binations and overtones) of a free pseudorotor can become very complicated.

Conclusions

We have carried out calculations to provide a descriptive picture of the energy level patterns expected for the ring-puckering vibrations of spiro compounds. Since the spectra of these molecules are expected to be complicated, it is necessary to have a basic understanding of how these levels will change as a function of the interaction between the two rings (i.e., the magnitude of the ccoefficient).

Since the vapor pressures of most spiro compounds are quite low, it is necessary in most cases to heat the samples in order to record their vapor-phase far-infrared spectra. We have constructed a special sample cell to do this and are initiating this work.

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for financial support. Dr. Lloyd F. Colegrove assisted with the preparation of the figures.

Registry No. SSH, 33317-66-7; CSC, 111769-82-5; silacyclobutane, 287-29-6.

Radical Cations of Bis(diphenylphosphino) Derivatives (Ph₂P-R-PPh₂): The Formation of Localized, Cyclic, and Dimeric Configurations. An ESR and Quantum Chemical Study

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

Laboratory of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands (Received: March 19, 1991)

A matrix ESR study on radiogenic radical cations of $Ph_2P-R-PPh_2$ derivatives with various linkers (R) is presented. The experiments show that in a frozen dichloromethane solution the radical cations can adopt localized (Ph2PR+), cyclic $(Ph_2P-R-PPh_2^{*+})$, and dimeric $(Ph_2RP-PRPh_2^{+})$ configurations, depending on the nature of the linker. The cyclic and dimeric products are formed in the reaction of a localized cation with a second free-electron pair, resulting in an intra- or intermolecular three-electron $P \perp P \sigma^*$ bond, respectively. The formation of the cyclic structure, with a strongly bent $P \perp P$ σ^* bond, requires a specific proximate position of the two phosphine moieties in the precursor molecule. The mutual orientation of the two free-electron pairs of the precursors is assessed by NMR via the "Jpp spin-spin coupling constant. Ab initio UHF quantum chemical calculations at the 3-21G*/SCF level support the assignments.

Introduction

During the last decade ESR spectroscopy has been successful in establishing and identifying the structure of numerous radical cations generated via X- or γ -irradiation of the parent substrate in a frozen dilute halocarbon solution at 77 K.^{1,2} As a result of the high ionization potential of the halocarbon, the substrate radical cations are effectively trapped in these frozen matrices. The following reaction scheme has been frequently invoked to explain the products in a CFCl₃ matrix:¹

> $CFCl_3 \rightarrow CFCl_3^{*+} + e^ CFCl_3 + e^- \rightarrow CFCl_3^{--}$ $CFCl_3 + CFCl_3^{\bullet+} \rightarrow CFCl_3^{\bullet+} + CFCl_3$ $CFCl_3^{++} + S \rightarrow CFCl_3 + \dot{S}^+$

By using dilute solutions, it has been possible to obtain the parent cations or their unimolecular decomposition products. It is well established that at higher concentrations cation-parent substrate dimerization occurs via the interaction of the singly occupied molecular orbital (SOMO) of the cation with a free-electron pair of the substrate. This results in a three-electron bond with the unpaired electron in a σ^* molecular orbital. In particular, Symons and co-workers have shown that in CFCl₃ γ -irradiated phosphines yield both parent $(R_3\dot{P}^+)$ and dimer $(R_3P\dot{-}PR_3^+)$ radical cations.³ Analogously, we recently established that in case two different substrates are present, mixed dimers can be formed.⁴ When diphosphines are irradiated in halocarbon solutions, the possibility exists that a phosphorus-centered radical cation reacts with the intact free-electron pair of the neighboring phosphine moiety. Such an intramolecular interaction of the SOMO results in a cyclic σ^* configuration. Accordingly, in a recent study on 1,2-bis(diphenylphosphino)ethane, Rhodes and Symons describe the parent localized cation Ph2PCH2CH2PPh2+ and an intramolecular reaction product, $Ph_2PCH_2CH_2PPh_2^{+}$. The latter possesses a cyclic σ^* structure and a bent P-P bond.⁵ Their evidence for the cyclic configuration is based on two facts. First, the spectral features of the dimer did not intensify relative to the signals of the localized cation on increasing the concentration, as would be required for a bimolecular reaction. Second, the $m_1 = \pm 1$ lines showed an unusual form exhibiting $A_{\perp} > A_{\parallel}$, which was elegantly interpreted by assuming a near-perpendicular orientation of the sp hybrids comprising the SOMO of the dimer. The postulated structure is depicted in Figure 1. A similar bent σ^* structure has previously been suggested for 1,4-dithiacyclohexane cations.⁶

Independently, we were investigating similar bis(diphenylphosphino) derivatives, $Ph_2P-R-PPh_2$, though with longer methylene linkers (R = (CH₂)_n, n = 4, 6). Our results obtained from frozen CH₂Cl₂ solutions, however, gave no evidence of an intramolecular reaction but revealed at higher concentrations besides localized cations (Ph_2PR^+) in fact intermolecular dimer products $(Ph_2RP - PRPh_2^+)$. In the present study we describe the results of X-irradiation experiments on several bis(diphenylphosphino) derivatives with various linkers. It will be shown that in principle intra- as well as intermolecular reactions can occur. The formation of the cyclic intramolecular reaction products requires a specific favorable orientation of the two phosphine moieties. In order to arrive at these conclusions we combine the ESR technique with several other methods. First, we use ESR

⁽¹⁾ Symons, M. C. R. Chem. Soc. Rev. 1984, 13, 393.

 ⁽¹⁾ Shiotani, M. Magn. Reson. Rev. 1987, 12, 333.
 (3) Hasegawa, A.; McConnachie, G. D.; Symons, M. C. R. J. Chem. Soc., Faraday Trans. 1 1984, 80, 1005.

⁽⁴⁾ Janssen, R. A. J.; Aagaard, O. M.; van der Woerd, M. J.; Buck, H. M. Chem. Phys. Lett. 1990, 171, 227.

⁽⁵⁾ Rhodes, C. J.; Symons, M. C. R. J. Chem. Soc., Chem. Commun. 1989, 1393.

⁽⁶⁾ Asmus, K. D.; Bahnemann, D.; Fisher, Ch.-H.; Veltwisch, D. J. Am. Chem. Soc. 1979, 101, 5322.

Radical Cations of Bis(diphenylphosphino)s



Figure 1. Schematic representation of the SOMO of the cyclic σ^* structure of Ph₂PCH₂CH₂PPh₂^{•+}.



Figure 2. Powder pattern simulations of a radical containing two identical ³¹P nuclei as a function of the angle θ between the two major axes of the ³¹P hyperfine tensors.

powder spectrum simulation to predict the spectra of specific cyclic and dimeric configurations. Second, the molecular conformation of the bis(diphenylphosphino) derivative is assessed via the nuclear spin-spin coupling $^{\prime\prime}J_{PP}$ or with X-ray structural data known from literature. Finally, quantum chemical calculations are employed to optimize the radical geometries and to calculate the hyperfine coupling constants.

