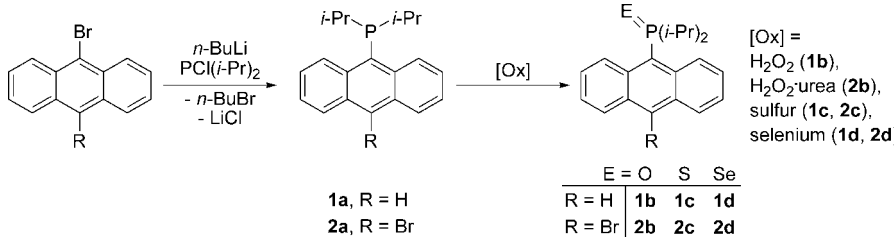
SCHEME 1. Syntheses of 1a−d and 2a−d



as tridentate ligands to stabilize metals with a σ-bond to the carbon atom in position 9.[7] Only marginally more publications deal with related naphthalene compounds. For example, isopropyl-substituted binaphthyl ligands were employed to catalyze the asymmetric synthesis of an axially chiral antimitotic biaryl via a Suzuki cross-coupling reaction[8] as well as to stabilize new dinuclear chloro-bridged ruthenium complexes.[9] Furthermore, the sterically strained 1,8-diisopropylphosphanylnaphthalene was characterized, showing remarkable through-space interactions as derived from the ^{31}P NMR spectrum.[10]

Interest in anthracenes bearing heteroatom-based substituents has increased due to their ability to act as chemosensors,[11] and particularly anionic targets can be detected by alterations of the fluorogenic quality in solution.[12] Recently we described the synthesis of the symmetrically substituted 9,10-bis(diphenylthiophosphoryl)anthracene demonstrating that the luminescence properties depend on the presence of an aromatic guest in the crystal lattice.[13] Therefore it might serve as a chemosensor for toluene and further investigations are under way.

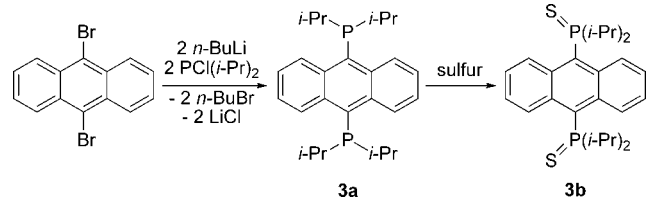
In this article we report studies on the diisopropyl-substituted analogue in order to compare the structural, spectroscopic, and fluorescence features. In addition, the monophosphorus-substituted compounds 9-diisopropylphosphanylanthracene and 9-bromo-10-diisopropylphosphanylanthracene as well as their oxidation products were synthesized and characterized, revealing interesting dynamic properties in solution as shown by low-temperature ^{1}H NMR experiments.

Results and Discussion

The synthesis of the parent compound **1a** was achieved by reacting 9-bromoanthracene in diethyl ether with *n*-BuLi and subsequent addition of chlorodiisopropylphosphane, as shown in Scheme 1. After concentration of the mixture, the precipitate was filtered off and dried in vacuo leaving **1a** in yields up to 86%. The oxidation reactions were achieved with H_2O_2 (**1b**), elemental sulfur (**1c**), and gray selenium (**1d**), respectively.

Recently we reported the synthesis and structural characterization of the first 9-bromo-10-phosphanylanthacene, obtained by monolithiation of 9,10-dibromoanthracene and subsequent reaction with chlorodiphenylphosphane.[14] To extend the selective monolithiation followed by substitution with different phosphorus electrophiles, we chose chlorodiisopropylphosphane (Scheme 1). After removal of the solvent **2a** was obtained as a yellow powder in good yield. The following oxidation reactions leading to **2b**–**d** were carried out as described for **1b**−**d**, with the modification of using $H_2O_2 \cdot (H_2N)_2C{=}O$ as a mild oxidizing reagent to give **2b**.

SCHEME 2. Syntheses of 3a and 3b



The 9,10-symmetrically-substituted compounds **3a** and **3b** were prepared similarly by 2-fold lithiation of 9,10-dibromoanthracene in diethyl ether (Scheme 2). According to our experience the highest yields were obtained when the chlorophosphane was added at room temperature and the mixture was then stirred for about 4 h before filtration and removal of the solvent. In analogy to the syntheses of **1c** and **2c**, the oxidation of **3a** was performed by treatment with elemental sulfur in toluene at reflux to give **3b** in almost quantitative yield.

