PERKIN 2

"Nibbering's C_7H_7N": an *ab initio* study of the structure and electronic properties of benzaldimine and its protonated ion[†]

Borislav Kovačević,[*a] **Joel F. Liebman**[*b] **and Zvonimir B. Maksić**[*a,c]

[a] *Quantum Organic Chemistry Group, Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, 10000 Zagreb-HR, Croatia*
[b] *Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, MD 21250, USA*
[c] *Faculty of Science and Mathematics, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia*

Received (in Cambridge, UK) 16th May 2002, Accepted 14th June 2002

Imines are an interesting but relatively poorly-characterized class of organic compounds: for example, is the gas phase ion-derived C_7H_7N species observed by Nibbering *et al.* benzaldimine or troponimine? Proton affinities are important quantities for the understanding of organic compounds. We have investigated the structure, energetics and proton affinities of benzaldimine, troponimine, and their carbonyl and olefinic analogs (benzaldehyde, tropone, styrene, heptafulvene) using G2(MP2) computational theory. We find the benzenoid species (benzaldimine, benzaldehyde, styrene) to be more stable by 20–25 kcal mol^{-1} than their nonbenzenoid isomers (troponimine, tropone, heptafulvene). From our calculations and analysis of literature data, we derive the enthalpy of formation and proton affinity of benzaldimine to be 39 ± 3 and 220 ± 3 kcal mol^{-1} respectively and conclude Nibbering's C_7H_7N is, in fact, this species.

Introduction

Imines are a large and important family of compounds, some of them exhibiting highly pronounced basicity. Consider C_7H_7N—there are many isomers—we feel the most interesting to be imines: benzaldimine C_6H_5CHNH (phenylmethanimine) and its nonbenzenoid isomer, troponimine cyclo-C_7H_6NH (cyclohepta-2,4,6-trien-1-imine). While either of these isomers is plausibly the deprotonation product of gas phase $C_7H_7NH^+$,[1] the former was suggested by Nibbering *et al.* to be the derived species. Is it? The current quantum chemical study contrasts these two isomeric imines and related pairs of isomeric species and provides a corroborative answer.

Compared to olefins and carbonyl compounds, imines are a comparatively ignored class of organic compounds: the study of their energetics even more so. For example, in a recent thermochemical review[2] that is part of the general "Patai" volume on double-bonded functional groups, only 10% was devoted to these species as opposed to olefins and carbonyl compounds.[3] We note specialized reviews in this context for dienes and polyenes,[4] and for enones.[5] Very few of the studied imines[6] have been aldimines as these are even more problematic with regards to synthesis, isolation and characterization; their relatively unsubstituted framework exacerbates problems of hydrolysis and oligomerization. We thus should not be disappointed that there are ambiguities in structure and energetics of even formally simple species. Consider the archetypical imine, CH_2NH, gaseous methanimine (formaldimine). Experimental gas phase chemists have offered a *ca.* 10 kcal mol^{-1} spread in recommended enthalpies of formation.[7] Calculational methods gave a plausibly definitive answer. Pople's G2 method[8] suggests a value of 20.6 ± 2.4 kcal mol^{-1}, while Martin's W2 theory[9] gives the nearly identical value of 21.2 ± 0.5 kcal mol^{-1}. (We acknowledge that "kcal" is not an SI unit: however, it remains very popular in the computational chemical literature, wherefore 1 kcal = 4.184 kJ.) Let us adopt a consensus value of 20.9 ± 2.5 kcal mol^{-1}. The aim of the present work is to discuss the structure and energetics of benzaldimine and troponimine as well as the related systems benzaldehyde, tropone, styrene and heptafulvene (1-methylenecyclohepta-2,4,6-triene) (Fig. 1).