Methods

Powder Pattern Simulation. The calculation of powder patterns for the simulation of ESR spectra of cyclic and dimeric radical cations, $R_3P \rightarrow PR_3^+$, was performed by using a computer program specifically tailored to the present spin system. As a result of the large hyperfine couplings of the two ³¹P nuclei, a pronounced second-order splitting of the central features is to be expected. In order to reproduce the spectra correctly, all terms of the spin Hamiltonian were treated exactly before full diagonalization. We have used the following Hamiltonian:

$$\mathcal{H} = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A}_1 \cdot \mathbf{I}_1 + \mathbf{S} \cdot \mathbf{A}_2 \cdot \mathbf{I}_2 - g_N \beta_N \mathbf{B} \cdot (\mathbf{I}_1 + \mathbf{I}_2)$$

The tensors g, A_1 , and A_2 are in principle rhombic and noncoincident. The electron spin S = 1/2, and the nuclear spins $I_1 = I_2 = 1/2$. The ³¹P g_N factor is taken isotropic. Figure 2 contains the simulated powder ESR spectra for a number of different mutual orientations of the A_1 and A_2 hyperfine tensors. The three principal values of A_1 and A_2 tensors were taken as identical, being 900, 900, and 1000 MHz, respectively. The g tensor was assumed to be isotropic ($g_{iso} = 2.00$). The angle θ is defined as the difference in orientation of the parallel components of A_1 and A_2 (Figure 3).

Before analysis of the results, it should be noted that under experimental conditions the central transitions are obscured by features of other radicals and the analysis is restricted to the lateral regions of the spectra. Figure 2 reveals that the simulated spectra can be divided into three different sets designated A-C. The first set, A, comprises the spectra for $\theta = 0-30^{\circ}$. The patterns belonging to set A are virtually identical. In an experiment it would



Figure 3. Definition of the angle θ used in the powder spectrum simulations.



Figure 4. Typical ¹³C NMR spectrum of the ortho carbon atom of *trans*-1,2-bis(diphenylphosphino)ethene. The spectral parameters D and N are indicated.

not be possible to attribute the slight decrease of the splitting between the parallel and perpendicular features unambiguously to either the increase of θ or a decrease of the difference between the parallel and perpendicular principal components of A_1 and A₂. The second set, B, ranging from $\theta = 40-80^{\circ}$, contains spectra that differ significantly from those of set A. For a hypothetical experimentally obtained powder ESR spectrum of type B, however, it would not be evident to assign the spectra to a nonalignment of two axially symmetric hyperfine tensors. Similar spectra, to those of set B, can also be expected for coincident rhombic hyperfine tensors with three distinct principal components. The third set, C, comprising the spectrum for $\theta = 90^{\circ}$, is unique in the sense that it is the only spectrum that ostensibly indicates that for the lateral regions the perpendicular transitions are further apart than the parallel absorptions $(A_{\perp} > A_{\parallel})$. In fact, the strong ("perpendicular") absorptions are the result of combined spectra in the geometric plane described by the vectors $A_{\perp 1} + A_{\parallel 2}$ and $A_{\parallel 1} + A_{\perp 2}$, whereas the adjacent small ("parallel") absorptions arise from a single spectrum described by the vector $A_{\perp 1} + A_{\perp 2}$, which is perpendicular to the above-mentioned plane.

NMR Conformation Analysis. Methods for determining ${}^{n}J_{PP}$ coupling constants in symmetrical bis(diphenylphosphino) derivatives are described in detail by Colquhoun and MacFarlane.⁷ In particular the ${}^{n}J_{PP}$ of the AXX' spin system is most readily obtained from the ${}^{13}C(A)$ spectra of the phenyl groups. A typical spectrum of the ortho carbon atom of *trans*-1,2-bis(diphenyl-phosphino)ethene is shown in Figure 4.

Since J_{CP} is small for the ortho, meta, and para carbon atoms, it is a good approximation to determine ${}^{n}J_{PP}$ from $(D^2 - 0.25N^2)^{1/2}$. For bis(diphenylphosphino) derivatives with two interjacent carbon atoms (C₂ linked), large positive values of ${}^{3}J_{PP}$ will arise when the two lone-pair P-C-C dihedral angles are small.⁷ This behavior is opposite to the conventional Karplus-type dependence of a three-bond coupling constant on the dihedral angle.

Computational Details. Open-shell calculations were performed by using the unrestricted Hartree–Fock (UHF) procedure of the GAUSSIAN88 program package.⁸ The molecular geometries were

⁽⁷⁾ Colquhoun, I. J.; McFarlane, W. J. Chem. Soc., Dalton Trans. 1982, 1915.

⁽⁸⁾ Frisch, M. J.; Head-Gordon, M.; Schlegel, H. N.; Raghavachari, R.; Binkley, J. S.; Gonzales, 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.; Pople, J. A. Gaussian 88. Gaussian, Inc., Pittsburgh, PA.

TABLE I: ESR Parameters of Ph2P-R-PPh2 Radical Cations (A in MHz)

linker	cation	A	A_{\perp}	Aiso	2A _{dip}	81	g⊥	A _H	ref
CH,	local	1456	778	1004	452	2.001	2.007	65	
-		1261	702	888	373	2.002	2.007		Ь
	dimer	1449	1147	1247	202	2.002	2.003		а
CHCH cis	cyclic	1242	834	970	272	1.999	2.004		а
CHCH trans	local	1298	811	973	325	2.002	2.004		а
	dimer	1333	1047	1142	191	2.001	2.004		а
CH ₂ CH ₂	local	1383	747	959	424	2.003	2.005	56	а
		1275	702	893	382	2.002	2.007		Ь
	cyclic	1240	882	1001	239	2.003	2.008		а
	•	1328	888	1035	293	2.002	2.007		Ь
	dimer	1394	1093	1193	201	2.002	2.005		а
CH(CH ₃)CH ₂	local	1339	720	926	413	2.004	2.009	59	а
	cyclic	1214	840	965	249	2.003	2.000		а
	dimer	1413	1106	1208	205	2.004	2.006		а
$CH(CH_3)CH(CH_3)$	local	1348	669	895	453	2.006	2.007	50	а
CC	local	1307	747	934	373	2.002	2.005		а
	dimer	1385	1103	1197	188	2.000	2.003		а
$CH_2CH_2P(Ph)CH_2CH_2$	local	1293	768	943	350	1.998	2.009	53	a
	cyclic	1287	881	1016	271	2.004	2.005		а
	dimer	1438	1076	1197	241	2.004	1.998		а
CH ₂ CH ₂ CH ₂	local	1381	728	945	436	2.005	2.008	59	а
	dimer	1455	1175	1268	187	2.002	2.008		а
CH ₂ CH ₂ CH ₂ CH ₂	local	1376	685	915	461	2.001	2.005	60	а
	dimer	1453	1138	1243	210	2.000	2.004		а
2,2'-(1,1'-binaphthyl)	local	1370	772	971	399	2.001	2.005		а
	dimer	1364	1044	1151	213	2.001	2.005		а
$CH_2CH(OC(CH_3)_2O)CHCH_2$	local	1394	784	987	407	2.003	2.008	50	а
	dimer	1554	1254	1354	200	2.003	2.006		а
CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	local	1378	731	947	431	2.003	2.008	61	а
	dimer	1481	1157	1265	216	2.003	2.008		а
CH ₂	local	1344	703	917	427	2.002	2.007	62	а
	dimer	1457	1156	1256	201	2.006	2.006		а

