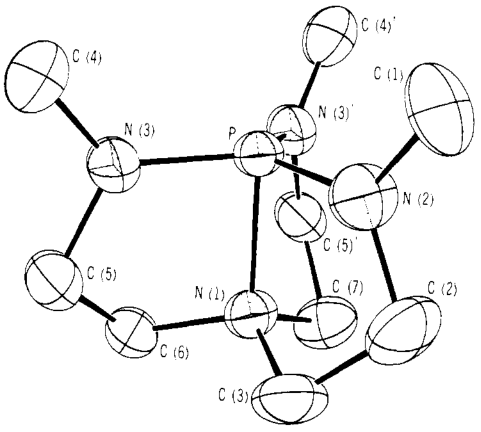
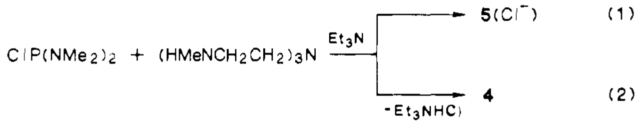


Figure 1. ORTEP drawing and atomic numbering scheme for **5**(BF$_4^-$). Pertinent bond distances are P–N(1), 1.967 (8); P–N(2), 1.62 (1); and P–N(3), 1.661 (7) Å; important bond angles are N(1)PN(2), 85.9 (4); N(1)PN(3), 86.5 (2); N(2)PN(3), 120.7 (3); and N(3)PN(3)', 117.5 (4)°.

pair toward the phosphorus is consistent with the H–P proton occupying the vacant axial position. The P–N$_{ax}$ bond distance in **5** (1.967 Å) is comparable to that in **3** (1.986 Å).[4] The considerably shorter P–N$_{eq}$ distances compared with the P–N$_{ax}$ distance in **5**(BF$_4^-$) may reflect a combination of the diminished σ bond order in the axial three-center four-electron system[9] and the lack of N$_{ax}$–P π bonding.

The first indication of the remarkable stability of **5** became evident in reaction 1. The presence of triethylamine was intended to remove HCl, thereby leading to the synthesis of the prophosphatrane **4** in reaction 2.[10] Instead, **5**(Cl$^-$) was isolated.



Furthermore, efforts to remove the proton in **5**(Cl$^-$) with DBU in DMSO, *n*-BuLi in THF, CaH$_2$ in CH$_2$Cl$_2$, or KOH in refluxing toluene led only to the recovery of **5**(Cl$^-$). Slowly heating **5**(Cl$^-$) with a large excess of anhydrous NaOH to 200 °C under vacuum over a period of several hours also gave no indication of reaction. Above 200 °C a sudden sublimation of **4** from the reaction mixture is observed. Extraction of the crude reaction mixture with benzene afforded a 53% yield of **4**.[11,12]

These results strongly imply that **4** is a powerful base. This was confirmed by monitoring with ^{1}H and ^{31}P NMR spectroscopy a CD$_3$CN solution of **4** to which excess weak acid was added. Indeed, **4** deprotonates PhOH (pK_a = 10), (CN)$_2$CH$_2$ (pK_a = 11),[13] protonated "Proton Sponge" (1,8-(bisdimethylamino)-naphthalene·HI, pK_a = 12.3),[14] (EtOOC)$_2$CH$_2$ (pK_a = 13),[13] and H$_2$O (pK_a = 15.7)[15] to give **5** as the only phosphorus-containing product. With 1 equiv of H$_2$O, an equilibrium mixture of **4** and **5** is observed in a ratio of ca. 4:1. It is noteworthy that the only product detected in the reaction with H$_2$O is **5** since P(NR$_2$)$_3$ systems are well known to be hydrolytically unstable, giving rise to P–N bond cleavage. The lack of reaction of **4** with *t*-BuOH (pK_a = 16.5)[16] indicates that the pK_a of **5** is approximately 16. Thus **5** is a weaker acid by at least ca. seven orders of magnitude compared with typical R$_3$PH$^+$ species (pK_a = 8–9[17]). The diverse chemistry of this versatile system is currently under further investigation.

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Supplementary Material Available: Tables of crystal data, positional and anisotropic thermal parameters, and bond lengths and bond angles (5 pages); tables of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

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[10] The reaction of P(NMe$_2$)$_3$ with (HMeNCH$_2$CH$_2$)$_3$N to form **4** is exceedingly slow.

