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(32) The HMO results for pyrrolo[3,2-*b*]pyrrole are $3a_u(\pi)$, −7.51 eV; $2a_u(\pi)$, −8.20 eV; $2b_g(\pi)$, −9.65 eV; $1b_g(\pi)$, −11.59 eV. This compound was not available for the measurements.
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Novel Aromatic Systems. 9.[1a] Proton and Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of the Heteroaromatic 6π 1,3-Dioxolium (Dithiolium) and 10π Benzo-1,3-dioxolium (Dithiolium) Ions

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Received December 23, 1976

The 6π heteroaromatic character of protonated (HSO_3F–SbF_5–SO_2) and methylated (CH_3F–SbF_5–SO_2) vinylene carbonate (**1a**) and its trithio analogue (**1b**) is investigated by ^{1}H and ^{13}C NMR spectroscopy. The 10π heteroaromatic character of the benzo derivative of **1a** in addition to the parent 1,3-benzodioxolium ion (**4**) and 1,3-benzodithiolium ion (**5**) has also been studied.

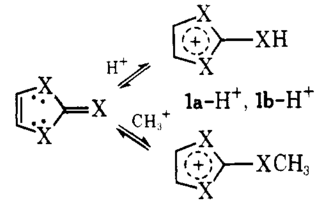
Aromatic character has been frequently attributed to molecules in which lone pair electrons on heteroatoms enter into conjugation with unsaturated bonds forming stable Hückel-type aromatic systems.[2] Heterocyclic compounds containing oxygen and sulfur represented by the 1,3-dioxolium and 1,3-dithiolium ions (as well as parent compounds) should, as 6π-electron systems, be quite stable. Few examples of substituted 1,3-dioxolium cations[3] have been reported in contrast to extensive reports concerning the 1,3-dithiolium salts.[4] The reactivity and electronic spectra of "pseudoaromatic" sulfur compounds have been studied using simple MO–LCAO methods.[5] We therefore thought it of interest to examine the ionic systems resulting from protonation and methylation of vinylene carbonate (**1a**) and 1,3-dithia-2-thione (**1b**). In addition, we have extended our studies to include 10π electron systems, 2-hydroxy-1,3-benzodioxolium ion (**2**-H$^+$), the parent 1,3-benzodioxolium ion (**4**), and 1,3-benzodithiolium ion (**5**).

Results and Discussion

Protonated and methylated ions, respectively, were prepared from their corresponding precursors with the general methods developed previously.[6a,b] ^{1}H and ^{13}C NMR data, for the precursors and the ions studied, are summarized in Tables I and II, respectively.

6π Heteroaromatic Ions. Stable ions result from protonation (**1a**-H$^+$, **1b**-H$^+$) using FSO_3H–SbF_5–SO_2 solution and, methylation (**1a**-$CH_3{}^+$) using CH_3F–SbF_5 "complex" in SO_2 solution at −60 °C. Methylated ion (**1b**-$CH_3{}^+$) was studied as the stable iodide salt[7] in SO_2 solution. Methylation of **1b** with CH_3F–SbF_5 "complex" in SO_2 solution resulted in, as yet, unidentifiable species in the ^{1}H NMR spectrum.

1a, X = O
1b, X = S



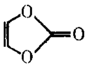
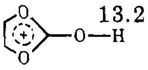
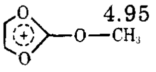
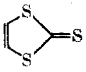
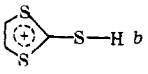
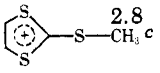
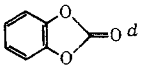
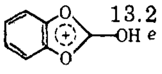
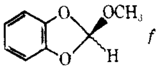
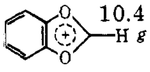
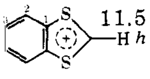
1a-H$^+$, **1b**-H$^+$

1a-$CH_3{}^+$, **1b**-$CH_3{}^+$

We consider the carbon-13 chemical shifts of ring carbons to be quite informative concerning trends of charge delocalization since extensive evidence has resulted indicating the sensitivity of charge and ^{13}C NMR shifts.[8] The assignment of resonances was made by the now familiar procedure of Grant and co-workers.[9,10] When needed, "off-resonance" proton decoupled spectra were obtained to assure correct peak assignments.