"This work, CH₂Cl₂ matrix. ^b Rhodes and Symons, CFCl₃ matrix.⁵

optimized at the 3-21G* SCF level in an analytical gradient procedure with respect to all parameters within the symmetry constraint. For the optimized geometries a subsequent vibration frequency analysis was performed to find the order of the stationary point. The isotropic and dipolar hyperfine couplings were calculated as

> $A_{\rm iso} = (8\pi/3)(g_{\rm e}/g_0)g_{\rm N}\beta_{\rm N}\langle\delta(r_{\rm N})\rangle_{\rm spin}$ $\mathcal{A}_{\rm dip}(ij) = -(g_{\rm c}/g_0)g_{\rm N}\beta_{\rm N}\left(\frac{r^2\delta_{ij}-3ij}{r^5}\right)_{\rm cain}$

The subscript "spin" refers to the fact that averaging occurs over the unpaired spin density of the UHF wavefunction. A_{dip} is a traceless tensor that can be diagonalized, giving three principal values, together with their directions.

Results and Discussion

Bis(diphenylphosphino)methane. The ESR spectrum of an X-irradiated frozen sample of Ph₂PCH₂PPh₂ in dichloromethane, recorded at 95 K, reveals the expected parallel and perpendicular features of the ³¹P doublet from a localized Ph₂PCH₂PPh₂⁺ radical cation. The isotropic (A_{iso}) and dipolar (A_{dip}) hyperfine couplings obtained from the spectrum (Table I) are significantly larger than the corresponding values reported by Rhodes and Symons.⁵ This can only be explained by taking into account an effect caused by the difference in host matrix in the respective experiments (viz., CH_2Cl_2 and $CFCl_3$). Similar differences in the hyperfine parameters of phosphorus-centered radicals due to the host matrix have been encountered for cations of $P(OMe)_3^3$ and $PCl_3^{.9}$ From the hyperfine couplings comprised in Table I, the spin density on both phosphorus atoms can be estimated (Table II).¹⁰

Furthermore, an additional doublet coupling of approximately 65 MHz was observed, in both CH₂Cl₂ and CD₂Cl₂ matrices.

TABLE II: Spin Density Distribution of Ph2P-R-PPh2 Radical Cations

		3s,	3р,	total,		
linker	cation	%	%	%	p/s	ref
CH ₂	local	7.5	61.6	69.1	8.2	a
		6.6	50.8	57.4	7.7	Ь
	dimer	9.3	27.5	73.6	3.0	а
CHCH cis	cyclic	7.3	37.0	88.6	5.1	а
CHCH trans	local	7.3	44.3	51.6	6.1	а
	dimer	8.5	26.0	69.0	3.3	а
CH ₂ CH ₂	local	7.2	57.8	65.0	8.2	а
		6.7	52.0	58.7	7.8	Ь
	cyclic	7.5	32.6	80.2	4.4	а
	•	7.7	39.9	95.2	5.2	b
	dimer	8.9	27.4	72.6	3.1	а
CH(CH ₃)CH ₂	local	6.9	56.3	63.2	8.2	а
	cyclic	7.2	33.9	82.2	4.7	а
	dimer	9.0	27.9	73.8	3.1	а
$CH(CH_3)CH(CH_3)$	local	6.7	61.7	68.4	9.2	а
CC	local	7.0	50.8	57.8	7.3	а
	dimer	9.0	25.6	69.2	2.9	а
CH ₂ CH ₂ P(Ph)CH ₂ CH ₂	local	7.1	47.7	54.8	6.7	а
	cyclic	7.6	36.9	89.0	4.9	а
	dimer	9.0	32.8	83.6	3.7	а
CH ₂ CH ₂ CH ₂	local	7.1	59.4	66.5	8.4	а
	dimer	9.5	25.5	70.0	2.7	а
CH ₂ CH ₂ CH ₂ CH ₂	local	7.4	62.8	70.2	8.5	а
	dimer	9.3	28.6	75.8	3.1	а
2,2'-(1,1'-binaphthyl)	local	7.3	54.4	61.7	7.5	а
	dimer	8.6	29.0	75.3	3.4	а
$CH_2CH(OC(CH_3)_2O)CHCH_2$	local	7.4	55.4	62.8	7.5	а
	dimer	10.1	27.2	74.6	2.7	а
CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	local	7.1	58.7	65.8	8.3	а
	dimer	9.5	29.4	77.8	3.1	а
CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂	local	6.8	58.2	65.0	8.6	а
	dimer	9.4	27.4	/3.0	2.9	а

^a This work, CH₂Cl₂ matrix. ^b Rhodes and Symons, CFCl₃ matrix.⁵

Interestingly, the same splitting was also reported by Rhodes and Symons and tentatively assigned to ¹⁹F coupling resulting from interaction of the cation with CFCl₃.⁵ Since similar couplings

⁽⁹⁾ Aagaard, O. M.; de Waal, B. F. M.; Cabbolet, M. J. T. F.; Janssen, (1) Morton, J. R.; Preston, K. F. J. Magn. Reson. 1978, 30, 577.

TABLE III: Results of Quantum Chemical Calculations on Model Radical Cations

cation	sym	$E(\mathrm{UHF})$, au $\langle S^2 angle$	vib, ^a cm ⁻¹	A _{iso} , MHz	A _{dip} , MHz	A _H , ^b MHz	P-P, Å	θ¢
CH₃PH₂⁺	C _s	-379.349975 0.7558	196 A″	907	520 -259, -261	86		
CH ₃ H ₂ P ⁺ PH ₂ CH ₃ ⁺	C24	-759.026921 0.7742	46 Au	1083	267 -112, -155	50	2.793	0
H ₂ PCHCHPH ₂ **	C_{2v}	-756.654139 0.7772	165i Az	983	301 -149, -152	21	2.821	77
	<i>C</i> ₂	-756.654864 0.7818	111 <i>i</i> B	925	293 -139, -154	14	2.794	80
	C_1	-756.654867 0.7976	111 A	857	272 -130, -142	-5	2.797	80
				979	313 -147, -166	31		
H ₂ PCH ₂ CH ₂ PH ₂ +	<i>C</i> ₂	-756.846510 0.7830	169 A	957	290 -128, -162	23	2.728	78

^a Frequency and irreducible representation of lowest vibration mode. ^b Hyperfine coupling of the CH₃, CH₂, or CH hydrogen nucleus trans to the phosphorus sp³ free electron orbital. Angle (deg) between the major axes of the two ³¹P dipolar hyperfine coupling tensors.