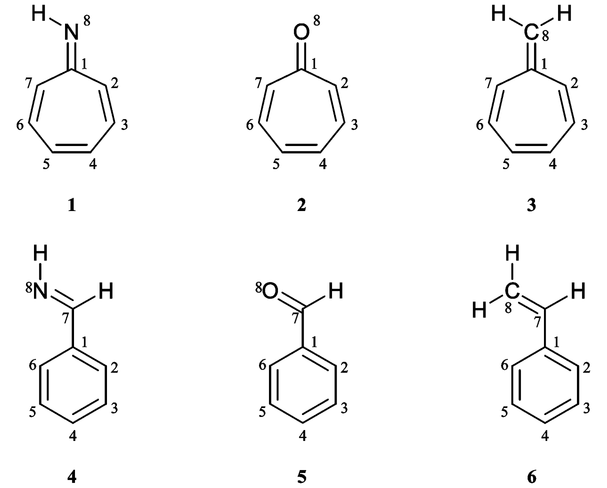

Fig. 1 Neutral species (and atomic numbering) discussed in the current study: **1** = troponimine, **2** = tropone, **3** = heptafulvene, **4** = benzaldimine, **5** = benzaldehyde, **6** = styrene.

Particular attention will be paid to their proton affinities, which are among the most important features of molecular species.

Computational methodology

Since some of the heats of formation of the studied compounds are unfortunately lacking, we shall employ the best possible theoretical model feasible in systems of their size. A

[†] This manuscript is dedicated to Professor Nico Nibbering on the occasion of his forthcoming 65th birthday and recent retirement.

DOI: 10.1039/b204766g

Table 1 Enthalpies (in hartree) and proton affinities (PA/kcal mol^{-1}) of species **1**–**6** and of CH_2NH and CH_2O

Molecule	G2(MP2) Enthalpy	PA(calc)	PA(exp)[a]
1	−325.02383		
1H$^+$(N)	−325.40172	238.6	
2	−344.90658		
2H$^+$(O)	−345.25269	218.7	220.1
3	−308.97040		
3H$^+$(C(8))	−309.33609	231.0	
4	−325.06670		
4H$^+$(N)	−325.42081	223.7	217.9
5	−344.94510		
5H$^+$(O)	−345.26031	199.3	199.3
6	−309.01537		
6H$^+$(C(8))	−309.33199	200.2	200.6
CH_2NH	−94.45726		
$CH_2NH_2^+$	−94.78584	206.2	203.8
CH_2O	−114.33226		
CH_2OH^+	−114.60143	168.9	170.4
C_2H_4	−78.41030		

[a] All experimental values of proton affinities are taken from ref. 12.

very reasonable compromise between accuracy and practicality is provided by the G2(MP2) procedure[10] by utilizing the GAUSSIAN 94 suite of programs.[11] This implies that the geometry is optimized at the MP2(full)/6-31G* level, whereas the zero point vibrational energy (ZPVE) is computed by utilizing the HF/6-31G* model and the resulting frequencies are scaled by a common factor 0.89. Further, corrections are introduced to remedy a deficiency of the incomplete basis set and a number of approximations are employed to estimate contributions of the electron correlation energy. Thus the final energy corresponds to the quadratic configuration interaction QCISD(T) plus some empirical high level corrections E^{HLC}. The resulting computational scheme is more economical than the G2 procedure with but a very small sacrifice in accuracy.

Calculational and experimental results

Neutral species

Results of our calculations related to molecular energetics are summarized in Table 1.

These calculational results can be used in various ways. The first is the direct difference of isomer enthalpies of formation. From our calculations, we find benzaldimine to be more stable than troponimine by some 26.9 kcal mol^{-1} and the isoelectronically related benzaldehyde to be more stable than tropone by 24.2 kcal mol^{-1}. Using archival enthalpies of formation[13] for the latter two species, we find a difference of 19.3 kcal mol^{-1}. While we do not understand the *ca.* 5 kcal mol^{-1} discrepancy between theory and experiment for the difference between the benzenoid and nonbenzenoid carbonyl compounds, benzaldehyde and tropone, we still feel confident that the former is considerably more stable than the latter. Equivalently, one can use the roughly thermoneutral isodesmic reaction (endothermic by 2.7 kcal mol^{-1}) of

$$\text{Cyclo-}C_7H_6O + C_6H_5CHNH \longrightarrow \text{Cyclo-}C_7H_6NH + C_6H_5CHO \quad (1)$$

to conclude that benzaldimine is more stable than troponimine by 20–25 kcal mol^{-1} admitting that benzenoid and nonbenzenoid species may be described with different accuracy by our calculational protocol.

