occurs from the tellurium atom to the sulfur atom of the methylsulfinyl group by means of intramolecular π-conjugation between the benzene rings and the sulfur atom. This sulfur atom is important in connecting the π-conjugated system on the tellurium atom with the sulfur atom of the methylsulfinyl group.

In summary, we have found a new remote oxidation reaction through π-conjugated bonds for the formation of dicationic telluranes.

Experimental Section

4: Tf_2O (4 µL, 0.024 mol) was added to a solution of **3** (14 mg, 0.02 mol) in dry CH_3CN at −40 °C under an argon atmosphere. The resulting solution was stirred for 12 h at room temperature, and the solvent was then evaporated to give **4** (15 mg, 86%) as the residue. M.p. 118–123 °C (decomp); ^1H NMR (270 MHz, CD_3CN): $\delta = 2.43$ (s, 3H), 4.42, 5.26 (AB q, $J = 18$ Hz, 2H), 4.90, 5.24 (AB q, $J = 17$ Hz, 2H), 6.86–8.23 (m, 17H, ArH); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 14.5$, 39.1, 39.9, 124.2, 124.9, 127.6, 128.7, 130.0, 131.0, 131.5, 132.2, 132.3, 132.8, 132.9, 134.8, 136.2, 147.5, 147.9, 150.5; ^{125}Te NMR (126 MHz, CD_3CN, 25 °C): $\delta = 1343.2$ (relative to Me_2Te); EI-MS: *m*/*z*: 574 $[M^+ - 2\,TfO^-]$; elemental analysis calcd for $C_{29}H_{24}F_6O_6S_5Te$: C 40.02, H 2.78; found: C 39.79, H 2.99.

6: M.p. 145–150 °C (decomp); ^1H NMR (400 MHz, CD_3CN): $\delta = 2.53$ (s, 3H), 4.45, 5.15 (AB q, $J = 18$ Hz, 2H), 5.03, 5.22 (AB q, $J = 17$ Hz, 2H), 6.81–8.16 (m, 21H, ArH); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 15.0$, 39.5, 40.3, 120.1, 122.3, 123.3, 124.6, 125.3, 127.7, 128.3, 129.0, 130.3, 131.0, 131.6, 132.1, 132.5, 132.8, 132.9, 135.3, 136.2, 136.5, 143.2, 147.7, 148.1, 150.0; ^{125}Te NMR (126 MHz, CD_3CN): $\delta = 1339.7$ (relative to Me_2Te); FAB-MS: *m*/*z*: 831 $[M^+ - TfO^-]$.

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[3] Since 2,6-bis[(phenylsulfanyl)methyl]phenyl 4-(methylsulfanyl)phenyl telluride has four chalcogen atoms which are susceptible to oxidation, it is difficult to selectively oxidize the S atom of the methylsulfanyl group. Therefore, the compound was initially converted to the corresponding dicationic tellurane, which was then treated with *m*-CPBA to oxidize the sulfur atom of the methylsulfanyl group. The telluride **3** was obtained by reduction of the dicationic tellurane with two equivalents of thiophenol.

[4] X-ray structure analysis of **4**: Selected bond lengths [Å] and angles [°]: Te1-S1 2.637(1), Te1-S2 2.730(1), S1-Te1-S2 160.60(3). Crystal data: $C_{29}H_{26}F_6O_7S_5Te$, crystal dimensions $0.75 \times 0.30 \times 0.25$ mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.822(3)$, $b = 16.531(3)$, $c = 10.187(2)$ Å, $\alpha = 99.65(1)$, $\beta = 103.81(2)$, $\gamma = 92.63(2)°$, $V = 1737.7(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.70\ \mathrm{g\,cm^{-3}}$, $2\theta_{max} = 60.0°$. Rigaku AFC-7R four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $\omega/2\theta$ scan mode, $T = 296$ K, 11109 measured reflections, Lorentzian and polarization corrections, absorption coefficient 12.3 $\mathrm{cm^{-1}}$, semiempirical absorption correction (ψ scans; transmission factors 0.93–1.00), structure solution with direct methods, program package teXsan(1992), full-matrix least-squares refinement on *F*, 7190 observed reflections ($I > 3.0\sigma(I)$), 440 parameters, hydrogen atoms included but not refined, $R = 0.041$, $R_w = 0.053$, residual electron density 1.07 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136391. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Pyrone-Like Structures as Novel Oxygen-Based Organic Superbases**