Comparison of the solubilities of the two bromoanthracene derivatives during the lithiation reactions shows different behavior. 9-Bromoanthracene is well soluble in diethyl ether, but during addition of 1 equiv of *n*-BuLi the resulting 9-lithioanthracenide is precipitated from the mixture as an orange solid. On the other hand the 9,10-dibromo-substituted analogue is almost insoluble in the same solvent, while the monolithiated species with one bromine atom remaining gives a clear orange solution. During addition of the second equivalent of *n*-BuLi at −15 °C the resulting 9,10-dilithioanthracenide again is precipitated from the clear solution as an orange solid.

The protons of the alkyl region of **1a** give rise to well-resolved signals in the ^{1}H NMR spectrum at room temperature. The methyl groups of one isopropyl substituent are diastereotopic, and thus produce two sets of doublets of doublets at δ_H 1.33 and 0.65 ppm with coupling constants of $^3J_{HP} = 17.4/^3J_{HH} = 6.7$ Hz and $^3J_{HP} = 13.5/^3J_{HH} = 7.0$ Hz, respectively. For the methine protons the doublet of septets is observed as a pseudo-octet, indicating that the values of the corresponding $^2J_{HP}$ and $^3J_{HH}$ couplings are identical (7.0 Hz).

However, integration of the signals in the aromatic region adds up to seven protons instead of the expected nine of the anthracenyl unit, meaning that the peaks of two aromatic hydrogen atoms are not resolved at room temperature. Broaden-

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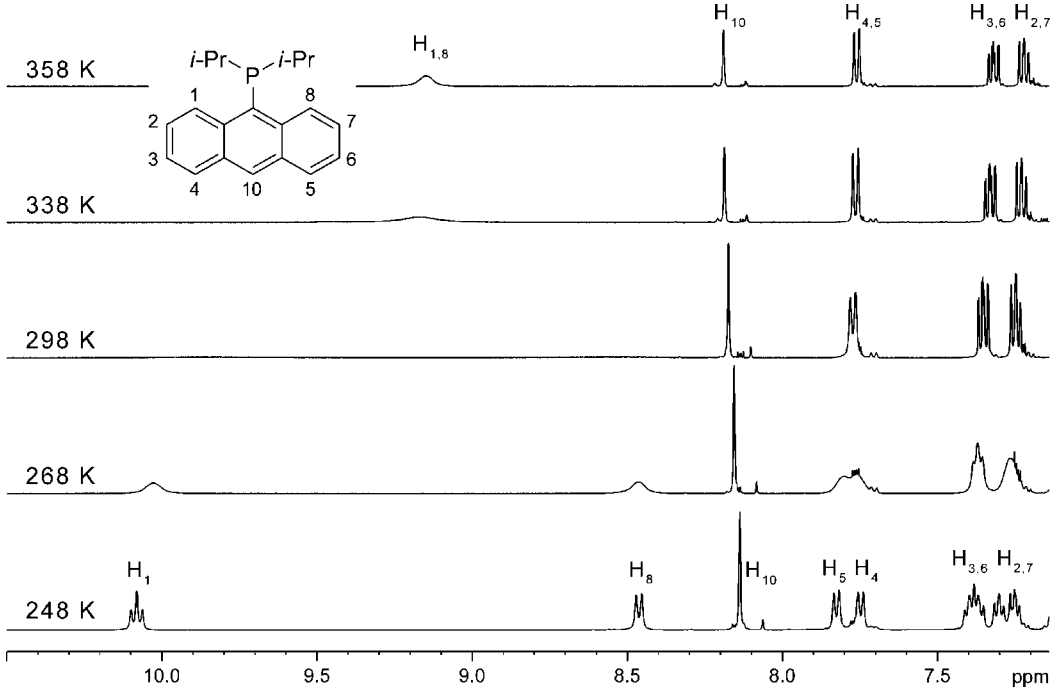

FIGURE 1. Variable-temperature ^{1}H NMR spectra (500 MHz) of **1a** in toluene-d_8.

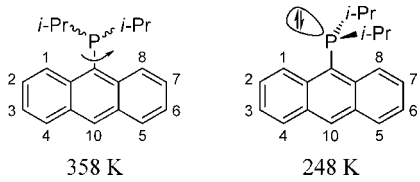

FIGURE 2. Temperature-dependent conformations of **1a**.

ing of the aryl signals suggests a dynamic process that was therefore investigated by variable-temperature ^{1}H NMR experiments. Figure 1 shows the aromatic region of ^{1}H spectra of toluene-d_8 solutions of **1a** at temperatures between 358 and 248 K.

