Radical cations in mixtures of Cl3P and Me2S: a combined ESR and quantum chemical study

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been neglected. For these compounds it has been shown that the latter "memory effects" may cancel the nearest neighbor control. Such processes have to be expected in compounds with "unstable" local electronic configurations in the absence of "memory effects".

VII. Final Outlook

The many-particle nature of π electron bonding in alternant hydrocarbon systems has been investigated by the method of the local approach supplemented by rather simple model Hamiltonians. The present authors believe that it is most convenient for the reader to review the principal findings in the form of characteristic catchwords. (i) The π electrons in annulenes and linear polyenes are sizaably localized. It seems to be necessary to substitute widely accepted traditional models for π compounds. (ii) Bond alternation leads throughout to an increase in the π electron delocalization. (iii) The respective enhancement of the charge fluctuations is probably the microscopic origin for the distortive nature of π networks. (iv) An enhancement of the charge fluctuations (decreasing electronic correlation-strength Δε) and increasing interatomic π correlation energies caused by bond delocalization are not mutually exclusive in larger hydrocarbons. The out-of-phase modulation is obviously the rule. (v) Cyclic 6π electron structures allow for the optimum possible π delocalization in alternant hydrocarbons; but even this takes place far from the "free-electron" limit. The latter process may lead to the situation that extended π systems prefer to form less or more decoupled spatially localized 6π subunits. (vi) Extension of linear monocyclic or polycyclic π systems is frequently not coupled to an increasing delocalization of the π electrons (effects due to the end atoms neglected); their fluctuations saturate quite early. Exceptions have been discussed in the above sections. (vii) The interatomic π correlation energy is one driving force for the bond length alternation in linear and monocyclic hydrocarbons exceeding a certain threshold dimension. (viii) Strong electronic correlations tend to attenuate Jahn–Teller or Peierls instabilities. The attenuation is maximized with increasing correlation strength; see the series C6H6, C10H14, C13H18, C16H22. (ix) The latter effect may be of some influence in "metastable" solids, i.e., solids where the instability is scarcely suppressed. In these compounds superconductivity under strong coupling conditions may become possible.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. M.C.B. acknowledges support due to a Heisenberg Fellowship. The drawings have been kindly prepared by Mr. H. A. Schmaltz.

Radical Cations in Mixtures of Cl3P and Me2S. A Combined ESR and Quantum Chemical Study

Olov M. Aagaard,* Bas F. M. de Waal, Marcoen J. T. F. Cabbolet, and René A. J. Janssen

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Exposure of phosphorus trichloride (Cl3P) and dimethyl sulfide (Me2S) dissolved in halocarbons (CFC13, CF3CC13, CF2C1CFCl2, and CH2Cl2) to X rays at 77 K results in the corresponding parent cations and several cation–substrate adducts. The radicals are detected and identified by ESR spectroscopy. In dilute solution exclusive formation of the parent Cl3P+• and Me2S+• radical cations is observed. In CFC13, Me2S+• exhibits superhyperfine interactions due to chlorine and fluorine nuclei of the matrix molecule(s). At increased concentration, or on warming the sample, the parent radical cations readily react with dissolved Cl3P or Me2S molecules to form homodimeric Cl3P–PCl3+• and Me2S•–SMe2+• and heterodimeric Cl3P–SMMe2+• radical cations with a two-center three-electron σπ+ bond. The heterodimer is formed in spite of a significant difference between the ionization potentials of the two reduced substrates (Ai, Aii). Therefore, formation of an ion–molecule adduct consisting of two equivalent molecular parts (homodimer) should be preferred over ion–molecule adducts comprised of two different molecular fragments (heterodimer). Accordingly, a large number of ESR studies describe homodimetric radical cations, whereas reports on heterodimers are few. However, this reflects the lack of systematic study rather than the alleged intrinsic instability of the heterodimers.

Recently we reported the results of radiogenic radical formation in a mixture of trimethylphosphine (Me3P) and dimethyl sulfide (Me2S) in Freon.3 We demonstrated that besides the well-known

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Introduction

The use of halocarbon matrices in combination with ESR spectroscopy has eminently contributed to the knowledge of radiogenic formation and reactivity of radical cations at low temperature. In general these experiments are conducted at low substrate concentration to ensure the detection of the parent radical cations and several cation–substrate adducts. The radicals are detected and identified by ESR spectroscopy. In dilute solution exclusive formation of the parent Cl3P+• and Me2S+• radical cations is observed. In CFC13, Me2S+• exhibits superhyperfine interactions due to chlorine and fluorine nuclei of the matrix molecule(s). At increased concentration, or on warming the sample, the parent radical cations readily react with dissolved Cl3P or Me2S molecules to form homodimeric Cl3P–PCl3+• and Me2S•–SMe2+• and heterodimeric Cl3P–SMMe2+• radical cations with a two-center three-electron σπ+ bond. The heterodimer is formed in spite of a significant difference between the ionization potentials of the two reduced substrates (Ai, Aii). Therefore, formation of an ion–molecule adduct consisting of two equivalent molecular parts (homodimer) should be preferred over ion–molecule adducts comprised of two different molecular fragments (heterodimer). Accordingly, a large number of ESR studies describe homodimetric radical cations, whereas reports on heterodimers are few. However, this reflects the lack of systematic study rather than the alleged intrinsic instability of the heterodimers. Recently we reported the results of radiogenic radical formation in a mixture of trimethylphosphine (Me3P) and dimethyl sulfide (Me2S) in Freon.3 We demonstrated that besides the well-known

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Radical Cations in Mixtures of Cl,P and Me2S


Radical cations (Me,P+ and Me2S+) and homodimers (Me,P-PMe,P+ and Me,S-SMe,S+) were obtained by changing the experimental conditions, such as temperature range between 90 and 130 K. It proved possible to study formation and reactivity of each individual radical by ab initio quantum chemical calculations.

Results and Assignment

A. Experimental

Cl,P (Merck) was distilled prior to use. Me2S, CFC1, solution, and Me,S-SMe,S radical cation formed after X-irradiation of a frozen 11% v/v CI,P/Me2S (1:1) CFC1, solution. Additional 35Cl and 19F superhyperfine couplings appear on the g, tensor direction.

The ESR spectra were recorded on a Bruker ER 200D spectrometer, operating with an X-band standard cavity and interfaced to a Bruker Aspect 3000 computer. The results were used to characterize the computed stationary points as local minima or saddle points.

Figure 1. (a) ESR spectrum, recorded at 98 K, of the Me2S+ radical cation formed after X-irradiation of a frozen 11% v/v CI,P/Me2S (1:1) CFC1, solution. Additional 35Cl and 19F superhyperfine couplings appear on the g, tensor direction. (b) ESR spectrum, recorded at 105 K, of the Me2S-SMe,S radical cation formed after X-irradiation of a 30% v/v CI,P/Me2S (1:1) CFC1, solution.

