# Protonation of 4H-Pyran-4-one and its Sulfur Analogues. MNDO Study

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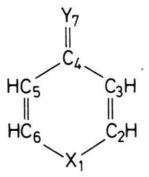
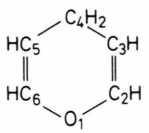
The molecular and electronic structure of 4H-pyran-4-one and its mono- and disubstituted sulfur analogues (**1**–**4**) are studied by the MNDO method. The salient structural features are qualitatively reproduced and the trend of changes of geometric parameters is in good agreement with experiment. The charge distributions exhibit strong polarization due to the large $\pi$-electron drift toward the exo-heteroatom. The protonated conjugated acids are considered too. It is found that exo-heteroatom protonation is favoured by 60–80 kcal/mol over the attachment of the proton to the intraring heteroatom. This is in accordance with experimental evidence. It is rationalized by the higher electron density centered on the exo-heteroatom and the appreciable increase in aromatic cyclic conjugation taking place upon the exo-protonation.

## Introduction

In the years since the basicity of 2,6-dimethyl-4H-pyran-4-one was recognized by Collie and Tickle [1], a large amount of work has been devoted to the elucidation of the protonation behaviour [2–4] of this and related systems. Particularly, the changes in molecular and electronic structure upon protonation of 4H-pyran-4-one and its derivatives, where one or both oxygens are substituted by sulfur atoms, have attracted considerable attention [2, 5]. Hitherto, the properties of neutral species have been the subject matter of both experimental [6–10] and theoretical studies [11–16], while information on the structural characteristics of protonated species was based exclusively on spectroscopic data [2, 5]. As a part of our continuing interest in the structural and energetic properties of protonated organic bases [17, 18], we applied the MNDO method [19] to 4H-pyran-4-one (**1**), 4H-pyran-4-thione (**2**), 4H-thiopyran-4-one (**3**), 4H-thiopyran-4-thione (**4**) and their conjugated acids. The model compounds 4H-pyran (**5**) and 4H-thiopyran (**6**) are considered too for comparative purposes. The MNDO method seems to be the most suitable approach since it is better than any of the current semiempirical theories in treating heterocyclic systems [17, 20–22].




1 $X_1 = O$, $Y_7 = O$
2 $X_1 = O$ $Y_7 = S$
3 $X_1 = S$ $Y_7 = O$
4 $X_1 = S$ $Y_7 = S$

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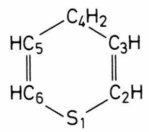


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## Calculations

The calculations were carried out by the modified version [22] of the standard MNDO program [19]. The geometries of all species were determined by minimizing the total SCF energy with respect to all geometrical variables. Calculations were performed on the Univac 1110 computer at the University Computational Centre in Zagreb.

## Results and Discussion

The calculated structural parameters of neutral bases **1**–**4** are summarized in Table 1. All calculated structures are found to be planar possessing $C_{2v}$ symmetry. The available experimental data [23]

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Table 1. The calculated structural parameters[a] of bases **1**–**4**, the formal atomic charges, gross $\sigma$- and $\pi$-populations and $\pi$-bond orders as obtained by the MNDO method.

