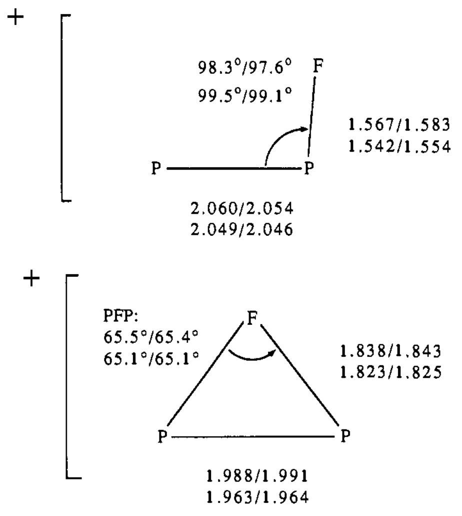


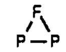
Top: CISD,TZ2P/CISD,DZP
Bottom: SCF,TZ2P/SCF,DZP

Figure 4. Theoretical geometris in ångströms and degrees for the bent and cyclic isomers of P_2F^+.

ring electrons, fulfilling the $4n + 2$ rule. Thus one would also predict P_2O^{2+} and P_2N^+ to be cyclic. Protonation at phosphorus weakens the P–P bond and the P_H–O bond substantially and shortens the P–O bond. One gives up P–P multiple bonding to gain P–O multiple bonding. Protonation at oxygen also strengthens the P–O bonds and weakens the P–P bond.

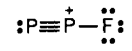
Another way to weaken the antibonding $3b_1$ interaction is to replace oxygen by fluorine. The energy of the fluorine atomic p orbital would be even further below the P–P π bonding orbital than the oxygen p orbital. If weakening the ring π interaction favors the cyclic structure, one might expect P_2F^+ to be cyclic. This hypothesis was tested theoretically by optimizing the structures of the isoelectronic P_2F^+. We found two stationary points, which are shown in Figure 4: a bent structure and a cyclic structure. The total energies and theoretical vibrational frequencies are given in Table V, and the relative energies are given in Table VI. At the SCF level, the bent structure is a minimum, and the cyclic structure is a transition state between the two equivalent bent structures. When correlation is included, however, the cyclic structure is not only a minimum, it is the global minimum, 4.4 kcal mol⁻¹ below the bent structure at the TZ2P CISD + Q level.

Table VI. Relative Energies of Bent and Cyclic P_2F^+ (kcal mol⁻¹)

	SCF		CISD	
	DZP	TZ2P	DZP	TZ2P
	0.0	0.0	0.0	0.0
	5.8	6.3	−3.4 −6.3[a]	−2.0 −4.4[a]

[a] Includes Davidson's correction for unlinked quadruple excitations.

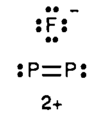
The linear structure was also a transition state at the DZP SCF level and was not investigated further. The highly electronegative fluorine will not form the linear structure (C), presumably because it would force a P–P triple bond:

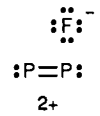


$$:P{\equiv}\overset{+}{P}{-}\ddot{\underset{\cdot\cdot}{F}}:$$

C

Viewed in terms of resonance structures, both cyclic and bent P_2F^+ contain ionic terms:





This is shown by the Mulliken populations which have a negative charge on the fluorine (−0.44 and −0.40 for cyclic and bent, respectively, at the TZ2P CISD level of theory).

If the key to stabilizing the cyclic structure is the weakening of the b_1 antibonding orbital interaction, one might expect that the groups NH and CH_2, which are isoelectronic to OH^+, might also prefer cyclic structures to linear ones when attached to P_2. In these cases the b_1 interaction would be weakened because the N–H and C–H bonds would polarize the N or C p_x orbital away from the phosphorus π orbitals. Although ring-opening polymerizations would certainly be energetically favored, if one could isolate these molecules (P_2F^+, P_2CH_2, or P_2NH) either in the gas phase, or in an inert matrix, they hold promise of being stable three-membered rings incorporating a P–P double bond.