Dimas Suárez, J. Angel Menéndez, Enrique Fuente, and Miguel A. Montes-Morán*

The concept of strong organic basicity is generally associated with proton sponge compounds.[1] An unexpectedly high pK_a value was reported for the parent compound of this class, 1,8-bis(dimethylamino)naphthalene (DMAN) by Alder et al. more than 30 years ago.[2] This high thermodynamic basicity arises from the interaction of basic groups in close proximity to each other. In contrast, the hydrophobic shielding of the basic centers in DMAN derivatives results in a weak nucleophilic character and low rates of proton transfer,[3] attributes which ultimately will decide the utilization of the organic superbases as proton scavengers in chemical and biochemical processes.[4]

The term “pyrone-like structures” (as used in this communication) was originally adopted by Voll and Boehm[5] to define a type of oxygen-containing functionality capable of acting as a basic center on carbon surfaces.[6] According to their definition[5] these pyrone-like compounds are combinations of non-neighbouring carbonyl and ether oxygen atoms at the edges of a graphene layer. Thus, this generic designation would include not only γ-pyrone derivatives but also structures where the two oxygen atoms are located in different rings. Although there are no reported data, within our knowledge, for these latter pyrone-like systems, we have recently demonstrated using ab initio calculations that they show a broad spectrum of base strength (around 12 pK_a units).[7]

Herein we report a systematic ab initio study of the gas-phase proton affinities (PAs) of mono- and polycyclic pyrone-like structures **1**–**7**. The structural and energetic results for compounds **1**–**7** will be compared with those of the prototypical proton sponge DMAN **8**, and thus support the title proposal of pyrone-like structures as organic superbases. In addition, some specific aspects justify the novelty of and interest shown in the comparison of these relatively simple organic compounds with conventional proton sponges. First, the proton acceptor atom corresponds to a neutral carbonyl oxygen atom in contrast to the predominance of amine and imine functionalities in the nitrogenated superbases. Second-

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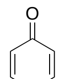
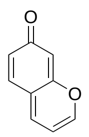


1

213.0 kcal mol^{-1}



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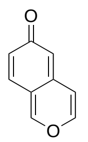
232.2 kcal mol^{-1}



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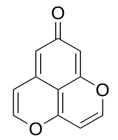
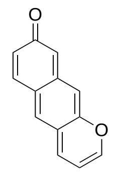
232.1 kcal mol^{-1}



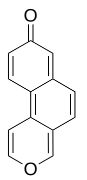
4

242.0 kcal mol^{-1}



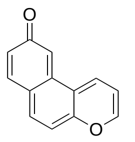
5

245.0 kcal mol^{-1}



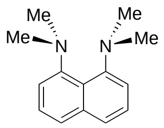
6

246.4 kcal mol^{-1}



7

251.9 kcal mol^{-1}



8 (DMAN)

243.8 kcal mol^{-1}

ly, both the polarity of the pyrone-like compounds and the easy access of solvent to their basic center may facilitate either an acceptable solubility or fast kinetics for proton transfer from and to the carbonyl functionality. Finally, the important control of resonance stabilization on the PAs of **1**–**7** supports a clear structure–basicity correlation for these and other pyrone-like structures of potential interest.

The corresponding gas-phase PAs for structures **1**–**8** were calculated at the MP2/6-311+G(2d,2p)//MP2/6-31G(d) level of theory. The simplest pyrone-like structure, γ-pyrone (**1**), has a PA of 213.0 kcal mol^{-1}, a value around 9–14 kcal mol^{-1} below typical PAs for weak nitrogen bases such as pyridine (PA = 222.3 kcal mol^{-1}), or trimethylamine (PA = 226.8 kcal mol^{-1}).[8] The PAs of these latter bases are taken here as an experimental reference because of the lack of data concerning the gas-phase basicity of γ-pyrone (or α-pyrone) compounds. Nevertheless, to further calibrate the methodology to be used in the determination of PAs for the rest of systems studied, we also calculated the PA of **1** with the G2(MP2,SVP) method.[9] The resultant G2(MP2,SVP) value is 213.0 kcal mol^{-1}, which matches perfectly the PA of **1** estimated at the MP2/6-311+G(2d,2p)//MP2/6-31G(d) level.