| Compound | Bond distances (Å) | | Bond angles (deg) | | Charges | | | | $\pi$-bond orders | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Bond | | Angle | | Atom | Form. ch. | $\sigma$ | $\pi$ | Bond | |
| **1** | $X_1C_2$ | 1.363 (1.358) | $X_1C_2C_3$ | 123.0 (123.9) | $X_1$ | − 0.19 | 4.40 | 1.80 | $X_1C_2$ | 0.34 |
| | | | | | $C_2$ | 0.12 | 2.94 | 0.94 | $C_2C_3$ | 0.91 |
| | $C_2C_3$ | 1.363 (1.344) | $C_2C_3C_4$ | 120.8 (120.9) | $C_3$ | − 0.22 | 3.11 | 1.11 | $C_3C_4$ | 0.26 |
| | | | | | $C_4$ | 0.30 | 2.94 | 0.76 | $C_4Y_7$ | 0.89 |
| | $C_3C_4$ | 1.489 (1.463) | $C_2X_1C_6$ | 119.3 (117.3) | $C_5$ | − 0.22 | 3.11 | 1.11 | | |
| | | | | | $C_6$ | 0.12 | 2.94 | 0.94 | | |
| | $C_4Y_7$ | 1.228 (1.226) | $Y_7C_4C_3$ | 123.6 – | $Y_7$ | − 0.31 | 4.96 | 1.34 | | |
| | $C_2H$ | 1.096 (1.079) | $HC_2C_3$ | 125.0 (125.2) | | | | | | |
| | $C_3H$ | 1.089 (1.082) | $HC_3C_2$ | 120.4 (120.0) | | | | | | |
| **2** | $X_1C_2$ | 1.360 (1.353) | $X_1C_2C_3$ | 122.5 (123.8) | $X_1$ | − 0.18 | 4.41 | 1.77 | $X_1C_2$ | 0.37 |
| | | | | | $C_2$ | 0.12 | 2.95 | 0.94 | $C_2C_3$ | 0.88 |
| | $C_2C_3$ | 1.368 (1.357) | $C_2C_3C_4$ | 121.2 (120.3) | $C_3$ | − 0.17 | 3.09 | 1.08 | $C_3C_4$ | 0.34 |
| | | | | | $C_4$ | 0.10 | 3.11 | 0.79 | $C_4Y_7$ | 0.83 |
| | $C_3C_4$ | 1.465 (1.431) | $C_2X_1C_6$ | 119.2 (116.9) | $C_5$ | − 0.17 | 3.08 | 1.08 | | |
| | | | | | $C_6$ | 0.12 | 2.95 | 0.94 | | |
| | $C_4Y_7$ | 1.567 (1.665) | $Y_7C_4C_3$ | 123.3 – | $Y_7$ | − 0.24 | 4.84 | 1.40 | | |
| | $C_2H$ | 1.095 (1.082) | $HC_2C_3$ | 125.1 (124.8) | | | | | | |
| | $C_3H$ | 1.090 (1.082) | $HC_3C_2$ | 120.1 (119.3) | | | | | | |
| **3** | $X_1C_2$ | 1.686 | $X_1C_2C_3$ | 125.4 | $X_1$ | 0.10 | 4.03 | 1.87 | $X_1C_2$ | 0.29 |
| | $C_2C_3$ | 1.348 | $C_2C_3C_4$ | 123.1 | $C_2$ | − 0.08 | 3.10 | 0.98 | $C_2C_3$ | 0.94 |
| | $C_3C_4$ | 1.494 | $C_2X_1C_6$ | 104.4 | $C_3$ | − 0.15 | 3.11 | 1.04 | $C_3C_4$ | 0.23 |
| | $C_4Y_7$ | 1.229 | $Y_7C_4C_3$ | 121.5 | $C_4$ | 0.29 | 2.95 | 0.76 | $C_4Y_7$ | 0.90 |
| | $C_2H$ | 1.090 | $HC_2C_3$ | 123.3 | $C_5$ | − 0.15 | 3.11 | 1.04 | | |
| | $C_3H$ | 1.094 | $HC_3C_2$ | 119.6 | $C_6$ | − 0.08 | 3.10 | 0.98 | | |
| | | | | | $Y_7$ | − 0.29 | 4.97 | 1.32 | | |
| **4** | $X_1C_2$ | 1.682 (1.759) | $X_1C_2C_3$ | 125.0 (122.4) | $X_1$ | 0.12 | 4.04 | 1.85 | $X_1C_2$ | 0.29 |
| | | | | | $C_2$ | − 0.08 | 3.10 | 0.98 | $C_2C_3$ | 0.92 |
| | $C_2C_3$ | 1.353 (1.342) | $C_2C_3C_4$ | 124.2 (128.1) | $C_3$ | − 0.11 | 3.08 | 1.03 | $C_3C_4$ | 0.32 |
| | | | | | $C_4$ | 0.08 | 3.13 | 0.80 | $C_4Y_7$ | 0.85 |
| | $C_3C_4$ | 1.470 (1.406) | $C_2X_1C_6$ | 104.0 (101.4) | $C_5$ | − 0.11 | 3.08 | 1.03 | | |
| | | | | | $C_6$ | − 0.08 | 3.10 | 0.98 | | |
| | $C_4Y_7$ | 1.567 (1.671) | $Y_7C_4C_3$ | 121.2 – | $Y_7$ | − 0.20 | 4.85 | 1.35 | | |
| | $C_2H$ | 1.090 – | $HC_2C_3$ | 123.2 – | | | | | | |
| | $C_3H$ | 1.090 – | $HC_3C_2$ | 119.4 – | | | | | | |
| **5** | $O_1C_2$ | 1.368 | $O_1C_2C_3$ | 123.2 | $O_1$ | − 0.21 | 4.38 | 1.83 | $O_1C_2$ | 0.30 |
| | $C_2C_3$ | 1.356 | $C_2S_1C_6$ | 118.7 | $C_2$ | 0.09 | 2.93 | 0.98 | $C_2C_3$ | 0.94 |
| | $C_3C_4$ | 1.504 | $C_4C_3C_2$ | 122.2 | $C_3$ | 0.20 | 3.10 | 1.10 | $C_3C_4$ | 0.15 |
| | $C_2H$ | 1.095 | $HC_2C_3$ | 125.1 | $C_4$ | 0.09 | 3.91 | 0.93 | | |
| | $C_3H$ | 1.089 | $HC_3C_2$ | 120.6 | $C_5$ | − 0.20 | 3.10 | 1.10 | | |
| | $C_4H$ | 1.115 | $HC_4C_3$ | 110.0 | $C_6$ | 0.09 | 2.93 | 0.98 | | |
| **6** | $S_1C_2$ | 1.689 | $S_1C_2C_3$ | 125.1 | $S_1$ | 0.06 | 4.04 | 1.90 | $S_1C_2$ | 0.22 |
| | $C_2C_3$ | 1.344 | $C_2S_1C_2$ | 104.2 | $C_2$ | − 0.11 | 3.09 | 1.02 | $C_2C_3$ | 0.96 |
| | $C_3C_4$ | 1.504 | $C_4C_3C_2$ | 125.3 | $C_3$ | − 0.12 | 3.08 | 1.03 | $C_3C_4$ | 0.15 |
| | $C_2H$ | 1.089 | $HC_2C_3$ | 123.6 | $C_4$ | 0.07 | 3.00 | 0.93 | | |
| | $C_3H$ | 1.093 | $HC_3C_2$ | 119.9 | $C_5$ | − 0.12 | 3.09 | 1.02 | | |
| | $C_4H$ | 1.116 | $HC_4C_3$ | 108.8 | $C_6$ | − 0.11 | 3.08 | 1.02 | | |

[a] Experimental values [23] are given in parentheses.

