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Onium Ions. 24.[1] ^{17}O NMR Spectroscopic Study of Oxonium and Carboxonium Ions

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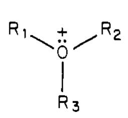
Abstract: A series of oxonium and carboxonium ions prepared from ^{17}O-enriched precursors was studied by ^{17}O NMR spectroscopy. A 240–250-ppm ^{17}O shielding effect is observed for ketones upon protonation, showing a decrease in the carbon–oxygen π bond order by about 40%. A similar shielding effect is also observed for protonated carboxylic acids. The ^{17}O chemical shifts of acyl cations show a 50-ppm shielding compared to the model compound carbon monoxide, indicating some contribution of oxocarbenium ion form to the overall onium ion structure. A small ^{17}O NMR deshielding (10–25 ppm) observed for trivalent oxonium ions when compared to their neutral precursors demonstrates the unimportance of charge effect on ^{17}O NMR chemical shifts. The peroxonium ion prepared by protonating hydrogen peroxide is 36 ppm more shielded than its progenitor. The hydrogen–oxygen coupling constant in peroxonium ion could not be determined due to fast proton exchange even at very high acidities.

Protonated heteroorganic compounds play key roles as intermediates in many acid-catalyzed reactions. Of particular interest are the oxonium ions that contain a positive trivalent oxygen with an electron octet.[2] Oxonium ions can be conveniently divided into several classes: saturated oxonium ions with three oxygen–ligand single bonds (**1**) and unsaturated oxonium ions with oxygen–ligand double (**2**) or triple (**3**) bonds. These ligands are most frequently either carbon substituents or hydrogen (acidic oxonium ions), although many other elements can be substituted.



1

$R_1-\overset{+}{\ddot{O}}=R_2 \longleftrightarrow R_1-\ddot{\underset{\cdot\cdot}{O}}-\overset{+}{R_2}$

2

$:\overset{+}{O}\equiv R \longleftrightarrow :\ddot{O}=\overset{+}{R}$

3

Numerous examples exist of the first class, the simplest being the parent oxonium ion H_3O^+.[3] Other examples of saturated oxonium ions include protonated alcohols[4] (alkyloxonium ions), important as intermediates in the acid-catalyzed dehydration[5] of alcohols, protonated ethers[4] (dialkyloxonium ions), and tertiary trialkyloxonium ions with three carbon–oxygen single bonds, which are among the most widely known onium ions (Meerwein's salts). Their general stability and alkylating ability have made them useful synthetic reagents.[6]

Unsaturated oxonium ions also play important roles as reaction intermediates. Protonated ketones[7] or aldehydes[7] are involved in the acid-catalyzed hydration, nucleophilic addition, and ketal-forming reactions of the carbonyl group as well as in the formation of semicarbazones, hydrazones, and Schiff bases. Acyl cations are intermediates in the formation and hydrolysis of esters and in Friedel–Crafts acylation reactions.[8]

Oxonium ions have been extensively studied previously, particularly by UV, IR, and ^1H and ^{13}C NMR spectroscopy.[2,4] Much information has been obtained from these studies about their structure and electronic properties. However, ^{17}O NMR spectroscopy has not yet been applied in a systematic study of oxonium ions. In fact, relatively few ^{17}O NMR studies have been reported[9,10] despite the enormous importance of oxygen-containing compounds in chemistry. From studies that have been reported, it is evident that ^{17}O NMR chemical shifts are very sensitive to changes in the nature of oxygen bonding. In particular, ^{17}O NMR chemical shifts are extremely good indicators of carbon–oxygen π bond order.[9] Aldehydes and ketones, having a π bond order of one, exhibit substantial downfield ^{17}O chemical shifts (510–660 ppm) from $H_2{}^{17}O$. Alcohols and ethers have a π bond order of zero and are shielded with respect to the carbonyl oxygens (−40 to 100 ppm relative to $H_2{}^{17}O$). Intermediate chemical shifts are observed for oxygen atoms exhibiting π bond orders between zero and one.

