Inorg. Chem. **1994**, *33*, 1153–1157

Calculated Properties of Triphospha[1.1.1]propellane

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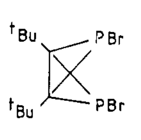
Received June 30, 1993®

Ab initio molecular orbital calculations at the MP2/6-31G* level of the structure, vibrational spectra, and thermochemical properties of triphospha[1.1.1]propellane (**4**), diphosphabicyclo[1.1.0]butane (**5**), and phosphirane (**6**) have been carried out and compared with those of their all-carbon analogues. **4** possesses a ring strain even smaller than that of [1.1.1]propellane and is characterized by a bridgehead C–C distance of 1.63 Å and a heat of formation ($\Delta H^\circ_{f,0}$) of 560 ± 20 kJ/mol. The observable IR bands of **4** are centered in the regions of 2291, 947, 755, and 459 cm^{-1}, while the first vertical UV absorption of **4** is expected at 5.3 ± 0.5 eV. Although the C–C bridgehead distance in triphospha[1.1.1]propellane (**4**) is rather long, it has been shown by atoms-in-molecule calculations that a bridgehead bond exits and has a pronounced covalent character.

Introduction

In recent years, a large number of three-membered rings containing both phosphorus and carbon atoms have been synthesized and characterized.[1] Efficient routes are now available for the preparation of substituted phosphiranes and diphosphiranes. Several polycyclic derivatives of the latter have also been described including the bicyclic compounds **1** and **2**.[2] As far as we are aware, phosphorus derivatives of propellanes are not known yet. It is needless to say that [1.1.1]propellanes form a class of intriguing molecules having inverted tetrahedral geometry at the bridgehead carbon atoms. The recent synthesis of a pentastanna[1.1.1]propellane[3] has stimulated a surge of interest in propellanes containing heavier group 14 elements (Si, Ge, Sn).[4] Successive substitution of carbon units by heteroatoms is another possible avenue leading to new derivatives. A recent theoretical study[5] pointed out that the sulfur analogue **3** is a tightly-bound molecule and should be experimentally accessible. Accordingly, **3** possesses a ring strain even smaller (about 11 kJ/mol) than that of the parent all-carbon species. Since phosphirane is also less strained than cyclopropane (by about 30 kJ/mol[6]), one might expect that triphospha[1.1.1]propellane (**4**) would have a ring strain at least comparable to that of [1.1.1]propellane. In an attempt to assess the stability of **4**, we have carried out a theoretical study of its structure and properties. Diphosphabicyclo[1.1.0]butane (**5**) and phosphirane (**6**) have also been considered and compared with their all-carbon analogues. Our thermochemical results suggest that triphospha[1.1.1]propellane (**4**) constitutes a viable candidate for a laboratory preparation. In addition, the electronic structure and bonding of these P-compounds have been analyzed using the theory of atoms-in-molecule.



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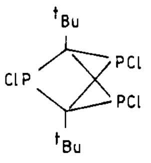

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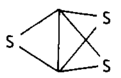

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Details of Calculations

To facilitate comparison, we have performed ab initio molecular orbital calculations at the same level as in a previous report.[5] Optimized geometries and harmonic vibrational wavenumbers of the species examined were obtained using second-order Møller–Plesset perturbation theory (MP2) with the d-polarized 6-31G* basis set. Thermochemical parameters were estimated from MP2/6-31G* total energies and zero-point vibrational corrections. The vertical excitation energies were calculated with the configuration interaction method including all monoexcitations (CIS) and the larger 6-311++G** basis (++ denotes a set of sp-diffuse functions). Molecular orbital calculations were performed making use of the Gaussian 90 program.[7] The electronic analysis has been carried out by employing the PROAIM program.[8]