Vinylene carbonate (**1a**) in 1:1 M/M FSO_3H–SbF_5 in SO_2 solution was found to be protonated on the carbonyl oxygen. The ^{1}H NMR spectrum at −60 °C consisted of two peaks, one at δ 8.2 ppm of relative area 2, and one at δ 13.2 ppm of area 1. In addition, the olefinic protons are deshielded by 1.3 ppm

Table I. ^{1}H NMR Parameters of Heteroaromatic Ions[a]

Precursor	Heteroaromatic ion	
7.2 	8.2  13.2	8.2  4.95
7.5 	8.5  [b]	8.1  2.8 [c]
7.2–7.25 (m)  [d]	8.0  13.2 [e]	
7.1 3.62  [f]	8.1–8.2  10.4 [g]	
	7.95–8.9  11.5 [h]	

[a] In parts per million (δ) from external Me_4Si (capillary). Protonated in $FSO_3H-SbF_5-SO_2$ at −60 °C. Methylated with CH_3F-SbF_5 "complex"$-SO_2$ at −40 °C. [b] Not observable. [c] Methylated species studied as stable iodide salt in SO_2 solution at −40 °C. [d] In SO_2ClF at −10 °C. [e] Protonated in $FSO_3H-SbF_5-SO_2ClF$ at −80 °C. [f] In CCl_4, ambient probe temperature. [g] Ion prepared in FSO_3H-SO_2 at −70 °C. [h] In CD_3CN, ambient probe temperature.

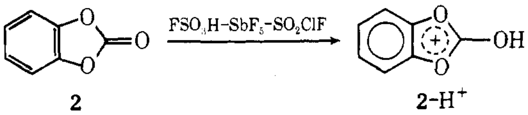
when compared to the neutral molecule in SO_2 solution. This additional deshielding suggests the presence of a significant ring current, the resulting ion being a 6π-electron heteroaromatic system. Methylation of **1a** resulted only by using CH_3F-SbF_5 "complex" in SO_2 solution while other methylating agents [$HC(OCH_3)_2^+PF_6^--SO_2$, $(CH_3)_3O^+BF_4^--SO_2$, $CH_3OSO_2F-SO_2$] proved unsuccessful. The ^{1}H NMR spectrum of **1a**-CH_3^+ at −60 °C consisted of two signals, one at δ 8.2 ppm with relative area 2, and one at δ 4.95 ppm of area 3. Again one observes the same downfield absorption of the olefinic protons due to significant charge delocalization into the ring.

^{13}C NMR parameters for vinylene carbonate (**1a**) show significant shielding of the carbonyl carbon (δ^{13}C 154.8) due most probably to the proximity of lone pair electrons on the adjacent heteroatoms. The carbonyl shift is very similar in ethylene carbonate, the saturated analogue of **1a**.[11] The olefinic carbons appear at δ^{13}C 132.2, a resonance value typical of sp^2 carbons of substituted alkenes and aromatics.[11] Upon protonation, the carbon-13 chemical shifts for the 1,3-dioxolium ion formed are deshielded by 6.1 ppm for the olefinic carbons and 9.5 ppm for the carbonyl carbon. Carbon-13 chemical shifts for methylated vinylene carbonate (**1a**-CH_3^+) show striking shift differences for the carbonyl carbon when compared to **1a** and **1a**-H^+, while the olefinic carbon shift is the same as that of **1a**-H^+. Carbon-13 chemical shifts for the 1,3-dioxolium ion formed are deshielded by 6.1 ppm for the olefinic carbons and 27.0 ppm for the carbonyl carbon.