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The Me$_2$S$^+$ and Me$_2$S$^+$-SeMe$_2$$^+$ Radical Cations. ESR studies on both radicals are numerous.$^{3,7}$ Table I lists some interesting literature data along with the results of the present study. The Me$_2$S$^+$ and Me$_2$S$^+$-SeMe$_2$$^+$ radical cations can be distinguished by the larger $^1$H hyperfine coupling of the Me$_2$S$^+$ radical cation (60 vs 18 MHz, Figure 1). Furthermore, the $g$ tensor of Me$_2$S$^+$ is strongly anisotropic whereas the $g$ value of Me$_2$S$^+$-SeMe$_2$$^+$ seems isotropic (Figure 1). In Figure 1a the ESR spectrum of the Me$_2$S$^+$ radical cation in CFC$_3$ at 98 K nicely illustrates the complex pattern caused by the overlapping $^1$H hyperfine couplings and the anisotropic $g$ tensor of the radical. Our assignment, indicated in Figure 1a, corresponds well with values reported by Bonazzola et al.$^5b$ Prior to annealing, the spectrum of Me$_2$S$^+$ at low Me$_2$S concentration, and an extra hyperfine splitting of 4.2 MHz (1.5 G) coupling was resolved on the $g$ tensor component. In agreement with previous studies, no extra hyper coupling was resolved on the $g_x$, $g_y$, and $g_z$ component, though no explicit pattern could be established. In Figure 2a, the ESR spectrum of the C$_{13}$P$^+$ radical cation generated from C$_{13}$P$_2$Cl$_4$ recorded at 98 K of the C$_{13}$P$^+$ radical cation formed in a 10% v/v solution of C$_{13}$P in CH$_2$Cl$_2$. Additional $^1$H$_{19}$C hyperfine interactions are present. (b) ESR spectrum of the C$_{13}$P$^+$ radical cation formed in a 10% v/v solution of C$_{13}$P in CH$_2$Cl$_2$.

With respect to formation and stability of these cations we find that X irradiation of a mixture of Me$_2$S and Cl$_2$P invariably leads to Me$_2$S$^+$ at low Me$_2$S concentration, and to Me$_2$S$^+$-SeMe$_2$$^+$ dimers at increased concentration. It is interesting to note that, in contrast to their concurrent detection in the mobile CF$_3$CCl$_2$ and CF$_2$ClCClF$_2$ matrices, we were not able to observe the monomer and dimer radical cations simultaneously in the more rigid CFC$_1$$_3$ or CH$_2$Cl$_2$ matrices. In CFC$_1$$_3$, e.g., formation of either the monomer or dimer radical cation is determined by the Me$_2$S concentration. If the concentration is below 10% v/v, only Me$_2$S$^+$ is observed; above 10% v/v, solely the Me$_2$S$^+$-SeMe$_2$$^+$ radical cation is detected. A similar behavior was recently noted by Ambroz et al.$^7m$ In

Table I: $^1$H Hyperfine Couplings* and $g$ Values of the Me$_2$S$^+$ Radical Cation, Its Homodimer Me$_2$S$^+$-SeMe$_2$$^+$ and Related Radical Cations Generated in Irradiated Halocarbon Solutions

<table>
<thead>
<tr>
<th>Radical</th>
<th>$T$, K</th>
<th>$A$, MHz</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$g_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_2$O$^+$</td>
<td>77</td>
<td>123; 119; 119</td>
<td>2.0138</td>
<td>2.0072</td>
<td>2.0045</td>
<td>2.0085</td>
</tr>
<tr>
<td>Me$_2$S$^+$</td>
<td>81$^a$</td>
<td>57</td>
<td>2.019</td>
<td>2.019</td>
<td>2.0023</td>
<td>2.0134</td>
</tr>
<tr>
<td></td>
<td>77$^d$</td>
<td>57</td>
<td>2.019</td>
<td>2.0145</td>
<td>2.0076</td>
<td>2.0137</td>
</tr>
<tr>
<td></td>
<td>77$^e$</td>
<td>61; 60; 57</td>
<td>2.033</td>
<td>2.016</td>
<td>2.001</td>
<td>2.017</td>
</tr>
<tr>
<td></td>
<td>130$^f$</td>
<td>59</td>
<td>2.019</td>
<td>2.0145</td>
<td>2.0076</td>
<td>2.0137</td>
</tr>
<tr>
<td></td>
<td>98$^f$</td>
<td>60; 60; 56</td>
<td>2.032</td>
<td>2.015</td>
<td>2.001</td>
<td>2.016</td>
</tr>
<tr>
<td></td>
<td>77$^f$</td>
<td>58; 58; 56</td>
<td>2.033</td>
<td>2.017</td>
<td>2.002</td>
<td>2.017</td>
</tr>
<tr>
<td></td>
<td>81$^f$</td>
<td>58</td>
<td>2.032</td>
<td>2.017</td>
<td>2.002</td>
<td>2.017</td>
</tr>
<tr>
<td>Me$_2$S$^+$-SeMe$_2$$^+$</td>
<td>77$^f$</td>
<td>44</td>
<td>2.1316</td>
<td>2.0647</td>
<td>1.999</td>
<td>2.0651</td>
</tr>
<tr>
<td>Me$_2$Se$^+$</td>
<td>77$^f$</td>
<td>13</td>
<td>2.0702</td>
<td>2.0366</td>
<td>1.9964</td>
<td>2.0344</td>
</tr>
</tbody>
</table>

* $A$(MHz) = 2.08247 (g/$g_x$) (g/$g_y$). CFC$_3$, ref 13. CF$_2$ClCCl$_2$, ref 7$e$. CFCl$_3$, refs 7$g$, 19. CFCl$_3$, ref 5$e$. CFCl$_3$, ref 5$g$. CFCl$_3$, this study. CF$_2$CClFCCl$_3$, ref 5$b$. CF$_2$CClFCCl$_3$, ref 5$k$. Cyclopropane, ref 7$d$. H$_2$O, ref 7$a$. CFCl$_3$, ref 1. *Single crystal of Me$_2$Se, ref 21.

![Figure 2a](https://example.com/figure2a.png) (a) ESR spectrum recorded at 98 K of the Cl$_2$P$^+$ radical cation formed radiogenically in a 1% v/v Cl$_2$P/Me$_2$S (1:10) CFC$_3$ solution. Additional $^1$Cl$^1$P hyperfine interactions are present. (b) ESR spectrum of the Cl$_2$P$^+$ radical cation formed in a 10% v/v solution of Cl$_2$P in CH$_2$Cl$_2$.