Results and Discussion

Molecular Structure. Figure 1 displays the optimized geometrical parameters of **4**–**6** as well as experimental data[9] for **6**. Calculated geometries for [1.1.1]propellane (**7**), bicyclo[1.1.0]butane (**8**), and cyclopropane (**9**) at the same level of theory have been previously reported and discussed in detail.[5,10] Unless otherwise noted, the theoretical parameters mentioned hereafter refer to the MP2/6-31G*-optimized values. As seen in Figure 1, there is good agreement between theory and experiment for the geometry of phosphirane (**6**). Such agreement is substantiated by rotational constants that can be compared as follows:

	calcd, MHz	exptl, MHz
A	20328	20094
B	9736	9801
C	7629	7634

The relative deviations on rotational constants are thus about 1%. Of particular relevance are the C–C and C–P bond distances. In the order from the monocyclic molecule **6** to the polycyclic **5**

® Abstract published in *Advance ACS Abstracts*, February 1, 1994.

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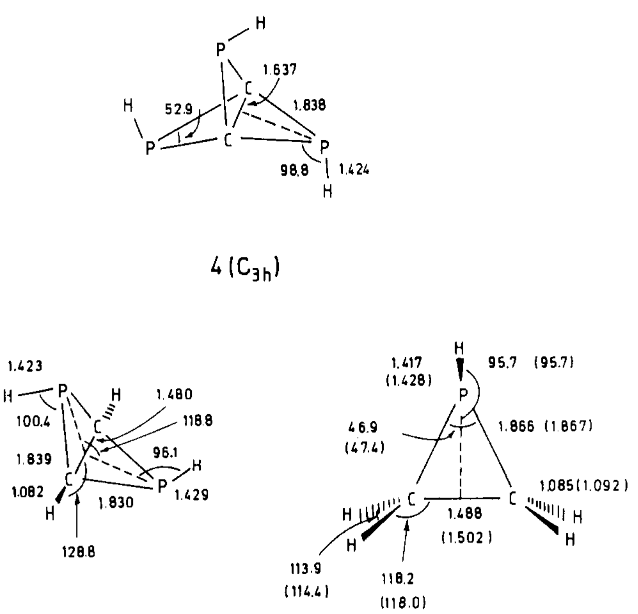

$4\ (C_{3h})$

$5\ (C_s)$

$6\ (C_s)$

Figure 1. MP2/6-31G*-optimized geometries of phosphorus cycles. Bond lengths are given in Å, and bond angles in deg. For **6**, experimental values in parentheses are from ref 9.

Table 1. Calculated Energies of Bond Separation Reactions (MP2/6-31G*)

	bond separation reacn	ΔE_r (kJ/mol)
A	**4** + $6CH_4 + 3PH_3 \rightarrow CH_3CH_3 + 6CH_3PH_2$	−232
B	**5** + $4CH_4 + 2PH_3 \rightarrow CH_3CH_3 + 4CH_3PH_2$	−150
C	**6** + $2CH_4 + PH_3 \rightarrow CH_3CH_3 + 2CH_3PH_2$	−66
D	**7** + $9CH_4 \rightarrow 7CH_3CH_3$	−314
E	**8** + $6CH_4 \rightarrow 5CH_3CH_3$	−231
F	**9** + $3CH_4 \rightarrow 3CH_3CH_3$	−100
G	**4** + $3CH_3CH_2CH_3 \rightarrow$ **7** + $3CH_3PHCH_3$	87
H	**5** + $2CH_3CH_2CH_3 \rightarrow$ **8** + $2CH_3PHCH_3$	84
I	**6** + $CH_3CH_2CH_3 \rightarrow$ **9** + CH_3PHCH_3	35

Table 2. Calculated and Experimental Vibrational Wavenumbers of Phosphirane (**6**) (in cm^{-1})

