3. The upfield shifts of the nitrogen resonances of **9**, on changing solvent from chloroform to acetic acid to water, again reflects diminishing ion pairing.

Proton Chemical Shifts. Table IV summarizes proton chemical shifts of imidazole and *N*-methylimidazole in several hydrogen-bonding and protonating solvents. Of the nonexchanging protons, only that at C2 appears to be sensitive to hydrogen bonding at nitrogen. Protonation affects all resonances, shifting them downfield, with H2 experiencing the largest change.

Addition of trifluoroethanol to a solution of imidazole in chloroform causes an upfield shift of the H2 proton, a possible result of disruption of the hydrogen bonds in associated imidazoles by the alcohol. This is supported by a change in the broad imidazole infrared absorption in the region 3400–2400 cm^{-1}. Furthermore, while the change of solvent from chloroform to trifluoroethanol in chloroform has no sizable effect on the proton resonances of *N*-methylimidazole, the infrared spectrum in the presence of trifluoroethanol shows a broad absorption from 3400 to 2400 cm^{-1} attributable to hydrogen bonds at nitrogen that is not present in the infrared spectra of either *N*-methylimidazole or trifluoroethanol by themselves. From this it appears that the position of the H2 resonance is not much affected by changes in hydrogen bonding at the pyridine-type nitrogen.

Hydrogen bonding and protonation of imidazoles strongly affect the proton resonances of the hydrogen-bonding and protonating agents. Thus, hydrogen bonding of trifluoroethanol, acetic acid, and trifluoroacetic acid with *N*-methylimidazole in chloroform causes downfield shifts of their OH resonances by 4.3, 2.4, and 5.0 ppm, respectively, relative to their positions in chloroform alone.

Experimental Section

The ^{15}N NMR spectra were obtained with a Bruker WH-180 NMR spectrometer operating at 18.25 MHz as previously described.[10] The shifts were measured relative to external 1 M $D^{15}NO_3$ in D_2O, using 25 mL of 2 M solutions of imidazoles and imidazolium salts in 25-mm o.d. spinning sample tubes. The reference was contained in a 5-mm o.d. NMR tube held in the center of the sample tube by means of a Teflon plug. The deuterium in the reference provided the field-frequency lock signal. The temperature was held near 25 °C, but the shifts reported are corrected to this temperature in cases where the temperature deviated from this value. Because of the long relaxation times and small, unfavorable nuclear Overhauser effects of the pyridine-type nitrogens in imidazoles, a pulse width of 12 μs was used with a repetition rate of 20 s and proton noise decoupling only during data acquisition, with an average of 500 accumulations at a sweep width of 7000 Hz. Continuous proton noise decoupling and faster pulsing were used in the measurements of the salts.

N-Methylimidazole and 4-methylimidazole were distilled under reduced pressure. Spectrograde chloroform was dried over anhydrous potassium carbonate and distilled. A center cut was stored over molecular sieves and used within a few days. Acetic acid was distilled and the fraction, boiling at 117.5–118.0 °C, stored in a desiccator and used within 1 day.

The hydrochloride and methyl iodide salts were prepared as previously described.[11]

Registry No. 1, 616-47-7; 4, 288-32-4; 4·HCl, 1467-16-9; 5, 822-36-6; 6, 4333-62-4.

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[10] Gust, D.; Moon, R. B.; Roberts, J. D. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4696–5700.

[11] Duthaler, R. O.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 4969–73.