Heating the solution to 358 K results in a broad singlet at δ 9.15 ppm that integrates to two protons assigned to H_1 and H_8. At room temperature the singlet disappears and by cooling to 248 K it is split into two well-resolved signals as a doublet of doublets at 10.08 ppm (H_1) and a doublet at 8.46 ppm (H_8). The assignment of the resonance signals to H_1 and H_8 was established by NOESY and ^{31}P-decoupled ^{1}H NMR experiments. In the case of H_8 the observed multiplicity results from the $^3J_{HH}$ coupling to the vicinal proton H_7 (8.9 Hz), and in addition, the NOESY NMR spectrum shows coupling with the CH and CH_3 protons of the isopropyl substituents. The signal of H_1 is moreover affected by a remarkable through-space interaction with the phosphorus nucleus. This was verified by the ^{1}H{^{31}P} NMR spectrum, where the multiplicity of the pseudotriplet is reduced to a doublet. Therefore H_8 must be in close proximity to the *i*-Pr groups, while H_1 must be close to the lone pair of the phosphorus atom, as shown in Figure 2 (right). An analogous temperature-dependent splitting of signals is observed for H_4 and H_5 showing isochronic resonance at room temperature (7.77 ppm, $^3J_{HH} = 8.2$ Hz). By cooling the solution the two protons lose their magnetic equivalency and are split into two new doublets at 7.83 and 7.57 ppm, respectively.

As probable mechanisms, the rotation of the *i*-Pr_2P group around the P−C_9 bond makes the protons H_1 and H_8 chemically equivalent and therefore they resonate as one broad singlet at higher temperatures (Figure 2, left). However, at 248 K in solution the molecule adopts the geometry shown in Figure 2 (right), with both isopropyl substituents arranged staggered with respect to the anthracene unit. This conformation explains the nonequivalency of all aromatic hydrogen atoms as well as the through-space coupling by an overlap of the lone electron pair on the phosphorus atom as already suggested for 1,8-phosphanylnaphthalene derivatives.[10,15] The rotational barrier was determined to be 56 kJ mol^{-1} (ΔG_{298K}), which is in very good agreement with the corresponding value found for 9-isopropylanthracene.[16]

Variable-temperature ^{1}H NMR spectra of $CDCl_3$ solutions of **2a** are shown in Figure 3. The temperature-dependent splitting of signals is in general in accordance with the spectral properties of **1a** and will therefore not be discussed in detail. According to the IUPAC nomenclature the numbering scheme of **2a** is different and the doublet of $H_{1,8}$ is shifted downfield to 8.68 ppm ($H_{4,5}$ in **1a**: 7.77 ppm) due to the electronic effect of the bromine substituent. Additionally, the chemical shifts of H_2, H_3, H_6, and H_7 are affected and the corresponding signals are closer together than in **2a**.

As shown in Figure 4, the ^{1}H NMR spectra of the 9,10-symmetrically phosphanyl-substituted compound **3a** are quite different from that of **1a** and **2a**. Assuming that the rotations about the P−$C_{anthracene}$ bonds are very fast on the NMR time scale, the aromatic hydrogens H_1, H_4, H_5, and H_8 are expected to be equivalent and undistinguishable. Nevertheless, this is only valid for higher temperatures and thus a broad singlet can be detected at 353 K. By cooling the solution to 183 K this peak is split into four new signals of different chemical shifts and different heights of the corresponding integrals.

This observation can be explained by considering the different conformations the molecule can adopt as shown in Figure 5. Provided that all isopropyl substituents are arranged staggered

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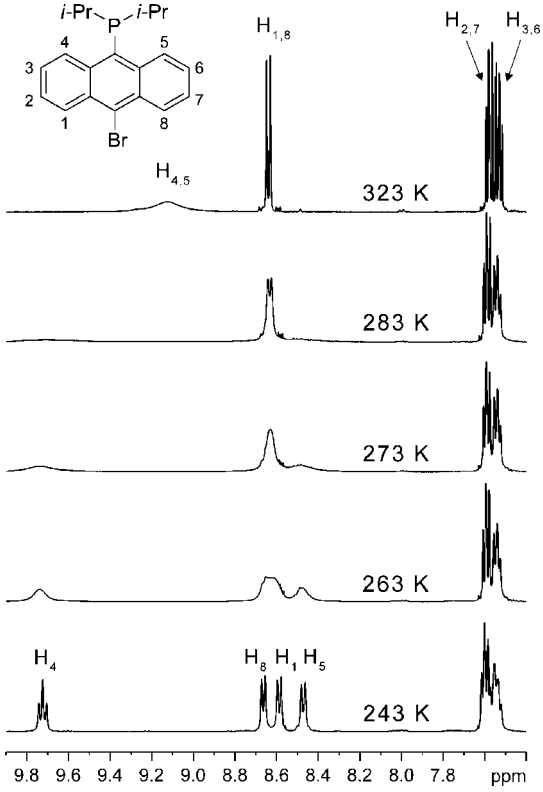

FIGURE 3. Variable-temperature ^{1}H NMR (500 MHz) spectra of **2a** in $CDCl_3$.