mode		phosphirane-d_0 calcd[a]	phosphirane-d_0 exptl[b]	phosphirane-d_1[c] calcd[a]	phosphirane-d_1[c] exptl[b]	isotopic shift calcd[a]	isotopic shift exptl[b]
a′	1	3109	3092	3109	3092	0	0
	2	3019	3012	3019	3012	0	0
	3	2247	2291	1616	1667	−631	−624
	4	1449	1437	1448	1435	−1	−2
	5	1075	1058	1075	1058	0	0
	6	1005	1004	1001	999	−4	−5
	7	974	969	913	913	−61	−56
	8	800	8004	791	792	−9	−12
	9	752	769	605	618	−147	−151
	10	604	598	594	595	−10	−3
a″	11	3097	3093	3097	3093	0	0
	12	3016	3016	3016	3016	0	0
	13	1424	1416	1425	1418	1	2
	14	1178	1232	1178	1233	0	1
	15	1021	1004	1016	999	−5	−5
	16	917	916	857	855	−60	−61
	17	647	657	634	643	−13	−14
	18	593	580	485	478	−108	−102

[a] MP2/6-31G* values and scaled by 0.94. [b] From ref 12. [c] Isotopic substitution on P.

Table 3. Calculated Vibrational Wavenumbers (in cm^{-1}) and IR Intensities of Triphospha[1.1.1]propellane (**4**)

mode[a]		**4**-d_0 calcd[b]	**4**-d_0 I[c]	**4**-d_3[d] calcd[b]	**4**-d_3[d] I[c]	isotopic shift
a	1	2278	0	1637	0	−641
	2	888	0	792	0	−96
	3	755	14	607	0	−148
	4	605	0	495	29	−110
	5	459	46	435	59	−24
	6	399	0	398	0	−1
e	7	2291	100	1646	100	−645
	8	947	26	828	55	−119
	9	848	0	776	0	−72
	10	771	0	650	9	−121
	11	598	0	474	0	−124
	12	293	1	281	2	−12

[a] Using C_3 symmetry. [b] MP2/6-31G* values and scaled by 0.94. [c] Normalized intensities. [d] Substitution on P.

and **4**, the C–P length actually decreases whereas the C–C distance is marginally compressed (0.008 Å) in **5** but markedly stressed in **6** (0.15 Å). A similar trend can also be observed for the bridgehead C–C bond in the carbon analogues **7**–**9** albeit to a lesser extent,[5,9] namely 1.502 Å (exptl, 1.512 Å) in cyclopropane (**9**), 1.496 Å (exptl, 1.497 Å) in bicyclobutane (**8**), and 1.592 Å (exptl, 1.596 Å) in [1.1.1]propellane (**7**). Thus, the bridgehead C–C distance in the phosphorus derivative **4** is predicted to be longer than that in its carbon analogue **7** or in the sulfur analogue **3** (1.562 Å). As a consequence, the bond angle at P within the three-membered rings in **4** is opened by 6° relative to that in **7**.

Thermochemical Properties. The thermochemical stability of the phospha derivatives **4**–**6** can be evaluated with the aid of a couple of bond separation reactions. The associated reaction energies are summarized in Table 1. The energy of each one of the isodesmic reactions A–F provides a measure of the ring strain of the corresponding cyclic system. This property is approximately additive. As a matter of fact, the ring strain in both propellane forms **4** and **7** is about three times as large as in both cyclopropanes forms **6** and **9**, respectively. Similarly, the ratio of ring strain energies between **5**/**6** and **8**/**9** is somewhat larger than two. More interestingly, the phosphorus systems **4**–**6** are found to be consistently less strained than their carbon analogues **7**–**9**. This is also in line with a significant endothermocity of the homodesmic reactions G–I, especially for the two reactions G and H that have similar reaction energies. Using the available experimental heats of formations for reference molecules,[11] the heat of formation of triphospha[1.1.1]propellane (**4**) is estimated to be $\Delta H°_f = 560 \pm 20$ kJ/mol at 0 K.