Reactions of Quinuclidine *N*-Oxide and Other Amine Oxides with Sulfur Dioxide. Structure of Quinuclidine Sulfur Trioxide

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Passage of SO_2 gas through solutions of quinuclidine *N*-oxide in water or undried organic solvents at ambient temperature resulted in precipitation of sparingly soluble colorless platelets of quinuclidine sulfur trioxide in 85–90% yields. Reaction in dry benzene gave a mixture of $QN{-}SO_3$, $QN{-}OSO_3$, and $QN{\cdot}H_2SO_3$ (QN = quinuclidine). Addition of SO_2 to a mixture of oxides of triethylenediamine in H_2O yielded $O_3SN(CH_2CH_2)_3NSO_3$. A kinetic study showed that hydrolysis of $QN{-}SO_3$ in water is exceedingly slow, even at 86 °C. The hydrolysis is first order and occurs at a rate (9.3×10^{-7} s^{-1}) which is *280* times slower than the analogous rate for $Et_3N{-}SO_3$. Alkaline hydrolysis of $QN{-}SO_3$ was moderately fast, yielding QN and sulfate. A single-crystal X-ray structure determination of $QN{-}SO_3$ confirmed the expected sulfamic acid type coordination of SO_3 to QN (N–S = 1.831(6) Å). Cell data: space group $P2_1/m$, $a = 7.955$ (4), $b = 8.829$ (3), $c = 6.100$ (4) Å, $\beta = 96.03$ (4)°, $R = 0.052$, $R_w = 0.031$ for 491 diffractometer-collected reflections with $I \geq 3\sigma(I)$ and symmetry-parameterized rigid-body model refinement.

The reaction of amine oxides with sulfur dioxide has been studied sporadically over the past several decades and found to give products quite dependent on both reaction condition and the nature of the oxide.[1,2] For example, trimethylamine oxide and SO_2 in dry benzene yield the sulfitoamine, $Me_3N{-}OSO_2$,[2] but in aqueous solution dimethylamine and formaldehyde result, presumably due to decomposition of the sulfitoamine intermediate via a Polonovski-type reaction.[3] Triethylamine oxide undergoes similar reaction with SO_2 in aqueous media, but, in dry benzene, triethylamine oxide–sulfur trioxide ($Et_3NO{-}SO_3$) was found to be a product.[3] Formation of the latter was rationalized by the reaction sequence in eq 1.

$$Et_3N{-}O + SO_2 \rightarrow Et_3N{-}SO_3$$

$$Et_3N{-}O + Et_3N{-}SO_3 \rightarrow Et_3N{-}OSO_3 + Et_3N \quad (1)$$

The ability of $Et_3N{-}O$ to take SO_3 from $Et_3N{-}SO_3$ was in

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[1] Edward, J. T.; Whiting, J. *Can. J. Chem.* **1971**, *49*, 3502, and references cited therein.

[2] Burg, A. B. *J. Am. Chem. Soc.* **1943**, *65*, 1629.

[3] Lecher, H. Z.; Hardy, W. B. *J. Am. Chem. Soc.* **1948**, *70*, 3789.

0022-3263/79/1944-3867$01.00/0

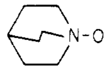
fact demonstrated by Lecher and Hardy in a separate experiment.[3] In yet a third case, strychnine *N*-oxide formed a sulfitoamine in dry benzene, but, in contrast to $Me_3N\text{-}O$ and $Et_3N\text{-}O$, gave a strychnine–SO_3 complex upon SO_2 addition in cold aqueous solution.[1] The reaction mechanism proposed for formation of the latter, a sulfamic acid derivative, involved the union of two radical ions according to eq 2.

$$R_3N^+\text{-}OH + SO_3^{2-} \rightarrow R_3N^{+\cdot} + OH^- + \cdot SO_3^- \rightarrow R_3N\text{-}SO_3 \quad (2)$$

The sulfitoamine was found to isomerize to strychnine–SO_3 in 24 h in boiling water according to the following proposed mechanism also involving free radicals:

$$R_3N\text{-}OSO_2 \rightarrow R_3N^{+\cdot} + \cdot SO_3^- \rightarrow R_3N\text{-}SO_3 \quad (3)$$

α-Isosparteine *N*-oxide and sparteine *N*-oxide had also been found to yield amine-SO_3 complexes, and it was suggested that the rigidity of the ring systems made Polonovski-type degradation to secondary amine and aldehyde unfavorable.[4] In order to further test this hypothesis as well as determine the feasibility of using certain structurally favorable amine oxides as SO_2 scavengers, we decided to investigate the reaction of SO_2 with selected amine oxides, in particular quinuclidine *N*-oxide (QN–O). The latter, like the strychnine and sparteine