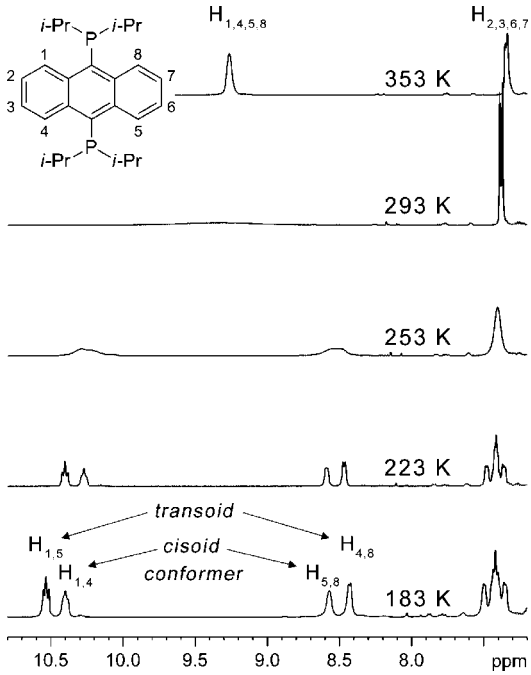

FIGURE 4. Variable-temperature ^{1}H NMR (500 MHz) spectra of **3a** in toluene-d_8.

with respect to the anthracene backbone, the nonbonding electron pairs of the two phosphorus atoms can be aligned either in a *cisoid* or in a *transoid* way. Chemical equivalency is now obtained for the hydrogen pairs H_1/H_4 and H_5/H_8 of the *cisoid* conformer and for H_1/H_5 and H_4/H_8 of the *transoid* conformer, respectively. As already discussed for **1a**, the ^{31}P-decoupled ^{1}H NMR spectrum of **3a** shows the reduction of the pseudotriplet

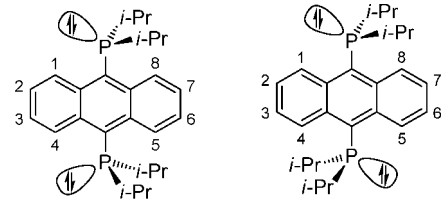

FIGURE 5. Conformational isomers of **3a** at 183 K.

of H_1 and H_5 to a doublet. The NMR signals of the different isomers integrate to 2.27 and 1.73 protons implying that the ratio is 57:43 in favor of the *transoid* conformer, which is expected to be more stable for steric reasons.

To examine the molecular configurations in the solid state, the structures of the compounds were determined. The results of the X-ray experiments are shown in Figures 6 and 7, and selected bond lengths and angles as well as crystallographic data are listed in Tables 1 and 2. In **1a** and **2a** the aromatic backbones are in plane with the phosphorus atoms and the isopropyl substituents are oriented staggered with respect to the anthracene plane, which bisects the *i*-Pr−P−*i*-Pr bond angle (**1a**: 105.9°; **2a**: 107.4°). These alignments reflect the results of the variable-temperature experiments suggesting that the staggered conformations are favored at lower temperatures. Unfortunately, we were yet not able to obtain suitable crystals of the phosphoryl species **1b** and **2b** due to the poor crystallization properties of phosphane oxides with large organic substituents. The crystal structures of **1c/1d** (*Pbca*) as well as **2c/2d** ($P2_1/c$) are isostructural, **2a** and **2c**,**d** crystallize with two almost identical molecules in the asymmetric unit. The anthracene units of the sulfur- (**1c**, **2c**) and selenium-oxidized (**1d**, **2d**) compounds are slightly folded and the phosphorus atoms are considerably out of the idealized aromatic planes with vertical distances between 81.7 (**1c**) and 126.6 pm (**2c**). The phosphorus−chalkogen bonds are not coplanar with the aromatic backbones, but distorted with dihedral angles at about 26°.