Vibrational and Electronic Spectra. Calculated and experimental[12] values for fundamental vibrational wavenumbers of phosphirane (**6**) in both isotopic H and D(P) forms are compared in Table 2. The harmonic wavenumbers obtained by MP2/6-31G* calculations have been scaled down by 0.94, a scaling factor suggested by earlier studies[5] on cyclopropane **9** and [1.1.1]-propellane (**7**), to account for the systematic overestimation at this level of theory. Similar to the earlier observations, the mean absolute error of 36 comparisons is just 13 cm^{-1} with a maximum deviation of 55 cm^{-1}. The calculated isotopic wavenumber shifts compare better with experiment. This satisfactory agreement lends confidence to the predictions for triaphospha[1.1.1]-propellane (**4**) given in Table 3. From these calculated results, a few points can be noted: (1) The PH stretching mode in **4** shows a small upward wavenumber shift (44 cm^{-1}) relative to that in **6**. (2) Only four vibrational modes of **4** are IR active. The asymmetric PH stretching mode is predicted to have the most intense absorption. (3) Isotopic wavenumber shifts due to deuterium atoms are present in all cases and are rather large. The shift associated with the PH stretching vibration is somewhat

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Table 4. Vertical Excitation Energies of P-Cycles **4**–**6** (in eV)

molecule	excitation energy[a]	f^b	main orbital transition[c]
4	5.3	0.026	$^1A''$: $9a' \rightarrow 4a''$
	5.9	0.000	$^1E''$: $7e' \rightarrow 4a''$
5	5.7	0.030	$^1A''$: $17a' \rightarrow 7a''$
	6.3	0.430	$^1A''$: $16a' \rightarrow 7a''$
6	6.4	0.015	$^1A''$: $5a'' \rightarrow 12a'$
	6.5	0.068	$^1A''$: $11a' \rightarrow 6a''$

[a] Based on CIS/6-311++G* * values and corrected by –0.5 eV for systematic overestimation. [b] Oscillator strengths. [c] The monoexcitation having the largest contribution into the CIS wave function.

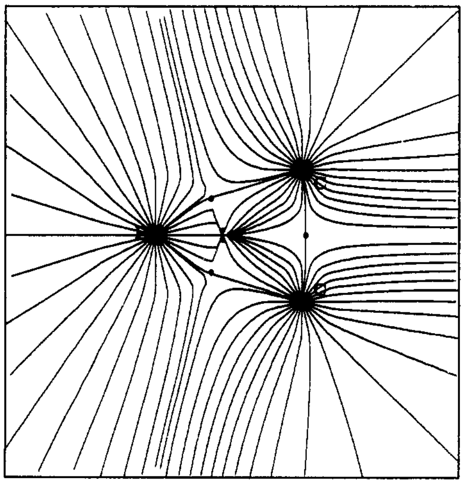

Figure 2. Bond path network of phosphirane (**6**) in the ring plane.

larger than that in **6** (645 versus 631 cm^{-1}). Thus both absorption intensity and isotopic shift make the PH stretching mode an important element of information to be used in an eventual identification of **4** by IR spectrometry.

Table 4 list the first two vertical excitation energies of **4**–**6**. CIS/6-311++G* calculations provide only upper bounds for this property. For bicyclobutane (**8**), the calculated value at this level is overestimated by about 0.5 eV[10] relative to the experimental value. To obtain more realistic predictions, we assume a systematic correction of 0.5 eV for the calculated values. In the order from the monocyclic species **6** to the tricyclic **4**, the UV absorption appears to shift toward a larger wavelength region. Unfortunately, as yet, the electronic spectrum of **6** is not available for comparison.

Evidence of a Bridgehead C–C Bond. As mentioned before, the C–C distance in **4** is rather long, about 0.15 Å longer than that in **6**. Therefore the question of interest is whether there is a bridgehead bond in triphospha[1.1.1]propellane (**4**). The formation of a bond between two atoms in a molecule can be viewed by means of a topological analysis of the electronic charge density.[13] In this approach, a "bond path" is defined as a unique line linking two nuclei in interaction, along which the electronic density ρ is a maximum with respect to any neighboring line. A bond path is determined by two vectors of $\nabla\rho$ which originate from the corresponding "bond saddle point" in ρ. The presence of such a critical point, usually denoted as a (3,–1) critical point since it is a maximum in ρ in two directions and a minimum in the third, implies that the electronic charge is accumulated between both nuclei along the bond path.