The powerful nature of oxygen-17 NMR spectroscopy as a structural tool prompted us to apply the method in an investigation of oxonium ions, including unsaturated oxonium ions such as protonated ketones, protonated carboxylic acids, and acyl cations as well as saturated oxonium ions, in order to determine the electronic and structural changes that occur on oxygen upon protonation.

Results and Discussion

It has been established[10] that the paramagnetic term σ_p is the major contributor to the total screening constant in ^{17}O nuclear shieldings. This paramagnetic term may be written as

$$\sigma_p{}^A = \frac{-2e^2\hbar^2}{3m^2c^2\Delta E}\langle r^{-3}\rangle \sum_B Q_{AB}$$

where A is the nucleus under investigation and B represents all other nuclei in the molecule. $\langle r^{-3}\rangle$ is the average value of r^{-3} for a 2p orbital and ΔE is the "mean" excitation energy of the molecule. Q_{AB} are bond order charge density terms and are a measure of the orbital angular momentum. It is through this parameter that the σ_p term increases in magnitude with π bonding. σ bonds have zero angular momentum about the bond axis, and consequently, the screening constant is dominated by the diamagnetic term. In contrast, the angular momentum for π bonds about the same axis is nonzero and a paramagnetic shift occurs.

A number of attempts to calculate oxygen shielding constants have appeared.[11] However, such calculations require a complete

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[1] For part 23, see: Watkins, M. I.; Ip, W. M.; Olah, G. A.; Bau, R. *J. Am. Chem. Soc.*, preceding paper in this issue.

[2] (a) Perst, H. "Oxonium Ions in Organic Chemistry"; Verlag Chemie: Weinheim, Germany, 1971. (b) Perst, H. "Carbonium Ions"; Olah, G. A.; Schleyer, P. v. R. Eds.; Wiley-Interscience: New York, 1976; Vol. 5, pp 1961–2047.

[3] Gold, V.; Grant, J. L.; Morris, K. P. *J. Chem. Soc., Chem. Commun.* **1976**, 397–398 and references therein.

[4] Olah, G. A.; White, A. M.; O'Brien, D. H. *Chem. Rev.* **1970**, *70*, 561–591 and references therein.

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[6] Reference 2a, pp 128–172. Meerwein, H. *Methoden Org. Chem. (Houben-Weyl), 3rd Ed.* **1965**, *6*, 325–365.

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[8] For a review, see: "Friedel-Craft and Related Reactions", Olah, G. A. Ed.; Interscience: New York, 1965, Vol. IV.

[9] For reviews, see: Klemper, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246–254. Silver, B. L.; Luz, Z. *Chem. Soc. Rev.* **1967**, *21*, 458–473.

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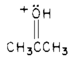
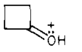
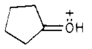
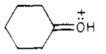
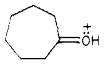
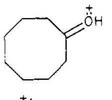
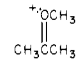
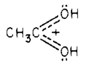
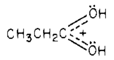
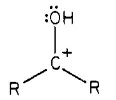
Table I. ^{17}O NMR Chemical Shifts of Oxonium Ions

ion	δ^{17}O NMR chemical shifts[a]	$\Delta\nu_{1/2}$, Hz
$H_3\ddot{O}^+$	10.2 (J_{OH} = 103.5 Hz)	59
$H_5\ddot{O}_2^+$	151.2	115
$CH_3\overset{+}{\ddot{O}}H_2$	−15.0 (J_{OH} = 107.6 Hz)	60
$(CH_3)_3\ddot{O}^+$	40.6	>400
 $CH_3\overset{+\ddot{O}H}{\overset{\parallel}{C}}CH_3$	310.3 (J_{OH} = 74 Hz)	110
	305.8	140
	287.5	140
	297.6	150
	299.2	150
	299.3	180
 $CH_3\overset{+\ddot{O}CH_3}{\overset{\parallel}{C}}CH_3$	306.6	280
	203.7 (J_{OH} = ca. 50 Hz)	300
	199.1 (J_{OH} = ca. 49.9 Hz)	280
$CH_3C\equiv\ddot{O}^+$	299.5	40
$CH_3CH_2C\equiv\ddot{O}^+$	300.1	50