QN-O

oxides, has nitrogen at a bridgehead position, but possesses a much simpler, symmetric structure. One of the products obtained from the SO_2 reaction, quinuclidine–SO_3 (QN–SO_3), was studied by X-ray crystallography in order to confirm that the sulfur bonds directly to the amine nitrogen. Although compounds of tertiary amines with sulfur trioxide have been known for nearly a century, a literature search revealed that a full three-dimensional X-ray structure of a molecule of this type has not previously been reported.[5]

Experimental Section

Pyridine *N*-oxide, 3-picoline *N*-oxide, triethylenediamine, and quinuclidine were purchased from Aldrich Chemical Co. Sulfur dioxide (99.98%) and a gas mixture containing 1.1% SO_2 in nitrogen were obtained from Matheson Gas Products. Pyridine–sulfur trioxide was prepared by a literature method.[6] Elemental analyses were performed by Galbraith Laboratories, Inc., and infrared and NMR spectra were recorded on Perkin-Elmer 521 and Varian EM-360 instruments, respectively.

Reaction of SO_2 with Pyridine *N*-Oxide and 3-Picoline *N*-Oxide. Passage of excess SO_2 through concentrated ethanol solutions of the title compounds at room temperature gave colorless solutions. In the case of pyridine *N*-oxide, addition of heptane gave an oil which crystallized on cooling in a freezer. The colorless hygroscopic crystals were filtered off and briefly dried in vacuo. The solid (1.65 g) was placed into a tube connected to a vacuum line. At room temperature, a significant dissociation pressure (>5 torr) was present and at 70 °C the pressure rose to approximately 100 torr. All volatiles (principally SO_2 and H_2O) were removed into a trap cooled with liquid nitrogen. SO_2 (7.66 mmol) was recovered from the latter by fractional distillation. The solid residue weighed 1.0 g, which corresponded to 10.4 mmol of pyridine *N*-oxide. Thus the original reaction product is undoubtedly a 1:1 SO_2 adduct since some SO_2 was lost upon drying.

For the 3-picoline *N*-oxide case, slightly off-white crystals of the SO_2 adduct formed on cooling the ethanol solution in a freezer. These were filtered off and dried in a nitrogen stream (the solid melts in a stream of SO_2). The dissociation pressure of a sample (0.855 g, 4.93 mmol assuming a 1:1 SO_2 adduct) was measured on a vacuum line to be ~15 torr at 20 °C. Overnight pumping at ambient temperature removed all but 0.1 mmol of volatiles (removed at 70 °C). The total amount of volatiles (primarily SO_2) removed was 4.51 mmol (91% of the amount expected for a 1:1 adduct).

Preparation of Quinuclidine *N*-Oxide (QN–O). Quinuclidine (QN) was oxidized to QN–O according to the procedure of Naumann et al.[7] The product was dried under high vacuum at ambient temperature over a 3-day period, taking care to crush any solid lumps formed. Elemental analysis of the resultant white free-flowing powder indicated that approximately $0.15H_2O$ was retained. Anal. Calcd for $C_7H_{13.3}NO_{1.15}$: C, 64.7; H, 10.3; N, 10.8; O, 14.2. Found: C, 64.7; H, 10.3; N, 10.7; O, 14.1. The ^1H NMR spectrum in $Me_2SO\text{-}d_6$ showed multiplets at τ 6.90 and 8.18.

Reaction of QN–O·$0.15H_2O$ with SO_2. Preparation of Quinuclidine–Sulfur Trioxide (QN–SO_3). A solution of QN–O·$0.15H_2O$ (0.190 g, 1.46 mmol) in ethanol (10 mL) was saturated with SO_2. The solution became warm, and about 15–30 s after addition, colorless platelets of QN–SO_3 rapidly began to form. Precipitation was complete within 5–10 min, and the product was collected on a frit, washed with ethanol, and air-dried. The yield was 0.249 g (89%). Anal. Calcd for $C_7H_{13}NSO_3$: C, 44.0; H, 6.9; N, 7.3; S, 16.8; O, 25.1. Found: C, 44.1; H, 7.1; N, 7.1; S, 16.6; O, 25.0.

