

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231403138>

Conformational stability and force field of short-chain linear chlorophosphazenes: MNDO calculations, ^{31}P NMR, vibrational spectra, and normal coordinate analyses of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_n\text{P}...$

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · OCTOBER 1992

Impact Factor: 2.78 · DOI: 10.1021/j100201a031

CITATIONS

14

READS

124

4 AUTHORS, INCLUDING:



Roger De Jaeger

76 PUBLICATIONS 851 CITATIONS

SEE PROFILE



Yahia Lemmouchi

British American Tobacco

34 PUBLICATIONS 460 CITATIONS

SEE PROFILE

Conformational Stability and Force Field of Short-Chain Linear Chlorophosphazenes: MNDO Calculations, ^{31}P NMR, Vibrational Spectra, and Normal Coordinate Analyses of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_n\text{P}(\text{O})\text{Cl}_2$ and $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_n\text{PCl}_3][\text{PCl}_6^-]$ ($n = 1, 2$)

Daniel Bougeard, Claude Brémard,* Roger De Jaeger, and Yahia Lemmouchi

Laboratoire de spectrochimie infrarouge et Raman, CNRS UPR 2631 L Bat. C5, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France (Received: May 27, 1992)

The Raman spectra of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_n\text{P}(\text{O})\text{Cl}_2$ and $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_n\text{PCl}_3]^+\text{PCl}_6^-$ ($n = 1, 2$) were recorded in the solid and liquid states at different temperatures. The qualitative depolarization ratios were obtained in the liquid phase. A ^{31}P NMR study for the molecular compounds showed a coalescence phenomenon near 220 K. The potential energy around the PN bonds for the $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ molecule and $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3]^+$ cation are derived from MNDO (modified neglect of diatomic overlap) calculations. The stable conformations are found to be trans-cis for $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ and $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3]^+$. The calculated structural parameters agree well with the X-ray experimental data. The frequencies obtained by normal coordinate analysis are in good agreement with the observed ones. The MNDO calculation of the harmonic force field is in reasonable agreement with the experimental values. The force constant values assigned to torsional modes around the PN bonds correspond to low barriers for the internal rotations. The easy internal rotation around the P—N and P=N bonds can explain the flexibility of the phosphazene backbone and the elastomeric properties of the phosphazene polymers.

Introduction

Polyphosphazenes represent a new class of inorganic polymers; they are characterized by a backbone of alternating phosphorus and nitrogen atoms with organic groups (R) attached to the phosphorus ($-\text{P}(\text{R})_2=\text{N}-$). Polyphosphazenes are unusual in polymer chemistry inasmuch various polymers are derived from a single polymeric intermediate, the polydichlorophosphazene, $(-\text{PCl}_2=\text{N}-)_n$.¹⁻⁹ Depending on the choice of substituents (R), the polymers have a wide range of properties⁸⁻¹⁵ and applications.¹⁶⁻²⁰ Some are elastomeric at room temperature. These elastomeric properties are in relation to the flexibility of the phosphazene backbones.^{10,14,15} Energy calculations based on molecular mechanics^{21,22} and semiempirical methods²³⁻²⁶ have been used in order to probe conformational preferences and chain flexibilities. Recently, experimental and theoretical conformational informations concerning the chloromonophosphazene compounds have been reported.²⁷

The vibrational spectroscopies, infrared and Raman, are efficient tools to study conformations in all phases. A lot of publications concern the investigations of the vibrational spectra and assignment of cyclic trimeric^{28,29} and tetrameric^{30,31} chlorophosphazenes, using normal coordinate analyses. The force fields of the cyclic compounds have also been transferred to the polydichlorophosphazene.³² This approach is only partially valid because in a cyclic molecule constraints affect bond angles and bond lengths.³³⁻³⁷ In a new approach to the problem, we have recently reported the Raman spectroscopic study and the normal coordinate analysis of chloromonophosphazenes $\text{Cl}_3\text{PNP}(\text{X})\text{Cl}_2$ ($\text{X} = \text{O}, \text{S}$) and $[\text{Cl}_3\text{PNPCl}_3][\text{Y}]$ ($\text{Y} = \text{Cl}, \text{PCl}_6$).²⁷

In this paper we use the MNDO method to examine the ground-state structures and vibrations of the following linear chlorodiphosphazene and triphosphazene compounds: $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_n\text{P}(\text{O})\text{Cl}_2$ ($n = 1, 2$) and $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_n\text{PCl}_3][\text{PCl}_6^-]$ ($n = 1, 2$). The Raman spectra of the linear-chain chlorophosphazenes are recorded in the liquid and solid states; the vibrational assignment is performed with the help of a force field derived from the normal coordinate analysis of the chloromonophosphazene compounds. The results are discussed under consideration of the ^{31}P NMR and X-ray diffraction data.^{36,37}

Experimental Section

Syntheses. $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{PCl}_3][\text{PCl}_6^-]$ (1) was synthesized by thermal treatment of $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ and $[\text{Cl}_3\text{PNPCl}_3][\text{PCl}_6^-]$,³⁸ which are both prepared by the procedure of Seglin.³⁹

$\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ (2) was prepared according to the method previously described by Riesel.⁴⁰

$[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3][\text{PCl}_6^-]$ (3) was prepared according to the procedure previously reported by Moran.⁴¹

$\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{P}(\text{O})\text{Cl}_2$ (4) was synthesized by reaction of $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ with $\text{HN}[\text{Si}(\text{CH}_3)_3]_2$ followed by treatment with $[\text{Cl}_3\text{PNPCl}_3][\text{Cl}]$ according to a home procedure.³⁸

The elementary analyses (P, N, Cl) of the compounds were in good agreement with the calculated values. All the compounds were carefully purified using distillation or vacuum sublimation or washed with anhydrous solvents to obtain good-quality Raman spectra. The samples were introduced into glass capillaries in a glovebox and sealed off under argon.