[a] Relative to SO_2 (505 ppm).[18]

knowledge of the molecular orbitals. In addition, all excited-state eigenvalues must be known. To a first approximation, the term ΔE can be equated to the excitation energy of the lowest lying excited state. In carbonyl compounds this corresponds to the n–π* transition.[12] Experimentally, it has been shown that carbonyl oxygen shieldings correlate approximately with $\lambda^{n-\pi^*}{}_{max}$ values. IR carbonyl stretching frequencies have also been related to ^{17}O NMR chemical shifts.[13]

Unsaturated Oxonium Ions. Protonated Ketones. Protonated ketones have been examined in the past by a variety of techniques, including NMR spectroscopy.[4,14] These studies have indicated that the carbonyl group retains substantial double-bond character upon protonation. The hydroxycarbenium ion resonance form **4** is a minor contributor to the overall structure of the protonated species, the main resonance form being the oxonium ion **5**.



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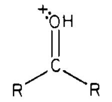

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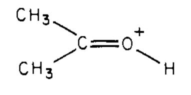
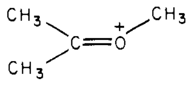
The spectra of a series of protonated ketones were obtained at −20 °C from SO_2 solutions of the ^{17}O-enriched ketone and HF–SbF_5. The spectra were recorded at this temperature in order to obtain the best possible resolution. Lower temperatures caused a significant line broading due to increased quadrupolar relaxation of the ^{17}O nucleus.[9] The chemical shifts obtained are listed in Table I.

The proton-decoupled ^{17}O NMR spectrum of protonated acetone **6**-H shows a very large shielding of the carbonyl oxygen resonance. The oxygen chemical shift is δ^{17}O 310.3, 249 ppm shielded with respect to acetone (δ^{17}O 559).[15] The proton-coupled spectrum shows an incompletely resolved doublet with a peak separation of 74 Hz. Whereas ^{1}H[4] and ^{13}C[14] NMR evidence indicates only a minor polarization, ^{17}O NMR spectroscopy reveals that there is substantially more modification of the carbonyl bond upon protonation than previously realized. The observed ^{17}O shielding implies a decrease in carbon–oxygen π bond order of about 40%. However, the carbonyl bond still retains substantial double–oxygen character as indicated by both the ^{17}O NMR chemical shift and the high rotational barrier of the C–O bond.[4]



6-H

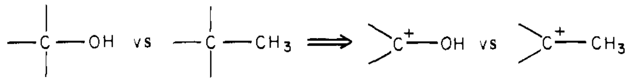


6-CH$_3$

The methylation of acetone was also studied. Addition of ^{17}O-labeled acetone to a solution of CH_3F–SbF_5 in SO_2 resulted in the formation of carboxonium ion **6**-CH_3. The ^{17}O chemical shift of **6**-CH_3 is δ^{17}O 306.6, again substantially shielded with respect to acetone and similar to the chemical shift of protonated acetone. It is apparent that both methylation and protonation affect the polarization of the carbonyl bond to a similar degree.

The ^{17}O NMR chemical shifts for a series of protonated cyclic ketones were also obtained and are given in Table I. The chemical shifts are shielded with respect to the neutral ketones by an amount similar to that of acetone. The chemical shifts for the five studied protonated ketones fall in a narrow range of 18 ppm, nearly the same range observed for the parent ketones (27 ppm).[15] No O–H coupling was observed in the proton-coupled spectra presumably due to the broad ($\Delta\nu_{1/2}$ = 140–180 Hz) line widths of the ions.