are included for the sake of comparison. Survey of the calculated bond distances and the experimental values shows that the MNDO method gives moderately good description of geometries of the studied systems. The carbon-sulfur distances are significantly underestimated. For example, the calculated C–S single bond length in **4** is shorter by 0.08 Å relative to the experimental value obtained by the MW technique [23], while the computed C=S double bond is compressed too much by 0.1 Å. This error is systematic in nature as observed also by Dewar et al. [24]. This is encouraging because the calculated values can be empirically corrected increasing thus the credibility of the MNDO results. Other bond lengths are quantitatively better reproduced e.g., the carbon-oxygen bond distances are within the deviation of 0.007 Å from the experimental findings. The carbon-carbon bonds exhibit generally somewhat larger error (0.02 Å) an exception being the $C_3C_4$ bond in **4** which is overestimated by 0.06 Å. The reason for this discrepancy is not obvious. Bond angles are reproduced much better than distances. This is however, a consequence of the rigid cyclic structures of the considered systems, which have only a few angular degrees of freedom. The errors are 2° and 4° for pyrone-type species and thiopyrone derivatives, respectively. Inspite imperfections inherent in the MNDO equilibrium structures one can expect that errors cancel out at least to the large extent when similar molecules are compared implying that trend of changes is well reproduced in most cases. As far as the single molecule is concerned, structural informations offered by the MNDO method should be qualitatively correct. Part of the differences between the theoretical and experimental values arises due to the fact that they correspond to different definitions of the molecular geometry. The MW data refer to $r_s$ structures, which are generally different from $r_e$ ones [25].

Inspection of the data displayed in Table 1 reveals two important features. Firstly, variation of structural parameters in the series **1**–**4** is compatible with that found experimentally [23]. For instance, replacement of the carbonyl group in **1** by thiocarbonyl shortens the $C_3-C_4$ bond by 0.026 Å according to the MNDO method. The corresponding MW estimate is 0.032 Å. Similarly, the intraring C–O distance is compressed by 0.03 Å and 0.005 Å as obtained by the MNDO method and MW technique, respectively. Both, theory and experimental measurements predict increase in the $C_2C_3$ bond distance. The MNDO yields 0.005 Å for this lengthening, while the corresponding MW value is 0.013 Å. These changes are compatible with differences in calculated bond orders for **1** and **2** (Table 2). Secondly, the studied molecules do not exhibit aromatic character to a significant extent as judged from the experimental and calculated bond distances as well as $\pi$-bond orders. Let us focus our attention to the $C_2=C_3$ double bond in **1**. The estimated interatomic distance is 1.363 Å which can be compared with the value of 1.356 Å calculated for model system **5**, where appreciable cyclic conjugation is prevented by the $CH_2$ group at the position 4. Another piece of evidence is $C_4=O_7$ bond distance (1.228 Å) which is virtually the same as that calculated in acetone [26] (1.227 Å). Similar conclusions can be drawn for other compounds of the present series by considering C=C $\pi$-bond orders. These are 0.91, 0.88, 0.94, and 0.92 for molecules **1**, **2**, **3** and **4**, respectively, which in turn are similar to those obtained for nonaromatic **5** (0.94) and **6** (0.96).

The fact that molecular geometry is little affected by mobile $\pi$-electrons does not imply that charge transfer is absent in the aforementioned compounds. On the contrary, they exhibit appreciable polarization. It is therefore of some interest to consider the calculated MNDO charge densities and their breakdown to $\sigma$- and $\pi$-contributions. They are presented in Table 1. The shift of electron density from the ring to the exo-heteroatom is apparent in all neutral bases. This is in accordance with previous semiempirical [10–12, 15] and STO-3G ab initio calculations [10] for **1**–**4** series and compound **1**, respectively, which could be expected for the $8\pi$

Table 2. The s-characters of the local hybrid orbitals in bases **1**–**4** as calculated by the MNDO method.

| Molecule | Bond | s-characters (%) | Molecule | Bond | s-characters (%) |
|---|---|---|---|---|---|
| **1** | $O_1-C_2$ | 13.5–21.4 | **3** | $S_1-C_2$ | 6.0–25.7 |
| | $C_2=C_3$ | 40.3–34.6 | | $C_2=C_3$ | 37.1–35.0 |
| | $C_3-C_4$ | 30.1–35.9 | | $C_3-C_4$ | 30.2–36.0 |
| | $C_4=O_7$ | 27.7–11.2 | | $C_4=O_7$ | 27.2–11.2 |
| **2** | $O_1-C_2$ | 13.7–21.3 | **4** | $S_1-C_2$ | 6.0–25.8 |
| | $C_2=C_3$ | 39.4–34.0 | | $C_2=C_3$ | 36.8–34.6 |
| | $C_3-C_4$ | 30.7–31.2 | | $C_3-C_4$ | 29.1–31.4 |
| | $C_4=S_7$ | 34.3– 6.4 | | $C_4=S_7$ | 33.6– 6.4 |