In the case of the 9,10-symmetrically-substituted compounds **3a** and **3b** the orientation of the phosphanyl groups with respect to the anthracene perimeter is in accordance with their monophosphorus-substituted analogues. For **3a** the two *i*-Pr_2P groups are arranged in a *transoid* way, confirming the conclusion from the low-temperature NMR experiments that this conformation is preferred upon cooling the solution. In contrast, the solid-state structure of **3b** reveals a *cisoid* orientation of the two P−S bonds causing a folding angle of 155.9° included by the two outer C_6-perimeters of the anthracene backbone.

3b is the isopropyl analogue of the previously reported 9,10-bis(diphenylthiophosphoryl)anthracene, which forms host−guest complexes with toluene to give intense solid-state fluorescence.[13] However, none of the isopropyl-substituted phosphanylanthracenes described in this paper show these effects in the solid state, even though **3b** was crystallized from toluene.

Conclusions

The 9,10-asymmetrically-substituted phosphanylanthracenes *i*-$Pr_2P(C_{14}H_9)$ (**1a**) and *i*-$Pr_2P(C_{14}H_8)Br$ (**2a**) as well as their chalcogene-oxidation products were synthesized straightforward with use of common reagents. The room temperature NMR spectra of **1a** and **2a** show broadening of aromatic signals, which can be attributed to fast rotations about the $P-C_{anthracene}$ bonds. By cooling the solutions the broad lines split into new peaks

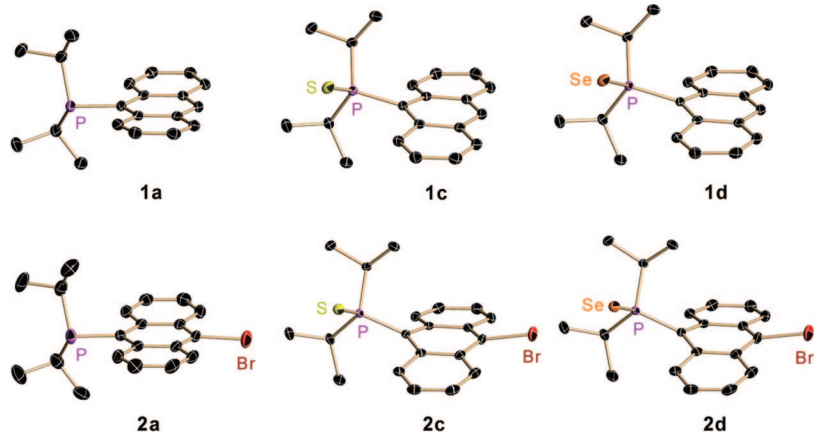

FIGURE 6. Molecular structures of **1a**, **1c**, **1d**, **2a**, **2c**, and **2d**. The anisotropic displacement parameters are depicted at the 50% probability level and hydrogen atoms are omitted for clarity.

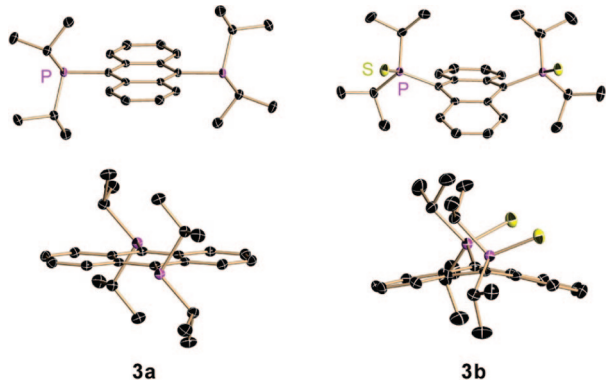

FIGURE 7. Molecular structures of **3a** and **3b** from different views. The anisotropic displacement parameters are depicted at the 50% probability level and hydrogen atoms are omitted for clarity.

that can be assigned to staggered conformational isomers of the molecules. The rotational barrier of this process, exemplary calculated for **1a**, was determined to be 56 kJ mol^{-1} (ΔG_{298K}).

In a similar manner the sterically more encumbered symmetrical 9,10-bis(diisopropylphosphanyl)anthracene (**3a**) was obtained from 9,10-dibromoanthracene and 2 equiv of *n*-BuLi and chlorodiisopropylphosphane, respectively; subsequent oxidation with elemental sulfur was achieved in almost quantitative yield. Variable-temperature NMR experiments for **3a** in solution show the coexistence of a *transoid* and a *cisoid* conformer at 183 K with marginal preference of the *transoid* form. Solid-state structures of the compounds were determined, verifying that the rotational conformations favored in solution at low temperature are maintained in the crystalline state.