It is argued that the existence of a bond path in an equilibrium structure is the necessary and sufficient condition for a chemical bond.[13] Figures 2–4 show the gradient vector fields that define the bond paths and atomic basins in the cycles **4**–**6**. Electronic densities are calculated using HF/6-31G* wave functions. The figures clearly demonstrate the presence of a bond path linking two C atoms forming a ring structure in each of the three molecules considered. In addition, a ring critical point, i.e. (3,+1) critical point, is also observed within the bonding triangle. In a topological approach, the number and type of critical points which can coexist in a system containing a finite number of nuclei is governed by the relationship[13]

$$n - b + r - c = 1 \tag{1}$$

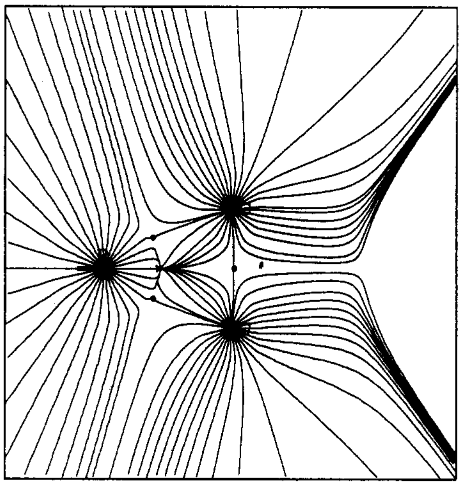

Figure 3. Bond path network of diphosphabicyclo[1.1.0]butane (**5**) in one C–P–C ring plane.

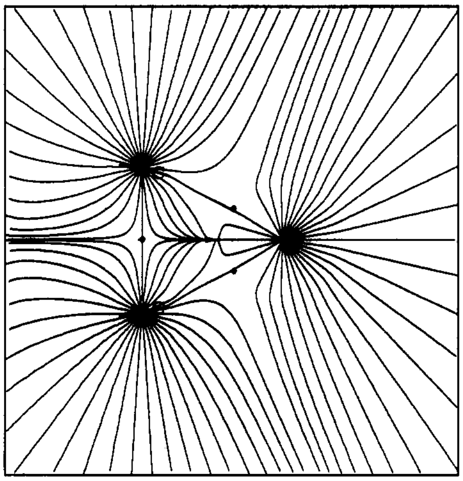

Figure 4. Bond path network of triphospha[1.1.1]propellane (**4**) in one C–P–C ring plane.

Table 5. Properties of the Bond Critical Point of Phosphorus Cycles **4**–**6** and Their All-Carbon Analogues **7**–**9** (HF/6-31G*)

	P-cycles				C-cycles			
bond A–B	compd[a]	ϵ	$\rho_b{}^b$	$\nabla^2\rho(r)^b$	compd	ϵ	$\rho_b{}^b$	$\nabla^2\rho(r)^b$
P–H/C–H[c]	**6**	0.03	0.16	0.02	**9**	0.03	0.28	–1.04
C–H[c]		0.03	0.29	–0.08		0.03	0.28	–1.04
C–P/C–C		0.50	0.14	–0.08		0.44	0.25	–0.53
C–C		0.23	0.24	–0.66		0.49	0.25	–0.53
ring			0.12				0.20	
C–P/C–C	**5**	0.58	0.14	0.07	**8**	0.53	0.25	–0.53
C–C(bridge)		0.19	0.26	–0.54		0.45	0.25	–0.38
ring			0.13				0.21	
C–P/C–C	**4**	0.78	0.14	0.07	**7**	0.55	0.25	–0.52
C–C(bridge)		0.00	0.18	–0.12		0.00	0.20	0.03
ring			0.14				0.20	

[a] Compounds: **4**, triphospha[1.1.1]propellane; **5**, diphosphabicyclo[1.1.0]butane; **6**, phosphirane; **7**, [1.1.1]propellane; **8**, bicyclo[1.1.0]butane; **9**, cyclopropane. [b] In au. [c] Similar values for bi- and tricyclic molecules.