Raman Measurements. The Raman spectra were recorded by using the dispersive technique on a Dilor RTI triple-monochromator spectrometer at different temperatures between 77 and 340 K with liquid or solid samples. The instrument is equipped to accumulate spectra. The Raman scattering was excited using argon laser lines (457.9, 488.0, 514.5 nm) with a power of 100–200 mW. The slit widths were typically 4 and 1.5 cm^{-1} for the liquid and solid samples, respectively. Sloping background in the Raman spectra was not corrected.

^{31}P NMR Measurements. ^{31}P NMR spectra were recorded with a Bruker WP400 spectrometer operating in the Fourier transform mode at 162 MHz. Chemical shifts were referred to external 85% H_3PO_4 .

Methods. The semiempirical calculations for the compounds under study (geometry optimizations, conformational analyses, and harmonic force fields) were performed with the MNDO option of the MOPAC package⁴² adapted to run on a Cyber 962.32 computer. The normal coordinate treatment used the SPSIM package,⁴³ which is a modified version of Shimanouchi's original programs.⁴⁴

Results and Discussion

Structural and Ground-State Properties. The molecular structures of some linear short-chain phosphazene oligomers have previously been determined by X-ray measurements³⁶ in the solid state where the molecular geometry of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ (2) is stabilized in a conformation close to the cis-trans arrangement, whereas the geometry of the $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3]^+$ cation of compound 3 is close to the all trans form. In order to obtain a quantitative description of the structures and dynamics of the isolated molecule 2 and cation 3, we performed the optimization of the geometries.

On the way to the polydichlorophosphazene $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ (2) is the first compound showing a $-\text{PCl}_2-$ group. Two planar conformations of the phosphazene skeleton are possible. P=O being in trans position to the $\text{N}_2=\text{P}_3$ bond as found in $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$,²⁷ the $\text{N}_4=\text{P}_5$ bond can be either cis or trans to the $\text{N}_2=\text{P}_3$ bond; these structures will be termed trans-cis and trans-trans, respectively. Starting from the solid-state param-

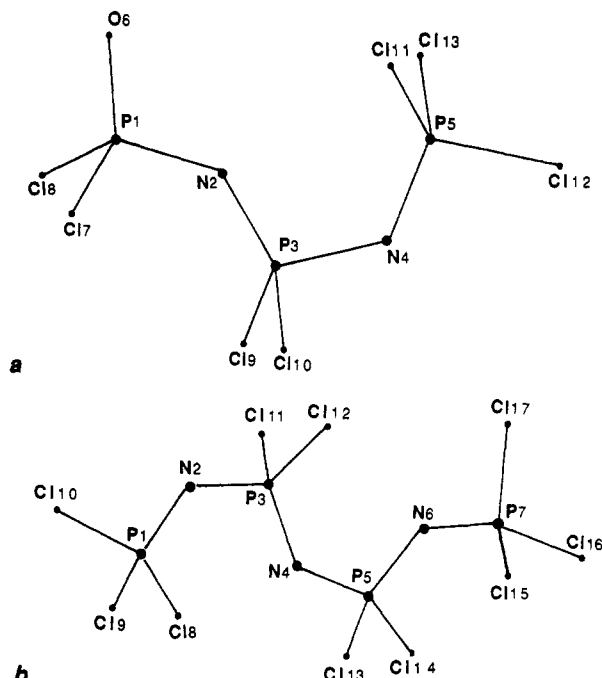


Figure 1. Molecular structures of the chlorophosphazene compounds with the corresponding atomic numbering schemes: (a) $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$; (b) $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3]^+$.

TABLE I: MNDO-Optimized Bond Lengths and Orders in the Conformers of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ (Lengths in angstroms)

bond	obs ^a	trans-trans		cis-trans	
		length	bond order	length	bond order
P ₁ -N ₂	1.546	1.626	0.92	1.615	0.94
N ₂ -P ₃	1.543	1.573	1.19	1.573	1.14
P ₃ -N ₄	1.537	1.629	0.99	1.633	0.98
N ₄ -P ₅	1.589	1.582	1.16	1.588	1.14
P ₁ -O ₆	1.456	1.480	1.45	1.480	1.44
P ₁ -Cl ₇	1.973	2.03	0.67	2.03	0.67
P ₁ -Cl ₈	1.989	2.03	0.67	2.03	0.67
P ₃ -Cl ₉	1.973	2.02	0.72	2.03	0.67
P ₃ -Cl ₁₀	1.989	2.02	0.72	2.03	0.67
P ₅ -Cl ₁₁	1.944	2.00	0.81	2.00	0.83
P ₅ -Cl ₁₂	1.966	2.00	0.92	2.01	0.92
P ₅ -Cl ₁₃	1.948	2.00	0.81	2.00	0.83
energy of formation, kJ/mol	-458 ^b	-474		-498	

^a Reference 36. ^b From MNDO calculation.

ters,³⁶ both conformers were optimized using MNDO calculations leading to the values listed in Table I. The energy of formation indicates that the trans-cis form is the most stable conformer as observed in the solid state. Starting from nearly equal PN bonds, the optimization process leads to two sorts of bonds: "double bonds" (between 1.573 and 1.588 Å) and "single bonds" (between 1.615 and 1.589 Å). The corresponding bond orders are in the range 1.14-1.19 and 0.92-0.99, respectively. Most of the calculated structural parameters listed in Table I are in reasonable agreement with the observed ones.³⁶ Nevertheless, the MNDO calculations lead to an overestimation of the bond distances, particularly of the PN bond lengths, but are in good agreement with earlier MNDO calculations concerning the shorter analog $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$.²⁷

Finally, the pathway from trans-cis to trans-trans conformation was studied in steps of 30° with relaxation of the structure at each step. It turns out that the trans-trans conformation is at the top of the barrier, so that an energy of 24 kJ/mol is necessary for the rotation around the P₃-N₄ bond (change of conformation), Figure 2. For the $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ compound, the trans-trans conformation is not a stable form, but only a transient state. The potential surfaces concerning the internal rotations

