Acta, **56**, 1741 (1973); B. Blank, P. G. Mennitt, and H. Fischer, XXIII IUPAC Congress, Boston, Mass., Vol. 4, Butterworths, London, 1971, p 1.
(54) N. C. Yang and R. H. Chen, *J. Am. Chem. Soc.*, **93**, 530 (1971).
(55) For a discussion of rotation vs. recombination in radical pairs, see R. A. Johnson and S. Seltzer, *J. Am. Chem. Soc.*, **95**, 938 (1973), and references cited therein.
(56) This figure assumes that **22** arises by cage recombination rather than by a concerted 1,3-acyl shift.
(57) A. J. Ultée, *J. Chem. Soc.*, 530 (1948).
(58) D. B. Bigley and R. W. May, *J. Chem. Soc. B*, 557 (1967).
(59) L. Carpino and E. G. S. Rundberg, *J. Org. Chem.*, **34**, 1717 (1969).
(60) A. Courtot, *Bull. Soc. Chim. Fr.*, **35**, 111 (1906).
(61) J. Colonge and P. Dumont, *Bull. Soc. Chim. Fr.*, **14**, 45 (1947).
(62) N. F. Cywinski and H. J. Hepp, *J. Org. Chem.*, **30**, 3814 (1965).
(63) C. E. Castro and R. D. Stephens, *J. Am. Chem. Soc.*, **86**, 4358 (1964); A. Zurqiyah and C. E. Castro, *Org. Synth.*, **49**, 98 (1969).
(64) W. B. Renfrow and A. Renfrow, *J. Am. Chem. Soc.*, **68**, 1801 (1946).
(65) K. von Auwers, *Chem. Ber.*, **46**, 508 (1913); W. Dieckmann and A. Wittman, *ibid.*, **55**, 3347 (1922).
(66) R. A. Letch and R. P. Linstead, *J. Chem. Soc.*, 443 (1932).
(67) E. N. Eccott and R. P. Linstead, *J. Chem. Soc.*, 2153 (1929); A. A. Goldberg and R. P. Linstead, *ibid.*, 2354 (1928).
(68) M. F. Shostakovskii, N. V. Komarov, V. P. Kuznetsova, and I. I. Igonina, *Akad. Nauk SSSR Bull. Div. Chem. Sci.*, 470 (1962).
(69) H. M. Schmidt and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **86**, 1142 (1967).
(70) G. Wittig and D. Wittenberg, *Justus Liebigs Ann. Chem.*, **606**, 1 (1957).
(71) R. V. Stevens, C. G. Christensen, W. L. Edmonson, M. Kaplan, E. B. Reid, and M. P. Wentland, *J. Am. Chem. Soc.*, **93**, 6629 (1971).
(72) M. Bertrand and R. Maurin, *Bull. Soc. Chim. Fr.*, 2779 (1967).
(73) J. S. Cowie, P. D. Landor, and S. R. Landor, *J. Chem. Soc., Perkin Trans. 1*, 720 (1973).
(74) J. E. Baldwin, J. E. Brown, and G. Hofle, *J. Am. Chem. Soc.*, **93**, 788 (1971).
(75) G. F. Hennion and C. V. DiGiovanna, *J. Org. Chem.*, **31**, 970 (1966).

CNDO/2 Calculations on Geometries of Tetra- and Pentacoordinated Phosphoranyl Radicals and UHF Calculations on Tetracoordinated π-Ligand Phosphoranyl Radicals

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Abstract: Open shell CNDO/2 calculations have been performed with geometry optimization. The calculated geometries are in agreement with the symmetry as derived from ESR data. Phosphoranyl radicals are found to have trigonal bipyramidal geometries, with the exception of π-ligand phosphoranyl radicals, which have tetrahedron-like geometries, when strong electron withdrawing ligands are absent. In a few calculations square pyramidal geometries were considered as deviations from ideal T or TBP structures. The spin densities, however, cannot be calculated accurately with CNDO/2. A π-electron model is proposed to calculate spin densities in tetracoordinated π-ligand phosphorus complexes, in which the five 3d orbitals of phosphorus are included in the calculation. These spin densities are found to be in good agreement with ESR experiments. The success of this model, where only π electrons are explicitly calculated, is explained.