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[13] Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893. Bader, R. F. W. *Atom in molecules. A quantum theory*; Clarenton Press: Oxford, U.K., 1990.

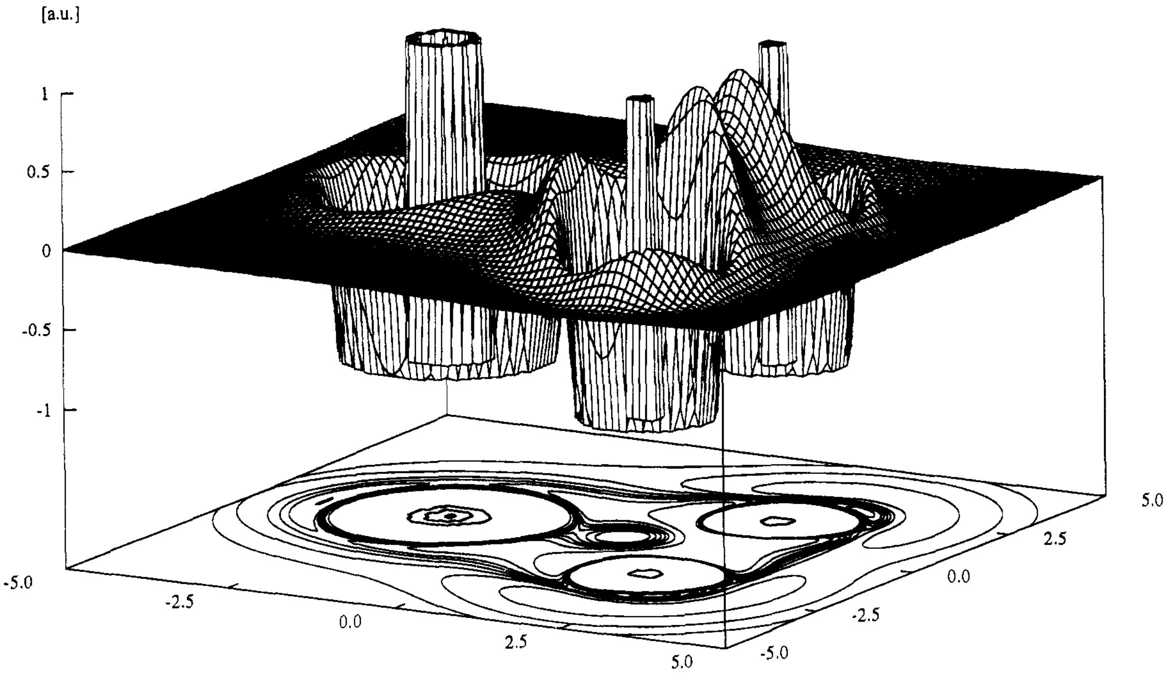

Figure 5. Contour maps of the Laplacian of the charge density in one C–P–C ring plane of phosphirane (**6**).