Protonation of 1,3-dithia-2-thione (**1b**) in 1:1 M/M FSO_3H-SbF_5 in SO_2 solution occurred on the thiocarbonyl sulfur. The ^{1}H NMR spectrum at −60 °C consisted of only one peak at δ 8.5 ppm assigned to the olefinic protons, while the protonated sulfur resonance could not be observed even at the lowest accessible temperatures. Methylation of **1b** with iodomethane yielded a stable iodide salt soluble in an SO_2 solution. Methylated species (**1b**-CH_3^+) at −40 °C showed two NMR signals, one at δ 8.1 ppm with relative area 2, and one at δ 2.8 ppm of area 3.

^{13}C NMR parameters for 1,3-dithia-2-thione (**1b**) show significant shielding of the thiocarbonyl group appearing 14.1 ppm upfield of the carbonyl carbon contained in the oxygen analogue. Protonated species (**1b**-H^+) resulted in downfield shifts of 6.3 ppm for olefinic carbons and 4.5 ppm for the thiocarbonyl carbon. The downfield shifts observed for olefinic carbons (4.0 ppm) and the thiocarbonyl carbon (8.8 ppm), along with protonation parameters, indicate greater ability of sulfur to accept a positive charge when compared to oxygen in this aromatic series.[12]

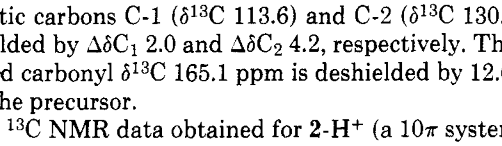
10π Heteroaromatic Ions. When catechol carbonate (**2**) in SO_2ClF is added to a $SO_2ClF-FSO_3H-SbF_5$ solution at −78 °C an amber-colored solution results which gave a ^{1}H NMR spectrum consisting of two singlets, one at δ 8.0 of relative area 4 corresponding to aromatic ring protons and δ 13.2 of area 1 assigned to the protonated carbonyl ($C{=}^{+}OH$). The aromatic protons of **2**-H^+ are deshielded approximately 0.8 ppm from precursor **2**. The protonated carbonyl was observed only at low temperatures (≤−80 °C), presumably a result of rapid exchange with the superacid solvent system. To verify the structure of **2**-H^+, the ^{13}C NMR spectrum was obtained. The aromatic carbons C-1 (δ^{13}C 113.6) and C-2 (δ^{13}C 130.3) are deshielded by $\Delta\delta C_1$ 2.0 and $\Delta\delta C_2$ 4.2, respectively. The protonated carbonyl δ^{13}C 165.1 ppm is deshielded by 12.6 ppm from the precursor.



2 **2**-H^+

The ^{13}C NMR data obtained for **2**-H^+ (a 10π system) are useful for comparison to the ^{13}C NMR data obtained for 2-hydroxy-1,3-dioxolium ion (**1**-H^+) (a 6π system). The protonated carbonyl of **2**-H^+ is only slightly deshielded from that of **1**-H^+, $\Delta\delta$C 0.8 ppm.

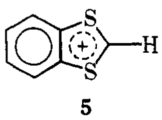
The parent 1,3-benzodioxolium ion (**4**) was prepared in FSO_3H-SO_2 from 2-methoxy-1,3-benzodioxole (**3**).[13,14]



3 **4**

The ^{1}H NMR spectrum of **4** consists of two singlets at δ 8.1 and 8.2 deshielded approximately 1.0 ppm from the precursor (**3**) and a sharp singlet for the methine H, δ 10.4. The ^{13}C NMR spectrum of **4** confirms the assigned structure since only four ^{13}C NMR peaks are observed for this symmetrical ion. Aromatic ring carbons C-2 (δ^{13}C 114.8) and C-3 (δ^{13}C 132.3) are deshielded 6.8 and 10.6 ppm from corresponding carbons of precursor **3**. The δ^{13}C 170.4 for C^+ is deshielded by 51.9 ppm from the precursor ^{13}C NMR value.