systems of the given geometry. The charge distribution within the ring is strongly influenced by the electronegativity of the endo-heteroatom. The salient feature of the intraring distribution of electron density in the "pyrone" type compounds (**1** and **2**) is the alternation of charges. The intraring oxygen carries the negative charge which is drifted from the neighbouring $C_2$ and $C_6$ atoms. Consequently, the latter are positively charged. The carbons $C_3$ and $C_5$ bear negative formal charge while $C_4$ atom is positive. Partitioning of the gross electron charge density to $\sigma$- and $\pi$-electron components for **1** shows that the endo-oxygen gains 0.4 e through two $\sigma$-channels but donates 0.2 e to the rest of a molecule by the $\pi$-electron back-bonding effect. The exo-oxygen exhibits the diametrically opposite behaviour. It loses a small amount of $\sigma$-electrons (0.04) but increases its $\pi$-density by 0.34 e. Thus, the $\sigma$- and $\pi$-electrons operate here in different directions. It is noteworthy that gain or loss of $\sigma$- and $\pi$-density is even at $C_3$ and $C_2$ positions, respectively. The appreciable positive charge at $C_4$ is mainly a consequence of the diminished $\pi$-density. The charge distribution in **2** fits the same pattern. The exo-sulfur loses more $\sigma$-electrons (0.16 e) but attracts more $\pi$-density (0.40 e) relative to its oxygen counterpart in **1**. It is worth mentioning that atoms in similar chemical environments have formal atomic charges which are very close. For instance, the endo-oxygen has practically the same charge in **1** and **2**. The same was found for carbon $C_2$. The electron density of the atom $C_3$ is smaller in **2** by 0.05 e which is caused by the perturbing exo-sulfur atom $S_7$. The largest difference is found for the $C_4$ carbon which is directly bonded to $S_7$ atom. Hence, the influence of the perturber dies off relatively quickly as a function of the distance from the substitution site. It turns out that formal atomic charges of atoms in similar environments, which are distant from the substitution functional groups, are transferable even in weakly delocalized systems like **1** and **2**. This conclusion holds also for compounds **3** and **4** e.g., the formal charges for intraring sulfur atoms are 0.10 and 0.12, respectively. It is interesting to mention that endo-sulfur $\sigma$ core is practically neutral. The formal positive charge arises due to the donation of $\sim 0.15$ $\pi$-electrons to the rest of the molecule. One observes also that the charge alternation in **3** and **4** does not occur since atoms $C_2$ and $C_3$ are both negative. Finally, it is noteworthy to mention that distribution of charge in considered bases is in accordance with their chemical reactivity [7] and spectroscopic properties [2, 5].

Another useful bond index is provided by the s-characters of the local hybrid orbitals forming the localised $\sigma$-bond [27]. The s-characters can be extracted directly from the charge density bond-order matrix of MOs without performing the actual localisation procedure [28, 29]. The calculated s-characters are given in Table 2. One observes that oxygen orbitals have high p-content because a large portion of s-orbital is absorbed in the formation of its lone pair(s). Even higher p-character has sulfur which in addition to lone pair(s) has orbitals much larger in size than carbon AOs. Since the similar size of AOs is a prerequisite for efficient two-centre overlapping and mixing of orbitals placed on the same nucleus [30], one can infer that sulfur will use less s-character than oxygen. Comparison of the hybridization parameters characterizing $C_4{=}O_7$ and $C_4{=}S_7$ bonds in **1** and **2**, respectively, is instructive. The s-character of the $C_4$ carbon in $C_4{=}O_7$ bond is significantly lower than in the $sp^2$ canonical state because the electronegative oxygen atom prefers p-type orbitals according to the well known Bent-Walsh rule [31]. In contrast, the more electropositive S atom will favour s-character which is indeed increased for the $C_4$ carbon in the $C_4{=}S_7$ bond. Further, the formal C=C double bonds have increased s-character as noticed in a number of maximum overlap [27, 32] and semiempirical calculations [28, 29, 33]. It should be stressed that the hybridization parameters are to a high degree transferable providing thus useful $\sigma$-building blocks even for delocalized molecular systems.

*Protonated Bases*

It is generally accepted that protonation of compounds **1**–**4** and related systems occurs exclusively at the exo-heteroatom yielding pyrilium and thiopyrilium salts [5, 9]. Recently, however, Gold and Mah [34] have reported another type of protonation of these compounds. They concluded on the basis of $^1H$ and $^{13}C$ NMR spectra of 2,6-dimethylderivatives of **1**, **2** and **3** in $SbF_5$-$HSO_3F$ (1 : 1) solution that dimethyl derivatives of **1** and **3** are doubly protonated under superacidic conditions, while the dimethyl analogue of **2** gives exclusively singly protonated ion [31]. The observed discrepancy in protonation behaviour has been attributed to the different basi-

cities of thiol- and hydroxy-group in pyrilium and thiopyrilium type conjugate acids [34].

We have examined in the present theoretical study both types of protonation. The considered monoprotonated species involve structures with proton attached to endo- and exo-heteroatoms. The calculated heats of formation are summarized in Table 3 together with the intrinsic proton affinities of exo-heteroatoms of neutral bases. Survey of the calculated heats of formation reveals that the exo-heteroatom protonation is more favourable than the attachment of the proton to the intraring heteroatom for all four bases **1**–**4**. This is in accordance with the experimentally observed mode of protonation. It can be rationalized by the higher electron density centered on the $Y_7$ heteroatom and increased aromaticity in cations as discussed below. It should be mentioned that the experimental heats of formation and proton affinities are not available. Thus it is hard to appraise the quality of the calculated thermochemical values in quantitative sense. Benson additivity rules [35] yield similar $\Delta H_f$ values for species with two heteroatoms of the same kind (**1** and **4**). Discrepancies of 10–15 kcal/mol were found for compounds **2** and **3** involving different heteroatoms. The absolute values of the proton affinities (PA) are probably too low as judged from PA values calculated by the MNDO method and compared with the experimental data for some related bases [24]. Some improvement in PA estimates might be obtained by using experimental $\Delta H_f$ for $H^+$ instead of the MNDO one [36]. Perusal of the results (Table 3) shows that the MNDO method ascribes higher intrinsic proton affinity to the carbonyl oxygen in **1** and **3** than to the thiocarbonyl sulfur in **2** and **4**. Finally, a slight decrease in proton affinity of "thiopyrone" type derivatives relative to the corresponding "pyrone" type bases is predicted by the calculations. It should be, however, pointed out that these bases exhibit reversed order of basicities in solution [4] presumably due to the solvent effect.