The Cl$_2$P$^+$ Radical Cation. X irradiation of Cl$_2$P results in the formation of the corresponding Cl$_2$P$^+$ radical cation in all halocarbons used. The ESR spectrum of this radical generated in CFC$_3$ is depicted in Figure 2a. The spectrum reveals a large, nearly isotropic, $^1$P doublet with some partially resolved chlorine hyperfine splittings. The isotropic $^1$P coupling derived from this spectrum is in agreement with values established for the related (HO)$_2$P$^+$ and (MeO)$_2$P$^+$ radical cations.$^{4,6,9}$ Interestingly, the ESR spectrum of the Cl$_2$P$^+$ radical cation generated from Cl$_2$P...
Radical Cations in Mixtures of Cl$_3$P and Me$_3$S

**TABLE II: Hyperfine Couplings$^a$ and g Values of the Radicals Detected in X-Irradiated Mixtures of Cl$_3$P and Me$_3$S, and Related Radical Structures Reported in the Literature**

<table>
<thead>
<tr>
<th>radical</th>
<th>T, K</th>
<th>$A_P$, MHz</th>
<th>$^3$Cl</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_3$P$^+$</td>
<td>75$^b$</td>
<td>739</td>
<td>40</td>
<td>2.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\perp$ $</td>
<td>$ -95</td>
<td>14 $</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\perp$ $</td>
<td>$ -75</td>
<td>-21  $</td>
</tr>
<tr>
<td></td>
<td></td>
<td>iso</td>
<td>190  $</td>
<td>$ 2 $</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2dip</td>
<td>549  $</td>
<td>$ 38 $</td>
</tr>
<tr>
<td>Cl$_4$P$^+$</td>
<td>77$^c$</td>
<td>3553</td>
<td>178</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\perp$ $</td>
<td>$ 3391</td>
<td>56 $</td>
</tr>
<tr>
<td></td>
<td></td>
<td>iso</td>
<td>3445 $</td>
<td>$ 96 $</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2dip</td>
<td>108  $</td>
<td>$ 82 $</td>
</tr>
<tr>
<td>Cl$_4$P$^{**}$</td>
<td>98$^d,^f$</td>
<td>2330</td>
<td>65</td>
<td>2.025</td>
</tr>
<tr>
<td>(HO)$_3$P$^{**}$</td>
<td>77$^g$</td>
<td>2605</td>
<td>2.025</td>
<td></td>
</tr>
<tr>
<td>(MeO)$_3$P$^{**}$</td>
<td>77$^h$</td>
<td>2524</td>
<td>2.0038</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\perp$ $</td>
<td>$ 1998</td>
<td>2.0026</td>
</tr>
<tr>
<td>Cl$_4$P$^{**}$</td>
<td>2dip</td>
<td>251</td>
<td>2.003</td>
<td></td>
</tr>
<tr>
<td>(MeO)$_3$P$^{**}$</td>
<td>77$^j$</td>
<td>2812</td>
<td>2.0049</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\perp$ $</td>
<td>$ 2255</td>
<td>2.004</td>
</tr>
<tr>
<td>Cl$_4$P$^{**}$</td>
<td>2dip</td>
<td>2441</td>
<td>2.0043</td>
<td></td>
</tr>
<tr>
<td>Me$_3$P$^+$</td>
<td>100$^i$</td>
<td>1636</td>
<td>2.002</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\perp$ $</td>
<td>$ 813</td>
<td>2.007</td>
</tr>
<tr>
<td>Cl$_4$P$^{**}$</td>
<td>2dip</td>
<td>1087</td>
<td>2.005</td>
<td></td>
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<tr>
<td>Me$_3$P$^+$</td>
<td>2dip</td>
<td>549</td>
<td>2.024</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $A_P$(MHz) = 2.80247($g/\mu g$) $a$(G).

$^b$ Single crystal of Cl$_3$P, ref 15i.

$^c$ Ref 15c, d, e, f. Cl$_4$P, this study.

$^d$ (CFCl$_3$, ref 3.

$^e$ (CFCl$_3$, ref 3.

$^f$ (CFCl$_3$, ref 3.

$^g$ (CFCl$_3$, ref 3.

$^h$ (CFCl$_3$, ref 3.

$^i$ (CFCl$_3$, ref 3.

$^j$ (CFCl$_3$, ref 3.

$^k$ (CFCl$_3$, ref 3.

$^l$ (CFCl$_3$, ref 3.

$^m$ (CFCl$_3$, ref 3.

$^n$ (CFCl$_3$, ref 3.

$^o$ (CFCl$_3$, ref 3.


Figure 3. ESR spectrum, recorded at 102 K, of the Cl$_3$P$^+$PCl$_3^+$ radical cation formed in a 10% v/v solution of Cl$_3$P in CFCl$_3$.

**TABLE III: $^3$P Hyperfine Couplings$^a$ and g Values of Homo- and Heterodimeric Radical Cations Detected in X-Irradiated Mixtures of Cl$_3$P and Me$_3$S, and Related Radical Structures Reported in the Literature**

<table>
<thead>
<tr>
<th>radical</th>
<th>T, K</th>
<th>x</th>
<th>$A_P$, MHz</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_3$P$^+$PCl$_3^+$</td>
<td>102$^b$</td>
<td>iso</td>
<td>2260</td>
<td>2.020</td>
</tr>
<tr>
<td>Me$_3$P$^+$PMel$_3^+$</td>
<td>100$^c$</td>
<td>$\perp$</td>
<td>1605</td>
<td>1.998</td>
</tr>
<tr>
<td>Me$_3$P$^+$PMel$_3^+$</td>
<td>2dip</td>
<td>1333</td>
<td>2.006</td>
<td></td>
</tr>
<tr>
<td>Cl$_3$P$^+$SMel$_2^+$</td>
<td>100$^d$</td>
<td>iso</td>
<td>3360</td>
<td>2.016</td>
</tr>
<tr>
<td>Cl$_3$P$^+$SMel$_2^+$</td>
<td>2dip</td>
<td>1385</td>
<td>2.006</td>
<td></td>
</tr>
<tr>
<td>Cl$_4$P$^{**}$SMel$_2^+$</td>
<td>120$^e,^f$</td>
<td>iso</td>
<td>5115</td>
<td>2.023</td>
</tr>
</tbody>
</table>

$^a$ $A_P$(MHz) = 2.80247($g/\mu g$) $a$(G).

$^b$ CFCl$_3$ and CH$_3$Cl$_3$, this study. CFCl$_3$, this study.

$^c$ CFCl$_3$, this study. CFCl$_3$, this study.

$^d$ CFCl$_3$, this study.

$^e$ CFCl$_3$, this study.

$^f$ CFCl$_3$, this study.

In the present case no chlorine hyperfine couplings were resolved. When generated in a CFCl$_3$ matrix, the ESR absorptions of Cl$_3$P$^+$ increase upon annealing. In this case Cl$_3$P$^+$ seems to be a secondary radical product because the rise of signal intensity coincides with the gradual loss of the Cl$_3$P$^+$PCl$_3^+$ radical (vide infra). The Cl$_3$P$^+$ radical was not observed in CF$_2$Cl$_2$ and CF$_2$Cl(CFCl)$_2$ matrices.