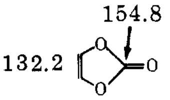
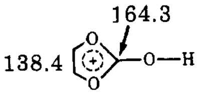
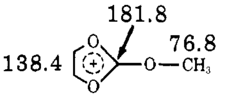
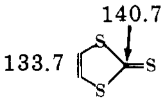
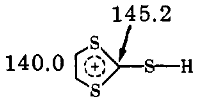
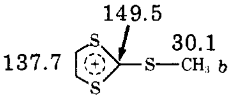
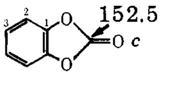
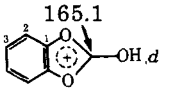
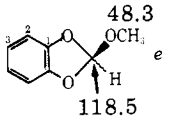
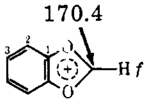
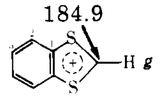
We also studied the sulfur analogue of **4**, the parent 1,3-benzodithiolium ion (**5**). Ion **5** was studied as the stable perchlorate salt[15] which proved to be readily soluble in CD_3CN.



5

The ^{1}H NMR spectrum of **5** consists of a series of multiplets δ 7.95–8.9 of relative area 4 and a sharp singlet at δ 11.5 of area 1 assigned to the methine proton. The ^{13}C NMR data for **5** may be compared to those of the all-oxygen analogue (**4**) as an indication of the extent of relative charge delocalization into the aromatic ring. Ring carbon C-2 (δ^{13}C 127.7) is deshielded by 12.9 ppm from the C-2 ^{13}C NMR value for **4** whereas ring carbon C-3 (δ^{13}C 131.8) is slightly shielded, $\Delta\delta$C 0.5. The C^+ ^{13}C NMR value (δ^{13}C 184.9) for **5** is deshielded by 14.5 ppm compared to the C^+ value for ion **4**, indicating rela-

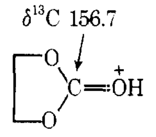
Table II. ^{13}C NMR Parameters of Heteroaromatic Ions[a]

Precursor		Heteroaromatic ion		
				
				
	C-1 144.4 C-2 111.6 C-3 126.1		C-1 143.7 C-2 113.6 C-3 130.3	
	C-1 146.0 C-2 108.0 C-3 121.7		C-1 144.4 C-2 114.8 C-3 132.3	
			C-1 145.5 C-2 127.7 C-3 131.8	

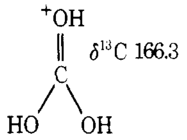
[a] In parts per million from external Me_4Si (capillary). Protonated in FSO_3H–SbF_5–SO_2 at −60 °C. Methylated with CH_3F–SbF_5 "complex"–SO_2 at −40 °C. [b] Methylated species studied as stable iodide salt in SO_2 solution at −40 °C. [c] In $CDCl_3$, ambient probe temperature. [d] Protonated in FSO_3H–SbF_5–SO_2ClF at −80 °C. [e] In SO_2ClF at −70 °C. [f] Ion prepared in FSO_3H–SO_2 at −70 °C. [g] In CD_3CN, ambient probe temperature.

tively more charge localized on the carbenium center in the all-sulfur analogue 5.

The protonated carbonyl of ethylene carbonate (6) and of carbonic acid (7) is analogous to that of protonated vinylene carbonate (1a-H$^+$) and protonated catechol carbonate (2-H$^+$). In fact, the ^{13}C NMR shifts $\delta^{13}C$ 156.7 and $\delta^{13}C$ (Me_4Si) 166.3 of 6 and 7 are similar to that of 1a-H$^+$ and 2-H^{+19} which at first would seem to indicate that 1a-H$^+$ and 2-H$^+$ are only simple protonated carbonates. However, in this case, it is not expected that there would be any charge delocalization into the π bond or the aromatic ring of 1a-H and 2-H$^+$H respectively. Such deshielding, however, evident from the ^{13}C NMR spectra of 1a-H$^+$ and 2-H$^+$ clearly indicate that 1a-H$^+$ and 2-H$^+$ are, indeed, 6π and 10π aromatic systems.