Table 3. The MNDO calculated heats of formation and proton affinities for **1**–**4** and their mono- and diprotonated ions.

| Position of protonation | $\Delta H_f$ (kcal mol$^{-1}$) | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| neutral | − 45.2<br>(− 46.3)[a] | 4.5<br>(14.2)[a] | − 4.3<br>(− 18.1)[a] | 46.2<br>(42.9)[a] |
| protonated at | | | | |
| X | 164.0 | 215.3 | 238.4 | 290.0 |
| Y | 108.2 | 164.8 | 154.8 | 211.9 |
| diprotonated at | | | | |
| Y | 414.3 | 472.6 | 459.3 | 517.9 |
| Proton affinity (kcal mol$^{-1}$) | 173.5 | 166.4 | 167.6 | 161.0 |

[a] Value calculated by Benson additivity rules [35].

Comparison of the calculated structural parameters of neutral bases with that of protonated species clearly shows that protonation perturbs the geometry of the parent molecule to a considerable extent. In exo-monoprotonated molecular ions lengthening of the $C_4$-exo-heteroatom bond as large as 0.09 Å takes place (Table 4). The increased $C_4$–Y bond distance and the reduced $\pi$-overlap population in ions **1A**–**4A** relative to neutral bases values conclusively shows that exo-protonation causes weakening of the $C_4$–Y bond. In addition, the $C_2$=$C_3$ bonds are lengthened by ~ 0.03 Å, while the $C_3$–$C_4$ and $X_1$–$C_2$ bonds are compressed by ~ 0.04 Å and ~ 0.02 Å, respectively. The CC distances become similar and close to the benzene value. They are more evenly distributed over the ring although some localization of double bonds remains e.g., $C_2$–$C_3$ in **1A** etc. Hence the aromatic character is increased. The $\pi$-bond orders indicate also substantial increase in the degree of the $\pi$-electron delocalization over the ring as compared to neutral bases (Tables 1 and 4) fully in line with results of spectroscopic studies [2, 5, 9]. It should be mentioned that the most dramatic change in $\pi$-bond orders is found in $C_4$–$Y_7$ bonds. They are smaller by ~ 50% in all protonated species. Additional piece of evidence indicating significant increase in cyclic conjugation is provided by the analysis of the formal atomic charges (vide infra).

The bond angles undergo significantly smaller changes upon protonation. The intra-ring angles are changed by at most 2.5° in considered conjugated acids, while the change in $YC_4C_5$ angle decreases by roughly 5°.

The protonated conjugated acids do not exhibit appreciable rehybridization although some redistribution of s-characters is noticable (Table 5). For instance, a small shift in s-content of the local $\sigma$-orbitals from double to single CC bonds is apparent. Similarly, an increase in s-character is observed in $O_1$–$C_2$ bonds. Interestingly, the protona-

Table 4. The calculated structural parameters of monocations **1A**–**4A** and dications **1B** and **3B**, the formal atomic charges, gross $\sigma$- and $\pi$-populations and $\pi$-bond orders as obtained by the MNDO method.