Recently much interest has arisen in the characterization of pentacoordinated phosphorus compounds. In the case of alkyl-alkoxy phosphoranyl radicals, Davies et al.[1] and Krusic et al.[2] have established by ESR measurements that the radicals have a trigonal bipyramidal (TBP) configuration, in which the unpaired electron is situated in an equatorial (basal) position. This was concluded from the large phosphorus splitting constants (a_P) of 700–1000 G.

Recent work by Schipper et al.,[3] Rothuis et al.,[4,5] and Boekestein et al.[6] and also results from Lucken and Mazeline[7,8] indicate that much smaller (<40 G) a_P's are found when one or more ligands consist of a π-electron system. This suggests an essential difference in coordination in both types of radicals. We performed CNDO/2 calculations[9-11] on these radicals. With the help of a SIMPLEX procedure[12] the energetically best configuration was calculated, with optimal distances and bond angles. The first type of phosphorus radicals was found to have a TBP geometry, in accordance with experimental data. The odd electron and the ligands were all found to be situated in the positions that were experimentally established by Krusic et al.[2] When one or more of the ligands consist of a π-electron system the configuration is confirmed to be tetrahedron (T) like.[3-6] Recently, it has been established by Davies et al.[13] that in the case of phenylphosphoranyl radicals high splitting constants (500–1000 G) can be observed with electron-withdrawing ligands (2,2,2-trifluoroethoxy, chlorine, hydrogen, and methyl sulfide) linked to phosphorus. By repeating Boekestein's[6] experiments, Davies et al.[13] confirmed his observations and proposal for T geometry if no electron-withdrawing substituent is present. In both cases the geometry of the phenylphosphoranyl radicals has been confirmed by our CNDO/2 calculations. From the calculated spin densities it was then attempted to calculate phosphorus splitting constants. The pentacoordinated radicals have high a_P's (∼700 G) and the tetracoordinated radicals have low a_P's (<80 G). The exact values of the small a_P's for some of the π-ligand radicals, in which we are especially interested, showed no good agreement with the results from the ESR experiments. In order to explain the low phosphorus splitting constants, we propose a model in which the phosphorus has sp_3 hybridization and the odd electron (the fifth "ligand") is delocalized over the five 3d orbitals of the phosphorus atom and the π-electron system. This implies a T-like configuration.[14]

Geometry Optimization with CNDO/2

In determining the geometry of the radicals, different trial configurations were chosen, i.e., T and TBP with different choices of apical (ap) and equatorial (eq) positions for the ligands. For some radicals we also calculated geometries which correspond with square pyramidal configurations. The bond lengths and a few bond angles were then optimized. This was not done for the bond angles at the phosphorus atom, which are determined by the chosen configuration: 109° for a T configuration and 90° and 120° for a TBP geometry.[32] (Gorlov et al.[15] have optimized the bond angles at phosphorus and silicon of tetraatomic radicals and found the CNDO/2 calculations adequate in this respect.) The trial structures with the lowest energy give the best fit with experimental data. In reality molecules will not have an exact T or TBP configuration. We expect them to have structures which closely resemble T or TBP.

In Table I a few typical distances and bond angles are shown, as calculated with the SIMPLEX procedure. For PH_2 and for biphenyl ligands the bond angles at phosphorus were also optimized.

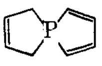
Table II shows the results of optimized calculations on pentacoordinated radicals, in which the ligands consist of various combinations of methoxy and methyl groups, hydrogen atoms, and the odd electron. From this table the following rules can be deducted:[2] these radicals have a trigonal bipyramidal geometry, the odd electron occupies an equatorial position, methyl (alkyl) groups prefer equatorial positions, methoxy groups occupy apical positions, hydrogen atoms occupy the remaining positions.

In the second group of radicals one or more of the ligands consist of a π-electron system, such as phenyl, biphenyl, ethenyl, and five-membered heterocyclic ring systems. In Table III the π-ligand radicals I–VII (see structures below), which have no strong electron-withdrawing ligands, are listed. The results of the calculations clearly indicate a T-like geometry.