The PA values for the possible pyrone-like structures with two fused rings, **2** and **3**, are 232.2 and 232.1 kcal mol^{-1}, respectively, which are around 10 kcal mol^{-1} above the experimental value for pyridine.[8] We also note from these values that the exact position of the ether oxygen atom has a very weak influence on the PA for the pyrone-like structures with two fused rings. Hence, our calculations predict that the gas-phase PA of **2** and **3** are reinforced by around 19 kcal mol^{-1} with respect to **1**. This large increment of the PA can be well understood in terms of the stability conferred to the protonated system by conjugation throughout the ether ring and the aromaticity of the resultant phenolic ring. A similar argument has been recently employed to explain the high basicity predicted for quinodiimine compounds.[10] Interestingly, the reported increase in the PA per quinoid ring ($\approx$20 kcal mol^{-1})[10] remains very close to the difference between the PA values of **1** and the pyrone-like molecules **2** and **3** ($\approx$19 kcal mol^{-1}). It is also worth noting that the stabilization of the protonated form by aromatization is significantly more important than the contribution of the strain energy to the basicity of conventional proton sponges (4–14 kcal mol^{-1}).[11] However, the formation of the intramolecular hydrogen bond in DMAN derivatives stabilizes the protonated species better by contributing 24 kcal mol^{-1} or more.[11]

It is clear from the PA calculations for structures **1**–**3** that the larger the conjugation gained upon protonation of pyrone-like structures the greater their PA and pK_a values, which eventually reaches the commonly accepted ranges of superbases (PA $\approx$ 240 kcal mol^{-1}). To further explore this possibility we considered four hypothetical superbases with three fused rings corresponding to the pryone-like structures **4**–**7**. Structure **4**, which represents the enlargement of **2** by addition of a second ether ring, has a PA of 242.0 kcal mol^{-1}, which is about 29 and 10 kcal mol^{-1} larger than those for **1** and **2**, respectively. However, when pyrone-like structures are grown by the appropriate insertion of sp^2 carbon atoms, a more important stabilization of the protonated forms results, with the calculated PA values for structures **5**–**7** being 245.0, 246.4, and 251.9 kcal mol^{-1}. Therefore the pyrone-like structures **4**–**6**, and especially **7**, should be considered as organic superbases in the gas phase.

Structure **7** is the pyrone-like structure with the largest PA reported in this work (Figure 1). From a comparison of the

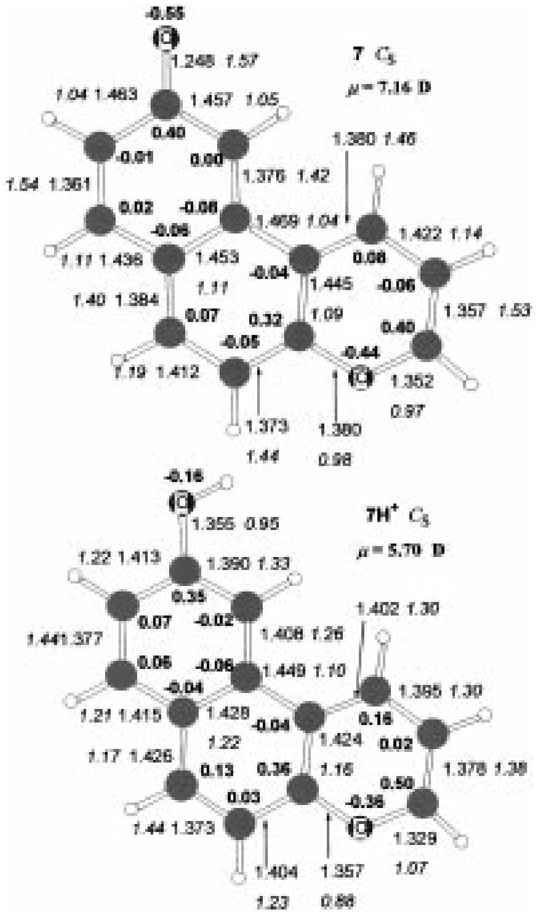
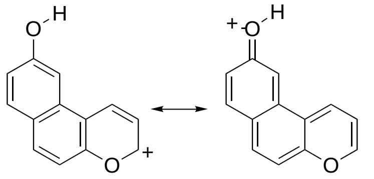