[11] Charring frequently occurs leading to low yields of **4** in this unreliable reaction.

[12] NMR data: ^{31}P (C$_6$D$_6$) δ 120.8; ^{1}H (CD$_3$CN) δ 2.60 (9 H, d, CH$_3$, $^3J_{PH}$ = 11.0 Hz), δ 2.76 (12 H, br, CH$_2$); ^{13}C (C$_6$D$_6$) δ 37.2 (CH$_3$, $^2J_{PC}$ = 41.0 Hz), δ 49.4 (d, N$_{eq}$CH$_2$, $^2J_{PC}$ = 6.7 Hz), δ 51.3 (s, N$_{ax}$CH$_2$).

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Definitive Characterization of the C$_3$H$_7^+$ Potential Energy Surface

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Because of its fundamental nature and small size, the C$_3$H$_7^+$ cation has been investigated extensively,[1] both experimentally[2-5] and computationally.[1,6-8] General features only have been established, not the detailed nature either of the two stable isomers (the 2-propyl cation and protonated cyclopropane) or of the related transition structures. The first minimum to be established by frequency analysis was published only very recently,[8] and this did not benefit from optimization at electron-correlated levels. The super acid study of Saunders et al.[2] led to three important conclusions, based on the results of multiple labeling and of kinetic analysis of ^{2}H and ^{13}C scrambling. Both protonated cyclopropane

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Table I. Total Energies[a] (hartree), Relative Energies[a] (E_{rel}, kcal/mol), Zero-Point Vibrational Energies[b] (ZPE, kcal/mol), and Number of Imaginary Frequencies (NIMAG)

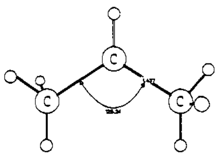
structure	MP2/6-311G**	ZPE(NIMAG)	MP4(FC)/6-311G**	E_{rel}
2-propyl (**1**)	−117.89053	53.4 (0)	−117.89267	0
corner-protonated I (**2**)	−117.88499	55.3 (0)	−117.88421	7.2
corner-protonated II (**3**)	−117.88437	55.1 (1)	−117.88368	7.3
edge-protonated (**4**)	−117.88320	55.2 (0)	−117.88179	8.6
1-propyl I (**5**)	−117.85857	53.1 (1)	−117.86142	19.3
1-propyl II (**6**)	−117.85782	54.0 (1)	−117.86089	20.5
TS corner-protonated → 2-propyl	−117.88296	54.9 (1)	−117.88163	8.4
propene	−117.59996	48.0 (0)	−117.59893	178.8[c]
cyclopropane	−117.59337	49.4 (0)	−117.59893	186.6[d]

[a] At MP2/6-311G** optimized geometries. [b] Computed at MP2/6-311G**. Scaled by a factor of 0.95, see: DeFrees, D. J.; McLean, A. D. *J. Chem. Phys.* **1985**, *82*, 333. [c] PA_{298} = 177.8 kcal/mol. [d] PA_{298} = 178.0 kcal/mol.

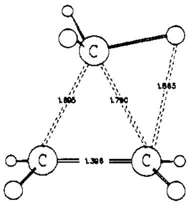
and 1-propyl cation species are involved, but proton scrambling via the latter is slightly faster. Corner-protonated cyclopropane is indicated to be slightly more stable than the edge-protonated isomer. We report computational results that substantiate and extend these findings and agree with the gas-phase experimental $C_3H_7^+$ energies.[3-5]

Standard but high levels of ab initio theory were employed for this study, using the IBM version of GAUSSIAN 86.[9] Structure optimizations and vibrational frequencies were calculated at the MP2/6-311G** level. Energy differences were calculated from MP4(FC)/6-311G** energies at the MP2 structures and zero-point energy corrections from the MP2 frequencies. The abbreviation FC indicates that the core 1s orbitals of the carbon atoms were frozen in the MP4 calculation. Our calculated 298 K proton affinities of propene and cyclopropane, 177.8 and 178.0 kcal/mol, respectively, suggest that the currently accepted experimental values, 179.5 ± 0.8 and 179.8 kcal/mol[3], respectively, may be in need of a small downward revision. Experimental estimates of the energy differences between the 2-propyl cation and protonated cyclopropane (ca. 8 kcal/mol)[4] and the 1-propyl cation (ca. 20 kcal/mol)[5] agree with our refined values (7.2 and 19.3 kcal/mol, respectively) for the most stable forms of the species (Table I).

