Harnessing Steric Strain to Obtain Superbases

Rafael Notario*[a] and José Elguero[b]

[a] *Instituto de Química Física 'Rocasolano', CSIC, Serrano 119, 28006 Madrid, Spain*
[b] *Instituto de Química Médica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

Theoretical calculations (G2 with complete optimization of the geometry) of tetrahedrane and its protonated form lead to the conclusion that tetrahedrane should be a superbase [proton affinity (PA) at 298 K, 252.0 kcal mol^{-1} (1 cal = 4.184 J)]; the performance of the G2 method was checked against 14 experimental PA values.

We recently reported[1] the results of an experimental (FT-ICR) and theoretical study in the protonation of the P_4 molecule in the gas phase. It was found that, while P_4 is a molecule with T_d symmetry,[2] in P_4H^+ the proton is bound to two P atoms, leading to a highly covalent P–H–P bond, similar to the B–H–B and C–H–C bonds in diborane[3] and $C_2H_5^+$,[4] respectively.

These results prompted us to study another molecule with T_d symmetry, tetrahedrane **1**, Fig. 1, the most highly strained of the saturated hydrocarbons. To our knowledge, this compound has not yet been isolated[5] and so we investigated its protonation by means of high level *ab initio* calculations.

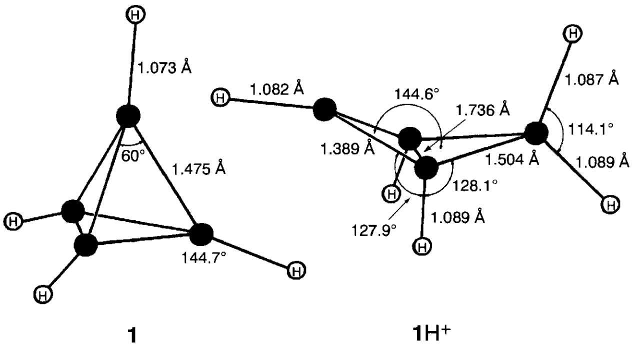
The proton affinities (PAs), have been calculated using G2 theory.[6] The PA of tetrahedrane, C_4H_4, is defined as the negative of ΔH^0_{298} for reaction (1):

$$C_4H_{4(g)} + H^+_{(g)} \rightleftharpoons C_4H_5{}^+_{(g)} \qquad (1)$$

The G2 level of theory corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G(d) calculations with HF/6-31G(d) scaled zero-point vibrational and 'higher level' corrections. As Smith and Radom[7] noted, in calculating proton affinities the empirical higher level correction cancels out, and the resulting proton affinity is thus purely *ab initio*.

Although G2-calculated energy changes for reaction (1) are generally referred to 0 K, we have also carried out the temperature correction leading to ΔH^0_{298} in order to directly compare our results with the experimental values for other compounds. To this end, the scaled vibrational frequencies were used.[7]

The total energies of tetrahedrane, C_4H_4, and the protonated form, $C_4H_5^+$, at the *ab initio* G2 level of theory are presented in Table 1, together with the corresponding proton affinities, PAs, at 0 and 298 K. All the calculations have been performed with the GAUSSIAN 92[8] system of programs. The optimized structures at MP2(full)/6-31G(d) are shown in Fig. 1. They are in very good agreement with previous calculations of the geometries of tetrahedrane[9] and cyclobutenyl (or homocyclopropenylium) cation,[10] *i.e.* the structure of protonated tetrahedrane, **1H**$^+$ in Fig. 1.



1 **1H**$^+$

Fig. 1 MP2(full)/6-31G(d) optimized structures of tetrahedrane **1** and the protonated form **1H**$^+$

Table 1 G2-calculated energies (Hartree) and proton affinities (kcal mol^{-1}) of tetrahedrane

	G2 (0 K)	G2 (298 K)	PA (0 K)	PA (298 K)
C_4H_4	−154.338343	−154.333647	250.5	252.0
$C_4H_5^+$	−154.737622	−154.732890		

In order to anchor our result to the experimental PA scale we have compared the G2 PA values at 298 K, calculated by Smith and Radom[7] for a set of 14 molecules, with the corresponding experimental values recently obtained by Szulejko and McMahon[11] by means of high pressure MS (HPMS) (see Fig. 2). There is an excellent linear correlation [slope = 0.992 ± 0.004, intercept = 1.68 ± 0.78 kcal mol^{-1} (1 cal = 4.184 J), R = 0.9999 and s.d. = 0.53 kcal mol^{-1}] between theoretical and experimental values. From this correlation, we can estimate an experimental PA value for tetrahedrane of 251.7 kcal mol^{-1}. This indicates that tetrahedrane would be a 'superbasic' molecule in the gas phase, with a proton affinity similar to that of the strongest 'superbases' studied very recently by Gal and Maria *et al.*[12] (they measure a PA of 251.9 kcal mol^{-1} for 7-ethyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene).

Why should the tetrahedrane display a 'superbasic' behaviour? There are two factors to expalin this fact.