Acknowledgment. This research was supported by the U.S. Air Force Office of Scientific Research, Grant AFOSR-87-0182.

Twisted Double Bond in Methylenephosphonium Ions. A Theoretical Investigation

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Received August 8, 1990

Abstract: Results of rigorous SCF calculations, including structure optimizations, are reported for $(R_2N)_2P^+{=}C(SiR'_3)_2$: R = H, Me, *i*-Pr; R′ = H, Me (and for $R_2P^+{=}CR'_2$ for comparison). Twisting of the $P^+{=}C$ double bond caused by steric hindrance of bulky groups R and R′ is facilitated by the electronic structure of the parent compound $(H_2N)_2P^+{=}C(SiH_3)_2$ which differs markedly from the genuine double-bond structure found in $H_2P^+{=}CH_2$.

I. Introduction

Igau, Baceiredo, Grützmacher, Pritzkow, and Bertrand[1] have recently reported the synthesis and crystal structure of the methylenephosphonium ion **1**, with R = *i*-Pr (C_3H_7) and R′ = Me with $CF_3SO_3^-$ as counterion. **1** could be simply considered as a phosphanylcarbene **2**, and the basic question addressed in the present work concerns the specific importance of amino and silyl groups for the properties of **1**.

The crystal structure of **1**, visualized in Figure 1a, shows re-

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[1] Igau, A.; Baceiredo, A.; Grützmacher, H.; Pritzkow, H.; Bertrand, G. *J. Am. Chem. Soc.* **1989**, *111*, 6853.

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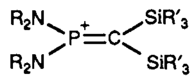
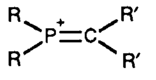


1



2

markable features;[1] despite a short PC distance (162 pm) and planar geometry at P and C (both indicative of a PC double bond), there is a twist angle of 60° for the "double bond", which raises questions about the electronic structure. To elucidate this problem we have performed SCF calculations for **1** and **2** for various R and R′. The calculations were performed with the program system TURBOMOLE[2] (on a workstation computer HP 835S) and employed an extended basis of DZP/TZP type[3] for P, Si, N, and C, and an STO-3G[4] basis for terminal Me and *i*-Pr groups. Equilibrium geometries were determined by a geometry relaxation procedure employing analytical gradients.[5] Whenever feasible, we computed second-order analytical gradients to confirm that a minimum was obtained.

II. Results and Discussion

The most instructive results of the present calculations are given in Table I. In agreement with previous theoretical studies,[6] we obtain a planar C_{2v} structure for phosphanylcarbene, i.e., **2** with R = R′ = H. The PC distance (162.3 pm) is rather shorter than found for phosphaalkenes[7] (164–169 pm), probably since P^+ has a smaller covalent radius than neutral P. According to population analyses, the PC double bond has slight polar character $P^{+0.7}C^{-0.2}$ (see Table I).

Substitution of C-bonded H by SiH_3, i.e., **2** with R = H, R′ = SiH_3, does not affect the planarity of the PC double bond. There is, however, an accumulation of electronic charge on C, $q_c = -0.7$ e, and a slight shortening of the PC distance, by 0.4 pm, probably arising from enhanced PC Coulomb attraction.

Substitution of P-bonded H in **2** by NH_2, i.e., **2** with R = NH_2 and R′ = H (diaminophosphanylcarbene), causes more pronounced changes; the double bond is twisted by 14.5°, the PC distance is shortened by 2.5 pm, as compared to R = H, and there is a marked increase of the charge of P, to $q_p = 1.3$ e. This leads to considerable Coulomb stabilization of PN bonds and the PC bond. Diaminophosphanylcarbene is isoelectronic to $[P(CH_2)_3]^-$, and the nonplanarity of these systems arises from nonbonding H–H repulsions[8,9] (distances of ≈ 174 pm; HH van der Waals distance 240 pm). $[P(CH_2)_3]^-$ can be considered as a Y conjugated system,[8,9] and this also holds for diaminophosphanylcarbene to some extent at least. The computed PN bond length of 159.8 pm (cf. Table II for PN distances in similar compounds) is markedly shorter than the typical single bond distance of ≈168 pm.[10] This is in line with the idea of Y conjugation; besides the PN σ bond and PN Coulomb attractions, the PN bond is stabilized by π-bonding effects. The increased electronic charge on C, $q_c = -0.5$ (versus −0.2 for R = H), also confirms this view since Y conjugated systems show electron accumulation on the ligands.[8,9]