$H_3PCH_2^+$ I

$(CH_3)_2P(biph)$ II

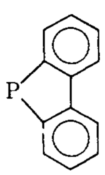
$(CH_3O)_3PPh$ III


IV

$(CH_3)_3PCHCH_3^+$ V

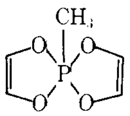
$(CH_3)_2PCHCH_3$ VI

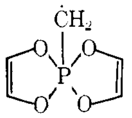
$(CH_3)_3PCH{=}CH_2$ VII

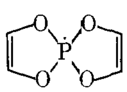
P(biph) =


When the radicals have electron-withdrawing ligands (in our calculations trifluoromethoxy and hydrogen), the calculations suggest a TBP geometry; see Table IV. $PhPH_2(OCH_3)$ is an exception, for which we have as yet no explanation.

Geometries, which differ both from T and TBP structures, are found in symmetric oxyphosphoranes[16] and possibly in their related radicals. See Table V for the energies calculated for VIII–X.


VIII


IX


X

Compound VIII has a square pyramidal geometry, as found by Holmes.[16] For the radical derived from this compound (IX) we also calculated a square pyramidal geometry. According to our calculations, X has a T geometry, which may be confirmed by an ESR experiment.

So far all these data on geometries are in agreement with experiments and with Muetterties' rules.[15,17] The possibility of a deviation from an ideal T or TBP structure can clearly be seen in the case of $PhP(OCH_3)_2OCF_3$, where the square pyramidal geometry has only a slightly higher energy than the TBP geometry. In the case of IV the difference between the T and square pyramidal geometries is rather large, indicating that the deviation from the T geometry is probably very small.

Table I. Bond Distances (Å) and Bond Angles (deg) Calculated with the CNDO/2–SIMPLEX Procedure

Bond	Group	T	TBP (ap)	TBP (eq)	Angle	Group	Deg
P–C	Alkyl	1.81	1.82	1.81	CPC	Biphenyl	~90
	Phenyl	1.73		1.70	POC	Methoxy	110.5
	Methylene	1.79	1.80	1.77	HPH	PH_2	91.5
	Ethylene	1.79	1.82	1.78			
P–O	Methoxy	1.81	1.80	1.77			
P–H		1.54	1.58	1.51			
	PH_2	-----	1.52	-----			
C–O	Methoxy	-----	1.40	-----			

Table II. CNDO/2 Results of Pentacoordinated Phosphorus Radicals without π-Ligands

Radical	Trial structure	Apical	Equatorial	E (au)
H_3POCH_3	TBP	OCH_3, H	H, H	−37.4525
	TBP	H, H	OCH_3, H	−37.4403
	T			−37.4421
$(CH_3)_2HPOCH_3$	TBP	OCH_3, H	CH_3, CH_3	−53.9320
	T			−53.9228
H_3PCH_3	TBP	H, H	CH_3, H	−18.5578
	TBP	CH_3, H	H, H	−18.5481
	T			−18.5524

Table III. CNDO/2 Results of π-Ligand Radicals without Strong Electron-Withdrawing Groups

Radical	Trial structure	Apical	Equatorial	E (au)
I	T			−17.2380
	TBP	CH_2, H	H, H	−17.1563
	TBP	H, H	CH_2, H	−17.1619
II	T			−119.1513
	TBP	biph, CH_3	biph, CH_3	−119.1338
III	T			−134.5585
	TBP	OCH_3, OCH_3	OCH_3, Ph	−134.5288
IV	T			−71.3923
	TBP[a]			−71.3147
	Square pyr			−71.2006
V	T			−52.1302
	TBP	CH_3, CH_3	CH_3, $CHCH_3$	−52.0348
	TBP	CH_3, $CHCH_3$	CH_3, CH_3	No convergence
VI	T			−42.9787
	Trigonal			−42.9497
VII	T			−51.5033
	TBP	CH_3, CH_3	CH_3, $CH{=}CH_2$	−51.4964
	TBP	CH_3, $CH{=}CH_2$	CH_3, CH_3	−51.4836

[a] Both rings have one apical and one equatorial P–C bond.