| Ion | Bond distances (Å) | | Bond angles (deg) | | Charges | | | | $\pi$-bond orders | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Bond | | Angle | | Atom | Form. ch. | $\sigma$ | $\pi$ | Bond | |
| **1A** | $X_1C_2$ | 1.345 | $X_1C_2C_3$ | 121.3 | $X_1$ | − 0.11 | 4.44 | 1.67 | $X_1C_2$ | 0.48 |
| | $C_2C_3$ | 1.391 | $C_2C_3C_4$ | 119.3 | $C_2$ | 0.25 | 2.97 | 0.79 | $C_2C_3$ | 0.77 |
| | $C_3C_4$ | 1.440 | $C_5C_6X_1$ | 121.4 | $C_3$ | − 0.24 | 3.10 | 1.14 | $C_3C_4$ | 0.52 |
| | $C_4C_5$ | 1.444 | $C_6X_1C_2$ | 121.8 | $C_4$ | 0.32 | 2.95 | 0.73 | $C_4C_5$ | 0.51 |
| | $C_5C_6$ | 1.389 | $Y_7C_4C_3$ | 125.4 | $C_5$ | − 0.17 | 3.08 | 1.09 | $C_5C_6$ | 0.79 |
| | $C_6X_1$ | 1.349 | $HC_2C_3$ | 125.3 | $C_6$ | 0.22 | 2.97 | 0.81 | $C_6X_1$ | 0.46 |
| | $C_4Y_7$ | 1.319 | $HC_3C_5$ | 125.3 | $Y_7$ | − 0.16 | 4.38 | 1.78 | $C_4Y_7$ | 0.53 |
| | $Y_7H$ | 0.954 | | | $HY_7$ | 0.26 | | | | |
| | CH | 1.096 | | | | | | | | |
| **1B** | $X_1C_2$ | 1.339 | $X_1C_2C_3$ | 120.2 | $X_1$ | − 0.05 | 4.47 | 1.58 | $X_1C_2$ | 0.54 |
| | $C_2C_3$ | 1.417 | $C_2C_3C_4$ | 117.8 | $C_2$ | 0.30 | 2.98 | 0.72 | $C_2C_3$ | 0.68 |
| | $C_3C_4$ | 1.419 | $C_5C_6X_1$ | 120.4 | $C_3$ | − 0.13 | 3.09 | 1.04 | $C_3C_4$ | 0.65 |
| | $C_4C_5$ | 1.420 | $C_6X_1C_2$ | 123.5 | $C_4$ | 0.23 | 2.83 | 0.94 | $C_4C_5$ | 0.65 |
| | $C_5C_6$ | 1.416 | $Y_7C_4C_3$ | 121.7 | $C_5$ | − 0.13 | 3.09 | 1.04 | $C_5C_6$ | 0.68 |
| | $C_6X_1$ | 1.338 | $HC_2C_3$ | 125.0 | $C_6$ | 0.30 | 2.98 | 0.72 | $C_6X_1$ | 0.54 |
| | $C_4Y_7$ | 1.400 | $HC_3C_5$ | 118.4 | $Y_7$ | − 0.06 | 4.11 | 1.95 | $C_4Y_7$ | 0.22 |
| | $Y_7H$ | 0.972 | | | $HY_7$ | 0.38 | | | | |
| | CH | 1.10 | | | | | | | | |
| **2A** | $X_1C_2$ | 1.343 | $X_1C_2C_3$ | 121.0 | $X_1$ | − 0.09 | 4.45 | 1.64 | $X_1C_2$ | 0.56 |
| | $C_2C_3$ | 1.397 | $C_2C_3C_4$ | 120.0 | $C_2$ | 0.23 | 2.97 | 0.80 | $C_2C_3$ | 0.75 |
| | $C_3C_4$ | 1.427 | $C_5C_6X_1$ | 121.0 | $C_3$ | − 0.17 | 3.09 | 1.08 | $C_3C_4$ | 0.57 |
| | $C_4C_5$ | 1.430 | $C_6X_1C_2$ | 121.5 | $C_4$ | 0.06 | 3.15 | 0.79 | $C_4C_5$ | 0.56 |
| | $C_5C_6$ | 1.395 | $Y_7C_4C_3$ | 125.7 | $C_5$ | − 0.13 | 3.09 | 1.04 | $C_5C_6$ | 0.76 |
| | $C_6X_1$ | 1.346 | $HC_2C_3$ | 125.3 | $C_6$ | 0.21 | 2.97 | 0.82 | $C_6X_1$ | 0.49 |
| | $C_4Y_7$ | 1.660 | $HC_3C_5$ | 125.4 | $Y_7$ | 0.19 | 3.98 | 1.83 | $C_4Y_7$ | 0.45 |
| | $Y_7H$ | 1.312 | | | $HY_7$ | 0.09 | | | | |
| | CH | 1.10 | | | | | | | | |
| **3A** | $X_1C_2$ | 1.664 | $X_1C_2C_3$ | 125.1 | $X_1$ | 0.33 | 3.98 | 1.69 | $X_1C_2$ | 0.45 |
| | $C_2C_3$ | 1.374 | $C_2C_3C_4$ | 122.3 | $C_2$ | 0.00 | 3.17 | 0.83 | $C_2C_3$ | 0.81 |
| | $C_3C_4$ | 1.446 | $C_5C_6X_1$ | 125.3 | $C_3$ | − 0.19 | 3.08 | 1.11 | $C_3C_4$ | 0.49 |
| | $C_4C_5$ | 1.451 | $C_6X_1C_2$ | 104.6 | $C_4$ | 0.33 | 2.96 | 0.71 | $C_4C_5$ | 0.48 |
| | $C_5C_6$ | 1.372 | $Y_7C_4C_3$ | 123.2 | $C_5$ | − 0.12 | 3.07 | 1.06 | $C_5C_6$ | 0.82 |
| | $C_6X_1$ | 1.668 | $HC_2C_3$ | 122.1 | $C_6$ | − 0.20 | 3.17 | 0.85 | $C_6X_1$ | 0.43 |
| | $C_4Y_7$ | 1.319 | $HC_3C_5$ | 122.3 | $Y_7$ | − 0.15 | 4.39 | 1.76 | $C_4Y_7$ | 0.55 |
| | $Y_7H$ | 0.954 | | | $HY_7$ | 0.26 | | | | |
| | CH | 1.095 | | | | | | | | |
| **3B** | $X_1C_2$ | 1.654 | $X_1C_2C_3$ | 125.1 | $X_1$ | 0.57 | 3.93 | 1.50 | $X_1C_2$ | 0.56 |
| | $C_2C_3$ | 1.398 | $C_2C_3C_4$ | 120.6 | $C_2$ | − 0.02 | 3.22 | 0.79 | $C_2C_3$ | 0.70 |
| | $C_3C_4$ | 1.421 | $C_5C_6X_1$ | 125.3 | $C_3$ | − 0.07 | 3.07 | 1.00 | $C_3C_4$ | 0.63 |
| | $C_4C_5$ | 1.421 | $C_6X_1C_2$ | 104.9 | $C_4$ | 0.20 | 2.83 | 0.79 | $C_4C_5$ | 0.63 |
| | $C_5C_6$ | 1.398 | $Y_7C_4C_3$ | 121.4 | $C_5$ | − 0.07 | 3.07 | 1.00 | $C_5C_6$ | 0.70 |
| | $C_6X_1$ | 1.653 | $HC_2C_3$ | 121.3 | $C_6$ | − 0.02 | 3.23 | 0.79 | $C_6X_1$ | 0.57 |
| | $C_4Y_7$ | 1.406 | $HC_3C_5$ | 117.6 | $Y_7$ | − 0.07 | 4.11 | 1.96 | $C_4Y_7$ | 0.22 |
| | $Y_7H$ | 0.971 | | | $HY_7$ | 0.38 | | | | |
| | CH | 1.10 | | | | | | | | |
| **4A** | $X_1C_2$ | 1.661 | $X_1C_2C_3$ | 124.7 | $X_1$ | 0.36 | 3.99 | 1.65 | $X_1C_2$ | 0.46 |
| | $C_2C_3$ | 1.379 | $C_2C_3C_4$ | 123.0 | $C_2$ | − 0.02 | 3.18 | 0.84 | $C_2C_3$ | 0.78 |
| | $C_3C_4$ | 1.430 | $C_5C_6X_1$ | 124.6 | $C_3$ | − 0.12 | 3.08 | 1.04 | $C_3C_4$ | 0.54 |
| | $C_4C_5$ | 1.434 | $C_6X_1C_2$ | 104.6 | $C_4$ | 0.06 | 3.16 | 0.78 | $C_4C_5$ | 0.54 |
| | $C_5C_6$ | 1.378 | $Y_7C_4C_3$ | 123.9 | $C_5$ | − 0.09 | 3.08 | 1.01 | $C_5C_6$ | 0.79 |
| | $C_6X_1$ | 1.664 | $HC_2C_3$ | 122.4 | $C_6$ | − 0.03 | 3.17 | 0.86 | $C_6X_1$ | 0.48 |
| | $C_4Y_7$ | 1.661 | $HC_3C_5$ | 122.5 | $Y_7$ | 0.20 | 3.99 | 1.81 | $C_4Y_7$ | 0.47 |
| | $Y_7H$ | 1.312 | | | $HY_7$ | 0.09 | | | | |
| | CH | 1.095 | | | | | | | | |