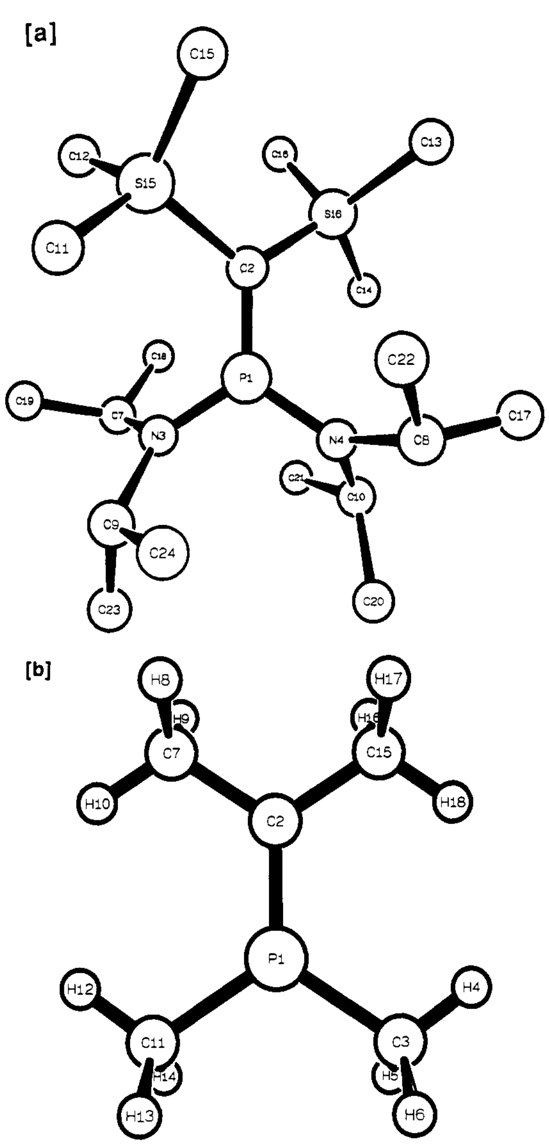


Figure 1. (a) Structure of **1** for R = *i*-Pr and R′ = Me, (hydrogen atoms omitted). (b) Structure of **2** for R = R′ = Me.

Table I. Computed Twist Angle θ, PC Distance, and Atomic Charges in Methylenephosphonium Ions[a]

no.	molecule (R/R′)	symmetry[b]	θ/deg	PC/pm	q_P[c]	q_C[c]	q_N[c]
1	**2** (H/H)	C_{2v}	0	162.3	0.7	−0.2	
2	**2** (H/SiH_3)	C_{2v}	0	161.9	0.7	−0.7	
3	**2** (NH_2/H)	C_2	14.5	159.8	1.3	−0.5	−0.4
4	**1** (H/H)	C_2	15.0	159.3	1.4	−1.0	−0.4
5	**1** (Me/H)	(C_2)	23.5	160.2	1.3	−1.0	−0.4
6	**1** (*i*-Pr/H)	(C_2)	31.5	161.1	1.3	−0.9	−0.5
7	**1** (*i*-Pr/Me)	(C_2)	38.1	161.6	1.3	−0.9	−0.5
8	**2** (Me/Me)	C_{2v}	0	164.2	0.9	−0.2	−0.3[d]

[a] As described in the text. [b] Symmetries given in parentheses have not been checked for (local) minimum character by second-order gradient calculations. [c] Atomic charges according to population analysis based on occupation numbers.[12] The trends of charges are close to those of a Mulliken population analysis, which gives q_C and q_N typically −0.3 e larger. [d] P-bonded carbon atom.