Figure 1. MP2/6–31G(d)-optimized structures for the neutral and protonated forms of the pyrone-like structure **7**. Distances are given in Ångstroms. Mayer bond orders and NPA atomic charges are shown in italic and bold characters, respectively. The dipole moment calculated by MP2/6-31G(d) is given in Debyes.

geometrical data and Mayer bond orders between **7** and the protonated form **7H**$^+$ we confirm that a certain aromatization of the all-carbon rings is induced upon protonation, which renders C–C distances in **7H**$^+$ lying within the range 1.36–1.45 Å (bond orders 1.44–1.10). Inspection of the corresponding changes in the charges in **7H**$^+$ by Natural Population Analysis reveals that 38 % and 34 % of the positive charge are delocalized throughout the ether ring and the hydroxyl groups, respectively. Thus, the nature of **7H**$^+$ can be better described in terms of the two resonance structures **7H**$^+$ (**I**) and **7H**$^+$ (**II**), with structure **7H**$^+$ (**I**) being the predominant one.



7H$^+$ (I) **7H$^+$ (II)**

For comparative purposes, we briefly discuss our calculations on the most prototypical proton sponge, DMAN (Figure 2). The calculated gas-phase PA for DMAN is 243.8 kcal mol^{-1}, 8.1 kcal mol^{-1} below that of **7**, and compares very well with the experimental value of 241.9 kcal mol^{-1}.[8] Similarly, the MP2/6-31G(d) geometrical data (see Figure 2) for the most stable conformers of DMAN and DMAN-H$^+$ with C_2 and C_S symmetry, respectively, are in good agreement with recent experimental results.[12] As discussed in previous work,[11, 12] various electronic and structural changes occur when DMAN accepts a proton. Most remarkably, the naphthalene ring becomes completely planar (although the corresponding C-C distances and bond orders suffer slight variations) and the proton is located asymmetrically between the N atoms with equilibrium distances of 1.108 and 1.561 Å, thus forming a short and strong N–H ⋯ N hydrogen bond.

In summary, the comparative analysis of the theoretical results for the pyrone-like structure **7** and DMAN clearly supports the prediction of pyrone-like structures as organic superbases. We expect that the theoretical results reported in this work will stimulate further work aimed at the synthesis of pyrone-like structures. This new type of reagents might expand the possibilities in the design of more specific oxygen-based superbases.

Experimental Section

Stable structures were fully optimized at the HF/6-31G(d) and MP2/6-31G(d) levels of theory[13] and characterized by calculating their HF/6-31G(d) frequencies. Proton affinities in the gas phase were obtained by combining MP2/6-311 + G(2d,2p)//MP2/6-31G(d) electronic energies and the corresponding HF/6-31G(d) thermal corrections at standard conditions. All the calculations were performed using the Gaussian 94 series of programs.[14]

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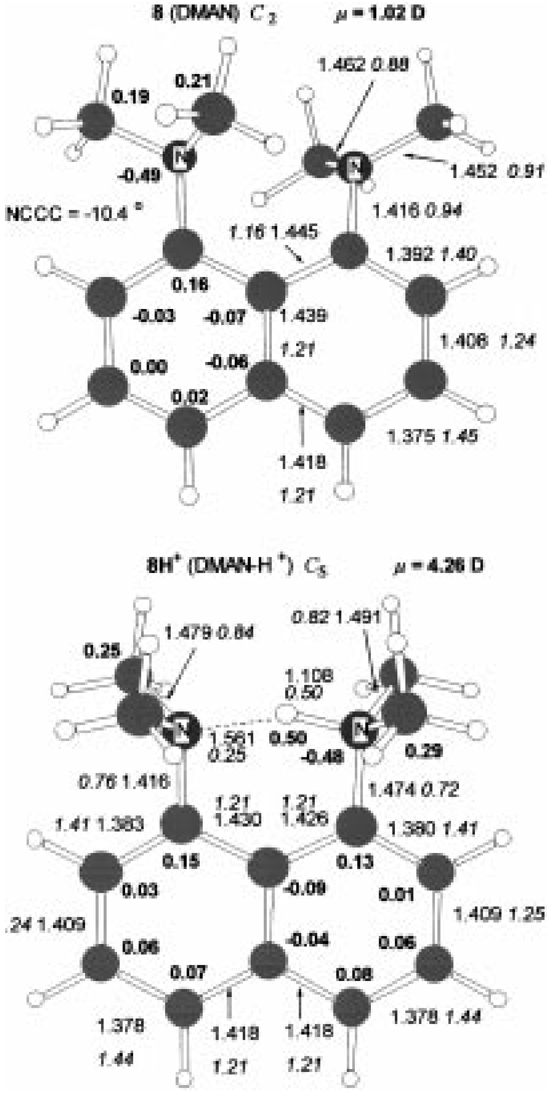

