

Systematic Investigation of PPV Analogue Oligomers Incorporating Low-Coordinate Phosphorus Centres

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Sterically-encumbered ligands tethered to conjugated segments have been developed and employed in concert with existing bulky ligands to prepare a series of *phospha*-PPV oligomers. A study of the variation of $\lambda_{\pi-\pi^*}$ values along this series indicates that low-coordinate phosphorus centres can support conjugation across extended systems, and generally confirms the expected red shift across the series from all-car-

bon oligomers to phosphaalkenes to diphosphenes. These findings provide experimental evidence that low-coordinate phosphorus centres are in fact capable of supporting electronic communication across extended π conjugated systems.

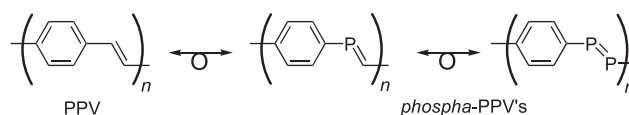
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Introduction

Since the discovery that selected polymers featuring extended π conjugation may exhibit conductivity^[1] and other fascinating properties and the subsequent integration of such materials into devices such as OLEDs,^[2] an explosion of research has emerged in the search for new systems with specifically desired properties.^[3] Efforts in this area have focused particularly on tuning the band gap (and therefore absorption and emission wavelengths and conductivity) by varying substitution patterns or exploring different conjugated linkers along the conjugated polymer chain.^[4] One of the most technologically promising classes of conjugated polymers are poly(*p*-phenylenevinylene)s (PPV)s.^[3] Hence, numerous efforts have been undertaken to create new polymers that incorporate the basic PPV framework with other conjugated linkers. However, comparatively little work has been carried out in this area in which heavier main group elements have been incorporated along the main chain, despite the success that has been achieved with polythiophene and polyaniline, in which accessible lone pairs may participate in π conjugation ($n-\pi$ interactions) giving rise to unique properties compared with their all carbon analogues.^[3d]

The success of PPV's and variations thereof, along with the established analogy between the chemistry of carbon and phosphorus (phosphorus is often referred to as a "carbon copy"^[5]) and the predicted π conjugative ability of phosphorus^[6] led to our interest in the synthesis and study of "*phospha*-PPV's" in which olefinic bonds are replaced by P=C or P=P bonds to yield main group $p\pi-p\pi$ conjugated materials. Such substitution may have a significant impact

on the properties of the polymers. The recent synthesis of the first poly(*p*-phenylenephosphaalkene), **P1**, did indeed provide evidence for π -conjugation involving P=C functional groups in a polymer.^[7]

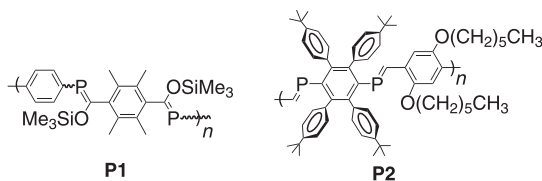


Another poly(*p*-phenylenephosphaalkene), **P2**, not only showed evidence for conjugation, but also revealed that such systems may also exhibit fluorescence,^[8] a property critical for LEDs. Particularly noteworthy is the very exciting breakthrough that phosphole-containing oligomers have been successfully used in LEDs.^[9] Several other investigations related to the incorporation of phosphorus into materials featuring possible π conjugation (in which phosphorus may contribute via $n-\pi$ interactions) have also been reported.^[10] Examples include polyarylyphosphanes,^[11] blue emitting polymers incorporating phosphole units,^[12] poly(ferrocenylphosphanes),^[13,14] and oligomers incorporating phosphirenes^[15] or phospholes.^[16–18]

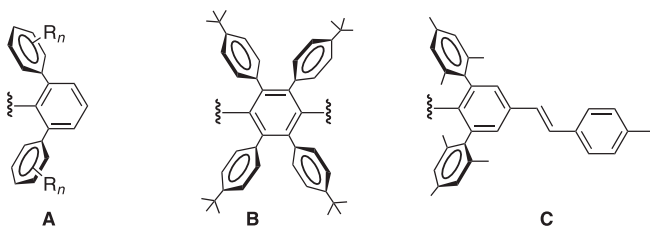
Substitution of the sp^2 carbon atoms along the path of conjugation in PPV's by heavier elements such as phosphorus thus has a significant impact on the properties of polymers. For example, simple differences in polarizability and electron affinity will effect the hole and electron transport properties. In addition, the HOMO–LUMO gaps may become increasingly smaller upon substitution with low-coordinate (formally sp^2) P atoms along the path of conjugation. One approach to gaining a fuller understanding of how molecular properties affect properties displayed by polymeric systems is the so-called "oligomer approach" that has been used for studying PPV and related organic

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conjugated materials.^[19] In this approach studies of discrete model oligomers of increasing size can yield correlations between small molecules and polymers.



Some work has been carried out towards developing such an analogy for phosphalkenes and diphosphenes, and towards drawing parallels between them and their all-carbon analogues. For example, discrete phosphalkenes and diphosphenes are more easily reduced than olefin analogues. Studies of the reduction of bifunctional conjugated phosphalkenes and diphosphenes have already revealed the additional possibilities of producing high-spin materials^[20] and even molecular switches.^[21] Further extensions of these studies require oligomers having longer conjugation paths and an increased phosphorus content. The longest π conjugated PPV-like molecules featuring phosphalkene or diphosphene units reported prior to this particular investigation were analogues of distyrylbenzene^[22,23] and stilbene.^[24,25]

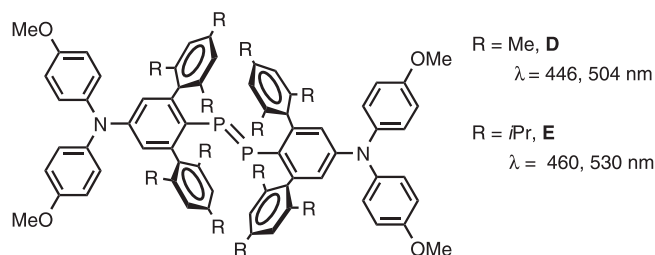


The absence of more ($p\pi-p\pi$ conjugated) extended systems with ($P=P$) and ($P=C$) linkages can possibly be attributed to difficulties associated with the synthesis of suitably bulky ligands required to prevent the redistribution reactions that phosphalkenes and diphosphenes are susceptible to in the absence of steric protection.^[26] The extent of steric bulk required can be illustrated by the fact that it was not until the 2,4,6-tri-*tert*-butylphenyl (Mes*) ligand was employed that the first isolable diphosphene (Mes*P=P Mes*) was reported.^[25] More recently, *m*-terphenyl ligands **A** have also been extensively employed in the steric shielding of multiple bonds between heavier main group elements.^[27]

In this report, routes to *m*-terphenyl ligands with conjugated groups tethered to the position *para* to the steric cleft (**C**) are detailed. These ligands, along with the existing ligands **A** and **B**, have enabled the preparation of a series of *phospha*-PPV oligomers as models for polymeric systems. The synthesis of this series of oligomers has allowed us to begin a systematic study of the effect of conjugation length and phosphorus for carbon substitution in PPV oligomers, the results of which are reported herein.