The substitution of C-bonded H by SiH_3 in diaminophosphanylcarbene causes effects similar to the corresponding substitution in phosphanylcarbene as is apparent from lines 3 and 4 in Table I (in comparison with the trend in going from line 1 to 2); there is virtually no change in the twist angle, 14.5° versus 15°, an increase of electronic charge on C (from −0.5 e to −1.0 e), and an accompanying slight reduction of the PC distance by 0.5 pm.

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(2) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(3) The contracted Gaussian basis set was of the type (9s, 5p, 1d)/[5s, 4p, 1d] for C, N, and (11s, 7p, 1d)/[6s, 4p, 1d] for Si and P, with s and p Gaussians from: Huzinaga, S. *Approximate Atomic Functions* **I and II**; University of Alberta: Edmonton, Alberta, Canada, 1971. The d exponents (C. 0.516; N, 0.976; Si, 0.449; P, 0.568) have been optimized for model systems, basically **1** for R = R′ = H.

(4) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(5) Geometry optimization terminated after the total gradient norm was smaller than 10^{-3} for Cartesian coordinates (in atomic units) and for internal coordinates (atomic units and radians).

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(8) Rajca, A.; Rice, J. E.; Streitwieser, A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1987**, *109*, 4189.

(9) Horn, H.; Ahlrichs, R. *J. Am. Chem. Soc.* **1990**, *112*, 2121.

(10) Cowley, A. H.; Mitchel, D. J.; Whangboo, M. H.; Wolfe, S. *J. Am. Chem. Soc.* **1979**, *101*, 5224.

Table II. Computed Properties (SCF Method) of Planar and Twisted $(CH_3)_2PC(CH_3)_2$ in Comparison with $(NH_2)_2PC(SiH_3)_2$[a]

molecule	θ, deg	G[b]	state[c]	ΔE	P–C	P–N	SEN (PC)	q_P[c]	q_C[c]
$(CH_3)_2PC(CH_3)_2^+$	0	C_{2v}[d]	$^1A_1$	0	164.2		1.96	0.86	−0.12
	90	C_{2v}	$^1A_1$[e]	71.4	186.5		1.19	0.25	0.32
	90	C_{2v}	$^3A_2$	33.8	178.4		1.36	0.95	−0.21
	90	C_{2v}	$^1A_2$[g]	35.2	178.4		1.36	0.95	−0.21
$(NH_2)_2PC(SiH_3)_2^+$	0	C_{2v}	$^1A_1$	0	159.0	160.5	2.02	1.42	−1.03
	15.0	C_2[d]	$^1A_1$	−1.7	159.3	160.6	2.04	1.39	−1.00
	90	C_{2v}	$^1A_1$[f]	18.2	158.8	159.3	1.96	1.56	−1.27
	90	C_{2v}	$^3A_2$	52.6	178.5	163.4	1.40	1.05	−0.62
	90	C_{2v}	$^1A_2$[g]	55.0	178.5	163.4	1.40	1.05	−0.62

[a] Distances in pm and relative energies in kcal/mol. [b] Molecular symmetry assumed if not stated othwerwise. [c] Atomic net charges according ref 12; see also footnote *c* of Table I. [d] Equilibrium geometry. [e] HOMO $7b_1$ dominantly located at P. [f] HOMO $8b_2$ dominantly located at C (see also Figure 2b). [g] Structure as in the $^3A_2$ state, not optimized.

The introduction of terminal groups bulkier than R = H and R′ = H leads to steady increases in the twist angle, paralleled by slight increases in the PC distance, whereas the charges on P, C, and N are virtually unchanged; cf. lines 4 to 7 in Table I. These changes are certainly due to the increased steric requirements of R and R′.

The computed net atomic charges, given in Table I, indicate that a useful representative of the class of compounds **1** is obtained for R = R′ = H, and that these are not typical phosphanylcarbenes. The importance of amino and silyl groups can be further tested if they are replaced by "electro neutral" methyl groups which have similar steric requirements. We have therefore also considered $Me_2P^+{=}CMe_2$, i.e., **2** with R = R′ = Me, in comparison with $(NH_2)_2P^+{=}C(SiH_3)_2$, i.e., **1** with R = R′ = H. Since we are mainly interested in properties of the PC double bond, we report in Table II computed data concerning the rotational barrier around the double bond axis. (A structure optimization has been carried out for the $^3A_2$ state of the 90° twisted geometry; the $^1A_2$ energy was computed at the same geometry.) The equilibrium structure of **2** with R = R′ = Me is shown in Figure 1b; any rotation of Me groups results in an energy increase.