Figure 2. MP2/6-31G(d)-optimized structures for the neutral and protonated forms of DMAN. Distances are given in Ångstroms. Mayer bond orders and NPA atomic charges are also shown in italic and bold characters, respectively. The dipole moment calculated by MP2/6-31G(d) is given in Debyes.

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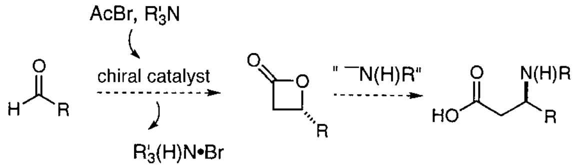
Enantioselective β-Amino Acid Synthesis Based on Catalyzed Asymmetric Acyl Halide–Aldehyde Cyclocondensation Reactions[**]

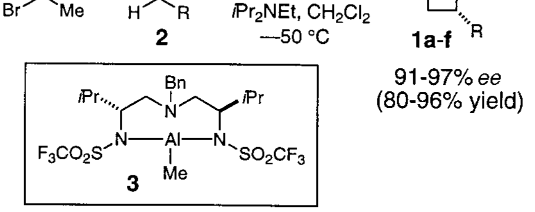
Scott G. Nelson[*] and Keith L. Spencer

Optically active β-amino acids have become increasingly prevalent features in small-molecule chemotherapeutic agents[1] and are integral components of peptidic materials that have unique structural properties.[2] As a result, efficient and economical preparation of enantiomerically enriched β-amino acids has become the focus of numerous synthesis studies.[3, 4] The amine-mediated S_N2 ring opening of β-lactones presents an especially attractive and straightforward entry to compounds that contain β-amino carbonyl functionalities [Eq. (1)].[5, 6] However, the evolution of this strategy as a general asymmetric synthesis of β-amino acids has been limited by the availability of the requisite optically active β-lactone electrophiles.[7] Herein we describe the union of catalytic asymmetric acyl halide–aldehyde cyclocondensation reactions with azide- or sulfonamide-anion-mediated ring opening of the derived enantiomerically enriched β-lactones as an economical and efficient asymmetric synthesis of N-protected β-amino acids.



(1)

Catalyzed enantioselective acyl halide–aldehyde cyclocondensation (AAC) reactions have recently been reported to provide convenient access to β-lactones with high enantiomeric purities [Eq. (2)].[8] We envisioned that integrating the catalytic asymmetric AAC reaction technology with the reactivity of nitrogen-based nucleophiles toward β-lactones would represent a general asymmetric synthesis of β-amino acid derivatives. Thus, a series of enantiomerically enriched β-lactones **1** were prepared by the asymmetric cyclocondensation of acetyl bromide and a variety of aldehyde electrophiles **2** catalyzed by the Al^{III} triamine complex **3** (Table 1). Based on pioneering observations by the groups of Vederas and Seebach,[5a–c] azide ion was evaluated initially as a suitable nucleophile for effecting the desired S_N2 mode of 2-oxetanone ring opening. Reacting the optically active β-lactones **1a–f** with sodium azide (2.0 equiv) in DMSO (50 °C) promoted efficient S_N2 lactone ring opening to directly afford the β-azido acids **4a–f** in 78–95 % yield [Eq. (3)].[9] Azide-induced ring opening was insensitive to the structure of the lactone alkyl substituent; lactones bearing aliphatic unbranched, alkoxy-substituted, α-branched,[10] and β-branched alkyl sub-



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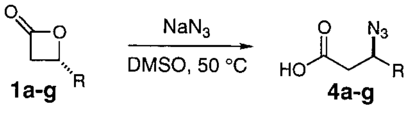

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