Table 5. The s-characters of the local hybrid orbitals in cations **1A**–**4A** as estimated by the MNDO method.

| Ion | Bond | s-characters (%) | Ion | Bond | s-characters (%) |
|---|---|---|---|---|---|
| **1A** | $O_1-C_2$ | 14.8–21.2 | **3A** | $S_1-C_2$ | 5.4–26.4 |
| | $C_2-C_3$ | 37.6–33.0 | | $C_2-C_3$ | 35.2–34.2 |
| | $C_3-C_4$ | 30.7–36.2 | | $C_3-C_4$ | 30.6–36.8 |
| | $C_4-C_5$ | 36.8–30.3 | | $C_4-C_5$ | 34.3–35.4 |
| | $C_5-C_6$ | 33.1–37.9 | | $C_5-C_6$ | 30.2–37.0 |
| | $C_6-O_1$ | 21.0–14.9 | | $C_6-S_1$ | 26.0– 5.5 |
| | $C_4-O_7$ | 25.2–13.2 | | $C_4-O_7$ | 24.6–13.5 |
| | $O_7-H$ | 15.0 | | $O_7-H$ | 15.2 |
| **2A** | $O_1-C_2$ | 15.0–21.1 | **4A** | $S_1-C_2$ | 5.6–26.2 |
| | $C_2-C_3$ | 37.5–32.3 | | $C_2-C_3$ | 35.1–33.5 |
| | $C_3-C_4$ | 31.5–33.1 | | $C_3-C_4$ | 31.5–33.4 |
| | $C_4-C_5$ | 32.7–31.1 | | $C_4-C_5$ | 33.0–31.1 |
| | $C_5-C_6$ | 32.4–37.7 | | $C_5-C_6$ | 33.6–35.3 |
| | $C_6-O_1$ | 21.0–15.0 | | $C_6-S_1$ | 26.0– 5.6 |
| | $C_4-S_7$ | 30.5– 4.9 | | $C_4-S_7$ | 29.7– 4.9 |
| | $S_7-H$ | 5.4 | | $S_7-H$ | 5.4 |

tion does not lead to dramatic rehybridization at the exo-heteroatom. Formation of the new O–H bond increases the s-character of the hybrid orbital directed toward the neighbouring $C_4$ carbon in **1** and **3**. However, the partner vis a vis hybrid orbital decreases its s-content. It appears that the average s-character of the $C_4-O_7$ bond is preserved during the protonation. Thus we can say that weakening of $C_4-O_7$ bond in **1** and **3** arises exclusively due to the decrease in $\pi$-bond order. On the contrary, the $C_7-S_7$ bond suffers a decrease in average s-character upon protonation (Table 5). Hence the weaker $C_4-S_7$ bond in **2** and **4** is a consequence of the decrease in bonding power of hybrids describing $\sigma$-bond and a simultaneous decrease in $\pi$-bond order. Survey of the data displayed in Table 5 reveals again a high degree of transferability of s-characters.

Properties of doubly protonated compounds **1B** and **3B** follow the same pattern as those of monoprotonated counterparts. The only difference is that all effects are enhanced almost twice. For example, the $\pi$-bond order of the $C_4-O_7$ bond is diminished to a quarter of the value found in the parent base compound. The extent of delocalization is further increased as evidenced by the calculated $\pi$-bond orders and intraring bond distances.