Analogously, from our calculations we find styrene is more stable than heptafulvene by 28.2 kcal mol^{-1}. Averaging the experimentally-derived enthalpy of formation of heptafulvene[4] and results derived from earlier high level *ab initio* calculational theory[14] of 60 ± 3 kcal mol^{-1} and the archival value[13] for styrene of 35.3 kcal mol^{-1}, a difference of 21.4 kcal mol^{-1} is obtained. Roughly the same discrepancy between calculation and experiment is found for the benzenoid and nonbenzenoid hydrocarbons (28.2–21.4 = 6.8 kcal mol^{-1}) as with the above carbonyl compounds (*ca.* 5 kcal mol^{-1}). The corresponding isodesmic reaction connecting benzaldimine and troponimine reads:

$$\text{Cyclo-}C_7H_6CH_2 + C_6H_5CHNH \longrightarrow \text{Cyclo-}C_7H_6NH + C_6H_5CHCH_2 \quad (2)$$

and is exothermic by 1.3 kcal mol^{-1}. Again we conclude that benzaldimine is more stable than troponimine by *ca.* 20–25 kcal mol^{-1}. All these data are consistent with intuition, which tells us that the aromatic benzene ring should be a more stabilizing fragment than a seven-membered ring because of the equivalent resonance structures in the former, and additionally the latter is destabilized because of some Baeyer or angle strain (*vide infra*). We note in passing that estimates of the aromatic stabilization of benzene fall in the range between 20–40 kcal mol^{-1} depending on its definition.[15] We thus conclude that the more stable C_7H_7N isomer is benzaldimine and not troponimine.

However, this does not answer the question of what is the enthalpy of formation of benzaldimine. Consider the isodesmic reaction

$$C_6H_5CHO + CH_2NH \longrightarrow C_6H_5CHNH + CH_2O \quad (3)$$

As written, the calculated enthalpy of reaction is endothermic by 2.1 kcal mol^{-1}: this sensibly suggests that phenyl stabilizes –CH=O more than –CH=NH *via* dipolar resonance structures. Using the consensus value for the enthalpy of formation of methanimine and the archival values for the two aldehydes, we derive an enthalpy of formation of 41.2 kcal mol^{-1} for benzaldimine. Alternatively, consider the isodesmic reaction

$$C_6H_5CHCH_2 + CH_2NH \longrightarrow C_6H_5CHNH + C_2H_4 \quad (4)$$

As written, the calculated enthalpy of reaction is exothermic by 2.7 kcal mol^{-1}: this sensibly suggests that phenyl stabilizes –CH=CH_2 less than –CH=NH *via* dipolar resonance structures. Using the consensus value for the enthalpy of formation of methanimine and the archival values for the two hydrocarbons, we derive an enthalpy of formation of 41.0 kcal mol^{-1} for benzaldimine. Finally, consider the difference of measured gas phase enthalpies of formation of benzophenone and benzaldehyde, and of 1,1-diphenylethylene and styrene. Chemically this corresponds to α-phenylation of $C_6H_5\mathit{C}H{=}O$ and $C_6H_5\mathit{C}H{=}CH_2$; numerically the differences are 21.9 ± 1.4 and 23.4 ± 1.1 kcal mol^{-1} using the requisite gas values from our thermochemical archives.[13] These two differences are close—let us adopt a consensus value of 22.6 ± 1.8 kcal mol^{-1}. Assume this difference is applicable to $C_6H_5\mathit{C}H{=}NH$. We have just seen before from the results of eqns. (3) and (4) that –CH=NH is quite comparable to those for –CH=O and –CH=NH. Then using the value reported in ref. 6 for the enthalpy of formation of gaseous benzophenone imine of 59.4 ± 0.3 kcal mol^{-1}, we obtain the value of 36.8 ± 1.9 kcal mol^{-1}. These two values for the enthalpy of formation of gaseous benzaldimine of 41.2, 41.0 and 36.8 kcal mol^{-1} are in satisfactory agreement with each other and the earlier suggested value[3] of 38.2 kcal mol^{-1} for this quantity; a value of 39 ± 3 kcal mol^{-1} is plausible and indeed is recommended here.