The Cl$_3$P$^+$PCl$_3^+$ Radical Cation. X irradiation of Cl$_3$P in CFCl$_3$ or CH$_3$Cl$_3$ at relatively low concentration (>3% v/v) results in the formation of the homodimeric Cl$_3$P$^+$PCl$_3^+$ radical cation from an ion-molecule reaction of Cl$_3$P$^+$ with Cl$_3$P. The presence of Cl$_3$P$^+$PCl$_3^+$ cations is readily identified by the degenerate triplet ESR spectrum shown in Figure 3, which is characteristic for a P+P type radical. As a result of the large hyperfine interaction to two identical $^3$P nuclei, the spectrum consists of four equally intense absorptions caused by a second-order splitting of the original degenerate central lines. In fact only three of the four lines can be identified because the fourth absorption is obscured by a strong central signal from the irradiated quartz tube. The $^3$P hyperfine interaction is listed in Table III. No $^3$Cl or $^3$Cl hyperfine interactions were resolved. Upon annealing, the radical can be detected up to 130–135 K. The decay of the radical cation seems to be coupled with the increase of the TBP-e Cl$_3$P$^+$ radical and another, as yet unidentified, phosphorus-centered radical (vide infra). In contrast to the parent radical cation Cl$_3$P$^+$, the magnitude of the $^3$P hyperfine interaction is identical in CFCl$_3$ and CH$_3$Cl$_3$. Surprisingly, the Cl$_3$P$^+$PCl$_3^+$ radical cation is not observed after X irradiation of Cl$_3$P$^+$ in the mobile CF$_2$Cl$_2$ and CF$_2$Cl(CFCl)$_2$ matrices.

The Cl$_3$P$^+$SMel$_2^+$ Radical Cation. The Cl$_3$P$^+$SMel$_2^+$ radical
of the parent substrate is sufficient compared to the homodimers Me$_2$S$^{-}$SM$_2$+ and c$_{13}$PLPc$_{13}$+. No C$_{13}$P is derived from CI$_3$P alone, and a relatively low concentration up to the melting of the matrix. The radicals are formed when different reaction pathways: C$_{13}$P$^{+}$, C$_{13}$P(SMe$_2$)$_2$$^{+}$, and CI$_3$P-.SMe$_2$+ heterodimer radical cation. Analogous to the CI$_3$P-.SMe$_2$+ radical cation formed in a 70% v/v solution of CI$_3$P and Me$_2$S (1:1) in CFCl$_3$, a C$_4$P trigonal-bipyramidal structure in which the odd electron is accommodated by a CI$_3$P- SM$_3$ substituents accommodate the valence electrons better than the chloride ion descendent from the irradiated solvent. However, at this moment no clear assignment can be made, and it is also conceivable that radical "X" does not correspond to either of the suggested structures.

The CI$_3$P(SMe$_2$)$_2$$^{+}$ Radical. Upon annealing an X-irradiated frozen mixture of CI$_3$P and Me$_2$S (for instance 70% v/v 1:1 in CFCl$_3$) a new phosphorus-centered radical is formed, exhibiting a very large $^{31}$P hyperfine coupling of 5115 MHz (Figure 6, Table III). The magnitude of the isotropic $^{31}$P hyperfine coupling points to a high contribution of the phosphorus 3s orbital to the SOMO. To our knowledge, the largest $^{31}$P hyperfine coupling reported until now amounts to 4555 MHz attributed to the CI$_3$P$^{+}$ radical anion which possesses an octahedral structure with the unpaired electron in a vacant position. This suggests that in our case the central phosphorus atom bears at least five substituents. We assign the new formed radical to the CI$_3$P(SMe$_2$)$_2$$^{+}$ radical cation formed by reaction of Me$_2$S-SM$_2$+ with a CI$_3$P molecule. Our assignment is based on several observations. First, the larger $^{31}$P hyperfine coupling of CI$_3$P(SMe$_2$)$_2$$^{+}$ compared to CI$_3$P$^{+}$ can be explained by the fact that the positively charged SM$_3$ substituents accommodate the valence electrons better than the chloride atoms of CI$_3$P$^{+}$ thereby increasing spin density on the hypervalent phosphorus nucleus in the antibonding SOMO. Second, the CI$_3$P(SMe$_2$)$_2$$^{+}$ radical is only detected when both Me$_2$S and CI$_3$P are present, which points to a hetero ion–molecule reaction. Furthermore, the increase of the CI$_3$P(SMe$_2$)$^{+}$ concentration is coupled with a rapid decrease of the Me$_2$S-SM$_2$+. In CFCl$_3$, the radical is absent if the concentration of Me$_2$S is below 10% v/v, regardless of the CI$_3$P concentration (only formation of Me$_3$S$^{+}$!). In addition, the radical is formed in CF$_3$CCl$_3$, although the heterodimer CI$_3$P-SM$_2$+ is not observed. This signifies that the ion–molecule reaction between the heterodimer CI$_3$P-SM$_2$+ and a molecule of Me$_2$S is unlikely. Apparently, the Me$_3$S-SM$_3$+ radical cation reacts with a CI$_3$P molecule giving the trimmer radical cation. Formation of this radical is observed in all halocarbon matrices used. The trimmer vanishes before the matrices melt without generating new phosphorus-centered radicals.

It is noted that Illies et al. report a similar reaction. In a mass spectroscopic study on the homoaossociation of Me$_3$S$^{+}$ to Me$_3$S, they observed at $-40\, ^\circ\text{C}$ a prominent peak at m/z 182. It is assigned to the monopositive trimer of Me$_3$S less four amu.

TABLE IV: Total Energies (au) and ($S^2$) UHF Expectation Values of the Radical Precursors and Radicals at Their Equilibrium Geometries (Figures 7-11) (All Structures Were Calculated with the 3-21G* Basis Set)

<table>
<thead>
<tr>
<th>compound</th>
<th>symmetry</th>
<th>UHF</th>
<th>ROHF</th>
<th>RHF</th>
<th>($S^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H,S,S**</td>
<td>C_2v</td>
<td>-396.476 386</td>
<td>-396.471 563</td>
<td>-396.819 637</td>
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<td>H,S</td>
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<td>-793.325 431</td>
<td>-793.325 431</td>
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<td>Me,S**</td>
<td>C_2v</td>
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<td>-474.169 419</td>
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<td>-948.656 055</td>
<td>-948.656 055</td>
<td>0.7734</td>
</tr>
<tr>
<td>Me,S-SMe^+</td>
<td>C_2v</td>
<td>-1253.922 205</td>
<td>-1253.913 335</td>
<td>-1253.913 335</td>
<td>0.7671</td>
</tr>
<tr>
<td>Cl,P</td>
<td>C_2v</td>
<td>-1711.015 964</td>
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</tr>
<tr>
<td>Cl,P^-</td>
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<td>-2168.714 223</td>
<td>-2168.714 223</td>
<td>0.7874</td>
</tr>
<tr>
<td>Cl,P^-SH_2^+</td>
<td>C_2v</td>
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<td>-2107.853 847</td>
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<td>Cl,PPPCl_3^-</td>
<td>C_2v</td>
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<td>Cl,P(SH_2)_2^-</td>
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<td>-2504.652 301</td>
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<td>-2504.651 054</td>
<td>0.7609</td>
</tr>
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</table>

*1 au = 627.5 kcal/mol. *2 Degenerate imaginary frequency 118i cm^-1. E. *3 Imaginary frequencies 92i cm^-1, 52i cm^-1, 81i cm^-1. *4 Imaginary frequencies 89i cm^-1 and 29i cm^-1, A*4. *5 No SCF convergence.