Previous attempts to correlate ^{17}O and ^{13}C NMR chemical shifts of analogous compounds have met with some success. For example, the ^{17}O shieldings of epoxides correlate well with the methylene carbon shifts of the structurally related cyclopropanes.[16] Similarly, the oxygen shifts of ketones and aldehydes correlate with the ^{13}C chemical shifts of the terminal carbon of the corresponding methylene compound.[12a,15] Finally, the ^{17}O chemical shifts of simple alcohols correspond to the ^{13}C chemical shifts of the analogous methyl-substituted compounds.[17] However, similar plots of protonated ketones do not correlate well. A plot of the ^{17}O chemical shifts of the protonated ketones and the ^{13}C chemical shifts of the related methyl-substituted cations[14] gave an extremely poor correlation. There should be a linear correlation if similar effects would occur in each of these two systems with the introduction of a positive charge; however, this was not the case. Differences occur among which is the substantial involvement of the oxonium ion resonance form. This is further evidence that the hydroxycarbenium ion structure is only a minor contributor to the total ion structure.



A plot of the ^{13}C chemical shifts of the carbonyl carbons and the ^{17}O chemical shifts of the carbonyl oxygens likewise shows a poor correlation. It is evident that protonation affects the carbon and oxygen shifts differently. In the neutral ketones, however, a similar plot showed a reasonable correlation.[12c]

On the basis of the O–H coupling constant, it has been suggested that the oxygen hybridization in protonated acetone is sp^3, indicating that the hydroxycarbenium ion form is dominant.[18] However on the basis of ^{17}O NMR results presented in this study, it is evident that there remains substantial carbon–oxygen π-bond character in the protonated carbonyl group and that the hy-

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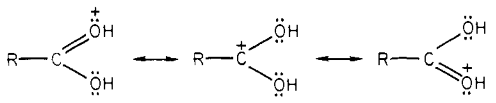
droxycarbenium ion resonance form is only a minor contributor.

Protonated Carboxylic Acids and Acyl Cations. The protonation of carboxylic acids results in the formation of the dihydroxycarbenium ions **7**.[4] As with protonated ketones, the charge is



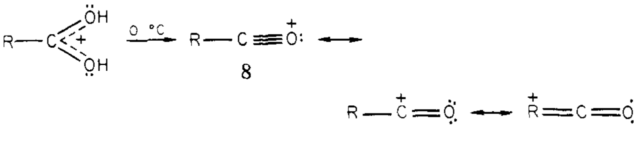
A 7 B

predominantly localized on oxygen (structures A, C). The ^{13}C NMR chemical shifts of the carboxylic carbon is slightly deshielded (~20 ppm)[19] upon protonation, indicating that less charge is localized on this carbon than on the carbonyl carbon in protonated ketones.

A ^{17}O NMR spectrum of protonated acetic acid obtained by the addition of ^{17}O-enriched acetic acid to a SO_2 solution of $HF-SbF_5$ at -25 °C showed a broad ($\Delta\nu_{1/2}$ = 300 Hz) resonance at 204 ppm. A similar spectrum was obtained upon protonation of propionic acid ($\delta^{17}O$ = 199, $\Delta\nu_{1/2}$ = 280 Hz). The proton-coupled spectra of both ions showed a small (~50 Hz) splitting of the peaks due to O–H coupling.

The chemical shifts observed for these ions are in accord with the preservation of substantial π-bond character in the carbon–oxygen bonds. The ^{17}O chemical shifts of acetic and propionic acids are 250.5 and 244 ppm, respectively.[20] Only one oxygen resonance is observed in these acids due to fast proton exchange leading to the equilibration of the two oxygen atoms.[10] A shielding of about 50 ppm is observed for each oxygen upon protonation. This implies a loss of about 20% of π bond order for each carabon–oxygen bond or a total of 40% for both. This is roughly the same loss observed in the case of the protonated ketones.