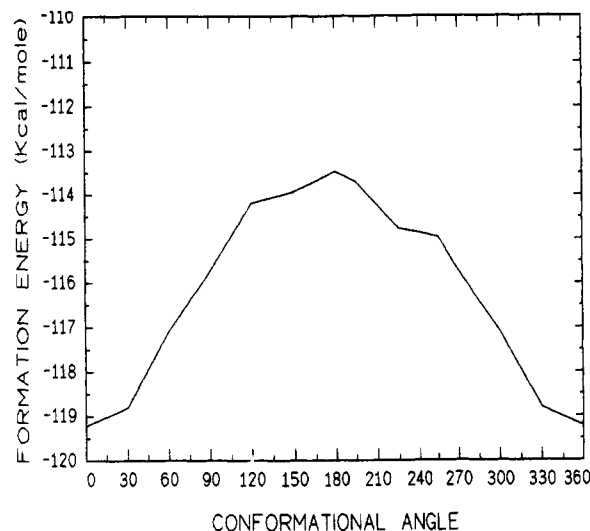


Figure 2. Relative energy as a function of the dihedral N₂P₃N₄P₅ angle of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$.

TABLE II: MNDO-Optimized Bond Lengths and Orders in the Conformers of $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{PCl}_3]^+$ (Lengths in angstroms)

bond	obs ^a	trans-trans		cis-trans	
		length	bond order	length	bond order
P ₁ -N ₂	1.498	1.603	1.09	1.588	1.11
N ₂ -P ₃	1.572	1.622	1.04	1.611	1.00
P ₃ -N ₄	1.527	1.616	1.07	1.605	1.06
N ₄ -P ₅	1.527	1.616	1.07	1.604	1.04
P ₅ -N ₆	1.572	1.622	1.04	1.614	1.02
N ₆ -P ₇	1.498	1.603	1.09	1.599	1.10
P ₁ -Cl ₈	1.93	2.00	0.84	2.00	0.85
P ₁ -Cl ₁₀	1.95	2.00	0.84	2.00	0.94 ^b
P ₃ -Cl ₁₁	1.97	2.01	0.77	2.00	0.82

energy of formation, kJ/mol

+236

+212

^a Reference 36.

of the $-\text{P}(\text{O})\text{Cl}_2$ and $=\text{PCl}_3$ groups were not studied in the present work. However, recently the corresponding potential surfaces have carefully been reported for the shorter $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ molecule and the energy barriers were found to be low.²⁷ Taking into account the analogy in structural and electronic properties of both molecules, the internal rotations around the P₁-N₂ and N₄-P₅ bonds are assumed to be faster than the rotational motion around the P₃-N₄ bond.

The $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3]^+$ cation of the $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3][\text{PCl}_6]^-$ (3) compound was treated by the MNDO method in a similar way. This longer oligomer could provide a more realistic model of the polymeric chain if the electrostatic forces are not too important. The molecular conformation was previously reported to be the all trans arrangement in the solid state from X-ray determination.³⁶ For this longer chain it was interesting to test the difference of energy between the two most probable conformations, all trans and cis-trans, Figure 1.

The data in Table II demonstrate that, under the assumption of an isolated ion, the cis-trans conformation is less instable in opposition to the solid-state structure. Obviously the intermolecular forces, most probably the electrostatic ones, are responsible for the stabilization of the all trans form in the solid state. All other structural parameters (bond lengths and angles) are in reasonable agreement with the experimental values in the solid state. The MNDO calculations lead again to an overestimation of the bond distances, particularly of the PN bond lengths. A consequence of these first results is that concerning the energy the molecular derivatives should be better models for the polymeric chain than the ionic substances which do not lead to the correct conformation.

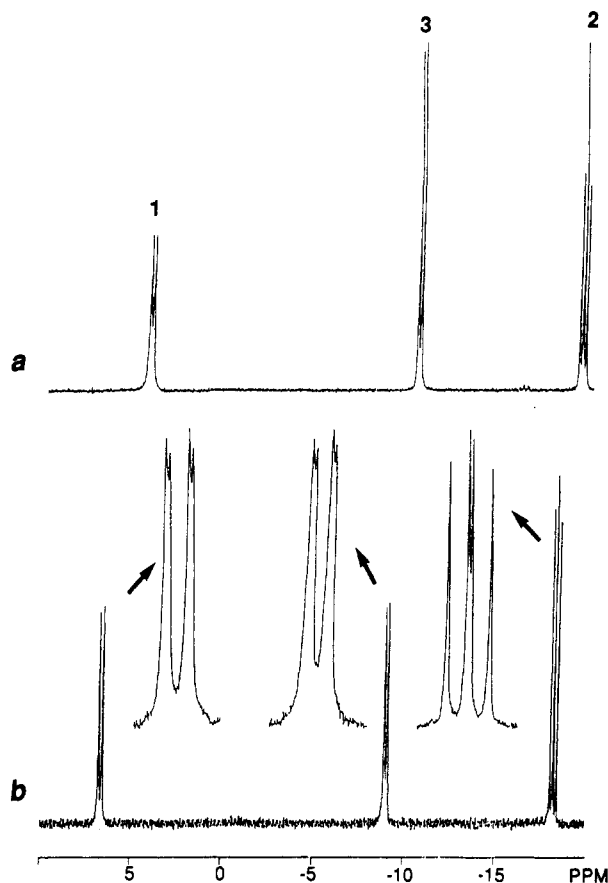


Figure 3. ^{31}P NMR spectra of $\text{Cl}_3\text{P}^1\text{NP}^2\text{Cl}_2\text{NP}^3(\text{O})\text{Cl}_2$ in CDCl_3 : (a) at 298 K; (b) at 220 K.