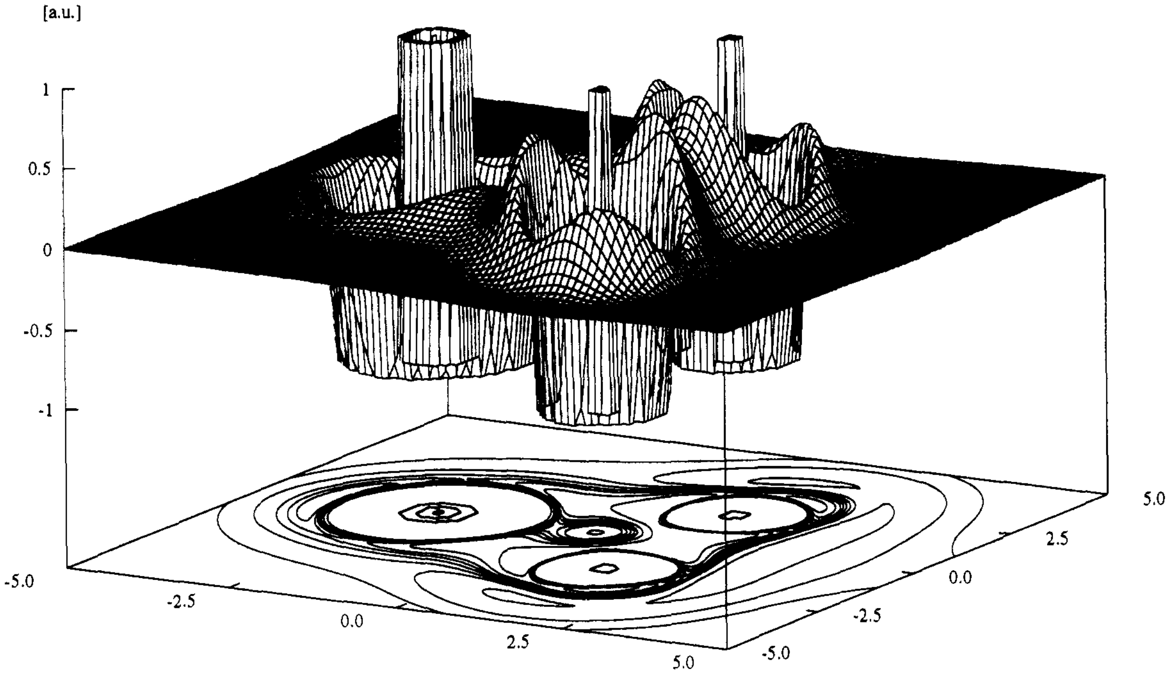

Figure 6. Contour maps of the Laplacian of the charge density in one C–P–C ring plane of diphosphabicyclo[1.1.0]butane (**5**).

where n is the number of nuclei, b is the number of bonds, r is the number of rings, and c is the number of cages. In **4**, $n = 8$, $r = 3$, and $c = 0$; thus, $b = 10$. Hence from a topological point of view, there has to be a bond path between the two bridgehead carbons.

Bonding Properties. Any deviation of the bond path from the corresponding internuclear line can be indicative of bond bending. The bent bond character is qualitatively assessed by comparing the bond path length (R_b) and bond length (R_e). For the C–C bonds, the bond paths are almost straight ($R_b \simeq R_e$). The curving of the C–P bonds, as measured by $R_b - R_e$, decreases from 0.054 Å in **6** to 0.018 Å in **5** and to 0.007 Å in **4**, indicating a uniform distribution of the strain over all C–P bonds in triphospha[1.1.1]propellane.

It is interesting to compare the bond properties of P-compounds **4**–**6** with their all-carbon analogues **7**–**9**. A topological analysis of the latter has been reported in a previous study.[14] As seen in Table 5, a similar trend in the bridgehead C–C bond properties in both series of rings can be noted. In the order from the monocycle to the polycycle, ϵ, the bond ellipticity, ρ_b, the charge density, and $\nabla^2\rho_b$, the Laplacian at the bond critical point, decrease in both systems.

Let us investigate these observations in somewhat more detail. The ellipticity of the bond critical point measures the rate of density fall off in the two directions. For the P–H and C–H bonds, ϵ is small but nonzero, indicating some axial distortion

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[14] Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985, 1001.