After a solution of either protonated acetic or propionic acid was warmed to 0 °C, a new signal appeared in the ^{17}O spectrum, which grew with time. These sharp ($\Delta\nu_{1/2}$ = 40–50 Hz) peaks were observed at $\delta^{17}O$ 299.5 and 300.1 for the acetic and propionic acid solutions, respectively, and correspond to the acyl cations formed via dehydration.[4] These acyl cations have been extensively studied by various techniques,[4,21] including IR, NMR, UV, X-ray, and ESCA[22] analysis. These studies have indicated that the acyl cations are resonance hybrids of the oxonium ion (**8**), oxocarbenium ion (**9**), and ketene-like (**10**) forms, with predominant charge localized on carbon (structure **9**). The infrared spectra[21] and X-ray structures of acyl cations reveal the substantial triple-bond character of the carbon–oxygen bond. However, NMR[21] and ESCA[22] methods seem to indicate that charge is also partially localized on carbon.



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While the ^{17}O NMR chemical shifts for the two studied acyl cations are similar to those of the protonated ketones, this does not mean that the two species are similar in either π bond order or charge distribution. Taking the ^{17}O chemical shift of carbon monoxide[23] as a model for carbon–oxygen triple bonds, one observes a shielding of approximately 50 ppm ($\delta^{17}O$ 350 - $\delta^{17}O$ 300) for the acyl cations. If one ignores the effect of charge, this shielding would indicate that there is a decrease in the total π bond order in the acyl cations as compared to carbon monoxide. In other words, the C–O bonding character in acyl cations is less than that of a carbon–oxygen triple bond but more than that of a carbon–oxygen double bond, which is in accord with previous conclusions. The relative contributions of the different resonance forms, however, is difficult to determine from the ^{17}O NMR data.

A striking feature of the ^{17}O spectra of the acetyl and propionyl cations is the narrow peak width observed ($\Delta\nu_{1/2}$ = 40–50 Hz). This is to be compared with the extremely broad (280–300 Hz) peaks observed for the protonated carboxylic acids. Reasonably sharp CO peaks ($\Delta\nu_{1/2}$ = 25–30 Hz) have been previously observed for metal carbonyl complexes[24] and may be attributed to the relatively spherical electron distribution about oxygen in these compounds.

Saturated Oxonium Ions. The hydronium ion, H_3O^+, is the parent of the saturated oxonium ions. It is readily observed as a static, nonexchanging species in superacid solutions. Recently, Mateescu and Benedikt[18] reported the characterization of the hydronium ion by ^{17}O NMR spectroscopy, including the oxygen–hydrogen coupling constant. On the basis of this coupling constant and the assumed linear relationship between coupling constants and s character of the oxygen σ orbitals, it was suggested that H_3O^+ is basically planar. Although this contention was subsequently questioned[25,26] on theoretical grounds, it called for an experimental reinvestigation.

The addition of 10% ^{17}O-enriched water to a SO_2 solution of $HF-SbF_5$ at -20 °C led to the formation of the parent oxonium ion H_3O^+. The proton-decoupled ^{17}O NMR spectrum displayed a narrow ($\Delta\nu_{1/2}$ = 59 Hz) absorption at $\delta^{17}O$ 10.2. The proton-coupled spectrum consisted of a quartet with an oxygen-hydrogen coupling constant of 103.5 Hz. This agrees well with the previously reported data of 9 ± 0.2 ppm and J_{OH} of 106 ± 1.5 Hz.[18] The observation of a quartet in the proton-coupled spectrum clearly indicates the presence of three equivalent hydrogen atoms covalently bound to oxygen. In addition, the nonexchanging nature of H_3O^+ in $HF-SbF_5$ at -20° implies a very significant proton-exchange barrier in this acid system.