The data for $Me_2P^+{=}CMe_2$ are analogous to those of C_2H_4 (which has higher symmetry of course). The lowest energy is obtained for the planar C_{2v} geometry with a PC bond distance of 164.2 pm, 2 pm longer than the one in $H_2P^+{=}CH_2$ (lines 1 and 8 of Table I) but still short for a PC double bond. There is, however, a normal mode with virtually zero vibrational frequency describing a distortion to C_s symmetry with pyramidal P, but no geometry leading to lower energy than found for C_{2v} could be located. The lowest singlet-state energy for the 90° twisted C_{2v} geometry was obtained for the open-shell $^1A_2$ state arising from singly occupied MOs $7b_1$ (phosphorus 3p) and $7b_2$ (carbon 2p), which is 33.8 kcal/mol above C_{2v}. The "ionic" closed-shell $^1A_1$ state requires an MCSCF treatment; as for ethene, a brute force SCF calculation yields an energy 71.4 kcal/mol above planar C_{2v} if $7b_1$ is doubly occupied (and 100 kcal/mol if $7b_2$ is doubly occupied). It should be noted that only C_2 symmetry is found (at most) during rotation and that A_1 and A_2 in C_{2v} both go to A in C_2.

The situation is completely different for **1** with R = R′ = H. The lowest energy for the 90° twisted molecule in C_{2v} is now found for the closed-shell $^1A_1$ state which is only 18.2 kcal/mol above planar C_{2v} and 20.0 kcal/mol above the C_2 equilibrium geometry. This result can be rationalized in the following way: (i) Coulomb bond stabilization acts independently of the twist angle; (ii) Y conjugation of the planar system leads to slightly reduced covalent PC bonding which facilitates rotation; and (iii) there is some degree of 2pπ3dπ bonding in the 90° structure. This is evident from the contour diagram of the doubly occupied HOMO $8b_2$ shown in Figure 2b. The nodal surface cuts through the location of P (and not the PC bond axis which would indicate anti bonding), as required for a bonding 3dπ contribution. The corresponding π MO $5b_2$ for planar C_{2v}, Figure 2a, shows a "normal" PC π bond with polarization toward C.

The 90° open-shell $^1A_2$ state (arising from singly occupied MOs $10b_1$ and $8b_2$ located on P and C, respectively) in **1** for R = R′ = H is 36.8 kcal/mol higher than the closed-shell $^1A_1$ state and 55 kcal/mol higher than the planar closed-shell ground state. This "anomalous" energetic ordering (as compared to ethene or $Me_2P^+CMe_2$ where the open-shell state is more stable) results from