Figure 5. UHF 3-21G^{*} optimized geometries for (a) $C_s CH_3 \dot{P}H_2^+$, (b) C_{2k} CH₃H₂P \pm PH₂CH₃⁺, (c) C_1 H₂PCHCHPH₂⁺⁺, and (d) C_2 H₂ PCH,CH,PH,+.

are observed in a variety of hosts, we attribute the extra splitting to one of the methylene hydrogen atoms.

At high gain the weak absorptions of an intermolecular $Ph_2RP \rightarrow PRPh_2^+$ dimer radical cation were identified. No major changes of the spectrum were observed on annealing until at 120 K all features were irreversibly lost.

The fact that no intramolecular reaction occurs can be rationalized on the basis of the molecular geometry of the parent substrate. The crystallographic analysis of Ph2PCH2PPh2 reveals that the free-electron pairs at the phosphorus atoms are on different sides of a plane through the phosphorus nuclei and the methylene carbon.¹¹ Hence intramolecular overlap is impossible without a substantial rearrangement of the molecular geometry involving a rotation of bulky PPh₂ moieties. The rotation might occur at ambient temperature as can be judged from the high ${}^{2}J_{PP}$ spin-spin coupling. At 77 K, however, such rotations are restrained. In addition, via an intramolecular reaction a threemembered ring would be formed. Such a ring will possess considerable strain and hence will be subject to ring opening at the relative weak P-P bond.

Open-shell quantum chemical calculations were performed on $CH_3PH_2^+$ and $CH_3H_2P \doteq PH_2CH_3^+$ as model compounds for the localized and dimer radical cations. The geometry of the $CH_3\dot{P}H_2^+$ prototype was optimized within the C_s symmetry constraint (Figure 5). The ground state is ²A'. Vibrational analysis confirms that this structure corresponds to a true minimum. The calculated values for A_{iso} and $2A_{dip}$ (907 and 520 MHz, respectively, Table III) are in fair agreement with the

(11) Schmidbaur, H.; Reber, G.; Schur, A.; Wagner, F. E.; Müller, G. Inorg. Chim. Acta 1988, 147, 143.

TABLE IV: "J_{PP} (Hz) of Bis(diphenylphosphine) Derivatives in **Dichloromethane Solution**

		"J _{PP}	
linker	″J _{₽₽}	determined from	lit.
CH ₂	a		125.07
CHCH cis	а		105.57
CHCH trans	13.5	¹³ C o-Ph carbon	13.47
CH,CH,	34.2	¹³ C o-Ph carbon	33.6 ⁷
CH(CH ₃)CH ₃	20.3	³¹ P	20.114
CH(CH ₃)CH(CH ₃)	6.6	¹³ C m-Ph carbon	
CC	5.6	¹³ C o-Ph carbon	6.17
CH ₂ CH ₂ P(Ph)CH ₂ CH ₂	28.7	31P	29.115
CH ₂ CH ₂ CH ₂	1.0	¹³ C o-Ph carbon	1.07
CH ₂ CH ₂ CH ₂ CH ₂	6.7	¹³ C o-Ph carbon	
$2.2' \cdot (1.1' \cdot \text{binanhthy})$	9.9	¹³ C o-Naph carbon	
CH-CH(OC(CH-)-O)CHCH-	<1	¹³ C o-Ph carbon	
CH_CH_CH_CH_CH_	<1	¹³ C o-Ph carbon	
CH ₂	<1	¹³ C o-Ph carbon	

^aCan only be determined from a triple-resonance experiment.⁷

experimental values for the localized Ph₂PCH₂PPh₂⁺ cation. For the dimer model $CH_3H_2P \rightarrow PH_2CH_3^+$ optimization within C_{2h} of the ${}^{2}B_{u}$ ground state results in the structure depicted in Figure 5. This structure corresponds to a minimum on the potential energy surface and possesses an elongated P-P three-electron σ^* bond of 2.793 Å, similar to that of the H₃PPH₃⁺⁺ dimer (2.802 Å at 6-31G*/SCF).¹² Again A_{iso} (1083 MHz) and $2A_{dip}$ (267 MHz) are comparable to the experiment. The principal directions of the two ³¹P dipolar hyperfine coupling tensors are aligned and make an angle of 30.3° with the P-P bond, in close agreement with previous experimental and theoretical results.¹³

cis-1,2-Bis(diphenylphosphino)ethene. According to Schmidbaur et al., the free-electron pairs of the two phosphino groups of cis-Ph2PCHCHPPh2 in the solid state are directed toward each other in the plane of the olefin skeleton.¹¹ Apparently this also holds for a dichloromethane solution of cis-Ph2PCHCHPPh2, where an unusually high ${}^{3}J_{PP}$ coupling of 105.5 Hz is reported⁷ (Table IV), indicating a small PCCP dihedral angle.

Considering the conformation of cis-Ph₂PCHCHPPh₂, it is not surprising that during X-irradiation in dichloromethane an intramolecular reaction occurs and that a cyclic structure is observed in the ESR spectrum (Figure 6a) at 95 K. No localized $Ph_2\dot{P}R^+$ cations or intermolecular dimers were observed, indicating a very

⁽¹²⁾ Clark, T. J. Am. Chem. Soc. 1988, 110, 1672.
(13) Janssen, R. A. J.; Sonnemans, M. H. W.; Buck, H. M. J. Chem. Phys. 1986, 84, 3694.

⁽¹⁴⁾ Morandini, F.; Consiglio, G.; Piccolo, O. Inorg. Chim. Acta 1982, 57, 15

⁽¹⁵⁾ Dubois, D. L.; Meyers, W. H.; Meek, D. W. J. Chem. Soc., Dalton Trans. 1975, 1011



Figure 6. ESR spectra of X-irradiated 1,2-bis(diphenylphosphino)ethene in a CH_2Cl_2 matrix. (a) Cyclic cation configuration of the cis isomer at 95 K. (b) Localized and dimeric centers of the trans isomer at 95 K.

efficient intramolecular process. The spectrum clearly shows the expected pattern with the parallel transitions on the inner flanks of the large perpendicular absorptions (cf. Figure 2, $\theta = 90^{\circ}$). This provides further support to the interpretation of Rhodes and

Symons regarding the cyclic structure of Ph2PCH2CH2PPh2+.5

The hyperfine couplings and spin density on both phosphorus atoms are listed in Tables I and II. The p/s ratio of 5.1 is intermediate to that of the prototype Me_3P^{+} (9.2) and the dimer $Me_3PPMe_3^{+}$ (2.3) radical cations.⁴

On annealing the sample, the radical can be detected up to 170 K, the melting temperature of the matrix. No other products were detected.