However, as they state: "the structure of this species is a tantalizing mystery.".

B. Quantum Chemical Calculations. All calculations employed the GAUSSIAN16(18) or GAMES UK19 series of programs using the 3-21G* basis set. Odd-electron systems were calculated using the unrestricted and restricted open-shell Hartree-Fock (UHF and ROHF) formalisms, and closed-shell systems with restricted Hartree–Fock (RHF). For open-shell systems geometry optimization was started at the UHF level. The resulting structure then served as input to the ROHF geometry optimization. Harmonic vibrational frequencies were calculated at the 3-21G* level in order to characterize stationary points as minima (representing equilibrium structures) or saddle points (transition states). Magnetic properties such as the isotropic and anisotropic part of the electron–nucleus hyperfine interaction were determined, where possible, from the spin-density matrix. The isotropic hyperfine coupling was calculated from

$$A_{iso} = \frac{1}{3} \pi \sum_{\sigma} g_{\sigma} \sum_{\nu} \frac{\langle \phi_{\nu} | \beta_{g} \beta_{s} | \psi_{\nu}(0) \rangle^2}{\langle \phi_{\nu}(0) | \phi_{\nu}(0) \rangle}$$

with

$$\langle \phi_{\nu}(0) | \phi_{\nu}(0) \rangle = \sum_{\sigma} P_{\nu}^{\sigma} \langle \phi_{\nu} | \beta_{\nu} \rangle$$

being the Fermi contact integral, and in which $P_{\nu}^{\sigma}$ is the spin-density matrix. It is noted that the GAMES UK program package gives the Fermi contact integral 1/\(\pi\) times its true value (in au). The magnetic dipolar hyperfine tensor was calculated as

$$A_{dp}(u,v) = -g_{\beta} g_{s} \sum_{\nu} P_{\nu}^{\sigma} \left( \frac{\langle \phi_{\nu}^* | \beta_{u} \beta_{v} | \phi_{\nu} \rangle}{r^5} \right) \phi_{\nu}$$

where $u, v$ are the Cartesian coordinates $x, y, z$.

(18) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. N.; Raghavachari, R.; Binkley, J. S.; Gonzalez, C; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pope, J. A. Gaussian 88; Gaussian, Inc.: Pittsburgh, PA, 1988. Calculations were performed on an Alliant FX/8 computer at our university.

Figure 7. Optimized geometries of the H2S, H2S+, and H2S-SH2+ structures calculated at ROHF/3-21G* SCF level within their respective symmetry constraints.

H2S+ + H2S → H2S-SH2+. The homodimer radical cation of H2S has been subject of many high-level quantum chemical studies.21,22 The two stable minima found are C2v and C3v structures, of which the C2v is the lowest in energy.7 The structures resulting after geometry optimization within the C2v symmetry constraint for H2S+ and H2S, and C3v symmetry constraint for H2S-SH2+ are depicted in Figure 7. Characteristic for the dimer $\sigma^{*}$ structure is the long S-S bond (2.826 Å). Furthermore, the H-S bond directions are nearly perpendicular to the S-S bond. The hydrogen hyperfine couplings calculated at ROHF/3-21G* level for both the monomer and dimer radical cations are listed in Table V. Sharing the odd electron between two sulfide moieties reduces the dipolar hyperfine coupling of the hydrogen atoms by half. Our calculations on the H2S-SH2+ radical reveal that the direction of the largest principal value of the sulfur dipolar hyperfine interaction (equivalent to the direction of the largest principal value of the $33\text{S}$ tensor) is not perfectly aligned with the S-S bond direction but makes a small angle (3.5°). The SOMO points away from the hydrogen substituents (Figure 7). Such a nonalignment is experimentally detected in the single-crystal ESR study on the Me2S-SeMe2+ radical cation.21 The direction of the largest principal value of the $77\text{Se}$ hyperfine tensor, corresponding to the direction of the SOMO on that nucleus, is inclined by 2.5° to the direction of the minimal g tensor component, which is assumed to correspond to the Se-Se linkage.21

Me2S+ + MeS → Me2S-SMe2+. Geometry optimization within C2v symmetry constraint for Me2S+ and MeS and within C3v for Me2S-SMe2+ results in the structures depicted in Figure 8. All structures are true minima, and their total energies are listed in Table IV. Our results are in excellent agreement with the calculations performed by Illies and co-workers for the same systems.7 However, in their article they do not state the symmetry constraints used and give little details on the optimized structures (Figure 8).7

The experimental ratio of the $\beta$-hydrogen hyperfine couplings of the monomer and dimer radical cations of Me2S or Me2Se is approximately 3.75+0.22. The calculated hyperfine couplings are listed in Table V. The ratio of the isotropic couplings of the monomer and the C2v dimer amounts to 2.5. Based on MNDO calculations,21 Williams suggested21 that the increased ratio (>2) is a consequence of the nature of the $\sigma^{*}$ orbital, rather than of a change in geometry at the heavy atoms. Our ab initio calculations on the C2v structure of Me2S-SMe2+, along with the computations performed by Illies and co-workers,7 show indeed that the bond angles and bond distances of the heavy atoms do not vary much between the monomer and dimer structures. In

Figure 8. Optimized geometries of the Me2S, Me2S+, and Me2S-SMe2+ structures calculated at ROHF/3-21G* SCF level with their respective symmetry constraints.

Figure 9. Optimized geometries, calculated at ROHF/3-21G* SCF level, of the structures containing one phosphorus and several chlorine atoms.

interestingly, in the C2v dimer the angles between the S-S bond and the bisectors of the C=S-C bond angles are significantly larger than in H2S-SH2+ (99.9° vs 91.4°, Figures 7 and 8).

The principal direction of the SOMO on the sulfur atoms is almost aligned with the S-S bond. We calculated a small angle of 0.8° in which the orbital points away from the CH3 substituents. In H2S-SH2+ the angle of the H-S-H bisector to the SOMO amounts 93.9°, comparable to the 90° of the 3p orbital in the monomer H2S+. In Me2S-SMe2+, however, this angle amounts
Radical Cations in Mixtures of Cl₃P and Me₂S

Figure 10. Optimized geometries of the three stationary points found for the Cl₃P=PCl₁⁺ structure (C₁₉ at ROHF, C₂ and C₃ at UHF) and the heterodimer Cl₃P=SH₂⁺ radical cation (ROHF). Structures calculated with the 3-21G* basis set.