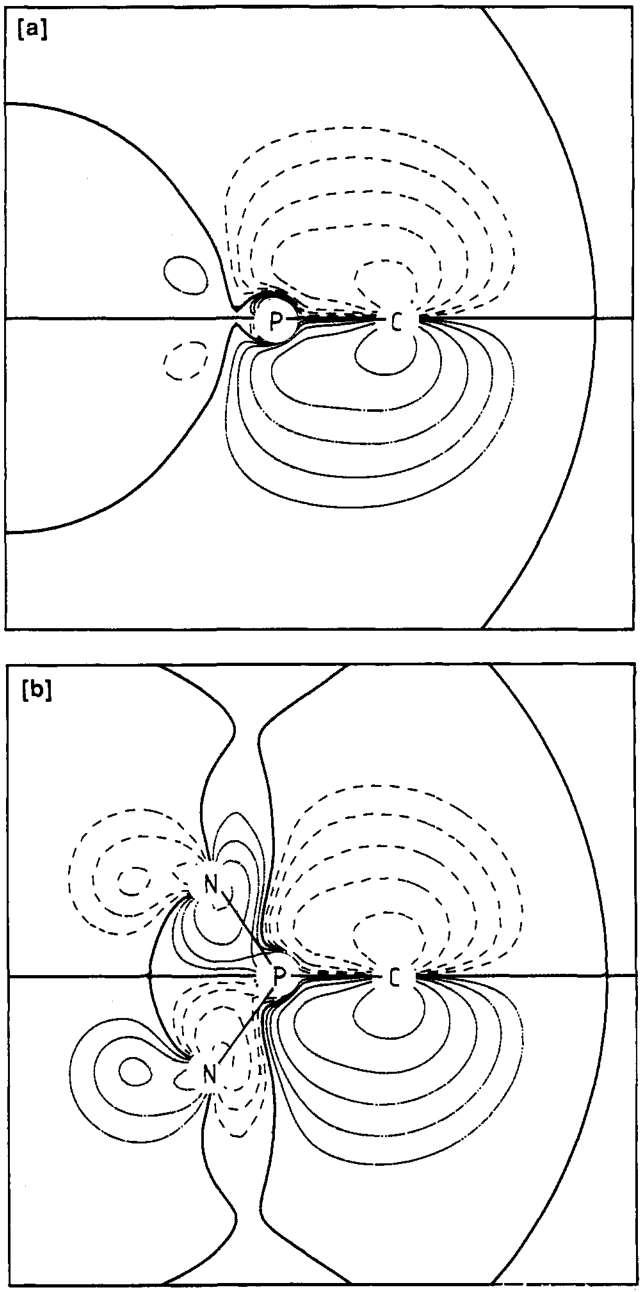

Figure 2. Contour diagrams of HOMO of **1**, R = R′ = H: (a) planar geometry, MO $5b_2$ describing the PC π bond; (b) MO $8b_2$ of the $^1A_1$ state in the 90° twisted geometry, describing the "2pπ3dπ bond". Plotted lines correspond to −0.16, −0.08, −0.04, −0.02, −0.01, 0.0, +0.01, +0.02, +0.04, +0.08, +0.16 a.u.

considerable destabilization of the $10b_1$ MO (dominantly phosphorus 3p) by the nitrogen lone pairs. One really has an NPN three-center, four-electron "π system" familiar from the allyl radical anion and other systems showing an NPN moiety.[11] The nitrogen lone pair electrons occupy the bonding $9b_1$ MO (and the formally nonbonding a_2 MO), and only the antibonding "π MO" ($10b_1$) of the three-center system is available on the P side for the open-shell state. This view is confirmed by the near planarity of N in the molecules investigated. The out-of-plane angle is 9° for the parent molecule **1** with R = R′ = H (at the C_2 equilibrium geometry) and only 0.2° for R = *i*-Pr and R′ = Me (the out-of-plane angle in ammonia is 61.4°). As further support we point out that the shortest PN distance (159.3 pm) of the cases considered in Table II occurs for the 90° twisted $^1A_1$ state, where the "allylic" system is unperturbed by the PC "double bond", whereas the longest PN bond occurs in the $^3A_2$ state where the singly occupied $10b_1$ MO is PN antibonding.

In Table II we have also given the PC "shared electron numbers" (SEN) of the population analysis,[12] which are a measure for covalent bond strength. We recall for comparison that SEN ≈ 1.4 and SEN ≈ 2.2 correspond to strong covalent single and double bonds. In the (almost) planar structures *and* the 90° $^1A_1$ structure of $(NH_2)_2P^+{=}C(SiH_3)_2$, we find SEN ≈ 2. The remaining cases yield SEN ≤ 1.4. The SEN(PC) are thus in line with the computed structure constants and the interpretations given above.

The comparison between **1** with R = R′ = H and **2** with R = R′ = Me confirms the conclusion drawn on the basis of net atomic charges presented in Table I: the amino and silyl groups in **1** are of great importance since they lead to a certain degree of Y conjugation resulting in properties which differ markedly from those expected for phosphanylcarbenes **2**.