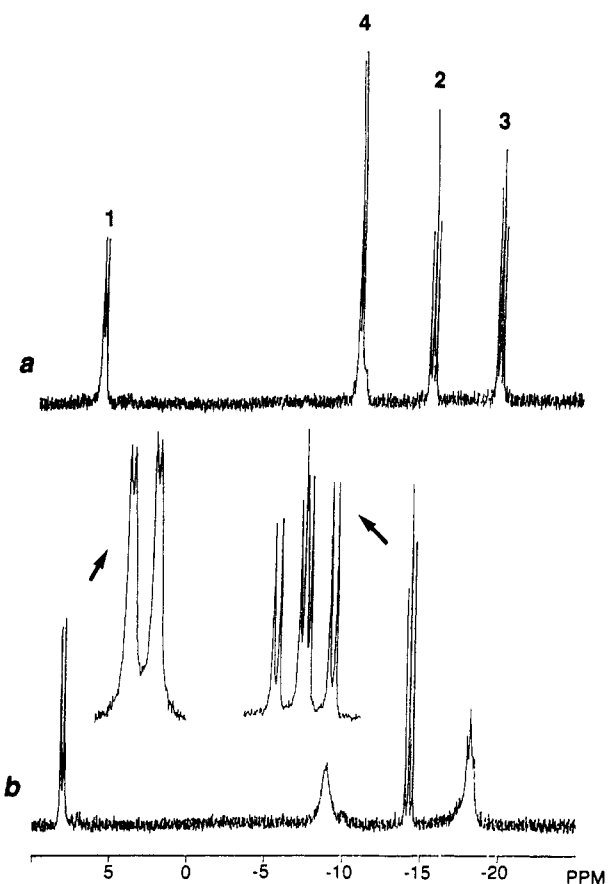


Figure 4. ^{31}P NMR spectra of $\text{Cl}_3\text{P}^1\text{NP}^2\text{Cl}_2\text{NP}^3\text{Cl}_2\text{NP}^4(\text{O})\text{Cl}_2$ in CDCl_3 : (a) at 298 K; (b) at 220 K.

^{31}P NMR Spectroscopy. The ^{31}P NMR spectra are important because they provide information about the bond flexibility and

TABLE III: Observed Raman and Calculated Frequencies and Vibrational Assignments for $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ ^a

observed	cryst (77 K)	melt (340 K)	calculated		potential energy distribution
			MNDO	NCA	
1323		1375	1294	1336	49 PO, 34 P=N
			1273	1276	54 PN, 31 PO
1237		1255	1290	1255	72 P=N
846			776	830	60 P—N, 34 bending
770		760	748	777	37 P—N, 40 bending
632		630	662	595	36 PCl, 26 NPCl
574			655	579	44 PCl, 44 NPCl
546			636	555	56 PCl, 35 NPCl
523		530	597	542	51 PCl, 25 NPCl
491		509	568	514	71 PCl
473		471	538	487	43 PCl, 22 NPCl
441		458	499	463	56 PCl
409		418	468	429	59 NPCl
379		379	354	412	49 NPCl, 34 PCl
355		355	338	379	57 PCl, 37 NPCl
314		319	297	302	31 PCl, 26 OPCI, 25 NPCl
268		286	290	297	67 OPCI, 31 PCl
249			263	283	27 NPCl, 27 OPCI, 26 PCl
237		235	232	244	29 ClPCI, 27 OPN, 23 PCl
224		222	200	222	59 ClPCI, 25 PCl
201		194	191	207	76 ClPCI, 25 PCl
			188	206	81 ClPCI, 21 NPCl
			163	199	52 ClPCI, 21 NPCl
187			150	183	65 NPCl
175		164	137	162	72 NPCl
160		152	118	157	63 NPCl
154			116	148	59 NPCl
n.o.	n.o.		90	90	51 PNP, 36 NPCl
n.o.	n.o.		65	57	22 PNP, 38 $\tau(\text{P}=\text{N})$
n.o.	n.o.		41	41	32 PNP, 28 $\tau(\text{P}=\text{N})$
n.o.	n.o.		30	32	47 $\tau(\text{P}-\text{N})$, 44 $\tau(\text{P}=\text{N})$
n.o.	n.o.		14	11	53 $\tau(\text{P}=\text{N})$, 35 $\tau(\text{P}-\text{N})$
n.o.	n.o.		-8 ^b	9	$\tau(\text{P}-\text{N})$ central

^a Only participations greater than 20% are included; NCA represents the results of normal coordinate analyses for the molecule assumed to have the structure observed in the solid state. n.o., not observed.
^b Imaginary value (see text).

the effect of the chain length and of the end groups on the structure of the backbone. The phosphorus atoms yielded different sets of resonance which depend on the spin-spin couplings. The $\text{P}(\text{O})\text{Cl}_2$ end groups of the $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ (2) and $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{P}(\text{O})\text{Cl}_2$ (4) molecules yielded a doublet of doublets around -12 ppm, whereas the PCl_3 end groups yielded a doublet of doublets immediately downfield from $\text{P}(\text{O})\text{Cl}_2$ (Figures 3 and 4).

Previous ^{31}P NMR spectra of linear phosphorylchlorophosphazenes do not indicate any rotational isomers in the temperature range 183–413 K.⁴⁵ With our experimental conditions the ^{31}P NMR spectrum of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{P}(\text{O})\text{Cl}_2$ (4) recorded at 223 K in $\text{CDCl}_3\text{-CHCl}_3$ mixture clearly exhibits the broadening of the two sets of resonance previously assigned to the $-\text{P}(\text{O})\text{Cl}_2$ and the nearest-neighbor $-\text{PCl}_2-$ groups. In addition, the ^{31}P NMR spectra of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ and $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ recorded in the same experimental conditions do not exhibit this behavior. Upon cooling no significant change, except some sharpening of the signals, is observed between 220 and 300 K. Because the cooling of the sample below 220 K induces the solidification of the solution, the coalescence phenomenon is not well established for the short molecules. However, it is tempting to attribute the broadening of the two sets of resonance to the hindered internal rotation around the $-\text{P}(\text{O})\text{Cl}_2$ bond. The internal rotation around the $=\text{PCl}_3$ bond remains too fast at 220 K to induce coalescence phenomena in the ^{31}P NMR spectra of all the linear phosphorylchlorophosphazenes under study. It should be noted that the calculated energy barriers (Tables I and II) corresponding to the isomerization cis-trans to all trans are too high to lead to a facile rotation around the $\text{PCl}_2\text{-N}$ bonds in the chain. Consequently in the time scale of the NMR the linear phosphazene backbone can be considered as rigid except for the two end groups. The temperature dependence of the ^{31}P NMR resonances cor-