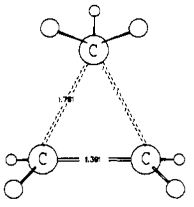
The 2-propyl cation prefers a *chiral* (C_2 point group) ground state (**1**), but the methyl rotation barriers are quite small (ca. 0.5 kcal/mol). In agreement with Dewar,[8] structure **2** is the lowest energy protonated cyclopropane, but the distortion from C_{2v} skeletal symmetry is less after MP2 optimization. Furthermore, methyl rotation (via **3**) is practically completely free. Movement of the hydrogens around the cyclopropane ring occurs via an edge-protonated cyclopropane, **4**, which lies only 1.4 kcal/mol above **2**. Structure **4** is a shallow minimum, but the transition structure for conversion into **2** (not shown) becomes a little lower in energy when zero-point-energy (ZPE) corrections are applied. Although we are not able to establish the nature of the edge-protonated cyclopropane conclusively, the point is moot as the potential energy surface (PES) is very flat, and **4** is higher than the corner-protonated forms (**2** and **3**) in energy.



1, C_2(0)

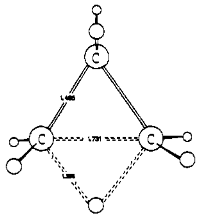


2, C_s(0)

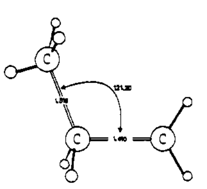


3, C_s(1)

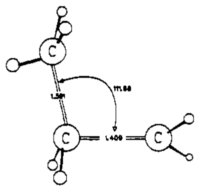
The isotope scrambling transition structures, **5** and **6**, both have 1-propyl cation geometries, but are distinct from one another. They differ primarily in the conformation of the terminal CH_2^+ group. The bisected structure (**5**) is slightly lower in energy than **6**, which is the transition structure for the conversion of protonated cyclopropane (**2**) into **1**. The latter process occurs by the widening of the C_1–C_2–C_3 angle of **2** with a concomitant rotation of the C_1 methylene group until **6** is reached. A hydrogen then migrates from C_2 without any barrier. Possible hydrogen bridged structures corresponding to protonated propene were probed carefully; a flat PES but no stationary point at either 6-31G* or MP2/6-31G* was found. A slight twisting of **5** from the perpendicular geometry initiates the process resulting in a 1,2-hydride shift to give the 2-propyl cation. This **1** → **5** interconversion results in hydrogen but not carbon scrambling. The alternative rearrangement of **1** via transition structure **6** and the protonated cyclopropanes (**2–4**) gives both carbon and hydrogen scrambling. In agreement with the observations of Saunders,[2] we find **6** to lie 0.8 kcal/mol above **5**. Our 19.3-kcal/mol relative energy of **5** is somewhat higher than the activation energy (16.3 ± 0.4 kcal/mol) determined in nonnucleophilic (super acid) media.[2] This could be due to differential solvation. However, this is not very likely because both **1** and **5** are "classical" (rather than bridged) carbenium ions. Other recent cases indicate the differential solvation of carbocation structures to be quite small energetically.[10]



4, C_{2v}(0)



5, C_s(1)



6, C_1(1)

This work characterizes several features of the $C_3H_7^+$ PES conclusively. The 2-propyl cation global minimum (**1**) has C_2 symmetry. The second minimum, corner-protonated cyclopropane (**2**), is an essentially symmetrical species with a rapidly rotating methyl group and a 1.4-kcal/mol barrier to hydrogen scrambling via edge-protonated cyclopropane (**4**). There are two different 1-propyl cation transition structures (**5** and **6**) but no 1-propyl cation minimum. These transition structures are involved in the hydrogen scrambling of the 2-propyl cation and in the interconversion of the 2-propyl cation (**1**) and corner-protonated cyclopropane (**2**) minima.

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Registry No. 1, 19252-53-0; propene, 115-07-1; cyclopropane, 75-19-4; protonated cyclopropane, 17806-70-1.

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