Results and Discussion

The protection of main group multiple bonds with *m*-terphenyl ligands featuring substitution *para* to the steric cleft is an underdeveloped area. Only a few 4-substituted 2,6-diarylphenyl ligands have been developed for use in low-coordinate phosphorus chemistry. Two relevant molecules bearing novel ligands have been pioneered by the Yoshifuji group.^[28] While compound **D** could not be fully purified, diphosphene **E**, having a greater degree of steric protection, was isolated in 11 % yield.

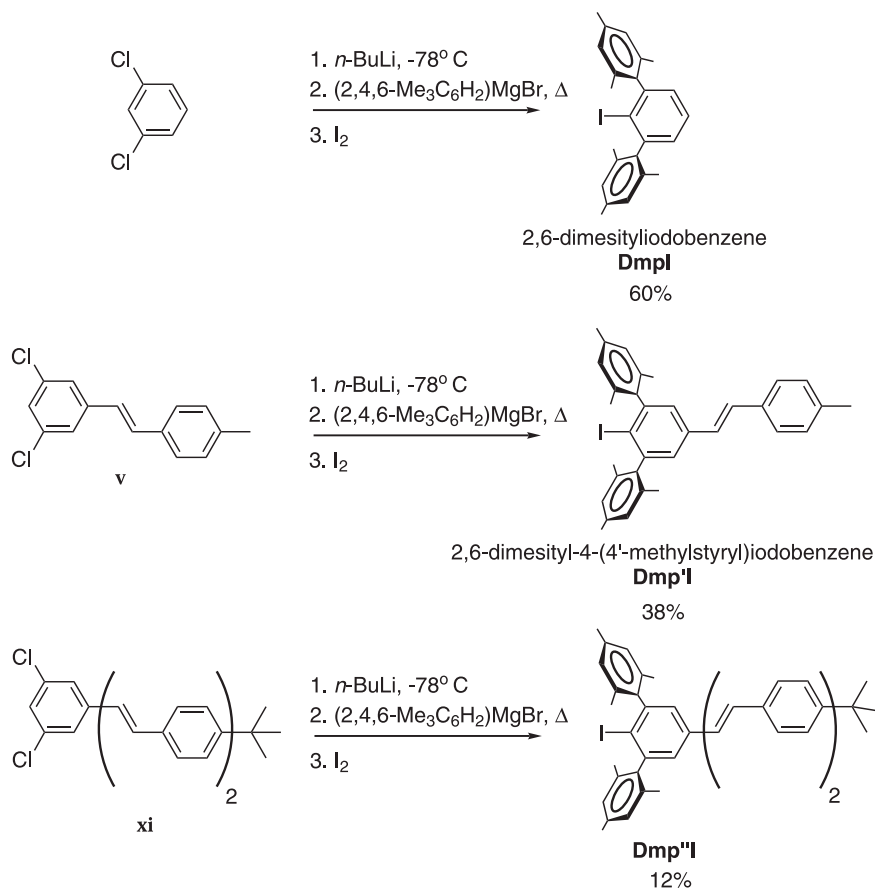


Both of these materials display impressive red shifts in their absorption spectra with data for **E** showing $\lambda_{\text{max}} = 460$ and 530 nm for the $\pi-\pi^*$ and $n-\pi^*$ bands, respectively. The approach to the amino functionalized terphenyl ligands was based upon introduction of the diarylamino functionality into preformed 1,4-diiodo-2,6-diarylbenzenes by a copper coupling step.

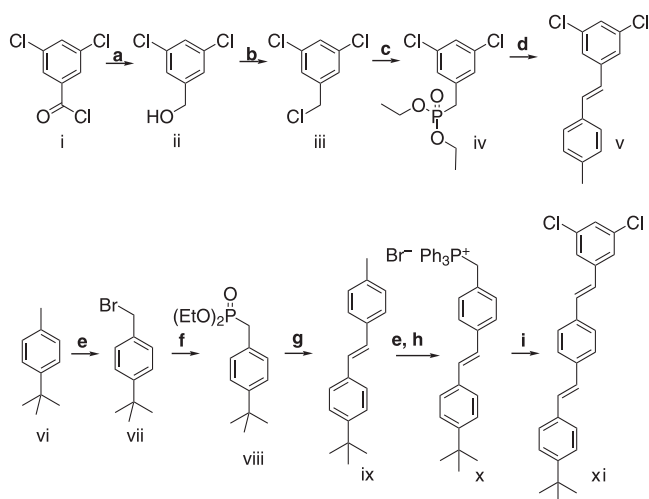
Our approach to functionalised terphenyls introduces functionality earlier in the synthesis. Specifically, 1,3-dichlorobenzene, the starting material for the simplest route to *m*-terphenyls (Scheme 1, top),^[29] was replaced with substituted 1,3-dichlorobenzenes (**v**, **xi**, Scheme 1).

These materials should enable common access to terphenyl ligands bearing different aromatic groups on the periphery of the ligand. Synthesis of precursor **v** has been previously reported and we have been able to effect its synthesis in an overall yield of 71 % in 4 steps from the commercially available 1,3-dichlorobenzoyl chloride.^[30,31] The more extended precursor **xi** could be prepared from the known intermediate phosphonium salt in an overall yield of 22 % in 6 steps starting with *p*-*tert*-butyltoluene.^[32,33] The syntheses of **v** and **xi** are summarized in Scheme 2.