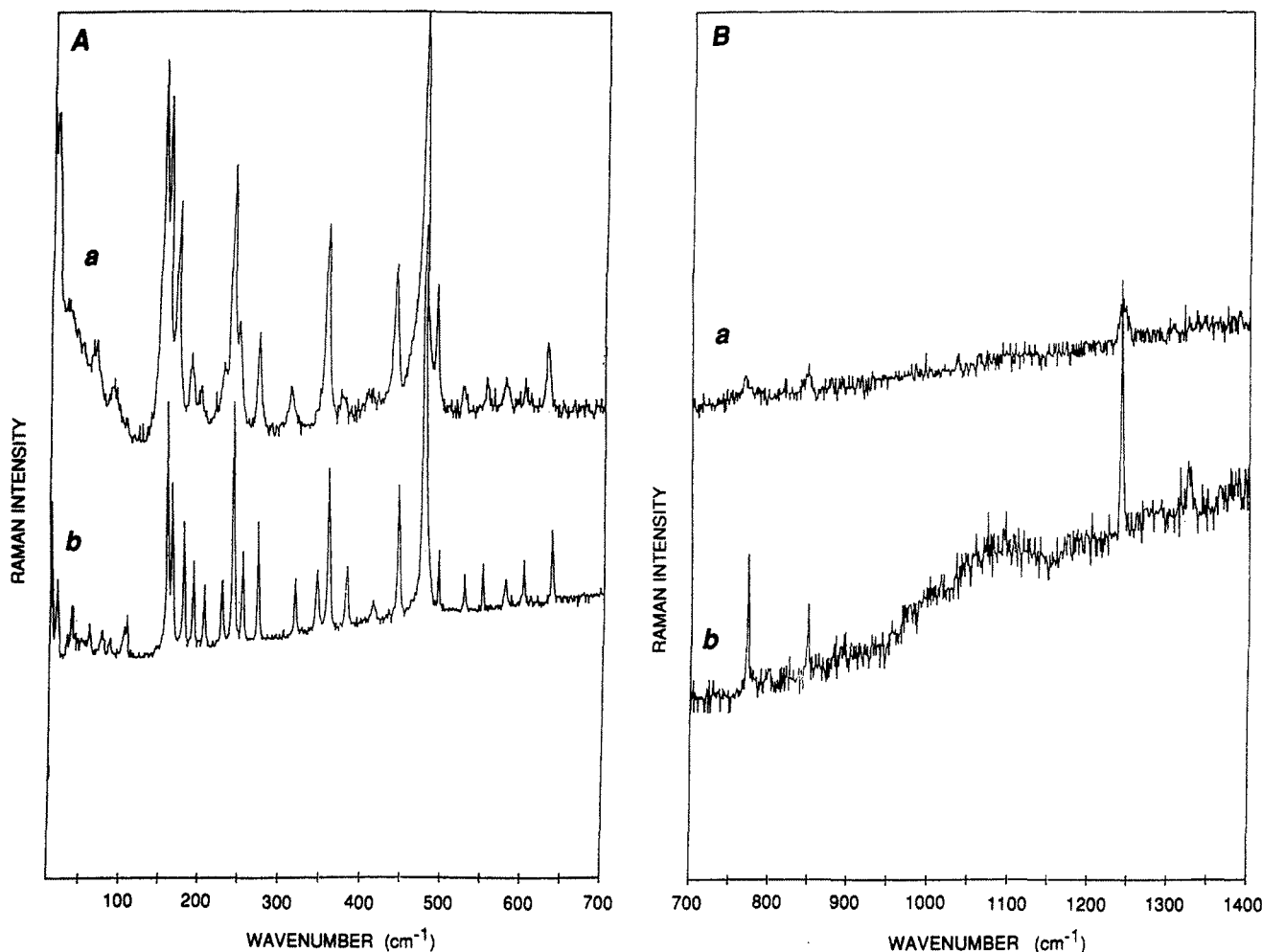


Figure 5. Raman spectra of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ in (A) high wavenumber range and (B) low wavenumber range: (a) in the solid state at 300 K; (b) in the solid state at 77 K (exciting radiation 457.9 nm).

responding to the end groups $-\text{P}(\text{O})\text{Cl}_2$ and $=\text{PCl}_3$ are in good agreement with the low energy barrier values calculated by the MNDO method for the shorter phosphorylchlorophosphazene molecules.

Raman Spectroscopy. Raman spectroscopy was used to obtain experimental information about the vibration frequencies, the structural properties, and the conformational properties of the linear chlorophosphazenes in the solid state as well as in the liquid phase.

According to the MNDO calculations the most energetically probable conformation of the $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ isolated molecule is the planar trans-cis form. The 33 normal modes of vibration are distributed between the two symmetry species of the C_s point group: $20A' + 13A''$; all these species are both Raman and infrared active. The A' modes are in plane vibrations and yield polarized Raman lines ($I_{\parallel}/I_{\perp} < 0.75$) whereas A'' modes are out of plane vibrations and should give rise to depolarized Raman lines ($I_{\parallel}/I_{\perp} = 0.75$). The compound $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ crystallizes in the triclinic system with two molecules per unit cell.³⁶ According to the factor group analysis the following internal vibrational modes are expected in the solid state: $33 A_g + 33 A_u$; only the g (gerade) modes are Raman active.

The study of the polarization of the Raman scattering points out that at least 6 Raman bands with depolarization ratio (I_{\parallel}/I_{\perp}) near 0.75 are detected among the 16 observed bands. This result is in good agreement with a C_s or pseudo- C_s molecular point group corresponding to a planar phosphorylphosphazene backbone of the isolated molecule. No supplementary bands due to rotamers are detected in the spectra of the melt. This indicates that either only one conformer is stable or the spectral differences between conformers are too small to be observed. As for $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ such conformers could be assumed for the rotation of the POCl_2 end group. The Raman spectrum of $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$,

recorded in the solid state, is analogous to that of the melt. However, the Raman bands are better resolved, particularly at low temperature (Figure 5).