Structural and electronic features

We shall now focus attention on the structural features of the studied systems and of related protonated species. Characteristic bond distances and bond angles obtained at the MP2(full)/6-31G* level for neutral and protonated species alike are given in Table 2.

Table 2 Geometric descriptors (bond lengths in Å, angles in °) and π-bond orders for species **1**, **2**, **3** and their protonated counterparts

Molecule	Bond or angle	Distance	π_{bo}
1	C(1)–C(2)	1.460	0.35
	C(1)–C(7)	1.463	0.35
	C(1)–N(8)	1.305	0.78
	C(2)–C(3)	1.360	0.78
	C(3)–C(4)	1.437	0.41
	C(4)–C(5)	1.362	0.77
	C(5)–C(6)	1.437	0.41
	C(6)–C(7)	1.361	0.79
	C(1)–C(2)–C(3)	130.9	
	C(2)–C(3)–C(4)	130.2	
	C(3)–C(4)–C(5)	127.8	
	C(4)–C(5)–C(6)	127.9	
	C(5)–C(6)–C(7)	130.1	
	C(6)–C(7)–C(1)	131.0	
	C(7)–C(1)–C(2)	122.1	
1H$^+$(N)	C(1)–C(2)	1.420	0.48
	C(1)–N(8)	1.342	0.57
	C(2)–C(3)	1.379	0.69
	C(3)–C(4)	1.407	0.53
	C(4)–C(5)	1.381	0.67
	C(1)–C(2)–C(3)	129.5	
	C(2)–C(3)–C(4)	130.2	
	C(3)–C(4)–C(5)	127.7	
	C(7)–C(1)–C(2)	125.3	
2	C(1)–C(2)	1.464	0.37
	C(1)–O(8)	1.245	0.74
	C(2)–C(3)	1.365	0.77
	C(3)–C(4)	1.429	0.45
	C(4)–C(5)	1.367	0.75
	C(1)–C(2)–C(3)	131.0	
	C(2)–C(3)–C(4)	130.9	
	C(3)–C(4)–C(5)	128.0	
	C(7)–C(1)–C(2)	122.0	
2H$^+$(O)	C(1)–C(2)	1.412	0.53
	C(1)–C(7)	1.412	0.53
	C(1)–N(8)	1.334	0.46
	C(2)–C(3)	1.386	0.65
	C(3)–C(4)	1.406	0.56
	C(4)–C(5)	1.390	0.64
	C(5)–C(6)	1.407	0.56
	C(6)–C(7)	1.386	0.65
	C(1)–C(2)–C(3)	128.6	
	C(2)–C(3)–C(4)	129.7	
	C(3)–C(4)–C(5)	128.0	
	C(4)–C(5)–C(6)	128.0	
	C(5)–C(6)–C(7)	129.6	
	C(6)–C(7)–C(1)	128.8	
	C(7)–C(1)–C(2)	127.2	
3	C(1)–C(2)	1.462	0.34
	C(1)–C(8)	1.355	0.80
	C(2)–C(3)	1.354	0.80
	C(3)–C(4)	1.447	0.38
	C(4)–C(5)	1.354	0.79
	C(1)–C(2)–C(3)	130.9	
	C(2)–C(3)–C(4)	130.0	
	C(3)–C(4)–C(5)	127.9	
	C(7)–C(1)–C(2)	122.4	
3H$^+$(C(8))	C(1)–C(2)	1.407	0.57
	C(1)–C(7)	1.407	0.57
	C(1)–C(8)	1.504	0.22
	C(2)–C(3)	1.396	0.61
	C(3)–C(4)	1.398	0.59
	C(4)–C(5)	1.396	0.60
	C(5)–C(6)	1.398	0.59
	C(6)–C(7)	1.396	0.61
	C(1)–C(2)–C(3)	130.1	
	C(2)–C(3)–C(4)	129.3	
	C(3)–C(4)–C(5)	127.9	
	C(4)–C(5)–C(6)	127.9	
	C(5)–C(6)–C(7)	129.3	
	C(6)–C(7)–C(1)	130.1	
	C(7)–C(1)–C(2)	125.3	