An ab initio quantum chemical calculation was performed on the radical cation of cis-H₂PCHCHPH₂. Full optimization within a C_{2v} symmetry constraint of the ²B₂ ground state results in a molecular arrangement with a single imaginary frequency of 165i cm^{-1} , corresponding to an A₂ vibration mode (Table III). The expectation values of the isotropic and dipolar hyperfine couplings calculated from the UHF wavefunction are $A_{iso} = 983$ and $2A_{dip}$ = 301 MHz, in good agreement with the experimental values for cis-Ph2PCHCHPPh2*+ (970 and 272 MHz, respectively, Table I), and confirm the assignment. The structure of cis-H₂PCHCHPH₂^{•+} is characterized by a reduced PCC angle of 114.4°. The resulting intramolecular P-P distance amounts to 2.821 Å. The principal directions of the dipolar hyperfine tensors on the two phosphorus atoms are inclined by an angle of 77°. Further optimization within C_2 symmetry results in a stationary point 0.45 kcal/mol below the C_{2v} geometry. Vibrational analysis, however, reveals a new imaginary mode (111*i* cm⁻¹), suggesting an overall C_1 point group. Subsequent reoptimization yields a C_1 geometry that is only 0.003 kcal/mol lower in energy (Figure 5, Table III). For this structure a significant difference in the spin density on the two ³¹P nuclei is predicted. The values of A_{iso} (979 and 857 MHz) and $2A_{dip}$ (313 and 272 MHz) remain in the experimental range. Further characteristics of the cyclic $C_{2\nu}$, C_2 , and C_1 structures of cis-H₂PCHCHPH₂^{•+} are compiled in Table Ш.

trans - 1,2-Bis(diphenylphosphino)ethene. The X-ray crystallographic data of Schmidbaur on the trans isomer reveal an approximate centrosymmetric structure with the free-electron pairs



Figure 7. ESR spectra of X-irradiated 1,2-bis(diphenylphosphino)ethane in a CH_2Cl_2 matrix. (a) At 100 K, showing localized and cyclic centers. (b) At 100 K, after recooling from 123 K, giving the secondary dimer radical cation.

pointing away from each other in a roughly orthogonal orientation with respect to the olefinic bond.¹¹ The ${}^{3}J_{PP}$ coupling constant determined from the ${}^{13}C$ NMR spectrum amounts to 13.5 Hz (Table IV).

X-irradiation of *trans*-Ph₂PCHCHPPh₂ predominantly results in the formation of localized Ph₂ PR^+ radicals together with some intermolecular dimerization (Figure 6b). Upon raising the temperature, a continuous increase of the dimer absorptions was observed at the expense of the initial product. At a temperature of 170 K all signals were irreversibly lost.

The ESR parameters and the corresponding spin densities are collected in Tables I and II. The p/s ratio of the intermolecular dimer is significantly less than that of the localized species, viz., 3.3 and 6.1.

It is clear that as a result of the rigidity of the substrate around the C=C bond, the large intramolecular distance between the two phosphorus atoms (4.56 Å), and the unfavorable orientation of the lone-pair electrons, no intramolecular reaction leading to a cyclic configuration is possible.

1,2-Bis(diphenylphosphino)ethane. Rhodes and Symons have shown that γ -irradiation of Ph₂PCH₂CH₂PPh₂ in CFCl₃ leads to the formation of both localized Ph_2PR^+ and delocalized cyclic Ph2PCH2CH2PPh2*+ radical cations.5 Their results are summarized in Tables I and II. The X-ray data of Pelizzi and Pelizzi show that in the solid state Ph2PCH2CH2PPh2 possesses an exact trans conformation of the PCCP chain as a result of a crystallographic center of symmetry on the C(sp³)-C(sp³) bond.¹⁶ The free-electron pairs are essentially oriented at different sides of the PCCP plane. Such a conformation would preclude an intramolecular reaction to a cyclic arrangement. However, in solution, a considerable degree of rotational freedom for the $C(sp^3)-C(sp^3)$ bond can be expected. The ${}^{3}J_{PP}$ coupling of 34.2 Hz in di-chloromethane obtained from the ${}^{13}C$ NMR spectrum lies between the corresponding values of cis- and trans-bis(diphenylphosphino)ethene (Table IV). Hence, in a rapidly frozen solvent different conformers can be expected, including a gauche orientation of the two phosphorus nuclei.

X-irradiation of $Ph_2PCH_2CH_2PPh_2$ in CH_2Cl_2 results in the formation of both $Ph_2\dot{P}R^+$ and cyclic $Ph_2PCH_2CH_2PPh_2^{++}$ centers, analogous to those detected in CFCl₃. The ESR spectrum recorded at 100 K is depicted in Figure 7a.



Figure 8. ESR spectrum of X-irradiated (R)-(+)-1,2-bis(diphenylphosphino)propane in a CH₂Cl₂ matrix at 100 K, exhibiting the strong absorptions of a localized center and the weak features of a cyclic cation product in the lateral regions.

On annealing to 112 K the signal intensity of the localized center gradually decreases. After further warming to 123 K and subsequent recooling to 100 K both initial cations are lost and a new radical product is formed (Figure 7b). The actual process taking place is that of a reaction of the initial cations with a second substrate molecule, leading to an intermolecular dimer $Ph_2RP - PRPh_2^+$. The experiment clearly demonstrates that a single substrate can give three different configurations, viz., a localized cation and delocalized cyclic and dimeric structures. The corresponding ESR powder patterns of the delocalized species are essentially identical with those in Figure 2 for $\theta = 0^{\circ}$ (dimer) and $\theta = 90^{\circ}$ (cyclic).

The spin density distribution of the three species (Table II) reveals a continuous decrease of the p/s ratio from 8.2 (localized), via 4.4 (cyclic), to 3.1 (dimer). This can be explained by an increasing pyramidalization at phosphorus, in accordance with the rise in 3s contribution.

The present ³¹P hyperfine couplings for the localized $Ph_2\dot{P}R^+$ radical in CH2Cl2 are significantly larger than those reported by Rhodes and Symons for a CFCl₃ matrix.⁵ The same result was obtained for the localized cation of Ph2PCH2PPh2. In contrast, the couplings for the cyclic radical cation are somewhat smaller than CFCl₃. The origin of these effects of the host matrix is not clear.

To investigate the cyclic configuration in more detail, we performed an ab initio UHF-SCF 3-21G* calculation on the H₂PCH₂CH₂PH₂⁺⁺ model. The molecular geometry, fully optimized within C_2 symmetry (Figure 5), is characterized by a P-P distance of 2.728 Å. The PCCP dihedral angle amounts to 32.2°, intermediate between a staggered and eclipsed conformation. The calculated hyperfine interactions $A_{iso} = 957$ and $2A_{dip} = 291$ MHz are in fair agreement with the experimental values of both the CH₂Cl₂ and CFCl₃ matrices (Table III). The two major principal components of the ³¹P hyperfine tensors make an angle of 78°.