In order to obtain a more accurate description of the fundamental vibrations a normal coordinate analysis was undertaken (see below). Analogous experimental results were obtained for the $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{P}(\text{O})\text{Cl}_2$ analog in the fused and solid states. The most striking analogy among all the linear phosphorylchlorophosphazenes under study is the planar arrangement of the skeleton of the molecules in the liquid and solid phases.

The poor solubility of the ionic compounds $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2][\text{PCl}_6]$ (1) and $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{P}(\text{O})\text{Cl}_2][\text{PCl}_6]$ (3) does not give the opportunity to obtain good-quality Raman spectra in solution. However, from the polarization measurements a planar backbone of the cations has been found in solution. This conformation was also found in the solid state, as previously demonstrated by X-ray determination.³⁶ The compound crystallizes in the quadratic system with four molecules per unit cell. However, the effects of the crystal field are very weak, and at room temperature the Raman spectrum exhibits only the characteristics of both cation and anion (Figure 6).

The Raman spectra of the ionic compounds show the general trends of the linear-chain chlorophosphazene molecules, but we are unable to assign the weak changes observed between the molecular and ionic compounds to the conformational changes only. Indeed, the electrostatic effects and the intermolecular couplings can induce analogous changes.

Force Field and Vibrational Assignment. Theoretical harmonic frequencies for trans-cis- $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ from MNDO calculations are listed in Table III and compared with the observed fundamental frequencies. The calculated values are in reasonable agreement with the observed Raman bands in the liquid and solid phases, though relatively large differences are found for some of

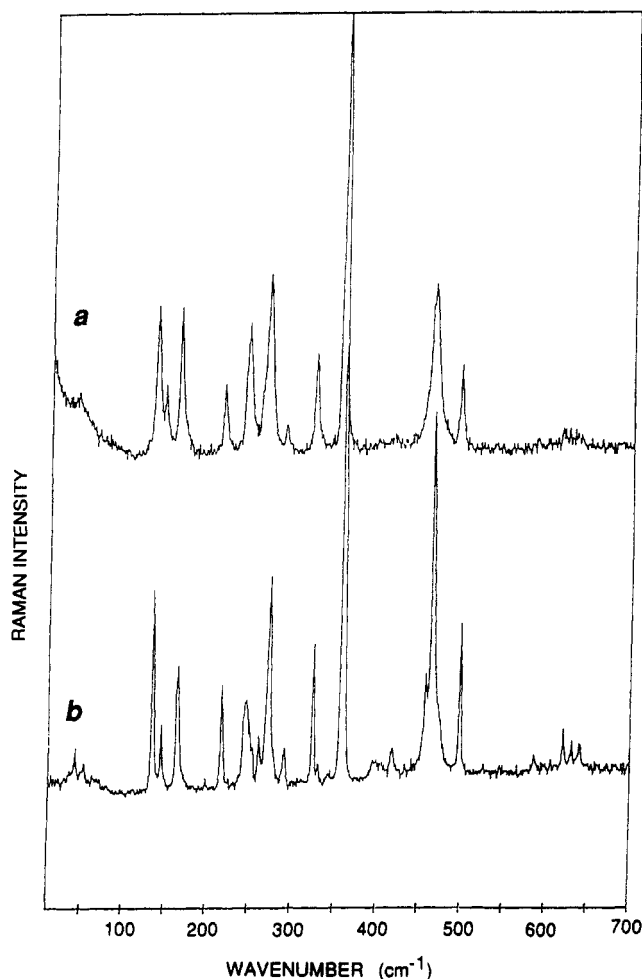


Figure 6. Raman spectra of $[\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})_2\text{PCl}_3][\text{PCl}_6]$: (a) in the solid state at 300 K; (b) in the solid state at 77 K (exciting radiation) 457.9 nm).

the vibrations, particularly the stretching modes involving the N, P, and O atoms. In addition, it should be noted that the last frequency corresponding to a torsional motion of the phosphazene skeleton is imaginary. This fact is caused by an insufficient optimization of the structure at the very flat bottom of the potential hypersurface. This observation confirms the fact that the theoretical treatment of the PN bonds is at the limit of applicability of the MNDO method.

In order to ascertain this result, a classical normal coordinate analysis of the vibrational modes of the *trans-cis*- $\text{Cl}_3\text{PN}(\text{PCl}_2\text{N})\text{P}(\text{O})\text{Cl}_2$ isolated molecule was performed. Further, the results of these calculations should help to better characterize the force field of the linear-chain phosphazenes. The calculations were carried out by the Wilson GF matrix method, and the structural parameters were taken from the X-ray data.³⁶ The observed and calculated frequencies along with approximate potential energy distributions are reported in Table III. By transferring the force field previously obtained for the shorter analogs, an average error of 10 cm^{-1} was obtained. Light modification of the force field and addition of more interaction force constants would probably improve the frequency fit, but it would not significantly increase the physical meaning of the information already acquired. In general, the mixing of internal coordinates in the A' normal modes is more extensive than the one found for the A'' modes. As expected, considerable mixing is found among the $\text{P}=\text{O}$, $\text{P}=\text{N}$, and $\text{P}-\text{N}$ stretches and the PNP and NPN bending modes. The force constants compare well with literature data concerning compounds with analogous functional groups. The main differences concern the PN bonds and are in good agreement with the structural and electronic differences exhibited by the linear-chain chlorophosphazene under study and the cyclic oligomers used as references.

Conclusions

The conformational and vibrational properties of linear-chain chlorodiphosphazene and chlorotriphosphazene compounds in their ground state have been analyzed in detail by the MNDO method, normal coordinate analysis, and ^{31}P NMR and Raman spectroscopies at variable temperature. The more stable conformation was found to be the planar *trans-cis* arrangement. This fact is in contradiction to the crystallographic results for the ionic derivatives for which we can therefore conclude that the all *trans* conformation is stabilized by the charges and intermolecular electrostatic forces. The energy barriers corresponding to the internal rotations around the P-N bonds of the backbone are relatively low (24 kJ/mol). The energy barriers to the internal rotation of the end groups $=\text{PCl}_3$ and $-\text{P}(\text{O})\text{Cl}_2$ remain very low but increase to a small extent with the length of the linear-chain chlorophosphazene molecule, as demonstrated by ^{31}P NMR spectroscopy. It turns out that the short linear molecular oligomers are better models for the polymeric chain than the cyclic oligomers or ionic derivatives. The highest mobility was found for the PCl_3 end group followed by the POCl_2 group and the chain P-N bond.