First, tetrahedrane is a highly strained hydrocarbon with an estimated strain energy of 130–140 kcal mol^{-1}.[13]

And secondly, the structure of the protonated tetrahedrane corresponds to that of cyclobutenyl or homocyclopropenylium cation, with C_s symmetry. This is the simplest homoaromatic carbocation, this contributing to its relatively high stability. Olah *et al.*[14] determined an 8.4 ± 0.5 kcal mol^{-1} ring inversion barrier, termed the 'homoaromatization energy',[15] and very

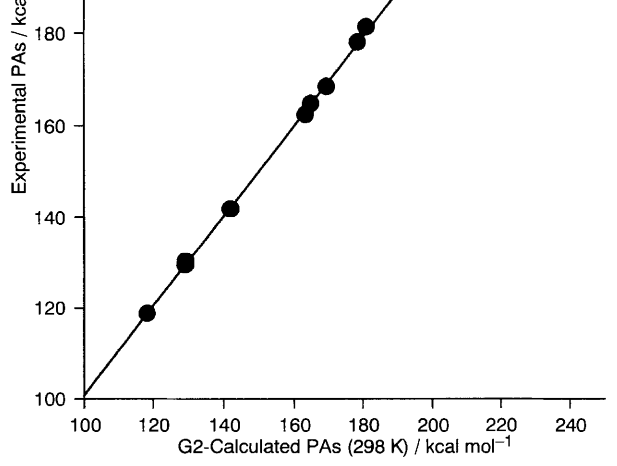


Fig. 2 Experimental (ref. 11) *vs.* G2-calculated (ref. 7) proton affinities for a set of selected compounds

recently, Schleyer *et al.*[10] have studied theoretically this carbocation at very high levels of calculation. They conclude that the homocyclopropenylium cation is a prototype for homoaromatic character, which is a result of strong through-space interactions caused by p–p overlap between the interacting centres, caused by delocalization of $(4n + 2)$ π-electrons accompanied by an equalization of atomic charges, bond lengths and ^{13}C chemical shifts.

Note added in proof: G2 calculations have been performed on C_4H_4.[16] The energies and enthalpies are in perfect agreement with our values.

We are very grateful to Centro de Supercomputación de Galicia (CESGA) for computing facilities, and to Dr V. Cruz and Professor J.-L. M. Abboud for their valuable discussions. This work was supported by Grant PB93-0289-C02-02 from the Spanish DGICYT.

Received, 13th April 1995; Com. 5/02391B

References

1 J.-L. M. Abboud, M. Herreros, R. Notario, M. Esseffar, O. Mó and M. Yáñez, submitted.

2 (*a*) S. Bhagavantam, *Ind. J. Phys.*, 1930, **5**, 35; (*b*) H. Zhang and K. Balasubramanian, *J. Chem. Phys.*, 1992, **97**, 3437, and references therein; (*c*) H. G. M. Edwards, *J. Mol. Struct.*, 1993, **295**, 95 and references therein.

3 (*a*) K. Hedberg and V. Schomaker, *J. Am. Chem. Soc.*, 1951, **73**, 1482; (*b*) E. Switkes, R. M. Stevens and W. N. Lipscomb, *J. Chem. Phys.*, 1969, **51**, 2085, and references therein.

4 K. Raghavachari, R. A. Whiteside, J. A. Pople and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1981, **105**, 5649, and references therein.

5 (*a*) G. Maier, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 309; (*b*) G. Maier, R. Wolf and F. Fleischer, *GIT Fachz. Lab.*, 1992, **36**, 506; 510.

6 (*a*) L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.*, 1991, **94**, 7221; (*b*) L. A. Curtiss, J. E. Carpenter, K. Raghavachari and J. A. Pople, *J. Chem. Phys.*, 1992, **96**, 9030; (*c*) L. A. Curtiss, K. Raghavachari and J. A. Pople, *J. Chem. Phys.*, 1993, **98**, 1293.

7 B. J. Smith and L. Radom, *J. Am. Chem. Soc.*, 1993, **115**, 4885.

8 GAUSIAN 92, Revision D.2, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wory, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Repogle, R. Gompers, J. L. Andrés, K. Raghavachari, J. S. Binkley, C. González, R. L. Martin, D.J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1992.

9 (*a*) J. M. Seminario and P. Politzer, *Chem. Phys. Lett.*, 1989, **159**, 27; (*b*) B. A. Hess Jr. and L. J. Schaad, *J. Am. Chem. Soc.*, 1985, **107**, 865.

10 S. Sieber, P. v. R. Schleyer, A. H. Otto, J. Gauss, F. Reichel and D. Cremer, *J. Phys. Org. Chem.*, 1993, **6**, 445.

11 J. E. Szulejko and T. B. McMahon, *J. Am. Chem. Soc.*, 1993, **115**, 7839.

12 E. D. Raczynska, P.-C. Maria, J.-F. Gal and M. Decouzon, *J. Phys. Org. Chem.*, 1994, **7**, 725.

13 (*a*) A. Greenberg and J. F. Liebman, *Strained Organic Molecules*, Academic, New York, 1978; (*b*) I. Alkorta, J. Elguero, I. Rozas and A. T. Balaban, *J. Mol. Struct.* (*Theochem*), 1990, **208**, 63, and references therein.

14 G. A. Olah, J. S. Staral, R. J. Spear and G. Liang, *J. Am. Chem. Soc.*, 1975, **97**, 5489.

15 R. C. Haddon, *J. Am. Chem. Soc.*, 1975, **97**, 3608.

16 M. N. Glukhotsev, S. Laiter and A. Pross, *J. Phys. Chem.*, 1995, **99**, 6828.