The substituted 1,3-dichloroarenes were thus employed for the synthesis of Dmp'I (Scheme 1, middle) and Dmp''I (Scheme 1, bottom) using essentially the same conditions employed in the synthesis of the DmpI ligand (Scheme 1, top), although yields became increasingly lower as the length of the conjugated tether was increased. The decrease in yield with increased conjugation length may be due to decreased reactivity of the intermediate arynes. Alternatively, arylene formation may be inhibited due to an increase in stability of the 2-chlorolithio (or magnesio) benzene and subsequent difficulty of metal halide elimination. Longer reaction times for Dmp'I and Dmp''I (10 and 16 hours, respectively) relative to DmpI (4 hours, ca. 60 % yield) partially compensate for less reactive substrates. Further increases in reaction times, however, did not provide increased



Scheme 1

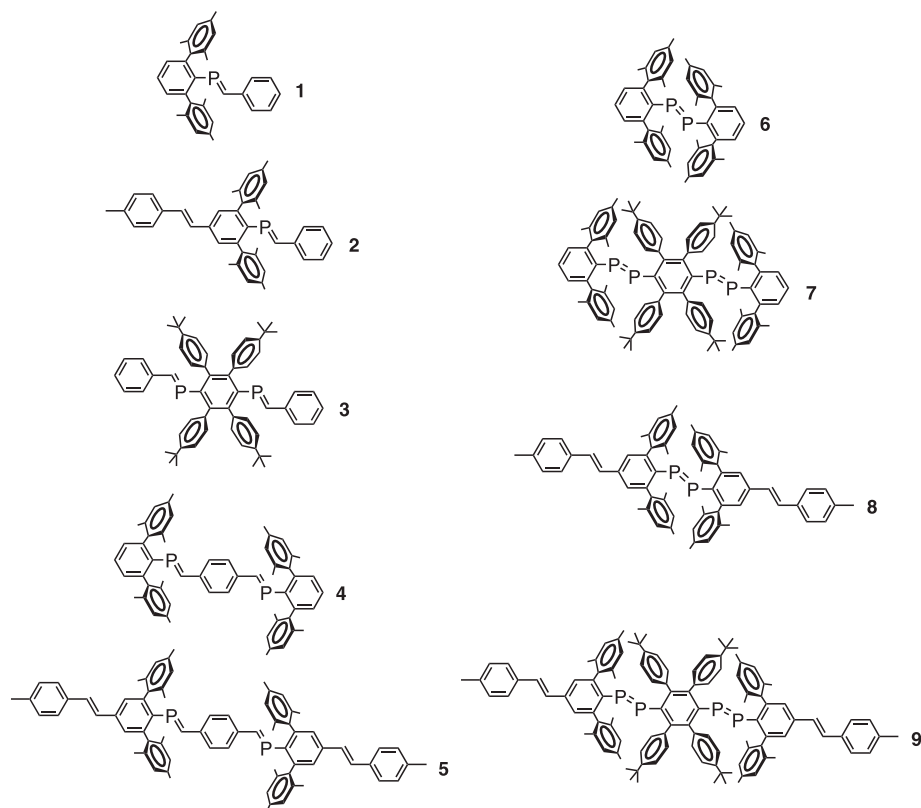


Scheme 2. Reagents and conditions: a) 1. LiAlH₄, 0°C , 2. H⁺; b) SOCl₂; c) P(OEt)₃, 160°C ; d) *p*-tolualdehyde, KO^tBu; e) NBS, BPO, reflux, 3 h; f) P(OEt)₃, 160°C ; g) *p*-tolualdehyde, KO^tBu; h) PPh₃, toluene, reflux; i) 3,5-dichlorobenzene, KO^tBu

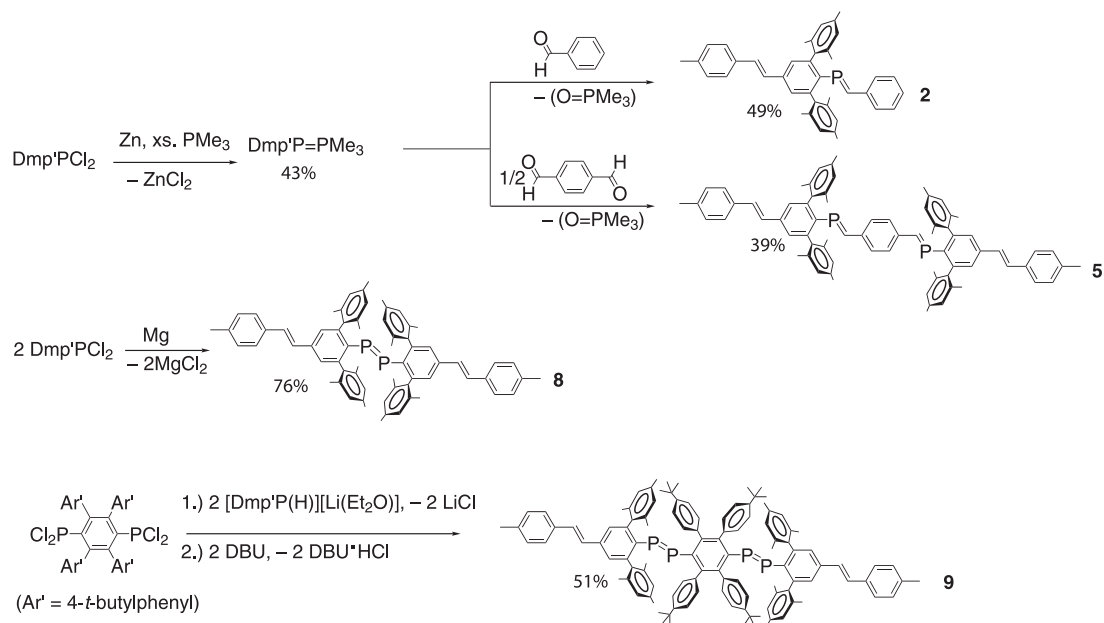
yields for Dmp' and Dmp''I beyond 38 % and 12 %, respectively. Due to the significant decrease in yield and time consuming preparation of more complex starting materials required to access Dmp''I compared with Dmp'I (Schemes 1 and 2), only the latter material has been pursued for utility in the current study.