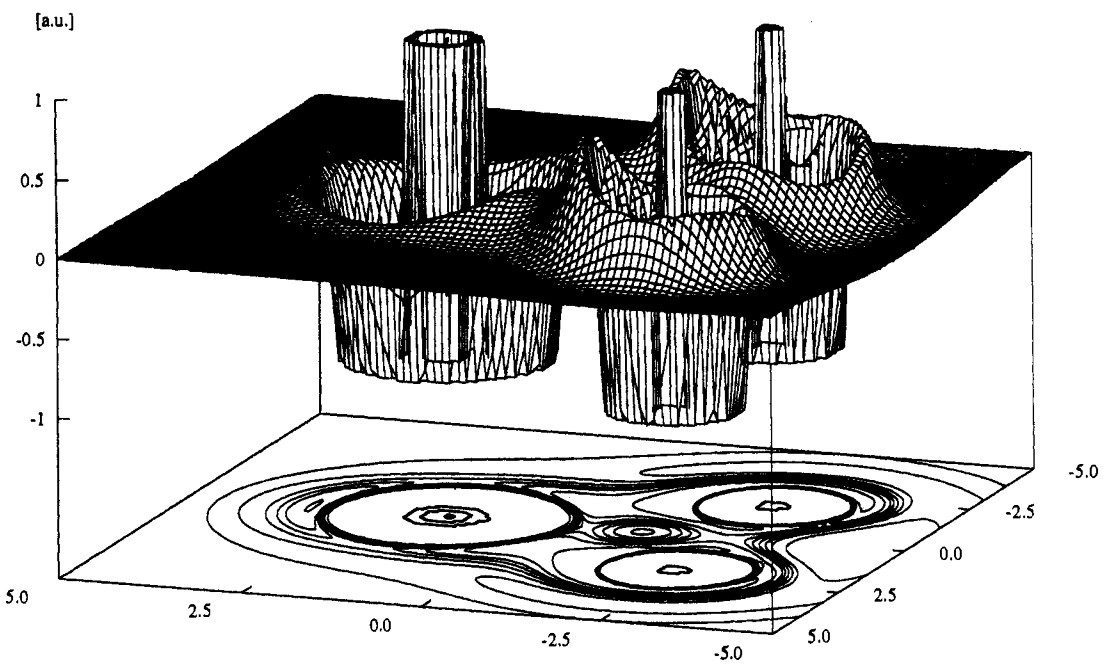

Figure 7. Contour maps of the Laplacian of the charge density in one C–P–C ring plane of triphospha[1.1.1]propellane (**4**).

from cylindrical symmetry. For C–C and C–P bonds, ϵ is much larger, showing considerable axial preference. The values of the C–C bond in the P-cycle are markedly smaller than those in C-counterparts suggesting a lower susceptibility of the bond to rupture.[13,14] ϵ of the bridgehead bond in both propellanes vanishes because of symmetry.

The value of ρ_b at the bridgehead bond is larger for P-cycles **5** and **6** but smaller for the P-propellane **4**, relative to their carbon analogues **7**–**9**. This is not inconsistent with the larger C–C distance in **4** mentioned above.

The Laplacian maps of **4**–**6** are displayed in Figures 5–7. It is apparent that the charge concentration decreases from **6** to **4**. Nevertheless, the existence of a bridgehead C–C bond in **4** can clearly be demonstrated. The Laplacian is negative in all C–C bonds except for the bridgehead bond in propellane (Table 5). A negative value for $\nabla^2\rho_b$, according to the topological analysis,[14] corresponds to a covalent bond interaction. Hence, the bridgehead bond in triphospha[1.1.1]propellane (**4**) has a more covalent character compared with that in [1.1.1]propellane (**7**). The consequence is that the former is more easily perturbed than the latter where the presence of a positive curvature along the bond path imparts a stiffness to the bond, making it more resistant to changes by substituent effects.[14,15] The most striking difference between both P- and C-cycles is the charge accumulation at the ring critical point. As seen in Table 5, the value ρ_b at this point is substantially larger in C-cycles than in P-cycles. Within the P-cycles, this quantity increases slightly but consistently in going from **6** to **4**, which is parallel with a charge increase in the C–P bonds. Another point worth noting is that, in P-cycles **4**–**6**, the ρ_{ring} values are not very different from those of ρ_b(C–P). As the reactivity of three-membered rings is very much a consequence of the charge concentration at the interior of the ring, this calculated result already emphasizes a difference in chemical behavior of phosphorus and carbon three-membered cyclic compounds.

In summary, this paper presents a detailed characterization of triphospha[1.1.1]propellane. We would hope that the results reported here will be useful in its experimental detection.

Acknowledgment. The authors are indebted to the Belgian National Fund for Scientific Research (NFWO), the Belgian Government (DPWB), the Institute for Nuclear Sciences (IIKW), and the KULeuven Computing Centre.

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