A striking structural feature of all the neutral molecules is that they are planar, thus enabling a fair amount of π-conjugation. Having said that, it should be noticed that our seven-membered rings exhibit a pronounced bond length alternation as one could have anticipated for the 8π-electron systems. Judging from the ring CC bond lengths, it appears that some π-conjugation is present and that it increases along the series heptafulvene, tropone and troponimine. In contrast, the bond length variation in the benzene rings of styrene, benzaldehyde and benzaldimine are negligible. The ring bond angles in seven-membered rings reveal some inherent angular strain, since they deviate from the ideal CCC angle of 120° for sp^2 carbons sometimes assuming angles as large as 131°, which implies some bent bonding inside the ring.[16] A conjecture that some π-conjugation occurs in these systems is supported by the π-bond orders calculated within the Löwdin partitioning scheme of the mixed interatomic densities.[17] Perusal of the data reveals that the π-bond orders of the formal single bonds are only 50% smaller than the corresponding values found in formal double bonds. In other words, the π-bond orders of formal single bonds are by no means insignificant.

Another index of π-electron delocalization is provided by the nucleus independent chemical shifts (NICSs).[18] They are calculated 1 Å above the geometric center of a given ring by using GIAO HF/6–311+G(2df,p) model. The equilibrium geometries are those estimated by the MP2(full)/6-31G* procedure. The gauge value for NICS indices is given by the value for benzene (−11.1), which reflects the ideal aromatic π-delocalization. The corresponding NICS results for **1**, **2**, and **3** assume values of 0.1, −3.1 and 4.2 (in ppm), respectively, thus indicating that troponimine is nonaromatic, tropone is somewhat stabilized, whereas heptafulvene should be partially antiaromatic. Increased stabilization of tropone can be deduced from a considerable contribution of dipolar resonance structure. On the other hand, the conjecture that heptafulvene is destabilized due to antiaromaticity should be taken with a due caution for two reasons. (1) Antiaromatic interaction would lead to the ring puckering in order to avoid π-delocalization and to diminish the angular strain. Obviously, this does not occur. (2) The antiaromatic 4$n\pi$ electrons possess in fact an appreciable amount of the nondynamical π-electron energy E(ND)$^{\pi}$ as shown by the CASSCF$^{\pi}$ calculations[19] In fact, the paradigmatic cyclobutadiene (CBD) has a higher E(ND)$^{\pi}$ energy than its linear zig-zag counterpart buta-1,3-diene. This finding can explain the fact that all seven-membered rings studied here are planar, despite unequivocal angular strain. It would then appear that a NICS value of 4.2 ppm found in **3** reflects perhaps the paratropicity of the ring, but not necessarily its inherent destabilization due to a presence of 8π electrons. In fact, a CASSCF(8,8)/cc-PVDZ//MP2(full)/6-31G* calculation[20] gave the nondynamical correlation energy E(ND)$^{\pi}$ as 69.5 kcal mol^{-1}. This is an appreciable amount of stabilization energy, which is higher by 2.7 kcal mol^{-1} that the value estimated by the additivity rule implying that $E(\mathrm{ND})^{\pi}$ is larger in heptafulvene than in the open chain zig-zag octa-1,3,5,7-tetraene.

Protonated species

Let us turn to proton affinities. Proton affinities (PAs) are of considerable interest and importance,[12] since this quantity determines basicity—one of the most fundamental properties of molecules. The G2(MP2) proton affinities are given in Table 1. It is well known that the proton affinities are affected by local hybridization.[21,22] The proton affinity of imines with their sp^2 hybridized nitrogens should thus be placed between PAs of amines and nitriles with their $N(sp^3)$ and $N(sp^1)$ atoms. However, a recent analysis has shown that the proton affinities could be decomposed into three components or contributions,[23] the first being the ionization potential of a neutral base B, estimated by the frozen molecule Koopmans' approximation $\mathrm{IP(B)}_n^{\mathrm{Koop}} = -\varepsilon_n$. Here, the index n stands for the nth ionization potential corresponding to either HOMO (n = 1) or to the ionization energy of the lone pair to be protonated (n > 1). For this purpose in our discussion we shall use $\mathrm{IP(B)}_n^{\mathrm{Koop}}$ calculated by the HF/6–311+G(3df,2p)//MP(full)/6-31G* model. The basis set employed is the one utilized in the electron correlation G2(MP2) calculations. From ref. 23 we find the corresponding triadic formula:

$$\mathrm{PA(B)} = -\varepsilon_n(\mathrm{B}) + E(\mathrm{ei})_{\mathrm{rex}}^{(n)} + (\mathrm{BAE})^{+\bullet} + 313.6\ \mathrm{kcal\ mol^{-1}} \quad (5)$$

wherein ε_n is the nth orbital energy of the initial base in Koopmans' approximation, $E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$ is the relaxation energy upon the electron ionization from the nth MO to infinity and $(\mathrm{BAE})^+$ is the homolytic bond energy of the newly formed bond between the hydrogen atom, the radical cation $\mathrm{B}^{+\bullet}$ and 313.6 kcal $\mathrm{mol^{-1}}$ is the ionization energy of atomic hydrogen. Formula (5) will be used in identifying the origin of a difference in PAs of troponimine and tropone, the former being higher by 20 kcal $\mathrm{mol^{-1}}$. For considering the difference between the proton affinities of two bases it is useful to introduce a triad $\Delta\mathrm{PA} = (-\Delta\varepsilon;\ \Delta E(\mathrm{ei})_{\mathrm{rex}};\ \Delta(\mathrm{BAE})^{+\bullet})$ in kcal $\mathrm{mol^{-1}}$, where all symbols have their obvious meaning and the difference in proton affinity ΔPA is given by a sum of the three components presented within the parentheses.

If we consider the difference between the proton affinities of troponimine and tropone, then a difference ΔPA = 20 kcal $\mathrm{mol^{-1}}$ can be resolved as (−2.8; 20.8; 2.0). It follows that a higher PA of **1** is a consequence of the larger relaxation effect upon the electron ejection. This finding is in harmony with a more pronounced π-electron delocalization in $\mathbf{1H^+}$(N) relative to $\mathbf{2H^+}$(O) triggered by the protonation as evidenced by inspection of both the CC bond distances and the corresponding π-bond orders in the protonated species (Table 2). This is also corroborated by the NICS values, which change in going from **1** to $\mathbf{1H^+}$(N) by −7.4 ppm, whilst the corresponding change for protonation of tropone yields a change of −6.1 ppm. Apparently, the aromatization of the ring in troponimine upon protonation is more significant.

The most relevant findings are the PAs of troponimine and benzaldimine, 238.6 and 223.7 kcal $\mathrm{mol^{-1}}$, respectively. The latter value is in reasonably good accordance with the experimental measurement, which gave 217.0 ± 1.7 kcal $\mathrm{mol^{-1}}$, meaning that the observed species was benzaldimine and not troponimine.[1] A consensus estimate of PA of benzaldimine derived by combining both theory and experiment would be 220 ± 3 kcal $\mathrm{mol^{-1}}$. Further, we derive proton affinity for benzaldehyde and tropone of 199.3 and 218.7 kcal $\mathrm{mol^{-1}}$, respectively, in fine agreement with the experimental values of 199.3 and 220.1 kcal $\mathrm{mol^{-1}}$.[24]

The protonation of heptafulvene (**3**) at the exocyclic C8 position yields a PA value of 231.0 kcal $\mathrm{mol^{-1}}$ and leads to a decrease in the NICS index by −5.8 ppm. Therefore, the aromatization is here the least in the series **1**–**3**. Nevertheless, it is safe to say that in all systems **1**–**3** protonation at the exocyclic atom induces the aromatic stabilization of the seven-membered ring by forming formally a 6π pattern delocalized over 7 carbon atoms.

It is important to realize that all protonated atoms in **1**–**3** retain practically all of their electron density after protonation. This is evidenced by Löwdin atomic densities of atoms N(8), O(8) and C(8) in the series **1**–**3**, which assume values 7.40 (7.39), 8.28 (8.31) and 6.38 (6.46) in $|e|$, respectively, where data for the conjugate acids are given within parentheses. Interestingly enough, the electron density of protonated oxygen and protonated carbon is higher than that in the corresponding neutral base.