The olefinic units in precursor materials (Scheme 2) were either prepared in the *E* form directly (via the Horner–Wittig reaction) or isomerized to the all-(*E*) conformation subsequent to synthesis. The retention of the all-(*E*) form in the course of the *m*-terphenyl synthesis and all subsequent steps was confirmed by the characteristic chemical shifts and coupling constants in ¹H NMR spectra. These diagnostic features were not resolved in the ¹H NMR spectrum of compound **9** (vide infra), however. Therefore the structural assignment of **9** was deduced using the known orientation of the starting material and the fact that a single species was observed in both ¹H and ³¹P NMR spectra. The *E* forms were highly desired for a useful comparison with organic PPV oligomers and derivatives in which the *E* forms are technologically far more relevant than corresponding *Z* isomeric materials.^[3]

Some differences in the general properties of Dmp' derivatives compared with those of known Dmp analogues are of note. For example, the conjugated segment tethered to the Dmp' ligand affords much greater solubility compared with analogous compounds featuring the simple Dmp ligand. Interesting colour differences can also be observed not only in the *phospha*-PPV oligomers that are the focus of the current study (vide infra), but also in the precursors. For example, while DmpLi is a white material,^[34] Dmp'Li is a red-brown colour, probably indicating that the



Scheme 3



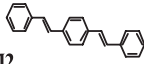
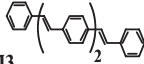
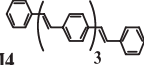
Scheme 4

extended conjugated system allows for delocalization of the anionic charge or possibly an ionic or charge separated structure. DmpPCl_2 (white) and $\text{Dmp}'\text{PCl}_2$ (pale yellow) (prepared from ArLi by known methods^[45]), however, differ only slightly in colour. Interestingly, a notable colour change is noted for the air- and moisture-sensitive phosphawittig reagents $\text{ArP}=\text{PMe}_3$. Whereas $\text{DmpP}=\text{PMe}_3$ is yellow

($\lambda = 348 \text{ nm}$, $\epsilon = 6021 \text{ M}^{-1}\text{cm}^{-1}$; $\lambda = 390 \text{ nm}$, $\epsilon = 2998 \text{ M}^{-1}\text{cm}^{-1}$), $\text{Dmp}'\text{P}=\text{PMe}_3$ is deep red ($\lambda = 332 \text{ nm}$, $\epsilon = 34,800 \text{ M}^{-1}\text{cm}^{-1}$; $\lambda = 432 \text{ nm}$, $\epsilon = 10,600 \text{ M}^{-1}\text{cm}^{-1}$).

The Dmp' ligand was thus used to produce a series of (P=C)- (Scheme 3, left) and (P=P)- (Scheme 3, right) containing phospho-PPV oligomers via the routes summarised in Scheme 4. These materials exhibit diagnostic bands in

Table 1. Absorption data (CHCl₃) for **1–9** and comparison to organic models

C=C model	$\lambda_{\pi-\pi^*}$ (nm) (log ϵ)	P=C	$\lambda_{\pi-\pi^*}$ (nm) (log ϵ)	P=P	$\lambda_{\pi-\pi^*}$ (nm) (log ϵ)	$\lambda_{n-\pi^*}$ (nm) (log ϵ)
	317 (4.53)	1	334 (4.59)	6	372 (3.63)	456 (2.56)
M1 						
	354 (4.77) ^[a]	2	341 (4.54)	7	398 (3.88)	476 (2.94)
		3	349 (4.60)			
M2 		4	411 (4.68)			
	384 (4.92) ^[b]			8	407 (4.68)	470 (3.72)
M3 						
	385 (5.10) ^[b,c]	5	417 (4.30)	9	422 (4.64)	481 (3.74)
M4 						

^[a] R. Erckel, H. Z. Fruehbeis, *Z. Naturforsch., Teil B* **1982**, 37, 1472–1480. ^[b] G. Drefahl, G. Plotner, *Chem. Ber.* **1961**, 93, 907–914.

^[c] Dioxane as solvent.

their visible absorption spectra. Phosphaalkenes commonly display a single characteristic absorption in the visible region normally assigned to a $\pi-\pi^*$ transition.^[5,6] Diphosphenes exhibit similar bands due to $\pi-\pi^*$ transitions but these are accompanied by a second absorption band of significantly lower intensity at higher wavelengths that have been assigned to $n-\pi^*$ transitions.^[24,25] The $n-\pi^*$ transition should be forbidden and therefore less intense. Following this convention, assignments of bands for **1–9** were made as summarized in Table 1. In accord with previous reports, the higher wavelength $n-\pi^*$ transitions for diphosphenes **6–9** have absorptivities approximately one order of magnitude lower than those of the corresponding $\pi-\pi^*$ transitions. This specific ordering has been the subject of some discussion, however.^[24,35] The most recent experimental (electron density deformation) and computational results (DFT) give most credence to the above ordering, that is, the HOMO of a diphosphene is more than likely the phosphorus lone pair orbital and the HOMO-1 is the π bond.^[36]

The set of diphosphene oligomers **6–9** enables one to test this ordering in a different fashion. Figure 1 portrays

two qualitative models for how the energies of pertinent frontier molecular orbitals should vary with increasing conjugation length. For the first model (Figure 1, left), the HOMO is assumed to be the π orbital and in the second model (Figure 1, right), the HOMO is assumed to be the phosphorus lone pair (n_+ combination). For both models the difference between the π and π^* orbitals is diminished with increasing conjugation length and the lone pairs are assumed to be relatively unaffected. The first model predicts that as the conjugation length increases, the HOMO–HOMO–1 gap (described by Δ in Figure 1) should increase. The second model predicts the exact opposite. The very crude model given in the right of Figure 1 fits the observed trends for compounds **6–9** nicely, as well as agreeing with the most recent computational and experimental data for simple diphosphenes.^[36]

A simple comparison of the absorption maxima ($\lambda_{\pi-\pi^*}$) for the all-carbon oligomers **M1–M4**, phosphaalkenes **1–5**, and diphosphenes **6–9** with central π -conjugated cores of equal length (Table 1) generally demonstrates the intended red shifts for the electronic transitions as either the phosphorus content or maximum conjugation length in-