The proton-coupled ^{17}O NMR spectrum of $CH_3O^+H_2$ obtained from 20% ^{17}O-labeled methanol in a $HF-SbF_5/SO_2$ solution consisted of a triplet with an oxygen–hydrogen coupling constant of 107.6 Hz, similar in magnitude to that of the parent oxonium ion. Proton decoupling gave rise to a singlet at $\delta^{17}O$ -15. This corresponds to a deshielding of approximately 25 ppm from neutral methanol ($\delta^{17}O$ -40). Again, the well-defined triplet in the proton-coupled spectrum indicates the presence of two equivalent hydrogens covalently bound to oxygen with a very slow exchange rate on the NMR time scale.

The deshielding observed upon the protonation of water and methanol is in contrast with the observed shielding of protonated ketones and carboxylic acids. This clearly demonstrates that the shielding effect is largely due to the decrease in oxygen π bond order and not to the effect of charge. It must be pointed out that the deshieldings observed for H_3O^+ and $CH_3O^+H_2$ are of the magnitude observed for solvent effects in many compounds.[12a,c,27,28] In fact, some solvent effects cause a greater shift than those observed for protonation. It is evident that not all the factors involved in determining ^{17}O chemical shifts are known, and much more work is needed in this area.

As previously mentioned, Mateescu and Benedikt[18] argued that H_3O^+ is planar on the basis of a 33% increase in the oxygen–hydrogen coupling constant upon going from H_2O to H_3O^+. They assumed a linear relationship between J_{OH} and the hybridization of oxygen and concluded that this increase in the coupling constant indicated that H_3O^+ is sp^2 hybridized and thus planar. They

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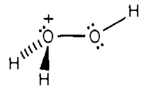
(28) Reuben, J. *J. Am. Chem. Soc.* **1969**, *91*, 5725–5729.

assumed that H_2O is sp^3 hybridized, which is, however, not the case.[25] It was subsequently pointed out by Symons[25] that the original ^{17}O data are supportive of a pyramidal geometry for H_3O^+ with a H–O–H bond angle of 111.3°. Indeed, Christe and coworkers[29] have previously isolated hydronium ion salts and have established by vibrational spectroscopy that H_3O^+ is pyramidal. Similar conclusions have been reached on the basis of quantum mechanical calculations.[26]

Attempts to prepare ^{17}O-labeled trimethyloxonium ion were somewhat inconclusive. The treatment of $CH_3{}^{17}OH$ with excess CH_3F–SbF_5 in SO_2 did not give rise to a clear enough absorption in the ^{17}O NMR spectrum that could be assigned to the ion. The methylation of $H_2{}^{17}O$ with excess dimethylchloronium ion was also attempted. In the ^{17}O NMR spectrum a broad absorption is observed around $\delta^{17}O$ 40.6 in addition to the $H_3{}^{17}O^+$ peak at $\delta^{17}O$ 10.0. The assignment of this signal to the trimethyloxonium ion can be, however, only tentative.

The Peroxonium Ion $H_3O_2{}^+$. The peroxonium ion $H_3O_2{}^+$ has been invoked as an intermediate in the electrophilic oxygenation of alkanes with hydrogen peroxide and strong acids.[30,31] Recently, Christe et al.[32] reported the isolation and characterization of several peroxonium salts. The infrared and Raman spectra of these salts indicated that $H_3O_2{}^+$ is isostructural with H_2NOH and has the geometry depicted.[32] However, no direct observation of the peroxonium ion by ^1H NMR spectroscopy[31,32] was possible due to rapid proton exchange with the solvent systems. When a mixture of equal volumes of 90% hydrogen peroxide and 30% $H_2{}^{17}O$ (stirred at room temperature for 12 h)[33] was added to a SO_2 solution of HF–SbF_5 at −25 °C, two absorptions were observed in the ^{17}O NMR spectrum. The major peak ($\delta^{17}O$ 10) is due to the oxonium ion $H_3{}^{17}O^+$. The second peak with a chemical shift of $\delta^{17}O$ 151 is attributed to the peroxonium ion $H_3O_2{}^+$. The peroxonium ion is shielded by 36 ppm with respect to hydrogen peroxide ($\delta^{17}O$ 187). This shielding is in contrast to the deshielding observed upon the formation of other oxonium ions such as H_3O^+ and $CH_3O^+H_2$ from their neutral precursors. No splitting was observed in the proton-coupled ^{17}O NMR spectrum of $H_3O_2{}^+$ (**11**), indicating an extremely fast proton exchange rate. This is consistent with the previously observed rapid exchange by ^1H NMR spectroscopy.[31,32]