References and Notes

- (1) Allcock, H. R. *Phosphorous-Nitrogen Compounds*; Academic Press: New York, 1972.
- (2) Stokes, N. S. *Am. Chem. J.* **1897**, *19*, 782.
- (3) Allcock, H. R.; Kugel, R. L. U.S. Patent 3370020, 1968.
- (4) Hornbaker, E. D.; Li, H. M. U.S. Patent 4198381, 1978.
- (5) De Jaeger, R.; Heloui, M.; Puskaric, E. Fr. Patent 2466435, 1981.
- (6) Heloui, M.; De Jaeger, R.; Puskaric, E.; Heubel, J. *Macromol. Chem.* **1982**, *183*, 113.
- (7) Abouchakra, T.; De Jaeger, R. Fr. Patent 2548652, 1985.
- (8) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
- (9) Allcock, H. R.; Kugel, R. L.; Valant, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
- (10) Allcock, H. R.; Connolly, M. S.; Sisko, J. T.; Al-Shall, S. *Macromolecules* **1988**, *21*, 223.
- (11) Thompson, J. E.; Sicka, R. W. U.S. Patent 3994838, 1976.
- (12) Vicio, J. C.; Reynard, K. A. *J. Appl. Polym. Sci.* **1971**, *21*, 3185.
- (13) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S. *Polym. News* **1978**, *5*, 1709.
- (14) Edwards, A. H. D.; Zitomer, F.; Sietz, D.; Singler, R. E.; Macaine, D. *Org. Coat. Prep.* **1976**, *36*, 737.
- (15) Allcock, H. R.; Mang, M. N.; Dembeck, A. A. *Macromolecules* **1989**, *22*, 4179.
- (16) Wade, C. W. R.; Gourlay, S.; Rice, R.; Heggli, A.; Singler, R. E.; White, J. *Organometallic Polymers*; Academic Press: New York, 1978; p 283.
- (17) Chattopadhyay, A. K.; Hinrichs, R. L.; Rose, S. H. *J. Coat. Technol.* **1979**, *51*, 87.
- (18) Suzuki, F.; Onozoto, K.; Yaegashi, H.; Masuko, T. *J. Appl. Polym.* **1987**, *34*, 2197.
- (19) Gettleman, G. L.; Vargo, J. M.; Gebert, P. H.; Farris, I. L.; Leboeuf, R. J.; Rawis, R. H. *Polym. Sci. Technol.* **1987**, *35*, 55.
- (20) Singler, R. E.; Willingham, R. A.; Friedrich, C.; Bosio, L.; Atkins, C. D. T.; Lenz, R. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, 491.
- (21) Allcock, H. R.; Allen, R. W.; Meister, J. J. *Macromolecules* **1976**, *9*, 950.
- (22) Allen, R. W.; Allcock, H. R. *Macromolecules* **1976**, *9*, 996.
- (23) Tanaka, K.; Yamashita, S.; Yamabe, T. *Macromolecules* **1986**, *19*, 2062.
- (24) Saiz, E. J. *Polym. Sci. Part B: Polym. Phys.* **1987**, *25*, 1565.
- (25) Uzaki, S.; Adachi, K.; Kotaka, T. *Macromolecules* **1989**, *21*, 153.
- (26) Aoki, Y.; Watanabe, F.; Imanurra, A. *J. Mol. Struct. (Theochem)* **1989**, *188*, 321.
- (27) Bougeard, D.; Brémard, C.; De Jaeger, R.; Lemmouchi, Y. *Spectrochim. Acta*, in press.
- (28) Huvenne, J. P.; Vergoten, G.; Legrand, P. *J. Mol. Struct.* **1980**, *63*, 47.
- (29) Painter, P. C.; Zarian, J.; Coleman, M. M. *Appl. Spectrosc.* **1982**, *36*, 265.
- (30) Zarian, J.; Painter, P. C.; Coleman, M. M. *Appl. Spectrosc.* **1982**, *36*, 272.
- (31) Varma, V.; Fernandes, J. R.; Rao, C. N. R. *J. Mol. Struct.* **1989**, *189*, 403.
- (32) Coleman, M. M.; Zarian, J.; Painter, P. C. *Appl. Spectrosc.* **1982**, *37*, 277.
- (33) Bullen, G. J. *J. Chem. Soc. A* **1971**, 1450.
- (34) Boyd, R. H.; Kensler, L. J. *Am. Chem. Soc.* **1977**, *99*, 4248.
- (35) Faggiani, R.; Gillespie, R. J.; Sawyer, J. P.; Tyrer, J. D. *Acta Crystallogr.* **1980**, *B36*, 1014.
- (36) Allcock, H. R.; Tollefson, N. M.; Arcus, R. A.; Whittle, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5165.
- (37) Chatani, Y.; Yatsuyamagi, K. *Macromolecules* **1987**, *20*, 1042.
- (38) Lemmouchi, Y. Thesis, Université des Sciences et Technologies de Lille, France, 1991.

- (39) Seglin, L.; Lutz, M. R.; Stauze, H. U.S. Patent 3231327, 1966.
 (40) Riesel, L.; Somieski, R. Z. *Anorg. Allg. Chem.* **1975**, *411*, 148.
 (41) Moran, E. F. J. *Inorg. Nucl. Chem.* **1968**, *30*, 1405.
 (42) Stewart, J. J. P. MOPAC Vers. 5. *QCPE* **1989**, 581.
 (43) Fischer, P.; Bougeard, D.; Schrader, B. In *Software-Entwicklung in der Chemie*; Gauglitz, Ed.; Springer-Verlag: Heidelberg, 1989.
 (44) Shimanouchi, T. *Computer programs for the normal coordinate treatment of polyatomic molecules*; University of Tokyo: Tokyo, 1968.
 (45) Schelling, G.; Rabanar, C. W.; Lehr, W. Z. *Naturforsch.* **1982**, *37B*, 38.
 (46) Durig, J. R.; James, G.; Hizer, T. J. J. *Raman Spectrosc.* **1990**, *21*, 155.