(R)-(+)-1,2-Bis(diphenylphosphino)propane. The ³¹P NMR spectrum of $Ph_2PCH(CH_3)CH_2PPh_2$ in CD_2Cl_2 gives a ${}^{3}J_{PP}$ coupling constant of 20.3 Hz, which is less than that of $Ph_2PCH_2CH_2PPh_2$. The reduced ${}^{3}J_{PP}$ value indicates a further increase of the time-averaged distance between the free-electron pairs of both phosphine moieties.

X-irradiation of Ph2PCH(CH3)CH2PPh2 in CH2Cl2 results in the formation of a localized Ph2PR+ radical cation center. In the lateral regions of the spectrum (Figure 8), weak absorptions are present, which can be ascribed to a cyclic configuration. The signal intensity, however, is too low to make this assignment without ambiguity. On annealing, the Ph₂PR⁺ cation is lost at 120 K. At 130 K, weak but clear signals of an intermolecular dimer were detected.

The hyperfine couplings and spin density distribution are similar to those encountered for Ph₂PCH₂CH₂PPh₂ (Tables I and II). (2S,3S)-(-)-Bis(diphenylphosphino)butane. For (S,S)-

 $Ph_2PCH(CH_3)CH(CH_3)PPh_2$ the ${}^3J_{PP}$ coupling constant is 6.6 Hz, the lowest value encountered for all C(sp³)-C(sp³)-linked

bis(diphenylphosphino) derivatives.

X-irradiation of Ph₂CH(CH₃)CH(CH₃)PPh₂ gives the corresponding localized structure Ph₂PR⁺ as the single product. On annealing, its ESR absorptions disappear at 120 K. No new radicals or rearrangement products were detected.

Bis(diphenylphosphino)acetylene. In the solid state the PCCP axis of this molecule is slightly bent with PCC angles of 173.5 and 175.3°.17 The torsion angle between the directions the free-electron pairs on the phosphorus atoms is approximately 90°. The ${}^{3}J_{PP}$ value is small and amounts to 5.6 Hz, in accordance with literature data.⁷ X-irradiation of Ph₂PCCPPh₂ in CH₂Cl₂ at 95 K leads to the predominant formation of the localized Ph_2PR^+ cation together with some intermolecular dimerization (Tables I and II). Raising the temperature to 125 K results in the loss of the localized center and the concurrent increase of the dimer species. Simultaneously, the complex patterns of a third radical product were observed, approximately at the positions where the initial localized cation was found. This species could not be identified unambiguously but seems to be an intermediate in the dimerization process. Similar hyperfine patterns were observed for 1.4-bis(diphenylphosphino)butane (Ph₂P(CH₂)₄PPh₂) and (-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (Ph₂PCH₂CH(OC(CH₃)₂O)CHCH₂PPh₂) (vide infra)

Bis(2-diphenylphosphinoethyl)phenylphosphine. The ${}^{3}J_{PP}$ coupling constant of Ph₂PCH₂CH₂P(Ph)CH₂CH₂PPh₂ is 29.1 Hz, comparable to that of Ph₂PCH₂CH₂PPh₂.

X-irradiation of the title compound in CH₂Cl₂ at 77 K yields all three possible radical configurations simultaneously: localized, cyclic, and dimeric. The abundant signals of the localized cation are rapidly lost on annealing to 120 K. The cyclic configuration and the dimer radical cation can be detected up to 140 K.

No signals were observed that can be attributed to a radical cation in which all three phosphorus atoms participate in the SOMO. The cyclic configuration probably comprises the central phosphorus atom and one of the terminal phosphorus nuclei.

1,3-Bis(diphenylphosphino)propane. In agreement with the value reported by Colquhoun and McFarlane, we obtained a small value of 1.0 Hz for the ⁴J_{PP} coupling constant of Ph₂P(CH₂)₃PPh₂.⁷ Although the dependence of ${}^{4}J_{PP}$ on the molecular conformation is not known, it is unlikely that there is a preference for a conformation in which the phosphorus atoms are sufficiently close to give an appreciable interaction between their free-electron pairs. Therefore it is not surprising that the ESR spectrum recorded at 100 K of an X-irradiated sample of Ph₂P(CH₂)₃PPh₂ in CH₂Cl₂ shows only the localized and dimeric radical cations and no cyclic configuration. The magnetic parameters obtained from the spectrum and the valence orbital spin densities are similar to those for the C₂-linked bis(diphenylphosphino) derivatives. At 120 K the localized center is irreversibly lost and a slight increase of the dimer absorptions is observed. The dimer can be detected up to 140 K.

1.4-Bis(diphenylphosphino)butane. The crystallographic structure of Ph₂P(CH₂)₄PPh₂ is characterized by an almost planar all-trans conformation of the PCCCCP fragment, with the two free-electron pairs on either side of the plane.¹⁸ In a frozen CH₂Cl₂ solution, however, a number of different rotameric conformations can be expected. Surprisingly, the ${}^{5}J_{PP}$ coupling amounts to 6.7 Hz (Table IV). X-irradiation of Ph₂P(CH₂)₄PPh₂ yields the corresponding localized and dimer radical cations (Tables I and II). At temperatures above 120 K the localized center disappears, whereas the dimer can be detected up the melting of the matrix (170 K). In the temperature range from 130 to 165 K, additional signals are present. These absorptions, which are not analyzed in detail, are tentatively assigned to an intermediate configuration of the dimerization reaction [cf. bis-(diphenylphosphino)acetylene and (-)-2,3-O-isopropylidene-2,3dihydroxy-1,4-bis(diphenylphosphino)butane].

⁽¹⁷⁾ Bart, J. C. J. Acta Crystallogr. 1969, 110, 1672.
(18) Rivera, A. V.; Gómez, D.; Rudolfo de Gil, E.; Suárez, T. Acta Crystallogr. 1988, C44, 277.

(R)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl. In contrast to $Ph_2P(CH_2)_4PPh_2$, (R)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl represents a C₄-linked derivative with a relatively rigid molecular structure. Unfortunately no crystallographic analysis is known. However, a single-crystal X-ray analysis of the corresponding oxidized form, 2,2'-bis(diphenylphosphinyl)-1,1'-binaphthyl, as a 1:1:1 complex with (1R)-(-)camphorsulfonic acid and acetic acid has been reported.¹⁹ The angle between the least-squares planes of the two naphthyl rings in this complex is 90.3° and the intramolecular P-P distance, calculated from the X-ray data, amounts to 4.57 Å. This means that, even when the free-electron pairs of the diphosphine possess a favorable mutual orientation, the two phosphorus atoms are probably too remote to form an intramolecular σ^* bond. The rigid conformation of the two free-electron pairs seems to increase the ${}^{5}J_{PP}$ coupling to 9.9 Hz with respect to the value of 1,4-bis(diphenylphosphino)butane (6.7 Hz, Table IV).