Most of the electron density shift to the protonated exo-atom comes from the mobile π-electrons of the ring, which in turn approach the aromatic sextet leading to considerable aromatization. This point will be discussed in some more detail below. Consequently, it is not surprising that protonation on the ring *e.g.* in tropone leads to appreciably lower PAs. For example, the PA values of **2** protonated at C2 and C4 are 180.2 and 167.9 (in kcal $\mathrm{mol^{-1}}$), respectively. Interestingly, protonation at the former site yields a PA that is equal to that of benzene 179.9 kcal $\mathrm{mol^{-1}}$. A considerable part of the difference between heteroatom and ring protonation comes from a lack of aromatic stabilization in the latter case. We should recall that the protonation on the ring should be preferred as far as Koopmans' theorem is concerned, since in this case the HOMO orbital energy (ε_1 = 202.5 kcal $\mathrm{mol^{-1}}$) is the price to be paid for protonation. The proton attack at oxygen requires HOMO-2 (ε_3 = 265.1 kcal $\mathrm{mol^{-1}}$) orbital energy, which is lower than HOMO by 62.6 kcal $\mathrm{mol^{-1}}$. Needless to say, protonation on the ring causes significant nonplanarity, which decreases stability of the protonated species together with a decrease in the π-electron conjugation.[25] Our previous study of the homolytic bond energies between the hydrogen atom and various radical cations has shown that they do not vary particularly. For example, the $(\mathrm{BAE})^{+\bullet}$ energies for imines are typically between 110–120 kcal $\mathrm{mol^{-1}}$. The same holds for oxygen–hydrogen bond association energies in alcohols and carboxylic acids. The $(\mathrm{C{-}H})^{+\bullet}$ bond energy in polyene radical cations has an average value[26] of about 75 kcal $\mathrm{mol^{-1}}$. Therefore, taking into account that $(\mathrm{BAE})_{\mathrm{OH}}^{\dot{+}}$ in tropone is 114.1 kcal $\mathrm{mol^{-1}}$ it appears that formation of the $(\mathrm{OH})^{+\bullet}$ bond in tropone is by 39 kcal $\mathrm{mol^{-1}}$ more advantageous than formation of the $(\mathrm{CH})^{+\bullet}$ on the ring. The residual difference between the PA($\mathbf{2H^+}$(O)) and PA($\mathbf{2H^+}$C(ring)) is given by the aromatization of the seven-membered ring upon exocyclic atom protonation and deformation of the ring induced by the ring protonation. In this connection it is worth mentioning that the difference in the protonation of styrene at the peripheral C(8) atom and *para*-C(4) carbon is 200.2 − 187.8 = 12.4 kcal $\mathrm{mol^{-1}}$. This is in harmony with chemical intuition, which says that the aromatic sextet should be preserved as much as possible.

Protonation of compounds **4**–**6** offers some very interesting pieces of information. The aromatic character of the benzene moiety is largely preserved after protonation as evidenced by the corresponding NICS values. They read: −10.8 (−10.2); −11.0 (−9.3) and −10.2 (−8.4) for compounds **4**, **5** and **6** respectively, where values for the conjugate acids are presented within parentheses as before. It is also clear that the aromatic stabilization exhibits a mild decrease along the series of conjugate acids $\mathbf{4H^+}$–$\mathbf{6H^+}$. However, the main conclusion is that protonation of troponimine, tropone and heptafulvene leads to aromatization of the seven-membered ring, which makes these compounds more basic relative to their benzenoid isomers and counterparts **4**–**6**.

Conclusion

We found that styrene, benzaldehyde and benzaldimine are all more stable then their isomeric counterparts heptafulvene, tropone and troponimine by the same *ca.* 24 kcal mol^{-1}. This is in accordance with intuition because the former compounds involve the aromatic benzene ring, while the latter embody the less delocalized and additionally, more angularly strained seven-membered ring. Benzaldimine has a proton affinity of *ca.* 220 ± 3 kcal mol^{-1} and a gas phase enthalpy of *ca.* 40 kcal mol^{-1}. On the basis of the calculated proton affinity, we conclude that the earlier studied compound C_7H_6NH under described experimental conditions[1] was benzaldimine.