Not unexpectedly protonation causes a pronounced electron charge redistribution in conjugated acids. Monoprotonation is accompanied by significant charge transfer from the base to a proton. In carbonyl containing species the incoming proton is shielded by 0.74 e while in thiocarbonyl acids the proton is almost neutral, the transfer of electron charge being 0.91 e. It is interesting to note that in **1A** species the transferred electron density comes mostly from the host $O_7$ atom and $C_2$, $C_6$ carbons. They donate about $\sim 0.15$ e each. In **3A** and **4A** the electron drift originates from both heteroatoms, the $S_7$ atom giving by far the largest share in the latter compound. Similarly, the largest portion of the electron density shifted to the proton in **2A** comes from the host sulfur atom $S_7$ while the contributions of $O_1$ oxygen and $C_2$, $C_6$ carbons are modest. Some atoms in the ring gain small amounts of charge density upon protonation to mention carbon atom at ipso-position in species **2A** and **4A**. Analysis of the $\sigma$- and $\pi$-charge redistribution is instructive. Inspection of the data given in Table 1 and 4 shows that protonated exo-heteroatoms lose a considerable amount of $\sigma$-charge density during the formation of the new Y–H covalent bond. It is found that oxygen $O_7$ and sulfur $S_7$ invest 0.58 e and 0.86 e, respectively, for that purpose. This electron density is conveniently used for shielding of the proton and buildup of charge in the region between the Y, H nuclei. A good deal of this charge ($\sim 0.44$ e) is recovered by the $\pi$-electron charge flow toward the protonated heteroatom. The most significant $\pi$-electron donors are intraring heteroatoms and carbon atoms at $C_2$, $C_6$ positions. The resulting formal charge of the exo-cyclic heteroatom depends strongly on its electronegativity. The exo-oxygen retains the negative charge in the "pyrilium" type ions, while the exo-sulfur atom in "thiopyrilium" types **2** and **4** becomes positively charged. This is in accordance with experimentally observed mode of diprotonation in dimethyl derivatives of **1**–**3**. The dimethyl derivatives of ions **1A** and **3A** undergo second protonation in strong acid solutions due to the formal negative charge of the exo-oxygen. In contrast, the dimethyl derivative of **2A** ion is resistant to the second protonation under the same conditions.

Double protonation leads to further charge reorganization. The MNDO method predicts a decrease of the positive charge placed on the carbon $C_4$ in dications **1B** and **3B** relative to parent bases. This is in qualitative agreement with $^{13}C$ NMR data [34] which exhibit a small upfield shift in the $C_4$ resonance when the solvent is changed from $CDCl_3$ to $HSO_3F$-$SbF_5$. However, a decrease of electron

density at $C_3$ and $C_5$ carbons is not corroborated by the $^{13}C$ NMR measurements, since an upfield shift is recorded upon second protonation for these nuclei [34].

Finally, it should be mentioned that a very simple criterion of delocalization in the considered species is offered by the $\pi$-electron charge density distribution. In the perfectly localized system one would have one $\pi$-electron per carbon atom and two $\pi$-electrons placed on intraring oxygen or sulfur atoms. Deviation of the gross $\pi$-electron density from these integers measures the extent of the $\pi$-conjugation. One observes, for example, that 0.33 $\pi$-electrons are released in **1A** by the $O_1$ atom as compared to the 0.2 e in the parent compound **1**. The carbon $C_2$ contributes 0.06 and 0.21 $\pi$-electrons to the delocalized system in **1** and **1A**, respectively. Analysis of this type gives immediately a contention that cyclic conjugation is increased by the protonation which is in agreement with other criteria provided by bond distances and $\pi$-bond orders.

## Conclusion

The MNDO method gives qualitatively a good description of the molecular geometries of the bases **1**–**4** and their mono- and diprotonated conjugate acids. The variation of the structural parameters in the bases is well reproduced and the most important features are in accordance with experimental findings. It is found that the bases **1**–**4** have small if not negligible aromatic character. Analysis of the charge distributions has shown that the molecules are considerably polarized mainly through the $\pi$-density flow from the ring to the exo-heteroatom. Protonation leads to a significant perturbation of the base ring. The calculated charge distributions and bond distances indicate substantial increase in aromaticity in the resulting mono- and dications. This finding is in qualitative agreement with results of spectroscopic studies. The heavy-atoms exo-bond $C_4{=}Y_7$ is destabilized by the protonation due to the appreciable decrease in $\pi$-bond order in **1** and **3**. This effect is enhanced in **2** and **4** by the simultaneous decrease in s-character. The formation of the new Y–H bond occurs at the expense of a considerable loss of Y $\sigma$-density. This is followed by a strong drift of the $\pi$-electrons toward the site of protonation, which partly compensates the serious decrease of electron density placed on Y. The calculations predict exo-heteroatom protonation to be more favourable by 60–80 kcal/mol than the attachment of the proton to the intraring heteroatom, in accordance with experiment. This can be rationalized by the higher electron density placed on the exo-heteroatom and the increased cyclic conjugation, which is a consequence of exo-protonation. On the contrary, intraring protonation leads to a highly pronounced localization in the $\pi$-system. As an illustration we mention that the $\pi$-lone pair populations of protonated $O_1$ and $S_1$ atoms in the endo-heteroatom protonated conjugate acids of **1** and **4** are 1.94 e and 1.96 e, respectively. It should be stressed that the exo-oxygen in **1A** and **3A** cations bears negative formal charge while exo-sulfur in **2A** and **4A** is found to be effectively positive. This result is in line with the different susceptibilities of these ions to the second protonation observed experimentally.

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