100.7°, which is considerably different. This could have a profound effect on the ratio of the β-hydrogen hyperfine couplings in Me₂S⁺⁺ and Me₂S⁻⁻Me₂S⁻⁻.

Cl₃P⁺⁺ + Cl₂P → Cl₃P=PCl₁⁺. Vibrational analysis shows that the C₁₉ structure of the Cl₃P⁺⁺ cation is a true minimum. Radical formation shortens the P-Cl bonds, with respect to its C₁₉ precursor Cl₂P, by about 0.2 Å. A flattening of the tetrahedral structure is also noted (Figure 9). The calculated C₁₉ structure for Cl₃P=PCl₁⁺ is a true minimum, and the optimized geometry is again characterized by a long σ⁺ bond (3.760 Å, Figure 10). Formation of the homodimer results in a stabilization of 9.0 kcal/mol at the UHF level (7.1 kcal/mol at ROHF, Table IV), which is almost half of the stabilization calculated for H₂P=PH₂⁺ at different levels (e.g. C₁₉ = 19.3 kcal/mol at UHF/6-31G*).2°

The calculated hyperfine couplings of Cl₃P⁺⁺ and Cl₃P=PCl₁⁺ are enumerated in Table V. The direction of the largest principal value of the 3¹Cl tensor in Cl₃P⁺⁺ is inclined by 29.2° with respect to the largest 3¹P hyperfine tensor component. In the dimer C₁₉, the Cl₂P atom is in the mirror plane (Figure 10) with a larger spin density than the Cl₂P atoms. The direction of the maximal principal value of the 3¹P hyperfine tensor is situated between the P-P and P-Cl bonds, inclined by 24.9° to the P-P bond. A similar orientation was established in single-crystal ESR work with related σ⁺ radical ions of substituted diphenyl disulfides. Experiment and ab initio calculations revealed an angle of 25 to 30°.2°

Cl₂P + H₂S⁺⁺ → Cl₂P=SH₂⁺ → Cl₂P⁺⁺ + H₂S. As a model for Cl₂P=SMMe₂⁺ we optimized the Cl₂P=SH₂⁺ structure. The heterodimer radical cation Cl₂P=SH₂⁺ can be formed following the two different pathways indicated in the heading. The energetic has been envisaged and resulted for respectively the left or right side of the reaction in -16.5 and -15.0 kcal/mol, respectively (Table IV). The C₁₉ staggered structure is computed to be a true minimum (see Figure 10), analogous to the H₂P=PH₂⁺ staggered C₁₉ structure.2° The stabilization is similar to or even slightly enhanced with respect to the latter one, depending on the theoretical level.

The calculated hyperfine couplings of the Cl₂P=SH₂⁺ radical are listed in Table V. In the C₁₉ structure, atoms in the mirror plane contain the highest spin density. The elongation of the P-S σ⁺ bond is in accordance with its antibonding character. The directions of the SOMO contributions of phosphorus and sulfur are not aligned with the P-S bond direction. The orientation of the anisotropic phosphorus and sulfur contributions to the SOMO (respectively 27.8° and 5.0°, Figure 10) are similar to the angular deviation noted earlier for their respective homodimers Cl₃P=PCl₁⁺ and H₂S=SH₂⁺ (vide supra).

TBP-e Cl₃P⁺⁺. Geometry optimization within C₃ symmetry constraint results in a true minimum for Cl₃P⁺⁺ (TBP-e, Figure 9). The hyperfine interactions are listed in Table V. In the TBP-e structure major spin density is primarily located on the axial chlorine atoms and the central phosphorus atom. In Cl₃P⁺⁺ phosphorus is formally hypervalent, and consequently the bonds to the axial chlorine atoms are elongated (Figure 9). Analogous to previous calculations on C₂H₆P⁺⁺ and F₂P⁺⁺ structures, the Cl₃P⁺⁺-Cl₁ bond angle in the Cl₃P⁺⁺ structure is less than 180°. The direction of the largest principal value of the axial chlorine atoms is inclined to the P-Cl bond direction by 21.4° and nearly orthogonal to the largest 3¹P hyperfine interaction (83.2°, Figure 9).

Attempts To Calculate the Structure "X". Based on the experimental hyperfine coupling, the structure of the unassigned radical "X" seems similar to the TBP-e Cl₃P⁺⁺ structure. Geometry optimization of Cl₃P⁺⁺ within C₃ symmetry constraint results in a stationary point (TBP-a, Figure 9). Unfortunately, vibrational analysis shows that it possesses a degenerate imaginary vibrational mode (1181 cm⁻¹, E). The small value of the force constant of the imaginary mode encountered indicates that the local hypersurface along the direction of this vibrational mode is quite flat. Attempts to minimize the energy of a Cl₃P⁺⁺ structure within C₃ symmetry constraint or without symmetry (C₃) result in dissociation into Cl₃P and a Cl⁺ atom. Similarly, attempts to optimize the C₁₉ σ⁺ Cl₃P⁺⁺-Cl₃P structure lead to such a dissociation. For the alternative conformation within C₃ symmetry, the TBP-a structure, maximal spin density is located at the equatorial chlorine atoms and the central phosphorus atom. The calculated 3¹P hyperfine coupling is larger than the interaction calculated for the Cl₃P⁺⁺ structure (Table V). This is in accordance with previous calculations and could possibly explain the experimental value of "X".

Since both TBP-e Cl₃P⁺⁺ and "X" radicals are formed on annealing of the homodimer Cl₃P⁺⁺ cation, we calculated several isomeric structures of Cl₃P=PCl₁⁺ by rearranging a chlorine atom from one phosphorus atom to the other. Only two stationary points were found, and their optimized geometries are depicted in Figure 10.

The first is a C₁₉ structure, composed of a TBP-e Cl₃P⁺⁺ molecule fragment and a Cl₁P⁺⁺ residue. No vibrational analysis could be performed because of computer limitations. The P-P distance of 3.75 Å clearly shows that the molecular fragments are loosely bound. The total energy of the C₁₉ structure has increased by 44.3 kcal/mol relative to optimized Cl₂P=PCl₁⁺.

The second stationary point found has been optimized within the C₃ symmetry constraint. The resulting structure is composed of two Cl₃P fragments (Figure 10) and represents an intermediate prior to dissociation into a Cl₃P⁺⁺ radical and a Cl₁P⁺⁺ molecule. Although the molecules are 3.22 Å apart, there is still mutual influence on the spin-density distribution. The chlorine atom of the Cl₃P molecule bears some spin density and likewise, the spin density on the central phosphorus atom of the Cl₃P⁺⁺ radical cation is increased. The total energy lies 6 kcal/mol below the sum of the total energies of the respective C₁₉ Cl₃P⁺⁺ and Cl₃P structures (Table IV).

Attempts to compute other stable geometries within C₃ symmetry constraint failed because of SCF-convergence problems.