X-irradiation of a 0.3 M solution (saturated solution) of the 1,1'-binaphthyl-linked diphosphine leads to the well-characterized localized and dimeric radical cations (Tables I and II). These species show the usual temperature dependence. The localized center is completely lost at 120 K, whereas the concentration of the dimer increases on warming prior to its disappearance at 170 K.

It is important to realize that the ESR spectrum of a cyclic delocalized configuration with a linker containing more than two interjacent carbon atoms like the 2,2'-substituted 1,1'-binaphthyl derivative will differ appreciably from the simulation depicted in Figure 2 for $\theta = 90^{\circ}$. The reason is that the increased size of the ring gives the possibility for a reduction of the angle θ between the polar directions of the two interacting free-electron orbitals. As a result, the spectrum of an intermolecular dimer and a cyclic structure cannot be easily distinguished. In the present case, but also for the 1,3-propane and 1,4-butane analogues, the intensity of the ESR spectrum assigned to the $P \rightarrow P \sigma^*$ configuration increases on annealing, along with the concurrent loss of localized cations. Above 120 K, only the σ^* configuration remains. For $Ph_2PCH_2CH_2PPh_2$ the cyclic σ^* configuration disappears at 120 K, in favor of the formation of an intermolecular σ^* structure. This behavior and the fact that the ratio of σ^* and localized centers seriously decreases at low concentration (10^{-2} M) lead to the conclusion that the P \perp P σ^* ESR spectrum is due to intermolecular dimer cations and does not originate from a cyclic intramolecular interaction.

(-)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane. X-irradiation of a 1 M CH₂Cl₂ solution of the title compound at 77 K results in the ESR spectrum shown in Figure 9a. This spectrum serves as a model for all C₃-, C₄-, C₅-, and C₆-linked bis(diphenylphosphino) derivatives, where invariably strong signals of a localized center are present, accompanied by much weaker absorptions in the lateral regions of the P \pm P σ^* dimer.

Upon warming to 120 K the localized center is rapidly lost and a new species gradually appears, reaching maximum intensity at 130 K (Figure 9b). A further rise of the temperature above 135 K eventually results in the spectrum shown in Figure 9c, where only the signals of the $P \pm P \sigma^*$ dimer remain. The interpretation of the spectrum of Figure 9b is not straightforward and is hampered by the interference of the σ^* dimer absorptions. Nevertheless, the complex appearance is reminiscent of a double doublet powder pattern and can in fact only be rationalized by assuming that the unpaired electron interacts with two magnetically different ³¹P nuclei. The spectrum is tentatively assigned to an intermediate of the conversion of a localized cation with one interacting ³¹P nucleus to a delocalized dimer with two identical ³¹P atoms.

1,5-Bis(diphenylphosphino)pentane. The ESR spectrum of X-irradiated $Ph_2P(CH)_5PPh_2$ in CH_2Cl_2 reveals the expected localized and dimeric radical cations (Tables I and II). Raising the temperature results in the irreversible loss of these two centers



Figure 9. ESR spectra of X-irradiated (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane in a CH₂Cl₂ matrix. (a) Initial spectrum at 100 K, localized center. (b) Spectrum at 130 K of an intermediate product (see text). Tentative assignment: $A_{z1} = 1778$, $A_{y1} = 1554$, $A_{x1} = 1466$, $A_{z2} = 298$, $A_{y2} = 293$, $A_{x2} = 458$ MHz; $g_z = 2.026$, $g_y = 2.030$, $g_x = 2.008$. (c) Spectrum recorded at 140 K of the P-P σ^* dimer radical cation.

at 125 and 130 K, respectively.

1,6-Bis(diphenylphosphino)hexane. The results for $Ph_2P-(CH_2)_6PPh_2$ are fully analogous to those described for $Ph_2P-(CH_2)_4PPh_2$ and $Ph_2P(CH_2)_5PPh_2$ (Tables I and II). Likewise, the temperature dependence of the centers is identical.

Conclusions

The present study shows that X-irradiation of bis(diphenylphosphino) derivatives in a frozen CH₂Cl₂ solution can result in localized, cyclic, and dimeric radical cation configurations, depending on the nature of the linker. The localized structures of precursors with a methylene linker exhibit beside the large ³¹P coupling an additional hyperfine interaction of 50-65 MHz (Table I). We conclude that this splitting originates from the methylene hydrogen trans to the SOMO, which is confirmed by quantum chemical calculations (Table III). In the cyclic structures the three-electron $P \doteq P \sigma^*$ bond is strongly bent (approximately 90°). The cyclic configuration is only observed in case the linker contains two interjacent carbon atoms and the two free-electron pairs on phosphorus are in a favorable mutual orientation to allow intramolecular overlap. In principle, the degree to which the two phosphorus free-electron pairs interact can be estimated from the $^{n}J_{PP}$ coupling constant. By comparison of Tables I and IV, it appears that the cyclic configurations are only observed when ${}^{n}J_{PP}$ is more than 20 Hz. If $^{n}J_{PP}$ is less, the cyclic centers are consistently absent. With respect to the UHF quantum chemical calculations, it is shown that prototype models of localized, cyclic, and dimer radical cations can be optimized to stable geometries. Furthermore, the calculated isotropic and dipolar hyperfine coupling constants at the optimized geometries are generally in good agreement with the experimental data, supporting the assignments. The calculations confirm the marked near-perpendicular orientation of the free-electron orbitals in the three-electron $P \doteq P \sigma^*$ bond of the cyclic center.

In addition to the well-established localized, cyclic, and dimer radical cations, a fourth configuration exists. Although the spectral

⁽¹⁹⁾ Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketoni, T.; Akatagawa, S.; Noyori, R. J. Org. Chem. **1986**, *51*, 629.

assignment of this species is far from conclusive, the spectrum can be interpreted in terms of two different ³¹P hyperfine interactions. A likely candidate for this species is an intermediate of the conversion of a localized center into a $P \doteq P \sigma^*$ dimer radical cation.

Experimental Section

Bis(diphenylphosphine)s were obtained from Aldrich and were used as received. Dichloromethane was dried by passing over a basic alumina column.

X-irradiation and ESR. Solutions of bis(diphenylphosphino) derivatives in CH₂Cl₂ (1 M) were degased by three consecutive freeze-pump-thaw cycles and subsequently frozen at 77 K in liquid nitrogen. The samples were X-irradiated at 77 K for 4 h using a Cu source, operating at 40 kV and 20 mA. X-band ESR spectra were recorded on a Bruker ER200D spectrometer, interfaced with a Bruker Aspect 3000 computer for digital storage. Typical spectra were recorded with 4K data points and a sweep width of 187.5 mT. Microwave power was 2 mW in most experiments. Temperature was controlled with the aid of a Bruker ER 4111 variable-temperature unit between 95 and 170 K. Hyperfine couplings and g values were determined from the spectra by using second-order corrections.²⁰

(20) Weltner, W. Magnetic Atoms and Molecules; Scientific and Academic Editions: New York, 1983.