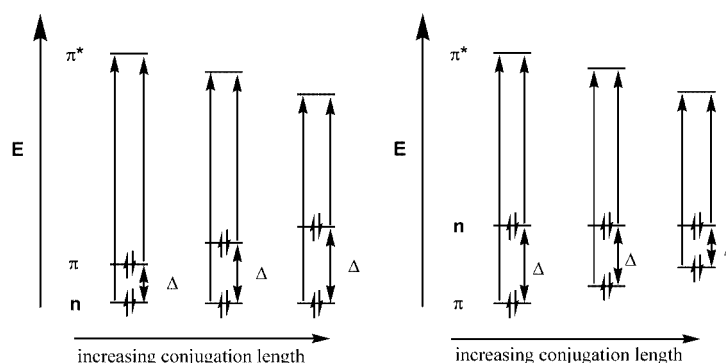


Figure 1. Simple MO diagrams for conjugated materials assuming the HOMO involves P=E π bonds (left) or n orbitals (right)

creases. A more detailed evaluation, however, reveals some discrepancies in these general trends. For example, although the $\lambda_{\pi-\pi^*}$ values for compounds **2** and **3** are consistent with the anticipated red shift with increasing P content (one P=C in **2** versus two P=C units in **3**), the values might also be expected to be red shifted with respect to the all-carbon analogue, distyrylbenzene (**M2**). The $\lambda_{\pi-\pi^*}$ values for compounds **2** and **3** are actually *blue* shifted by 13 nm and 5 nm, respectively, relative to distyrylbenzene. Compound **4**, however, which is also of the same geometric conjugation length, is quite significantly red shifted by 57 nm. These large differences exhibited by molecules of equal conjugation length demonstrate the striking effects that steric influences can produce. Specifically, such deviations can be attributed to deflections of some portions of the conjugated system out of ideal coplanarity with one another in response to steric clashes. In this manner, the *effective* conjugation length is lowered relative to that expected for an entirely coplanar conjugated core. A simple example of this effect is the observed 33 nm blue shift in the $\lambda_{\pi-\pi^*}$ value of (*E*)-2,6-dimethylstilbene with respect to (*E*)-stilbene.^[37]

Steric disruptions to coplanarity have in fact been intentionally incorporated into organic conjugated polymers and have been observed to provide a significant enhancement of electroluminescent efficiency.^[38] In other cases, steric distortions induced by binding events along conjugated polymer backbones have led to significant changes in absorption maxima, a property routinely taken advantage of in the design of molecular sensors.^[39] Such steric effects were also discussed in the analysis of the properties of a poly(*p*-phenylenephosphaalkene),^[7] and we have previously observed this effect (at least in the solid state) by X-ray crystallographic analysis of diphosphene **7** and phosphalkene **3**.^[22]

The effect of such sterically-induced noncoplanarity may not have as great an impact on the $\lambda_{\pi-\pi^*}$ of **4** since, in that case, the steric bulk is located on the outer rings rather than on the central ring such that the latter may easily maintain conjugation with at least the two flanking P=C units without steric interference. A direct comparison of **4** can also be made with 1,4-[Mes*P=C(H)]₂C₆H₄ (Mes* = 2,4,6-tri-*tert*-butylphenyl),^[40] in which the only difference is the replacement of Dmp with Mes* ligands. The Mes*-containing system has a $\lambda_{\pi-\pi^*}$ of only 326 nm, closer to that of stilbene than the all-carbon analogue, distyrylbenzene. Distortions of the phosphorus centre from the plane of the attached phenyl ring in the Mes* components are common due to the extreme steric pressure in such systems^[41] and such distortions may complicate comparisons of the type made here. Regardless of the explanation, similar large differences can be observed when comparing $\lambda_{\pi-\pi^*}$ values for other materials featuring the two sets of ligands such as **6** (372 nm) with Mes*P=PMes* (340 nm) or **1** (334 nm) with Mes*P=C(H)Ph (259 nm).^[38]

Another example of steric effects on effective conjugation is evident from the observed $\lambda_{\pi-\pi^*}$ value in **7**. Whereas a red shift of **7** with respect to **2**, **3**, or **4** might be expected, the observed value is actually within the range spanned by these three materials (390 nm for **7**, compared with 341 nm,

349 nm, and 411 nm for **2**, **3**, and **4**, respectively). This observation may not be altogether surprising in light of the much greater steric bulk about the P=P units in **7** compared with that about the P=C units in **2–4**.

Such minor and explainable deviations do not, however, detract from the overall trend observed when comparing systems with comparable steric positioning. For example, a comparison of **1** with **2**, **4** with **5**, **6** with **8** or **7** with **9**, where the pairs of compounds differ only by the addition of simple styryl units, all exhibit red shifts with increased conjugation length (15, 6, 35, and 32 nm, respectively). These data indicate that the incorporation of low-coordinate phosphorus centres into conjugated materials is a viable strategy for accessing materials featuring smaller band gaps than those observed in all-carbon analogues. Indeed, the $\lambda_{\pi-\pi^*}$ of 426 nm observed for simple (*E*)-PPV^[42] is practically equalled by the comparatively small (P=P)-containing analogue **9** ($\lambda_{\pi-\pi^*}$ = 422 nm) despite steric influences.

In addition to changes in $\lambda_{\pi-\pi^*}$ with increasing length or P content, observed differences in absorptivity (given as log ϵ , Table 1) are also noteworthy. For instance, while ϵ for **1** is similar to that of stilbene, the diphosphene analogue **6** has a value approximately eight times lower, and whereas ϵ increases uniformly with oligomer length for the organic models, the same trend does not hold for *phospha*-PPV analogues. These observations may again be due to steric factors. The sterically-induced perturbations from coplanarity which lead to a truncated effective conjugation length, as previously discussed, are synonymous with decreasing the cross section of the chromophore responsible for the $\pi-\pi^*$ transition, and the molar absorptivity of the band associated with this transition will therefore diminish (in the event that all else is held fairly constant). This proposition is supported by previously reported data on 2,6-disubstituted stilbenes.^[37] For example, simple 2,6-dimethyl substitution leads to approximately half as much absorptivity as unsubstituted stilbene, along with the aforementioned blue shift in the absorption maximum. Even a single bulky substituent, as in (*E*)-2-*tert*-butylstilbene ($\lambda_{\pi-\pi^*}$ = 285 nm, ϵ = 22,650 M⁻¹cm⁻¹), has a significant impact.^[43] Clearly such an effect would be more pronounced in diphosphenes **6–9** than in phosphalkenes **1–5** due to the greater steric crowding in the former. Based on such a steric argument, it would also be expected that for molecules of the same approximate *geometric* size there should be a correlation between $\lambda_{\pi-\pi^*}$ and ϵ . This premise is qualitatively demonstrated by the series of phosphalkene distyrylbenzene analogues **2–4** in which $\lambda_{\pi-\pi^*}$ and ϵ both increase across from **2–4**. Certainly many more complex factors, such as polarity/polarizability and solvation effects of both ground and excited states (to mention a few), are involved in determining the absorptivity of a given system as well. Although the perhaps oversimplified steric arguments presented here are merely qualitative assessments based on rational conjecture, they seem in line with data on substituted stilbenes.