Table IV. CNDO/2 Results of π-Ligand Radicals with Strong Electron-Withdrawing Ligands

Radical	Trial structure	Apical	Equatorial	E (au)
$H_3PCH{=}CH_2$	TBP	H, H	H, $CH{=}CH_2$	−25.5071
	TBP	H, $CH{=}CH_2$	H, H	−25.4941
	T			−25.5008
$PhP(OCH_3)_2$-OCF_3	TBP	OCH_3, OCF_3	OCH_3, Ph	−217.9811
	Square pyr			−217.9796
	T			−217.9585
$PhPH_2(OCH_3)$	TBP	H, OCH_3	H, Ph	−82.6907
	TBP	H, H	OCH_3, Ph	−82.7031
	T			−82.7102

Table V. CNDO/2 Results of Some Oxyphosphoranes

Radical or compound	Trial structure	E (au)
VIII	TBP	−121.3162
	Square pyr	−121.4781
IX	TBP	−120.3384
	Square pyr	−120.4935
X	T	−112.0541
	TBP	−112.0465
	Square pyr	−112.0296

Table VI. Comparison of Experimental a_P's (G) with Those Derived from CNDO/2 Calculations

Radical	a_P (exptl)	a_P (calcd)	Ref
I	41	55	7, 8
II	18	2.7	20
V	41	9.3	21
VI	32	1.8	21

Table VII. Semiempirical Constants Used in the UHF Calculations

Orbital	γ_{ii} (eV)	α_{core} (eV)	β_{C-C} (eV)
C_{2p}	11.13	−11.16	−2.32
P_{3d}	6.3	−2.86	

Spin Density Calculations with CNDO/2

To check the calculated spin densities, radicals I, II, V, and VI were used since the a_P's were known experimentally. All these radicals have a T-like configuration. To calculate the a_P's from the calculated spin densities we used the following formula[18]

$$a_P = Q_{Ps}\rho_s$$

in which ρ_s is the spin density in the 3s orbital of phosphorus. The value we used for the Q-interaction constant is Q_{Ps} = 3600 G, which is derived from theory.[19] The results are listed in Table VI. The a_P (exptl) value is the splitting constant as found in ESR experiment. For I the value of a_P (exptl) is that of $Ph_3PCH_2^+$ which should not differ too much from $H_3PCH_2^+$.

Evidently, CNDO/2 calculations cannot be used to calculate spin densities in phosphorus radicals.[15,18] This is presumably also true for other second-row atoms. Another difficulty is that with CNDO/2 it is only possible to calculate relatively small-sized radicals because of the long computer times. It will therefore be convenient at this point to introduce our π-electron UHF calculations.

Details Concerning the UHF Calculations

The computer program was based on the spin-projected semiempirical UHF method of Amos and Snyder.[22,23] For calculation of the two-center repulsion integrals (γ_{ij}) we used the formula of Nishimoto and Mataga[24]

$$\gamma_{ij} = \frac{14.397}{R_{ij} + (28.794/(\gamma_{ii} + \gamma_{jj}))}$$

in which γ_{ii} and γ_{jj} are one-center repulsion integrals and R_{ij} is the distance between the atomic orbitals i and j. The γ between two d orbitals was assigned the value of the one-center repulsion integral of the d orbital.

The resonance integrals (β_{ij}) between the phosphorus 3d orbitals and the adjacent carbon p orbitals were calculated from

$$\beta_{ij} = S_{ij}(\alpha_i + \alpha_j)/2(1 + |S_{ij}|)$$

in which S_{ij} is the overlap integral, calculated by integrating over the corresponding STO's, and α_i and α_j are the one-center core integrals. The β between two d orbitals is zero as a consequence of the orthogonality of the d orbitals. In Table VII the relevant parameters are listed. Those for phosphorus are the values calculated by Levinson and Perkins.[25] Phosphorus splitting constants were obtained from the calculated spin densities with

$$a_P = \sum_i (Q_{C-P}\rho_{ii}{}^C) + \sum_j (Q_{Pd}\rho_{jj}{}^P)$$

in which $\rho_{ii}{}^C$ is the spin density on a carbon atom attached to the phosphorus atom and $\rho_{jj}{}^P$ is the spin density in one of the five 3d orbitals of the phosphorus atom. The best fit values for Q_{C-P} and Q_{Pd} are −42 and 68 G, respectively. The value of $|Q_{C-P}|$ is very close to 40.68 G as suggested by Lucken and Mazeline.[7,8] The sign difference is consistent with the theories about spin polarization.