NMR Conformation Analysis. NMR spectra were recorded on a Bruker AM400 spectrometer, at frequencies of 400.1, 162.0, and 100.6 MHz for ¹H, ³¹P, and ¹³C, respectively. In all NMR experiments we used CD_2Cl_2 as solvent.

Acknowledgment. This investigation has been supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for Scientific Research (NWO). We thank Dr. A. E. H. de Keijzer for performing some of the preliminary experiments in this field.

Registry No. Ph2PCH2PPh2**, 126435-46-9; (Z)-Ph2PCH= CH2PPh₂⁺⁺, 136655-40-8; (*E*)-Ph₂PCH=CHPPh₂⁺, 136655-41-9; Ph₂P-(CH₂)PPh₂⁺⁺, 126575-31-3; (*R*)-Ph₂PCH(CH₃)CH₂PPh₂⁺⁺, 136655-42-9; (*S*,*S*)-Ph₂P(CH(CH₃)₂)PPh₂⁺⁺, 136655-43-1; Ph₂PC=CPPh₂⁺⁺, 13655-43-1; Ph₂PC=CPPh_2^{++}, 13655-43-1; Ph_2^{++}, 13655-43-1; Ph_2^{ 0, (3,3)-Ph₂P(CH(CH₃)₂)P(Ph₂, (3,3)-Ph₂P(CH₂)₂P(Ph)(CH₂)₂PPh₂⁺⁺, 136546-99-1; Ph₂P-(CH₂)₃PPh₂⁺⁺, 136547-00-7; Ph₂P(CH₂)₄PPh₂⁺⁺, 136547-01-8; Ph₂PCH₂CH(OC(CH₃)₂O)CHCH₂PPh₂⁺⁺, 136655-45-3; Ph₂P-(CH₂)₅PPh₂⁺⁺, 136547-02-9; Ph₂P(CH₂)₆PPh₂⁺⁺, 136547-03-0; CH₃PH₂⁺⁺, 91391-14-9; MePH₂, 593-54-4; (Z)-H₂PCH=CHPH₂⁺⁺, 136655-46-4; H₂P(CH₂)₂PH₂⁺⁺, 136547-04-1; Ph₂PCH₂PPh₂, 2071-20-7; (Z)-Ph₂PCH=CHPPh₂, 983-80-2; (E)-Ph₂PCH=CHPPh₂, 983-81-3; Ph₂P(CH₂)₂PPh₂, 1663-45-2; (*R*)-Ph₂PCH(CH₃)CH₂PPh₂, 67884-32-6; (S)-Ph₂PCH(CH₃)CH(CH₃)PPh₂, 64896-28-2; Ph₂PC=CPPh₂, 5112-5-8; Ph₂P(CH₂)₂P(Ph)(CH₂)₂PPh₂, 23582-02-7; Ph₂P(CH₂)₃PPh₂, 6737-42-4; Ph₂P(CH₂)₄PPh₂, 7688-25-7; Ph₂PCH₂CH(OC(CH₃)₂O)-CHCH₂PPh₂, 32305-98-9; Ph₂P(CH₂)₅PPh₂, 27721-02-4; Ph₂P-(CH₂)₆PPh₂, 19845-69-3; (R)-(+)-2,2'-bis(diphenylphosphino)-1,1'-dinaphthyl*+, 136655-44-2; (R)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, 76189-55-4.

Ab Initio Study of Argon and Nitrogen Ionic Clusters

Vladimir Frecer,*,†

Department of Physiology and Biophysics, Mount Sinai School of Medicine of the City University of New York, 1 Gustave L. Levy Place, New York, New York 10029

Duli C. Jain,

Natural Sciences Department, City University of New York, York College, Jamaica, New York, New York 11451

and Anne-Marie Sapse*

Department of Chemistry, City University of New York, Graduate School, New York, New York, and John Jay College, 445 W 59th St., New York, New York 10019, and Rockefeller University, New York, New York 10021 (Received: March 28, 1991)

Ab initio calculations up to the MP4 level of theory were performed for the ArN_2^+ , Ar_2^+ , and $(N_2)_2^+$, molecular ions. These species play an important role in the chemistry of the atmosphere. While the first two clusters are linear, the last is predicted to have a Z - shaped form. Calculated dissociation enthalpies of the clusters correspond well to experimentally observed binding energies. Theoretical reaction enthalpies and equilibrium constants were estimated for a set of reactions involved in the formation of these clusters.

Introduction

Small ionic clusters, which play an important role in stratospheric chemistry,^{1,2} have formed the object of numerous experimental^{3-11,26-28} as well as theoretical¹² studies. Among these species, the ionic clusters ArN_2^+ , Ar_2^+ , or $(N_2)_2^+$ have been $72^{-11}2^{-28}$ experimentally shown to feature large binding energies.7,9-11,26-28 As far as the simple homoatomic cluster Ar_2^+ is concerned, the large binding energy typical for this category of homonuclear complexes, is related to the electron delocalization.^{13,14,28} The ArN_2^+ complex also belongs to this category of clusters since the ionization potentials of Ar and N_2 are almost the same.^{9,28}

Experimental observations have shown dissociation energies for the $(N_2)_2^+$ cluster ranging from 11.5 to 24.5 kcal mol^{-1,9,13,26,27}

^{*} Permanent address: Cancer Research Institute, Slovak Academy Sciences, CS-81232 Bratislava, Czechoslovakia.

Ferguson, E. E. In Kinetics of Ion-Molecule Reactions; Ausloos, P., Ed.; Plenum Press: New York, 1979.
 Bowers, M. T. In Ion and Cluster Ion Spectroscopy and Structure;

Maier, J. P., Ed.; Elsevier: Amsterdam, 1989; p 241. (3) Lindinger, W.; Dotan, I.; Albritton, D. L.; Fehsenfeld, F. C. J. Chem.

Phys. 1978, 68, 2607.

 ⁽⁴⁾ Arnold, F.; Krankowsky, D.; Marieu, K. J. Nature 1977, 267, 30.
 (5) Smith, D.; Adams, N. G.; Miller, T. M. J. Chem. Phys. 1978, 69, 308.

⁽⁶⁾ Jarrold, M. F.; Illies, A. J.; Bowers, M. T. J. Chem. Phys. 1983, 79, 6086; 1984, 81, 214; 1985, 82, 1832.

 ⁽⁷⁾ Kim, H. S.; Bowers, M. T. J. Chem. Phys. 1990, 93, 1159.
 (8) Mielke, Z.; Andrews, L. J. Phys. Chem. 1990, 94, 3519.

⁽⁹⁾ Teng, H. W.; Conway, D. C. J. Chem. Phys. 1973, 59, 2316.