In summary, we have developed novel sterically-encumbered ligands tethered to conjugated segments and have employed these ligands in concert with existing bulky ligands

to prepare a series of *phospha*-PPV oligomers. A study of the variation of $\lambda_{\pi-\pi^*}$ values along this series indicates that low-coordinate phosphorus centres can support conjugation across extended systems, and generally confirms the expected red shift across the series from carbon oligomers **M1**–**M4** (Table 1) to phosphalkenes **1**–**5** to diphosphenes **6**–**9**. Importantly, these findings provide experimental evidence that such low-coordinate phosphorus centres are in fact capable of supporting electronic communication across extended π conjugated systems, a criterion required of any moiety viable in the type of materials of interest in the current investigation. Some noteworthy differences between the optical properties of these *phospha*-PPV oligomers and those of related organic systems may be explainable in terms of their inherent steric bulk.

Experimental Section

All manipulations were carried out in a dry box under an atmosphere of N_2 . Acetonitrile was distilled from CaH_2 under nitrogen and all other solvents were distilled from sodium benzophenone ketyl prior to use. Compounds **1** and **4**,^[44] **3** and **7**,^[22] and **6**^[45] were prepared as previously reported. Absorption spectra were carried out in degassed HPLC grade $CHCl_3$ on a Lambda 25 spectrophotometer. NMR spectra were recorded on a Varian Gemini instrument operating at 300 MHz for proton and 121.5 MHz for phosphorus. Proton and phosphorus spectra are referenced to residual solvent signals and 85 % phosphoric acid, respectively.

(E)-3,5-Dichloro-4'-methylstilbene (v): To a suspension of potassium *tert*-butoxide (18.7 g, 165 mmol) and 18-crown-6 (ca. 0.4 g) in THF (150 mL) was added dropwise over 30 minutes a solution of diethyl(3,5-dichlorobenzyl)phosphonate (44.6 g, 150 mmol) and 4-tolualdehyde (18.0 g, 150 mmol) in THF (300 mL). The mixture was then stirred for 24 hours at room temperature, after which time the reaction was quenched by pouring into 10 % methanolic HCl (500 mL). The mixture was filtered and diethyl ether (300 mL) and water (300 mL) were added to the filtrate. The organic layer that separated was washed with water (2 $\times$ 300 mL aliquots), neutralized (determined using pH paper) by addition of 5 % sodium hydrogencarbonate solution then rinsed with water (300 mL). Removal of volatiles from the organic solution yielded a sticky yellow solid. Triturating this solid in hexanes followed by filtration and drying of the solid in vacuo yielded the product as a pale yellow powder (30.2 g, 76.4 %). 1H NMR ($CDCl_3$, ppm): δ = 2.36 (s, 3 H), 6.88 (d, J = 16 Hz, 1 H), 7.07 (d, J = 16 Hz, 1 H), 7.17 (d, J = 8 Hz, 2 H), 7.20 (t, J = 2 Hz, 1 H), 7.34 (d, J = 2 Hz, 2 H), 7.38 (d, J = 8 Hz, 2 H); m.p. 78–80 °C (ref.^[30] 80–82 °C).

(E)-4-Iodo-3,5-dimesityl-4'-methylstilbene (Dmp'I): A solution of (E)-3,5-dichloro-4'-methylstilbene (**v**) (10.0 g, 38.0 mmol) in THF (125 mL) was cooled to –78 °C whereupon *n*-butyllithium (16.0 mL, 2.5 M in hexanes, 39.9 mmol) was added dropwise via cannula. After 1 hour of stirring at –78 °C, a solution of mesitylmagnesium bromide [prepared by the reaction of 2-bromomesitylene (26.5 g, 133 mmol) and Mg turnings (4.26 g, 190 mmol) in THF (150 mL)] was added dropwise via cannula at –78 °C. After warming to room temperature over a 3 hour period, the solution was heated to reflux for an additional 10 hours. After cooling to room temperature, the flask was placed in an ice bath and iodine (19.3 g, 76.0 mmol) was added in 5 g portions. After the exothermic reaction was complete and the characteristic iodine colour persisted in

solution for 15 minutes, 5 % Na_2SO_3 (250 mL) was added to quench excess iodine and the solution became yellow. The organic layer was extracted with diethyl ether (250 mL), rinsed with water (2 $\times$ 250 mL aliquots) and volatiles removed to yield a sticky solid. The solid was dissolved in boiling hexanes and precipitated at –7 °C to yield the product as an off-white powder (8.15 g, 38.5 %). 1H NMR ($CDCl_3$, ppm): δ = 2.12 (s, 3 H), 2.14 (s, 12 H), 2.23 (s, 6 H), 6.85 (d, J = 16 Hz, 1 H), 6.92 (s, 4 H), 6.97 (d, J = 16 Hz, 1 H), 6.98 (d, J = 8 Hz, 2 H), 7.13 (s, 2 H), 7.27 (d, J = 8 Hz, 2 H); m.p. 165–168 °C. HRMS(FAB, m/z): calcd. for $C_{33}H_{33}I$, 556.1627; found, 556.1628.