Results of the UHF Calculations

Radicals XI–XVI were calculated by the method indicated above.

$Ph_3PCH_2^+$	$Ph_3PCPh_2^+$	PPh_4
XI	XII	XIII
Ph_2P(biph)	P(biph)$_2$	(biph)PPh·benzyl
XIV	XV	XVI

All P–C distances were taken as 1.85 Å. Ylides have P–C distances of about 1.80 Å, these radicals are expected to have slightly larger distances; see also ref 14a and 14b. In Table VIII the measured and calculated phosphorus splitting constants are compared. In XV the calculated a_P deviates from the measured value, because the calculation was performed with one biphenyl group omitted from the molecule. The reason is that the molecule with two biphenyl groups is electronically degenerated[29] and therefore calculations give solutions with no physical sense. In XVI the benzyl group was omitted in the calculation because of the π character of the calculation. The calculated a_P value indicates that the benzyl group does not have a significant effect upon the α_P and γ_{PP} values. Inspection of Table VIII shows a reasonable quantitative agreement between theory and experiment.

Table VIII.[28] Comparison of Experimental a_P's (G) with Those Computed with the UHF Method

Radical[a]	a_P (exptl)	a_P (calcd)	$\Sigma\rho_{ii}{}^C$	$\Sigma\rho_{ii}{}^P$	Temp, °C	Preparation solvent	Lit.
XI	40.7	38.7	0.968	0.029	20	—	7, 8
XII	26.0	26.8	0.677	0.024	20	Benzene	3
XIII	4.0	3.8	0.372	0.173	−60	DMF	26, 27
XIV	9.5	10.0	0.348	0.067	−90	THF–DMF 1:1	26
XV	14.5	10.2	0.358	0.071	−60	THF–DMF 1:1	4, 5
XVI	9.6	9.9	0.350	0.070	−90	THF–DMF 1:1	26

[a] All radicals were prepared by electrochemical reduction with platinum electrodes, except for XI which was prepared by X-ray irradiation in a crystalline matrix.

The low splitting in XIII is caused by the fact that the spin density is delocalized over the whole molecule because of its symmetry. This causes a relatively high spin density on the phosphorus atom, which substantially lowers the a_P, because of the opposite signs of $Q_{C\text{-}P}$ and Q_{Pd}.

Though XV is also symmetric, the spin density is here localized on just one of the biphenyl groups, because the symmetry of the molecule is lowered by a strong Jahn-Teller effect.[30] In all the other compounds the spin density is localized in one ligand: in the one with the highest electron affinity. In XI and XII these are the methylene and diphenylmethylide groups, respectively, because these ligands have a positive charge without the unpaired electron, as a result of the odd number of carbon atoms they have. In the other compounds the biphenyl group has the highest electron affinity. The high splittings in XI and XII with respect to the other compounds, exist because the spin density in the ligand is mainly localized on the carbon atom adjacent to the phosphorus atom.

Discussion

It has been clearly shown that odd electron delocalization with the aid of π ligands leads to T configurations.[3-6] On the other hand, introduction of electron-withdrawing ligands even in phenylphosphoranyl radicals gives rise to a TBP configuration,[13] in which the odd electron is strongly localized on the phosphorus atom. When an electron-withdrawing substituent is introduced at the phosphorus, a T configuration will be unfavorable because in that case an electronegative ligand is linked to a positively charged phosphorus atom. In general the CNDO/2 method gives good results in calculating the geometries of phosphorus radicals. From ESR experiments we found that the approximations used in the CNDO/2 calculations make this method unsuitable for calculating spin densities. It might be better to perform INDO calculations where the calculated spin density in the 3s orbital of phosphorus looks more realistic. The phosphorus splitting constant could then be derived with more accuracy,[15,31] but even the INDO method uses a constant exponent for the wave function of the 3d-orbitals, while this exponent is dependent on the effective charge of the phosphorus atom.[11]