By lithiation of the remaining bromo-substituent and subsequent reaction with electrophiles, the 9-bromo-10-phosphanylanthracenes **2a**−**d** might be precursors for the syntheses of asymmetrically substituted anthracenes, for example, with mixed P/B-, P/N-, P/C-, or P/Si-centered substituents. Future work will place emphasis on the photonic properties of these derivatives as well as their coordination behavior toward *d* and *f* block elements.

Experimental Section

9-Diisopropylphosphanylanthracene (1a). *n*-BuLi (7.74 mL, 15.6 mmol) in *n*-hexane (2.01 M) was slowly added (30 min) to a solution of 4.00 g (15.6 mmol) of 9-bromoanthracene in 100 mL of diethyl ether at 0 °C. The reaction mixture was stirred for 30 min before slow addition of 2.37 g (15.6 mmol) of chlorodiisopropylphosphane. After stirring for 30 min the mixture was concentrated by evaporation. The resulting precipitate was separated by filtration and dried in vacuo. Crystals were obtained from a saturated solution in diethyl ether upon storage at rt for a few days.

Yield: 3.93 g (86%). ^{1}H NMR (500.134 MHz, $CDCl_3$): δ 8.17 (s, 1H, H_{10}), 7.77 (d, $^3J_{HH}$ = 8.17 Hz, 2H, $H_{4,5}$), 7.35 (ddd, $^3J_{HH}$ = 8.17 Hz, $^3J_{HH}$ = 6.48 Hz, $^4J_{HH}$ = 1.43 Hz, 2H, $H_{3,6}$), 7.25 (ddd, $^3J_{HH}$ = 9.00 Hz, $^3J_{HH}$ = 6.48 Hz, $^4J_{HH}$ = 1.06 Hz, 2H, $H_{2,7}$), 2.79 (dsept, $^2J_{HP}$ = $^3J_{HH}$ = 7.01 Hz, 2H, C*H*), 1.33 (dd, $^3J_{HP}$ = 17.4 Hz, $^3J_{HH}$ = 6.74 Hz, 6H, CH_3), 0.65 (dd, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 6.98 Hz, 6H, CH_3). ^{31}P{^{1}H} NMR (121.494 MHz, $CDCl_3$): δ −0.1 (s). MS (EI, 70 eV): *m*/*z* (%) 294 (53) [M]$^+$, 252 (14), 209 (100), 178 (22). Anal. Calcd for $C_{20}H_{23}P$: C, 81.60; H, 7.88. Found: C, 80.99; H, 7.33.

9-Diisopropylphosphorylanthracene (1b). Hydrogen peroxide (0.14 mL, 1.60 mmol, 35% in water) was added dropwise to a solution of 470 mg (1.60 mmol) of **1a** in 20 mL of methanol/dichloromethane (1:1) at −10 °C. After 2 h at −10 °C the solvent was removed in vacuo and the resulting residue was washed with dichloromethane, yielding **1b** as a pale yellow powder.

Yield: 422 mg (85%). ^{1}H NMR (500.134 MHz, $CDCl_3$): δ 9.25−9.10 (br s, 2H, $H_{1,8}$), 8.58 (s, 1H, H_{10}), 8.00 (d, $^3J_{HH}$ = 8.35 Hz, 2H, $H_{4,5}$), 7.52 (ddd, $^3J_{HH}$ = 9.10 Hz, $^3J_{HH}$ = 6.50 Hz, $^4J_{HH}$ = 1.53 Hz, 2H, $H_{2,7}$), 7.46 (ddd, $^3J_{HH}$ = 8.35 Hz, $^3J_{HH}$ = 6.50 Hz, $^4J_{HH}$ = 1.06 Hz, 2H, $H_{2,7}$), 2.79 (dsept, $^2J_{HP}$ = 1.59, $^3J_{HH}$ = 7.08 Hz, 2H, C*H*), 1.49 (dd, $^3J_{HP}$ = 14.9 Hz, $^3J_{HH}$ = 6.94 Hz, 6H, CH_3), 0.90 (dd, $^3J_{HP}$ = 16.3 Hz, $^3J_{HH}$ = 7.20 Hz, 6H, CH_3). ^{31}P{^{1}H} NMR (81.014 MHz, $CDCl_3$): δ 60.5 (s). MS (EI, 70 eV): *m*/*z* (%) 310 (42) [M]$^+$, 267 (39), 225 (40), 178 (100). Anal. Calcd for $C_{20}H_{23}OP$: C, 77.40; H, 7.47. Found: C, 76.57; H, 7.13.