Electron Capture of Dopants in Two-Photonic Ionization in a Poly(methyl methacrylate) Solid

Akira Tsuchida, Wataru Sakai, Mitsuru Nakano, and Masahide Yamamoto*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan (Received: November 4, 1991; In Final Form: June 5, 1992)

Behavior of the electron produced by two-photon excitation of an aromatic donor in a poly(methyl methacrylate) solid was studied by the addition of the electron scavengers to the system. According to the Perrin type analysis for the two-photonically ejected electron, the capture radii (R_c) of the scavengers examined were estimated to be from 8 to 40 Å. For the two-photonically ejected electrons, R_c is a capture radius for thermalized electrons. In this case the parent electron donor is not necessarily within this radius. On the other hand, for the fluorescence quenching, the distance between the donor and acceptor is within the static quenching radius (R_q) of the donor.

Introduction

Two-photon excitation of an aromatic dopant in a polymer solid results in the release of an electron to the polymer matrices. We have already reported the two-photon excitation of aromatic dopants and the resulting photochromic properties of the produced radical cations.¹ Intense laser pulse excitation of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) doped in poly(methyl methacrylate) (PMMA) develops a deep blue color in the sample instantaneously. This blue color is caused by the radical cation formation of TMPD (TMPD^{•+}) in PMMA. The produced TMPD^{•+} is very stable as the ejected electron is trapped in the polymer matrix as an anionic species of the polymer. Though the color may fade by the recombination of the TMPD^{•+} with the electron in the polymer, the color lasts long and can be seen even after a year's storage at room temperature. Thus far, many combinations of chromophore and polymer have been examined, and the polymers having some electron-accepting groups, such as carbonyl or ester group, were found to form the stable chromophore radical cations.^{1c}

In most studies for the ionization in polymers, the γ -ray or electron beam has been used as a radiation source.² These radiations have high energies, on the order of megaelectronvolts, and the energy is initially absorbed by the polymer matrix itself. Then, succeeding processes such as secondary electron generation, energy transfer, and charge transfer take place.³ In such a condition the final electron distribution around the parent hole was reported as an exponential or center-Gaussian type.^{4,5} The capture radii of TMPD triplet and positive ions by TMPD itself in PMMA solid were estimated as ca. 25 Å by using pulse radiolysis.⁶ On the other hand, the two-photon energy for ¹TMPD* or ³TMPD* excited by 351-nm light is 6.9 or 6.4 eV, respectively.^{1c} The ionization potential of TMPD is ca. 5.9 eV,⁷ and hence the initial kinetic energy of the ejected electron is estimated as ca. 0.5–1.0 eV. This low-excess-energy electron gives a far-Gaussian type distribution,^{1c} and such an ionization process makes it possible to estimate the electron-capture radii of scavengers. In this study, the meaning of the capture radii is discussed and the two-step capturing mechanism of the two-photonically ejected electron is shown.

Experimental Section

Chemicals. Methyl methacrylate (MMA, Wako Pure Chem. Ind., Ltd.) monomer was initially washed with an aqueous 5%

NaOH solution and then dried by Na₂SO₄ for 2 days. MMA was purified by distillation under reduced pressure with care taken to eliminate the remaining water as the azeotrope. TMPD (Aldrich Chem., Inc.), 1,3- and 1,4-dicyanobenzene (*m*- and *p*-DCNB, Wako), and dimethyl terephthalate (DMTP, Wako) were purified by recrystallization several times. Methyl benzoate (MBA, Wako) was purified two times by distillation under reduced pressure. 1,2,4,5-Tetracyanobenzene (TCNB) was synthesized from pyromellitic dianhydride⁸ and was purified by recrystallization three times.

Polymer Sample Preparation. Polymer samples for measurements were prepared by the bulk polymerization of MMA.¹ TMPD (1.2×10^{-4} M) and an appropriate amount of acceptors was dissolved in MMA with 2,2'-azobisisobutyronitrile (5×10^{-4} M) as an initiator. The solution was degassed and was polymerized in a Pyrex cell ($3 \times 1 \times 1$ cm) for 10 h at 333 K, then 10 h at 343 K, and finally 10 h at 393 K. The concentration increase of dopants due to the shrinkage upon polymerization ($\times 0.82$) was corrected,² and the thermostability of the chromophore during polymerization was checked by the absorption and emission spectra. All polymer samples used for the measurements were colorless, although at a very high acceptor concentration the sample showed white turbidity after the polymerization. No evidence of the ground-state interaction of TMPD with acceptors in the polymer could be found by the spectroscopic examinations. Probably the low concentration of TMPD (1.2×10^{-4} M) and the solidification of the matrix at a high polymerization temperature (393 K) prevented the aggregation or complex formation of the added chromophores.

Measurements of Fluorescence Quenching. Static fluorescence quenching of one-photonically excited TMPD in the PMMA matrix was measured by a spectrofluorophotometer (Hitachi, 850). Fluorescence spectra were obtained with a 2-nm slit width by the excitation of TMPD at 360-nm light (2-nm slit width) at 298 K.

Two-Photonic Excitation of Samples. Photoionization of TMPD in PMMA by the two-photon excitation was done by focused laser pulses emitted by an excimer laser (Lambda Physik, EMG101MSC). The XeF excimer laser light pulse (351 nm) had ca. 20-ns fwhm and ca. 60-mJ photon energy. The PMMA polymer matrix and dopant acceptors have no absorption at 351 nm, and the chromophore TMPD was selectively photoexcited. The photoexcitation of samples was carried out in a Dewar cell at 77 K: the decay of the radical ions produced by the recom-