6



7

Conclusions

Stable oxygen and sulfur heteroorganic ions such as the 1,3-dioxolium ion (6π), 1,3-dithiolium ion (6π), and the 1,3-benzodioxolium ion (10π) result from the protonation in superacid [FSO_3H–SbF_5–SO_2 (SO_2ClF)] of their carbonyl precursors. Vinylene carbonate is methylated with CH_3F–SbF_5 complex in SO_2 solution, whereas 1,3-dithia-2-thione forms a stable iodide salt upon methylation with methyl iodide.

The parent 1,3-benzodioxolium ard 1,3-benzodithiolium ions were also prepared and studied by ^1H and ^{13}C NMR spectroscopy. The NMR data indicate significant delocalization of charge over the 6- and 10π systems, respectively. However, at this stage of our understanding of chemical shifts vs. charge distribution relationships, no conclusion can be reached as to the exact nature of the ring currents involved and relative contribution of resonance forms.

Experimental Section

Materials. Starting materials used were commercially available of the highest purity (Aldrich and Strem Chemical Co.).

2-Methylthio-1,3-dithiolium Iodide (1b-CH_3^+). The stable iodide salt was prepared according to the procedure of Klingsberg.[6]

Catechol Carbonate (2). The carbonate was prepared according to the procedure of Huismann.[16]

Preparation of Ions. The protonated ions were prepared by adding the precursor (0.5 mL) to a stirred solution of 1:1 M/M FSO_3H-SbF_5 (1.5 mL) in an equal volume of SO_2 or SO_2ClF at −78 °C. Samples prepared in this manner gave spectra which showed no appreciable chemical shift differences with temperature or small concentration variations. The acid was always in excess as indicated by an acid peak at about δ 10.9 in the ^1H NMR spectrum. The ^{13}C NMR spectra of heteroorganic ions were recorded only if the ^1H NMR data matched the reported values in the literature. For ions not yet reported, the structure of the protonated forms could be established from the ^1H NMR spectral data (chemical shifts, multiplicity patterns, and peak area integration). After obtaining the ^{13}C NMR spectrum, the sample was checked again by ^1H NMR spectroscopy to determine if any decomposition had occurred. Samples studied in FSO_3H-SO_2 solution were prepared by dissolving the precursor (0.5 mL) in SO_2 (0.5 mL). This solution was added dropwise to a rapidly stirred solution of FSO_3H (2 mL)-SO_2 (1 mL) at −78 °C. The acid was always in excess as indicated by an acid peak at about δ 10.8 in the ^1H NMR spectrum.

The methylated ions were prepared by reacting the precursors with the "methyl fluoride–antimony pentafluoride complex" in SO_2 solution, under conditions previously described.[6b]

NMR Spectroscopy. ^1H NMR spectra were obtained on a Varian Associates Model A56/60-A spectrometer equipped with a variable temperature probe. ^{13}C NMR spectra were obtained in part on a modified Varian Associates Model HA-100 spectrometer equipped with a FT-100 Fourier transform accessory (V-4357 pulsing and control unit); a broad-band proton decoupler of 25.14 MHz was derived from a gated power amplifier capable of putting out approximately 80 W into the transmitter coils. The pulse width used was 35 μs, and the pulse interval, 1.5 s. The available computer memory (4000 input channels) and the need to provide multichannel excitation over the region of interest (sweep width 6800 Hz) limited the data acquisition time to 0.2 s.