9-Diisopropylthiophosphorylanthracene (1c). Elemental sulfur (130 mg, 4.07 mmol) was added to a solution of 1.09 g (3.70 mmol) of **1a** in 25 mL of toluene. Subsequently the reaction mixture was heated to reflux for 4 h and filtered over celite. After removal of the solvent, the product was obtained by crystallization from hot toluene.

Yield: 870 mg (72%). ^{1}H NMR (500.134 MHz, $CDCl_3$): δ 9.39 (d, $^3J_{HH}$ = 8.98 Hz, 2H, $H_{1,8}$), 8.55 (s, 1H, H_{10}), 7.99 (d, $^3J_{HH}$ = 8.24 Hz, 2H, $H_{4,5}$), 7.51 (ddd, $^3J_{HH}$ = 8.98 Hz, $^3J_{HH}$ = 6.56 Hz, $^4J_{HH}$ = 1.60 Hz, 2H, $H_{2,7}$), 7.45 (ddd, $^3J_{HH}$ = 8.24 Hz, $^3J_{HH}$ = 6.56 Hz, $^4J_{HH}$ = 1.15 Hz, 2H, $H_{3,6}$), 3.28 (dsept, $^2J_{HP}$ = 3.96, $^3J_{HH}$ = 6.76 Hz, 2H, C*H*), 1.46 (dd, $^3J_{HP}$ = 17.7 Hz, $^3J_{HH}$ = 6.67 Hz, 6H, CH_3), 0.88 (dd, $^3J_{HP}$ = 18.5 Hz, $^3J_{HH}$ = 6.95 Hz, 6H, CH_3). ^{31}P{^{1}H} NMR (81.014 MHz, $CDCl_3$): δ 71.2 (s). MS (EI, 70 eV) *m*/*z* (%) 326 (100) [M]$^+$, 284 (29), 241 (85), 209 (17), 178 (68). Anal. Calcd for $C_{20}H_{23}PS$: C, 73.59; H, 7.10. Found: C, 71.03; H, 6.53 (deviations are likely due to impurities of elemental sulfur).

TABLE 1. Selected Averaged Bond Length (pm) and Angles (deg) for 1a, 1c, 1d, 2a, 2c, 2d, 3a, and 3b

	1a	**1c** (E = S)	**1d** (E = Se)	**2a**	**2c** (E = S)	**2d** (E = Se)	**3a**	**3b** (E = S)
P−$C_{anthracene}$	185.7(2)	185.5(1)	185.7(1)	189.1(3)[a]	185.5(2)[a]	185.5(2)[a]	186.4(2)	186.5(2)[a]
P–E		197.3(5)	212.9(1)		196.8(6)[a]	212.4(5)[a]		196.6(6)[a]
out-of-plane[b] P	2.26	51.13	56.15	3.42	84.02	87.38	1.95	88.21
P−E torsion angle		17.6(1)	18.3(1)		12.5(2)[a]	12.9(2)[a]		12.7(2)[a]
folding angle[c] An	175.2	172.3	172.0	175.6	163.9	163.9	180.0	156.1

[a] The esds are quoted as extremes. [b] Vertical distance (av) between P and plane spanned by C_{4a}, C_{8a}, C_{9a}, and C_{10a}. [c] Angle enclosed by the two outer C_6-perimeters.

TABLE 2. Selected Crystallographic Data for 1a, 1c, 1d, 2a, 2c, 2d, 3a, and 3b

	1a	**1c**	**1d**	**2a**	**2c**	**2d**	**3a**	**3b**
formula	$C_{20}H_{23}P$	$C_{20}H_{23}PS$	$C_{20}H_{23}PSe$	$C_{20}H_{22}BrP$	$C_{20}H_{22}BrPS$	$C_{20}H_{22}BrPSe$	$C_{26}H_{36}P_2$	$C_{26}H_{36}P_2S_2$
CCDC no.	667520	667521	667522	667523	667524	667525	667526	667527
space group	*C*2/*c*	*Pbca*	*Pbca*	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a/Å	33.822(4)	10.918(10)	11.021(2)	8.3327(7)	22.595(2)	22.613(1)	11.564(2)	7.3333(12)
b/Å	8.1720(9)	14.544(1)	14.570(2)	15.557(2)	11.053(1)	11.197(1)	8.2911(12	15.522(3)
c/Å	12.113(1)	21.061(2)	21.206(3)	27.197(2)	14.548(1)	14.575(1)	11.950(2)	21.997(4)
β/deg	102.965(1)	90	90	93.059(2)	93.023(1)	93.468(1)	94.953(2)	90
V/Å^3	3262.7(6)	3344.4(4)	3405.4(8)	3520.6(5)	3628.1(3)	3683.6(4)	1141.4(3)	2503.8(7)
Z	8	8	8	8	8	8	2	4
R_1 [$I > 2\sigma(I)$][a]	0.0454	0.0298	0.0215	0.0373	0.0232	0.0212	0.0352	0.0245
wR_2 [$I > 2\sigma(I)$][b]	0.1199	0.0796	0.0586	0.0918	0.0624	0.0544	0.0873	0.0609
R_1 (all data)	0.0574	0.0315	0.0230	0.0512	0.0257	0.0235	0.0432	0.0258
wR_2 (all data)	0.1265	0.0809	0.0595	0.0961	0.0634	0.0553	0.0906	0.0615