Dmp'PCl₂: A solution of Dmp'I (4.0 g, 7.2 mmol) in THF (125 mL) was cooled to –78 °C whereupon *n*-butyllithium (3.0 mL, 2.5 M in hexanes, 7.5 mmol) was added dropwise via cannula. After 1 hour of stirring at –78 °C, PCl_3 (1.9 mL, 22 mmol) was added rapidly with a syringe. After the resultant solution was allowed to warm to room temperature over three hours, volatiles were removed in vacuo. The resultant orange solid was stirred with acetonitrile (150 mL) for 15 minutes and filtered. Removal of volatiles in vacuo gave a yellow solid which was dissolved in diethyl ether and filtered to remove salts. Removal of the diethyl ether in vacuo gave the product as a pale yellow powder (0.93 g, 24 %). 1H NMR ($CDCl_3$, ppm): δ = 2.01 (s, 12 H), 2.09 (s, 6 H), 2.36 (s, 3 H), 6.96 (s, 4 H), 7.03 (d, J = 16 Hz, 1 H), 7.13 (d, J = 16 Hz, 1 H), 7.17 (d, J = 8 Hz, 2 H), 7.25 (d, 2 H, $^4J_{H,P}$ = 3 Hz), 7.39 (d, J = 8 Hz, 2 H). ^{31}P NMR ($CDCl_3$, ppm): δ = 162.0.

Dmp'P=PDmp' (8): Magnesium turnings (15 mg, 0.62 mmol) were added to a solution of Dmp'PCl₂ (0.30 g, 0.56 mmol) and the resultant mixture sonicated for approximately 3 hours during which time the solution became an orange-red colour. The solution was decanted from a small amount of remaining magnesium and volatiles were removed in vacuo. The crude solid was extracted with hexanes and filtered. Removal of the solvent in vacuo gave the product as a red-orange powder (0.26 g, 76 %). 1H NMR ($CDCl_3$, ppm): δ = 1.73 (s, 24 H), 2.33 (s, 18 H), 6.77 (s, 8 H), 6.95 (d, J = 16 Hz, 2 H), 7.07 (d, J = 16 Hz, 2 H), 7.09 (s, 4 H), 7.13 (d, J = 8 Hz, 4 H), 7.33 (d, J = 8 Hz, 4 H). ^{31}P NMR ($CDCl_3$, ppm): δ = 490.8. HRMS (FAB, m/z): calcd. for $C_{66}H_{67}P_2$, 921.4718; found, 921.4672.

Dmp'P=PMe₃: To a stirred suspension of zinc dust (0.030 g, 0.46 mmol) and Dmp'PCl₂ (0.20 g, 0.38 mmol) was added trimethylphosphane (0.11 g, 1.4 mmol). The mixture was stirred for 3 hours during which time a red colour developed. The mixture was filtered, volatiles removed in vacuo and the crude solid dissolved in hexanes. The solution was then filtered and solvent removed in vacuo. The product was precipitated from a saturated *n*-pentane solution at –35 °C as a red solid (0.087 g, 43 %). 1H NMR ($CDCl_3$, ppm): δ = 1.07 (d, 9 H, J = 12 Hz), 2.08 (s, 12 H), 2.34 (s, 9 H), 6.95 (s, 4 H), 6.94 (d, J = 16 Hz, 1 H), 7.01 (d, J = 16 Hz, 1 H), 7.05 (s, 2 H), 7.12 (d, J = 8 Hz, 2 H), 7.32 (d, J = 8 Hz, 2 H). ^{31}P NMR ($CDCl_3$, ppm): δ = –0.7 (d, J = 560 Hz), –110.4 (d, J = 560 Hz).

Dmp'P=C(H)Ph (2): Trimethylphosphane (0.11 g, 1.4 mmol) was added to a mixture of zinc dust (0.03 g, 0.46 mmol), Dmp'PCl₂ (0.20 g, 0.38 mmol) and benzaldehyde (0.042 g, 40 mmol). A yellow colour developed almost immediately and after stirring for 6 hours the mixture was filtered and the solvent removed in vacuo. The crude solid was dissolved in hexanes, filtered and the solvent removed from the filtrate in vacuo. The product was precipitated from a saturated *n*-pentane solution at –35 °C as a yellow solid (0.10 g, 49 %). 1H NMR ($CDCl_3$, ppm): δ = 2.03 (s, 12 H), 2.21

(s, 6 H), 2.28 (s, 3 H), 6.81 (s, 4 H), 6.97 (d, $J = 16$ Hz, 1 H), 6.81 (d, $J = 16$ Hz, 1 H), 7.04 (m, 5 H), 7.08 (d, $J = 8$ Hz, 2 H), 7.18 (s, 2 H), 7.31 (d, $J = 8$ Hz, 2 H), 8.59 (d, 1 H, $J_{\text{H,P}} = 25$ Hz). ^{31}P NMR (CDCl_3 , ppm): $\delta = 239.2$ ppm. HRMS (FAB, MH^+ , m/z): calcd. for $\text{C}_{40}\text{H}_{40}\text{P}$, 551.2868; found, 551.2864.

1,4-[Dmp'P=C(H)]₂C₆H₄ (5): Trimethylphosphane (0.17 g, 2.3 mmol) was added to a mixture of zinc dust (0.074 g, 1.1 mmol), Dmp'PCl₂ (0.30 g, 0.56 mmol), and terephthalaldehyde (0.038 g, 0.28 mmol). A yellow-orange colour developed almost immediately and after stirring for 10 hours the mixture was filtered and the solvent removed in vacuo. The crude solid was dissolved in boiling hexanes, filtered, and the solvent removed in vacuo. The resultant solid was then rinsed with a small amount of warm acetonitrile and the final product was precipitated from diethyl ether/hexanes solution at -35°C as a yellow-orange solid (0.11 g, 39 %). ^1H NMR (CDCl_3 , ppm): $\delta = 1.98$ (s, 24 H), 2.18 (s, 12 H), 2.26 (s, 6 H), 6.77 (s, 8 H), 6.94 (d, $J = 16$ Hz, 2 H), 7.02–7.08 (m, 10 H), 7.15 (s, 4 H), 7.29 (d, $J = 8$ Hz, 4 H), 8.40 (d, 2 H, $J_{\text{H,P}} = 19$ Hz). ^{31}P NMR (CDCl_3 , ppm): $\delta = 242.3$. MS (FAB, MH^+ , m/z): calcd. for $\text{C}_{74}\text{H}_{73}\text{P}_2$, 1024; found, 1024.