The free induction signal derived after each pulse is signitized and accumulated in a Varian 620/i computer (8K). Approximately 5000–7000 accumulations were made to obtain each spectrum. Field/frequency regulation was maintained by a homonuclear internal lock system. The lock used was the proton decoupled carbon-13 resonance of a 60% carbon-13 labeled methyl iodide sample contained in a precision coaxially spaced capillary (o.d. ca. 0.2 and 0.4 mm) inserted in the sample NMR tube (5 mm o.d.).

Fourier transformation of the accumulated free induction signal gave the frequency spectrum[17,18] from which was measured the chemical shift of each signal, relative to the reference methyl iodide signal. All the chemical shifts reported here have been corrected to a Me_4Si reference by the relationship

$$\text{ppm}\ (Me_4Si) = \frac{H_2\ (\text{obsd}) - 977 - T(°C) \times 0.70}{25.2}$$

The ^{13}C NMR spectra for the remaining heteroorganic ions and precursors were obtained on a Varian Associates Model XL-100 spectrometer equipped with a broad decoupler and variable temperature probe. The instrument operates at 25.2 MHz for carbon-13, and is interfaced with a Varian 620L computer. The combined system was operated in the pulse Fourier transform mode, employing a Varian Fourier transform accessory. Typically 3000–5000 pulses, each of width 20–30 μs, needed to be accumulated in order to give a satisfactory signal to noise ratio for all signals of interest. Field frequency stabilization was maintained by locking on the fluorine-19 external sample of fluorobenzene. Chemical shifts were measured from the carbon-13 signal of 5% carbon-13 enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No.—**1a**, 288-53-9; **1a**-H^+, 62139-47-3; **1a**-CH_3^+, 62139-48-4; **1b**, 930-35-8; **1b**-H^+, 62139-49-5; **1b**-CH_3^+, 56125-66-7; **2**, 2171-74-6; **2**-H^+, 62139-50-8; **3**, 6823-42-3; **4**, 39525-29-6; **5**, 274-31-7.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Bridgehead Substituted Bicyclo[3.3.1]nonanes

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Received February 22, 1977

The ^{13}C NMR spectra of several bicyclo[3.3.1]nonanes, 9-methyl-9-azabicyclo[3.3.1]nonanes, 9-oxabicyclo[3.3.1]nonanes, and 9-thiabicyclononanes with bridgehead substituents are interpreted. Heteroatom bridgehead substituents cause downfield shifts of the resonances for γ-anti carbons 3, 5, and 7 in agreement with previous results for bridgehead substituents and in contrast to the upfield γ-anti shifts induced by heteroatoms in monocycles. Equatorial tertiary hydroxyl groups in cyclohexanols cause downfield shifts of the γ-anti carbons.

Within the last several years, ^{13}C NMR spectroscopy has emerged as a very powerful tool for structural analysis in organic chemistry.[1] The power of this technique derives in large measure from several empirically determined, rather well-ordered types of effects exerted by substituents on the chemical shifts of the various carbon atoms in a particular molecule. For example, it has been demonstrated on numerous occasions that a carbon atom disposed γ-gauche to a methyl group resonates at a relatively higher magnetic field than when it is located γ-gauche to a hydrogen or γ-anti to a methyl group.[2] Steric interactions are usually cited as being responsible for such *upfield* shifts. Interestingly, it has also been found that downfield shifts are observed when the encumbered carbon is separated from its steric antagonist by four bonds.[3] While the experimentally obtained γ and δ "steric" shifts are opposite in direction (thus indicating that the shielding mechanisms include significant contributions from terms of other than a steric nature), their individual consistencies render them very valuable in stereochemical assignments.

Recently, Eliel and co-workers have disclosed their intriguing findings related to the upfield chemical shifts observed for carbon nuclei γ to a heteroatom.[4] Briefly, their data have confirmed that a *gauche heteroatom* (N, O, F, S, Cl) produces an upfield (steric) shift of a ^{13}C NMR signal *greater* than the upfield shift caused by a gauche carbon group