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = {}^1/_3[\max(F_o^2,0) + 2F_c^2]$.

9-Diisopropylselenophosphorylanthracene (1d). This compound was prepared in analogy to **1c** from 1.03 g (3.50 mmol) of **1a** and 410 mg (5.25 mmol) of gray selenium in 25 mL of toluene and subsequent crystallization from toluene.

Yield: 980 mg (75%). ^{1}H NMR (300.130 MHz, $CDCl_3$): δ 9.40 (d, $^3J_{HH}$ = 8.90 Hz, 2H, $H_{1,8}$), 8.56 (s, 1H, H_{10}), 7.99 (d, $^3J_{HH}$ = 8.17 Hz, 2H, $H_{4,5}$), 7.52 (ddd, $^3J_{HH}$ = 8.17 Hz, $^3J_{HH}$ = 6.58 Hz, $^4J_{HH}$ = 1.72 Hz, 2H, $H_{3,6}$), 7.45 (ddd, $^3J_{HH}$ = 8.90 Hz, $^3J_{HH}$ = 6.58 Hz, $^4J_{HH}$ = 1.23 Hz, 2H, $H_{2,7}$), 3.36 (dsept, $^2J_{HP}$ = 5.23, $^3J_{HH}$ = 6.77 Hz, 2H, C*H*), 1.45 (dd, $^3J_{HP}$ = 18.4 Hz, $^3J_{HH}$ = 6.65 Hz, 6H, CH_3), 0.88 (dd, $^3J_{HP}$ = 19.0 Hz, $^3J_{HH}$ = 6.90 Hz, 6H, CH_3). ^{31}P{^{1}H} NMR (121.495 MHz, $CDCl_3$): δ 64.4 (s). ^{77}Se{^{1}H} NMR (95.382 MHz, $CDCl_3$): δ −368.5 (d, $^1J_{SeP}$ = 708.8 Hz). MS (EI, 70 eV): *m*/*z* (%) 374 (48) [M]$^+$, 331 (16), 294 (31), 209 (74), 178 (100). Anal. Calcd for $C_{20}H_{23}PSe$: C, 64.34; H, 6.21. Found: C, 63.07; H, 6.55 (deviations are likely due to impurities of gray selenium).

2a−d and 3a,b. For **2a−d** and **3a**,**b** see the Supporting Information.

Crystal Structure Determination. All data were collected from shock-cooled crystals on Bruker SMART-APEX II diffractometers with D8 goniometers at 100 K[17] [Mo K_α radiation, λ = 71.073 pm; all except **2a**, which was irradiated with INCOATEC Helios mirrors, are graphite-monochromated. The data were integrated with SAINT,[18] and an empirical absorption correction (SADABS) was applied.[19] The structures were solved by direct methods (SHELXS)[20] and refined on F^2 using the full-matrix least-squares methods of SHELXL.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp^2 (sp^3) carbon atoms were assigned ideal positions and refined by using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{eq} value of the parent carbon atom. The absolute structure of **3b** was determined unambiguously by refining the Flack *x* parameter[22] to −0.01(5).

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre, the CCDC numbers are listed in Table 2. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: General methods concerning the Experimental Section, preparation procedures, and analytical data for **2a–d** and **3a**,**b**, copies of ^{1}H, ^{31}P NMR spectra for all depicted compounds, as well as ^{77}Se spectra for **1d** and **2d**, X-ray crystallographic data of **1a**, **1c**, **1d**, **2a**, **2c**, **2d**, **3a**, and **3b** (CIF), and a ln(*k*/*T*) plot for determination of the rotational barrier for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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