Cl₃P + H₂S=SH₂⁺ → Cl₃P(SH₂)⁺⁺. As model compound for Cl₃P=SMMe₂⁺ we calculated the structure of the Cl₃P(SH₂)⁺⁺ radical cation was optimized. Geometry optimization of the heterotrimer Cl₃P(SH₂)₂⁺ resulted in four stationary points (Figure 11, Table IV). We performed vibrational analyses on the C₂₃(1) and C₂₃ structures. Both resulted in two small imaginary frequencies, indicating no true minima (C₂₃(1), 921 cm⁻¹ B₂, 521 cm⁻¹ B₁; C₂₃, 893 cm⁻¹ and 291 cm⁻¹ A₁). The small size of the negative eigenvalues again indicates that the hypersurface for the corresponding vibrational modes is flat.
The experimental $\text{C}_1\text{P} \left(\text{SMe}_2\right)^{+\cdot}$ radical structure is analogous to the $\text{C}_1\text{P}^-$ radical anion. In order to provide a comparison, we computed the structure of the $\text{C}_1\text{P}^+$ radical anion. Geometry optimization within $\text{C}_3v$ symmetry constraint gives a true minimum (Figure 9, Table IV). The spin density is located at the equatorial chlorine atoms and the phosphorus atom, similar to the $\text{C}_3\text{P}^+$ radical anion$^{4a}$ and $\text{C}_{12}\text{P}^+$ radical. Therefore, the $\text{P}^-$ bond lengths are longer than the $\text{P}^-\text{Cl}_3$ bond. The SOMO on phosphorus points away from the $\text{P}^-\text{Cl}_3$ bond. The calculated hyperfine couplings are listed in Table V.

The calculated $\text{C}_1\text{P} \left(\text{SH}_2\right)^{+\cdot}$ radical structures are indeed reminiscent of the $\text{C}_1\text{P}^+$ radical anion (Figure 11) with exception of the $\text{C}_3$ structure. In the latter the $\text{P}^-$ bond length of 3.16 Å indicates an intermediate structure prior to dissociation into $\text{Cl}_3\text{P}^+$ and 2H$_2$S. Likewise, the calculated $^{31}\text{P}$ hyperfine coupling deviates seriously from the experimental value. The other three structures ($\text{C}_3(1)$, $\text{C}_3(2)$, and $\text{C}_3(3)$) result in large $^{31}\text{P}$ hyperfine couplings as also found experimentally. However, they are not larger than the $\text{P}^-\text{Cl}_3$ bond. The hyperfine interaction calculated for $\text{C}_1\text{P}(\text{SH}_2)^{+\cdot}$ (Figure 9, Table IV). The spin density is located at the equatorial chlorine atoms and the phosphorus atom, similar to the $\text{C}_3\text{P}^+$ radical anion$^{4a}$ and $\text{C}_{12}\text{P}^+$ radical. Therefore, the $\text{P}^-$ bond lengths are longer than the $\text{P}^-\text{Cl}_3$ bond. The SOMO on phosphorus points away from the $\text{P}^-\text{Cl}_3$ bond. The calculated hyperfine couplings are listed in Table V.

Discussion

It has been shown that X irradiation at low temperature of mixtures of $\text{Me}_2\text{S}$ and $\text{Cl}_3\text{P}$ leads to several ion–molecule adducts. The adducts are detected and identified by ESR spectroscopy. In addition, ab initio quantum chemical calculations were performed to provide further insight into the radical structures.

The radiogenic production of the $\text{Cl}_3\text{P}^+$ radical cation from $\text{Cl}_3\text{P}$ is straightforward. Analogous to trialkylphosphine radical cations,$^{14}$ $\text{Cl}_3\text{P}^{+\cdot}$ reacts with its precursor to yield the homodimeric $\text{Cl}_3\text{P}^-\text{Cl}_3^+$ radical cation. Similarly for $\text{Me}_2\text{S}$, we observe the well-known monopositive cation $\text{Me}_2\text{S}^+$ and the corresponding homodimer $\text{Me}_2\text{S}^-\text{Me}_2\text{S}^+$. In mixtures of $\text{Cl}_3\text{P}$ and $\text{Me}_2\text{S}$ the heterodimer $\text{Cl}_3\text{P}^-\text{Me}_2\text{S}^+$ radical cation is formed, in spite of a significant difference in ionization potential of the two participating molecular fragments. Its formation indicates that, in frozen solution, ionization potential differences are less important for the stability of $\sigma^*$ bonds. At high solute concentrations we detected an ion–molecule reaction between the homodimer $\text{Me}_2\text{S}^-\text{Me}_2\text{S}^+$ and a molecule of $\text{Cl}_3\text{P}$. The adduct is assigned to a heterotrimmer $\text{Cl}_3\text{P} \left(\text{SMe}_2\right)^{+\cdot}$ radical cation in which the central phosphorus atom bears five substituents. The configuration of this radical is reminiscent of the octahedral $\text{Cl}_3\text{P}^-$ radical anion. The experimental $^{31}\text{P}$ hyperfine coupling of the heterotrimmer exceeds the value$^{15b}$ of $\text{Cl}_3\text{P}^+$ (Table III). In addition, two radical structures arise from a rearrangement of the homodimer radical cation $\text{Cl}_3\text{P}^-\text{Cl}_3^+$. First, the TBP-e $\text{Cl}_3\text{P}^+$ radical can clearly be identified. Secondly, a possibly related radical structure can be observed ("X"). Until now no final assignment is made for "X". Candidates are a $\text{C}_6\text{H}_{15}$ (TBP-a) $\text{Cl}_3\text{P}^+$ radical structure and a $\sigma^*$ $\text{Cl}_3\text{P}^-\text{Cl}$ radical.