Dmp'PH₂: To a stirred suspension of LiAlH_4 (0.18 g, 4.7 mmol) in THF (25 mL) was added solid Dmp'PCl₂ (1.2 g, 2.3 mmol) in small portions over 5 minutes. After stirring for 6 hours the mixture was filtered and volatiles removed in vacuo to give an off-white solid. This material was then dissolved in diethyl ether and filtered through alumina twice. Removal of volatiles in vacuo gave the product as an off-white powder (0.89 g, 85 %). ^1H NMR (C_6D_6 , ppm): $\delta = 2.12$ (s, 3 H), 2.14 (s, 12 H), 2.23 (s, 6 H), 3.31 (d, 2 H, $J_{\text{PH}} = 212$ Hz), 6.92 (s, 4 H), 6.98 (d, $J = 7$ Hz, 2 H), 7.02 (d, $J = 16$ Hz, 1 H), 7.16 (d, $J = 16$ Hz, 1 H), 7.18 (d, 2 H, $^4J_{\text{H,P}} = 2$ Hz), 7.28 (d, $J = 7$ Hz, 2 H). ^{31}P NMR (C_6D_6 , ppm): $\delta = -146.3$ (t, $J = 212$ Hz).

1,4-[Dmp'P=Pl]₂C₆Ar₄ (Ar = 4-*tert*-butylphenyl) (9): A solution of $[\text{Li}(\text{Et}_2\text{O})][\text{P}(\text{H})\text{Dmp}']^{[45]}$ (0.19 g, 0.35 mmol) in diethyl ether (20 mL) was added at room temperature to a rapidly stirred suspension of $\text{Cl}_2\text{P}-(p\text{-C}_6\text{Ar}_4)\text{-PCl}_2^{[22]}$ (0.14 g, 0.17 mmol) in diethyl ether (20 mL) over a 10 min period. During this time a fine white precipitate formed. The solvent was reduced in volume to 20 mL and a solution of DBU (0.053 g, 0.35 mmol) in diethyl ether (5 mL) was added. Upon addition, the solution became orange and eventually nearly red over a 1 h period after which time the reaction mixture was filtered and the solvent removed in vacuo. The solid material was precipitated from *n*-pentane at -35°C to give 0.18 g of red powder (51 %). ^1H NMR (C_6D_6 , ppm): $\delta = 1.13$ (s, 36 H), 1.93 (s, 24 H), 2.09 (s, 6 H), 2.33 (s, 12 H), 6.65 (d, $J = 8$ Hz, 8 H), 6.86 (d, $J = 8$ Hz, 8 H), 6.91–6.95 (m, 16 H), 7.11 (s, 4 H), 7.20 (d, $J = 8$ Hz, 4 H). ^{31}P NMR (CDCl_3 , ppm): $\delta = 479.7$ (d, $J = 570$ Hz), 524.8 (d, $J = 570$ Hz).

(*E,E*)-3,5-Dichloro-4'-(4-*tert*-butylstyryl)stilbene (xi): A solution of (*E*)-4-bromomethyl-4'-*tert*-butylstilbene (29.6 g, 89.9 mmol)^[32] and triphenylphosphane (25.8 g, 98.2 mmol) was heated to reflux in toluene (200 mL) for four hours. The resultant suspension was cooled to room temperature and the fine white precipitate collected by filtration. The solid was rinsed with *n*-pentane and dried, giving 49.9 g (67.4 %) (*E*)-4-(4-*tert*-butylstyryl)benzyltriphenylphosphonium bromide. A suspension of this material (35.0 g, 59.2 mmol) and 3,5-dichlorobenzaldehyde (11.4 g, 65.1 mmol) in THF (200 mL) was added over 30 minutes to a THF (50 mL) solution of *t*BuOK (7.36 g, 65.1 mmol) containing 18-crown-6 (0.160 g, 0.605 mmol). The mixture was then stirred for 12 hours, and quenched by pouring into an equal volume of 10 % methanolic HCl, upon which

a pale yellow solid precipitated. The precipitate was collected by filtration, rinsed with ethanol and dried. Proton NMR spectroscopic analysis of the crude solid indicated a mixture of *E* and *Z* isomers. Complete isomerization to the *E* form was successfully carried out by heating a toluene solution of the crude solid to reflux for 3 hours in the presence of a crystal of iodine, followed by rinsing with 5 % Na_2SO_3 and removal of volatiles in vacuo. Compound **xi** was isolated as a yellow powder (12.5 g, 51.9 %). ^1H NMR (CDCl_3 , ppm): $\delta = 1.34$ (s, 9 H), 6.95, d, 1 H, $J = 16$ Hz), 7.05 (d, $J = 16$ Hz, 1 H), 7.09 (d, $J = 16$ Hz, 1 H), 7.14 (d, $J = 16$ Hz, 1 H), 7.22 (s, 1 H), 7.36–7.40 (m, 4 H), 7.45–7.52 (m, 6 H); m.p. 139–141 $^\circ\text{C}$.

(*E,E*)-4-Iodo-3,5-dimesityl-4'-(4-*tert*-butylstyryl)stilbene (Dmp''D): A solution of (*E,E*)-3,5-dichloro-4'-(4-*tert*-butylstyryl)stilbene (**xi**) (10.0 g, 24.5 mmol) in THF (125 mL) was cooled to -78°C and *n*-butyllithium (10.3 mL, 2.5 M in hexanes, 25.8 mmol) was added dropwise via cannula. After 1 hour of stirring at -78°C , a solution of mesitylmagnesium bromide [prepared by reaction of 2-bromomesitylene (17.1 g, 85.9 mmol) and Mg turnings (2.98 g, 123 mmol) in THF (85 mL)] was added dropwise via cannula at -78°C . After warming to room temperature over a 3 hour period, the solution was then heated to reflux for an additional 10 hours. After cooling to room temperature the flask was placed in an ice bath and iodine (15.6 g, 61.4 mmol) was added in 3 g portions. After the exothermic reaction was complete and the characteristic iodine colour persisted in solution for 15 minutes, 5 % Na_2SO_3 (200 mL) was added to quench excess iodine and the solution became yellow. The organic layer was extracted with diethyl ether (200 mL), rinsed with water (2 $\times$ 200 mL aliquots) and volatiles removed to yield a viscous oil. Three precipitations of the material from a boiling ethanol solution subsequently cooled to -7°C gave the product as a pale yellow powder (2.05 g, 11.8 %). ^1H NMR (CDCl_3 , ppm): $\delta = 1.35$ (s, 9 H), 2.05 (s, 12 H), 2.39 (s, 6 H), 6.90 (s, 4 H), 7.03–7.14 (m, 4 H), 7.39–7.42 (m, 4 H), 7.46–7.52 (m, 6 H).

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