The model we used for our π-electron calculations is defective, because the 3d orbitals mix with the core (hyperconjugation). From the eigenvalues and eigenvectors calculated with CNDO/2 it follows that it is not always possible to make a distinction between π- and σ-molecular orbitals. Most of the molecular orbitals have a π symmetry in one part of the radical and a σ character in another part. Notwithstanding these defects, it was possible to infer phosphorus splitting constants which were in close agreement with the ESR data. This is due to the fact that the core participation in the highest molecular orbital (which is the most important one in determining the spin densities) of the tetracoordinated π-ligand complexes is always of the same low order. In these radicals the HOMO consists of approximately 6% of phosphorus core orbitals, 9% of other core orbitals, and 85% of carbon p_π and phosphorus 3d orbitals. This means that the differences of the spin densities on phosphorus in these molecules are mainly determined by the differences in energy of the ligand π orbitals relative to the phosphorus 3d levels.

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References and Notes

(1) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 2224 (1972).

(2) P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 6033 (1972).

(3) H. M. Buck, A. H. Huizer, and P. Schipper, *Phosphorus*, **1**, 97 (1971).

(4) R. Rothuis, T. K. J. Luderer, and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **91**, 836 (1972).

(5) R. Rothuis, J. J. H. M. Font Freide, and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **92**, 1308 (1973).

(6) A low phosphorus doublet splitting in compounds with one π-electron ligand was measured by G. Boekestein, E. H. J. M. Jansen, and H. M. Buck, *J. Chem. Soc., Chem. Commun.*, 118 (1974).

(7) E. A. C. Lucken and C. Mazeline, *J. Chem. Soc. A*, 1074 (1966).

(8) E. A. C. Lucken and C. Mazeline, *J. Chem. Soc. A*, 439 (1967)

(9) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

(10) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.

(11) D. Kilcast and C. Thompson, *J. Chem. Soc., Faraday Trans. 2*, 435 (1972).

(12) J. Nelder and R. Mead, *Comput. J.*, **7**, 308 (1964).

(13) A. G. Davies, M. J. Parrott, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 973 (1974).

(14) (a) H. L. Ammon, G. L. Wheeler, and P. H. Watts, *J. Am. Chem. Soc.*, **95**, 6158 (1973); (b) L. D. Cheung and L. M. Trefonas, *J. Heterocycl. Chem.*, **9**, 991 (1972).

(15) Y. I. Gorlov, I. I. Ukrainsky, and V. V. Penkovsky, *Theor. Chim. Acta*, **34**, 31-38 (1974).

(16) R. R. Holmes, *J. Am. Chem. Soc.*, **96**, 4143 (1974).

(17) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); **3**, 1298 (1964).

(18) Reference 10, p 178.

(19) R. Watson and A. Freeman, *Phys. Rev.*, **123**, 521 (1961); **124**, 1117 (1961).

(20) Thesis, R. Rothuis, Eindhoven, 1974.

(21) A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc. A*, 2388 (1971).

(22) T. Amos and L. C. Snyder, *J. Chem. Phys.*, **41**, 1773 (1964).

(23) L. C. Snyder and T. Amos, *J. Chem. Soc.*, **42**, 3670 (1965).

(24) K. Nishimoto and M. Mataga, *Z. Phys. Chem. (Frankfurt am Main)*, **12**, 335 (1957).

(25) K. A. Levinson and P. G. Perkins, *Theor. Chim. Acta*, **14**, 206 (1969).

(26) R. Rothuis, J. J. H. M. Font Freide, J. M. F. van Dijk, and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **93**, 128 (1974).

(27) H. Gilman and G. E. Brown, *J. Am. Chem. Soc.*, **67**, 824 (1945).

(28) Of course the a_P's are larger than a_H values calculated by other π-electron calculations. Therefore the differences between experimental and calculated a_P's are somewhat larger than usual, but still the relative error is rather small.

(29) From the ESR experiment one infers that in XV the odd electron is confined in one biphenyl part of the molecule, which means that XV exhibits a strong Jahn-Teller or solvent effect. See also ref 30.

(30) C. Kooistra, J. M. F. van Dijk, P. M. van Lier, and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **92**, 961 (1973).

(31) D. L. Beveridge, P. Dobosh, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1968).

(32) Square pyramidal geometries were taken from ref 16.