Open-shell quantum chemical calculations on the expectation values of the isotropic and dipolar hyperfine coupling constants were performed on the optimized structures of the various monomer and dimer radical structures. The computed values are in general in qualitative agreement with the experimental data and confirm the assignments. Additional analyses show that $\text{C}_1\text{P}^-\text{P}-\text{CI}_3^+$ homodimer and the $\text{C}_1\text{P}^-\text{CI}_3\text{P}^+$ are true minima. Calculations on the heterotrimer structure did not lead to a true minimum, although vibrational analysis reveals two small imaginary frequencies, indicating that the potential hypersurface for these vibrational modes is flat. It should be emphasized that substitution of $\text{Me}_2\text{S}$ by $\text{H}_2\text{S}$ in the calculations affects the electronic distribution within the radical due to the higher ionization potential of $\text{H}_2\text{S}$ ($\text{IP} = 10.4$ eV). Likewise, it is well known that hyperconjugation of the methyl protons provides significant stabilization for such radical cation complexes despite long central bonds. Moreover, solvent interactions with the calculated structures can play a decisive role in stabilizing the radical configuration. However, such a stabilization is not yet amenable to computation. Efforts to find a satisfactory $\text{Cl}_3\text{P}^+$ structure for radical "X" did not yield a true minimum. For the $\text{C}_6\text{H}_{15}$ (TBP-a) $\text{Cl}_3\text{P}^+$ structure a small degenerate negative eigenvalue is encountered. Geometry optimization of the $\text{C}_6\text{H}_{15} \sigma^* \text{Cl}_3\text{P}^-\text{Cl}$ structure leads to a dissociation of the radical in $\text{Cl}_3\text{P}$ and $\text{Cl}^-$. Interestingly, we find that the extra $\text{CFCl}_3$ superhyperfine interactions on $\text{Me}_2\text{S}^+$ descend from both chlorine and fluorine of the $\text{CFCl}_3$ molecule(s). Usually such ion–molecule interaction is observed along the minimal g direction,$^{14}$ whereas it now coincides with the maximal g direction. Clark$^{2a}$ suggested that the bond strength of a $\sigma^*$ bond depends on $\Delta\text{IP}$. Likewise, Clark, Hasegawa, and Symons investigated the change in $\sigma^*$ bond formation from chlorine to fluorine as a function of the difference in ionization potential between $\text{CFCl}_3$ and the dissolved molecule.$^1$ They predict that there should be a certain $\Delta\text{IP}$ at which interaction switches from chlorine to fluorine. Indeed the $\text{Me}_2\text{S}^+$ radical cation seems to be this point ($\Delta\text{IP} = 3.18$ eV). This is illustrated in Figure 12, where the parallel superhyperfine coupling vs $\Delta\text{IP}$ is displayed. Two straight lines can be drawn illustrating either hyperfine interaction to either $^{35}\text{Cl}$ or $^{19}\text{F}$. However, there seems to be a paradox, since the $^{19}\text{F}$ hyperfine coupling increases with increasing $\Delta\text{IP}$, i.e. with decreasing $\sigma^*$ bond strength. Perhaps it is possible to rationalize this discrepancy by assuming a negative sign for the $^{19}\text{F}$ hyperfine coupling. Yet we cannot explain the mechanism involved.
The type of matrix clearly influences radical formation. In the more mobile\(^3\) matrices, CF\(_2\)C\(_6\)I\(_2\) and CF\(_2\)C\(_6\)F\(_7\)Cl\(_3\), the Me\(^{35}\)S\(^-\) and Me\(^{35}\)S-SMe\(^{35}\)\(^-\) radicals are observed simultaneously after X irradiation, whereas in the rigid, more crystalline, CFC\(_3\)I\(_4\) or CH\(_3\)Cl\(_2\) frozen solutions, they are detected separately depending on the concentration. Surprisingly, formation of the CI\(_3\)P–P=CI\(_3\) homodimer is not observed in the mobile matrices, whereas in spite of ionization potential differences, the CI\(_3\)P–SMe\(^{35}\)\(^+\) heterodimer is readily detected in CFC\(_3\)CIF\(_3\) (but not in CF\(_3\)CIF\(_3\)).

The exact mechanism controlling these phenomena is not clear. As a consequence of the absence of CI\(_3\)P–P=CI\(_3\) radical cation in the mobile matrices, the secondary TBP–CI\(_3\)P and “*” radicals are also not detected in these frozen solvents. The experiments show that hyperfine couplings are fairly invariant to the type of solvent. In CH\(_3\)Cl\(_2\) the coupling for the same radical structure is usually slightly increased. It is noted that by following the reactions in different halocarbon solvents a consistent description of radical formation and reactivity is obtained.

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**Registry No.** Cl\(_3\)P, 7719-12-2; Me\(_2\)S, 75-18-3; Cl\(_3\)P radical cation (1+), 136889-80-0; Me\(_2\)S radical cation (1+), 34480-65-4; Cl\(_3\)P dimer radical cation (1+), 136804-95-0; Me\(_2\)S dimer radical cation (1+), 76796-56-0; Cl\(_3\)P–Me\(_2\)S radical cation (1+), 136804-91-6; Cl\(_3\)P radical, 20762-59-8; Cl\(_3\)P–Me\(_2\)S–Me\(_2\)S radical cation (1+), 136804-92-7; Cl\(_3\)P–H\(_2\)S radical cation (1+), 136804-93-8; Cl\(_3\)P–H\(_2\)S–H\(_2\)S radical cation (1+), 136804-94-9; H\(_2\)S radical cation (1+), 77544-69-5; H\(_2\)S, 7783-06-4; H\(_2\)S dimer radical cation (1+), 13604-96-1; Cl\(_3\)P, 58765-98-3; Cl\(_3\)P\(^{+}\), 75001-84-2; Cl\(_3\)P radical, 20762-58-7.

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### Electronic Structure and Aromaticity of 1,3-Azaphosphole and 1,3-Azarsole

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Three different aspects of the aromaticity have been studied for 1,3-azaphospholes and azarsoles, namely the molecular geometry, the bond separation reactions, and the UV photoelectron spectra. Ab initio molecular orbital theory has been used to calculate the geometrical and electronic structure of the molecules. Comparing the two possible tautomeric forms, the 1H derivatives (type I) have planar structures while the 3H derivatives (type II) show a puckered structure. The C–P or C–As bond lengths in the type I molecules are definitely shorter and the aromatic stabilization energies calculated from the bond separation reactions are larger than in type II molecules. Within each type I or type II molecules no characteristic difference in the aromaticity could be found. The band structure of the photoelectron spectra of type I molecules is similar to that of pyrrole, and the respective aromatic bands could be recognized.

The large variety of nitrogen-containing heteroaromatic systems inspired chemists dealing with organophosphorus compounds to synthesize heteroaromatic systems containing heavy atoms which replace the nitrogen. The achievements of the synthetic chemists in the 1980s have not been accompanied by widespread theoretical investigations. The photoelectron spectrum of the unstable parent compound phosphabenzene\(^4\) has been observed, and numerous quantum-chemical calculations have been conducted on this compound.\(^2\) Among the potentially aromatic metalacyclics, phosphabenzenes\(^3\) and phospholes\(^4\) have been studied. In our recent work, investigations of 1,3-benzazaphosphole and -benzoxaphosphole have been reported.\(^5\) The photoelectron spectra of methyl-substituted 1,2,4,3-triazaphosphole isomers have been studied, and on the basis of the change of some close-lying states the failure of Koopmans' theorem has been observed.\(^6\)

In a simple description of the electronic structure of nitrogen-containing heteroaromatic compounds two different types of nitrogen atoms are considered. For the first type the simplest example is pyrrole. The nitrogen atom in pyrrole is substituted by hydrogen, so that it is easily replaceable by bases possessing acidic character to the parent molecule. In terms of MO theory the aromaticity and stability of pyrrole is the consequence of the interaction of the nitrogen lone pair with the cis-butadiene backbone forming a six-electron \(\pi\)-system. For the second type pyridine is the most common example. In this compound nitrogen possesses a basic character. In terms of MO theory this is a consequence of the free lone pair in the plane of the molecule.

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