References

1 R. A. L. Peerboom, S. Ingemann, N. M. M. Nibbering and J. F. Liebman, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1825.

2 S. W. Slayden and J. F. Liebman, in *The Chemistry of Functional Groups Supplement A3: The Chemistry of Double-Bonded Functional Groups*, ed. S. Patai, John Wiley & Sons, Chichester, 1997.

3 This assertion was made from simple page count, not references nor compounds cited.

4 J. F. Liebman, in *The Chemistry of Functional Groups Supplement A2: The Chemistry of Dienes and Polyenes*, ed. Z. Rappoport, Wiley, Chichester, 1997, Vol. 1.

5 J. F. Liebman and R. M. Pollack, in *The Chemistry of the Enone Functional Group*, eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1989.

6 S. P. Verevkin, J. Morgenthaler and C. Rüchardt, *J. Chem. Thermodyn.*, 1997, **29**, 1175.

7 See the discussion in ref. 2, p. 594.

8 B. J. Smith, J. A. Pople, L. A. Curtiss and L. Radom, *Aust. J. Chem.*, 1992, **34**, 285.

9 G. de Oliveira, J. M. L. Martin, I. K. C. Silwal and J. F. Liebman, *J. Comput. Chem.*, 2001, **22**, 1297.

10 L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.*, 1991, **94**, 7221.

11 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheesman, T. A. Keith, G. A. Peterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. J. Peng, P. J. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Gordon, C. Gonzales and J. A. Pople, GAUSSIAN 94. Revision A.1, Gaussian. Inc., Pittsburgh, PA, 1995.

12 E. P. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data*, 1998, **27**, 413. All experimentally derived proton affinities are assumed to come from this source.

13 J. B. Pedley, R. D. Naylor and S. P. Kirby, *Thermochemical Data of Organic Compounds*, Chapman & Hall, New York, 1986.

14 A. Skancke, R. S. Hosmane and J. F. Liebman, *Acta Chem. Scand.*, 1998, **52**, 967. See also J. F. Liebman and A. Skancke, *Mol. Phys.*, 1997, **91**, 491.

15 See the various contributions to the "Aromaticity" thematic issue of *Chem. Rev.*, 2001, **101**(5), edited by P. von Ragué Schleyer, for a variety of definitions, assumptions and numerical values.

16 We remind the reader that the angle in a regular (equiangular, equilateral) heptagon is $5\pi/7$ radians or *ca.* 128.6°.

17 P. O. Löwdin, *J. Chem. Phys.*, 1950, **18**, 63.

18 P. v. R. Schleyer, Ch. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317.

19 Z. B. Maksić, D. Barić and I. Petanjek, *J. Phys. Chem. A*, 2000, **104**, 10873.

20 D. Barić, MSc thesis, Zagreb, 2002;, unpublished results.

21 F. Ijaali, O. Mo, M. Yañez and J. L. M. Abboud, *J. Mol. Struct. (THEOCHEM)*, 1995, **338**, 225.

22 C. Hillebrand, M. Klessinger, M. Eckert-Maksić and Z. B. Maksić, *J. Phys. Chem.*, 1996, **100**, 9698.

23 Z. B. Maksić and R. Vianello, *J. Phys. Chem. A*, 2002, **106**, 419.

24 Experiment and theory are in good accord for the simplest carbonyl compound and imine, CH_2O and CH_2NH. The recommended experimental values are 170.4 and 203.8 kcal mol^{-1} while our calculations give values of 168.9 and 206.2 kcal mol^{-1} respectively.

25 We recognize the ring protonated species as being derivatives of the homoaromatic tropilidine, *cf.* D. W. Rogers, A. Pododensin and J. F. Liebman, *J. Org. Chem.*, 1993, **58**, 2589, but we then recognize that homoaromaticity is of less energetics consequence than the "corresponding" aromaticity, *cf.* R. V. Williams, *Chem. Rev.*, 2001, **101**, 1185.

26 Z. B. Maksić and R. Vianello, unpublished results.