The computed twist angle for **1** with R = *i*-Pr, R′ = Me is 40°, in relatively poor agreement with the experimental value of 60°. There are various possible sources for this discrepancy. We have assumed C_2 symmetry (leading already to 102 internal degrees of freedom), whereas a slight distortion to C_1 is found in the crystal. More important is the relatively small rotational barrier of the PC double bond in **1**, discussed above, which makes the twist angle sensitive to approximations inherent in the present approach (small basis sets for Me and *i*-Pr which underestimate steric requirements, neglect of electron correlation), and possibly also to crystal-packing effects. The remaining computed structure parameters deviate only by a few picometers or degrees from experiment[1] (in parentheses) for **1** with R = *i*-Pr, R′ = Me (in picometers and degrees, atoms labeled as in Figure 1a if confusion is possible): PC = 161.6 (162.0), PN = 162.8 (161.5/161.0), SiC2 = 195.0 (187.5/191.3), ∠NPN = 114.3 (112.2), ∠C2PN = 122.8 (123.4/124.4), ∠PNC7 = 122.6 (121.0/124.4), ∠PNC9 = 124.9 (120.2/123.1) ∠C7NC9 = 112.4 (115.1/115.6), ∠PC2Si = 121.6 (119.3/121.7), ∠SiC2Si = 116.8 (119.1); sum of bond angles at N is 359.9 (359.7).

III. Summary

The combination of a short PC bond distance and a large twist angle in **1** may be rationalized in the following way. The Coulomb bond stabilization acts independently of the twist angle. The slight polarity of the PC bond in phosphanylcarbenes **2** becomes much more pronounced in **1**, which has some degree of Y conjugation and is further enhanced by silyl groups. This together with some degree of PC $2p\pi 3d\pi$ bonding in the 90° twisted structure leads to a rotational barrier around the PC bond of only 20 kcal/mol, in **1** with R = R′ = H, which facilitates twisting due to steric requirements of bulky groups R and R′ in **1**.

The remarkable structural features of **1**, R = *i*-Pr and R′ = Me, found by Bertrand et al.,[1] are thus essentially due to pronounced changes in molecular electronic structure effected by the electronegative NR_2 groups at P and the electropositive SiR_3 groups at C, which facilitate twisting caused by steric hindrance of bulky groups R and R′ in **1**. The present discussion of structural features of **1** is based on trends in computed properties (structure, atomic charges) resulting from changes in substituents. This view is complementary to—certainly not in contradiction with—the model of Trinquier and Malrieu[13] based on properties of the radicals obtained by breaking the double bond.

Acknowledgment. The authors thank Dr. G. Bertrand for valuable discussions. This work has been supported by the Fonds der Chemischen Industrie.

Supplementary Material Available: Listing of Cartesian coordinates of atoms, basis sets, and SCF energies of all molecules treated in this paper (11 pages). Ordering information is given on any current masthead page.

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MNDO Study of Large Carbon Clusters

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Received October 22, 1990

Abstract: MNDO calculations with complete geometry optimization are reported for 30 polyhedral carbon clusters C_n ($20 \leq n \leq 540$). The MNDO results for a planar graphite sheet are extrapolated from calculations on D_{6h} hydrocarbons C_nH_m ($n = 6k^2$, $m = 6k$, $k = 1$–6) and used as a reference for discussing the properties of the clusters. The structural features of the clusters are correlated with their stability. The relative MNDO energies with respect to graphite are compared with curvature-corrected Hückel calculations and with force field estimates, and criteria for the stability of the clusters are discussed. Infrared spectra are predicted for six stable clusters. Several cationic lithium complexes and their interconversions are investigated for C_{60} and C_{42}. Finally, computational aspects and performance data are considered, particularly for the largest clusters studied.

1. Introduction

Over the past years there has been considerable interest in pure carbon molecules. A comprehensive review[1] has recently documented the structural, electronic, and spectroscopic properties of small C_n molecules ($n < 20$) whose most stable isomers are usually either linear chains or monocyclic rings. Larger carbon clusters with $n \leq 190$ have been generated[2] by laser vaporization of graphite into a supersonic beam, followed by photoionization and

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