11

Experimental Section

Oxygen-17-enriched water (10% and 30%, methanol (20%), acetone (20%), and acetic and propionic acids (30%) were commercially available. The enriched ketones were prepared by adding equal volumes (0.05 mL) of ketone and enriched $H_2{}^{17}O$ to dioxane (0.1 mL) and warming for several hours. The resultant solution was used directly in preparing the ions.

Preparation of Oxonium Ions. The oxonium ions were prepared by the addition of the ^{17}O-enriched precursor to a 1:1 mixture of SO_2 and HF–SbF_5 (1:1) or the appropriate methylating agent at −78 °C. Enriched $H_3O_2{}^+$ was prepared by the addition of equal volumes of 90% normal H_2O_2 and 30% enriched $H_2{}^{17}O$ (which had previously been stirred together for 12 h) to a HF-SbF_5/SO_2 solution at −78 °C.

The ^{13}C and ^{17}O NMR spectra were obtained by using a Varian Associates Model FT-80 NMR spectrometer equipped with a broad-band variable-temperature probe. The oxygen shifts were referenced to the SO_2 solvent peak ($\delta^{17}O$ 505 ppm[18]).

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Registry No. H_3O^+, 13968-08-6; $H_5O_2{}^+$, 22206-74-2; $CH_3OH_2{}^+$, 17836-08-7; $(CH_3)_3O^+$, 43625-65-6; $CH_3C(=OH)CH_3{}^+$, 43022-03-3; c-$C_4H_6=OH^+$, 64725-63-9; c-$C_5H_8=OH^+$, 64725-64-0; c-$C_6H_{10}=OH^+$, 64725-65-1; c-$C_7H_{12}=OH^+$, 75032-00-7; c-$C_8H_{14}=OH^+$, 80954-12-7; $CH_3C(=OCH_3)CH_3{}^+$, 41798-19-0; $CH_3C(=OH)OH^+$, 18639-92-4; $CH_3CH_2C(=OH)OH^+$, 18639-93-5; CH_3CO^+, 15762-07-9; $CH_3CH_2CO^+$, 17158-30-4.

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Crystal and Molecular Structure of 2,2,8,8,12,13,17,18-Octamethylisobacteriochlorin

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Abstract: The X-ray structure determination of 2,2,8,8,12,13,17,18-octamethylisobacteriochlorin has been carried out to a resolution of 0.85 Å. The compound crystallizes in the rhombohedral space group $R\bar{3}$, with cell constants $a = b = c = 16.926$ (3) Å and $\alpha = \beta = \gamma = 109.72$ (2)°. It contains one molecule of $C_{28}H_{34}N_4$ in the asymmetric unit. The structure was solved by direct methods and refined to $R_w = 4.9\%$. Four half-hydrogen atoms, within bonding distance of the nitrogen atoms, were located experimentally from a difference Fourier map. The X-ray structure is thus a superposition of two tautomeric forms in which diagonally opposed nitrogen atoms have bonded hydrogen atoms. The macrocycle is planar in contrast to metalated isobacterochlorins which are generally domed or buckled.

The isobacteriochlorin macrocycle **1** has recently become a center of chemical, structural, and biochemical interest. This is due to two developments. One was the discovery[1] that the prosthetic group of sulfite and nitrite reductases is the iron complex of an isobacteriochlorin. From the sulfite reductase of *E. coli* was isolated the iron-free form, sirohydrochlorin[1] (**2a**). A second advance was the proof that **2a**, probably as its dihydro derivative, is an important intermediate on the biosynthetic pathway to vitamin B_{12};[2,3] this work also led to the illustrated complete structure

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