The above reaction can also be carried out using $CHCl_3$, benzene, or water as solvents. In benzene, a finely divided white precipitate formed immediately in ~90% yield. However, the product contained small amounts of impurities, possibly QN–OSO_3. In aqueous solution, crystallization of the QN–SO_3 is much slower, requiring several hours. QN–SO_3 (mp 282–284 °C) is nonhygroscopic, resistant to hydrolysis, and can be recrystallized from boiling water. It is sparingly soluble in H_2O, nearly insoluble in alcohols, and slowly sublimable in vacuo at 140–150 °C. The ^1H NMR spectrum of QN–SO_3 in $Me_2SO\text{-}d_6$ showed multiplets at τ 6.58 and 8.15. A Nujol mull gave IR absorptions at 1293 (br), 974, and 593 cm^{-1} due to SO_3 and at 786 cm^{-1}, assignable to ν(S–N). Raman peaks (polycrystalline sample) were observed at 269 s, 331 m, 338 m, 416 m, 530 m, 561 m, 665 s, 784 m, 813 s, 916 m, 919 m, 1007 s, 1032 s, 1040 m, 1057 s, 1120 m, 1212 m, 1287 m, 1298 m, 1313 m, 1452 s, and 1465 s cm^{-1}.

Preparation of QN–SO_3 from Quinuclidine *N*-Oxide Hydrochloride. The hydrochloride was prepared by the reaction of HCl gas with QN–O·$0.15H_2O$ in ethanol–diethyl ether. The white precipitate which formed immediately was filtered off and washed with ether. Passage of SO_2 through an aqueous solution of the hydrochloride gave on standing colorless crystals identified by IR to be QN–SO_3.

Preparation of QN–SO_3 from QN and Pyridine–SO_3. QN (0.5 g; 4.5 mmol) was added to a solution of pyridine–SO_3 (0.72 g; 4.5 mmol) in 50 mL of dry pyridine. A precipitate (0.1 g) formed, which was removed by filtration and found to have an infrared spectrum distinct from that of QN–SO_3. Solvent removal from the filtrate yielded 0.34 g of colorless crystals which gave an infrared spectrum identical with that of QN–SO_3 prepared from QN–O and SO_2.

Reaction of QN–O with SO_2 in Dry Benzene. A solution of QN–O·$0.15H_2O$ (3.14 g, 24.3 mmol) in 75 mL of benzene was dried over BaO overnight. The filtered solution (nitrogen atmosphere) was treated with a slow stream of SO_2 at 20 °C, resulting in the formation of 2.1 g of a white precipitate (A) and a light yellow solution. Upon standing for 2 days, the solution further deposited colorless crystals (0.15 g) later identified by IR to be QN–SO_3. Partial solvent removal followed by heptane addition yielded 0.75 g of a white solid (B). IR and NMR in $Me_2SO\text{-}d_6$ showed that A was a mixture consisting of approximately 60% QN–SO_3 (1.26 g) and 40% QN–OSO_3 (0.84 g). The latter was not isolated but was identified by the following evidence.

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(4) Wiewiorowsky, M.; Baranowski, P. *Bull. Acad. Pol., Sci. Ser. Sci. Chim.* **1962**, *10*, 549.

(5) A *c*-axis projection of the structure of Me_3NSO_3 was carried out by Shimizer, H.; McLachlan, D., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4352. However, no interatomic distances could be determined.

(6) Sisler, H. H.; Audrieth, L. F. *Inorg. Synth.* **1946**, *2*, 173.

(7) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.

IR peaks at 618 and 705 cm^{-1} are comparable to those reported[1] for the strychnine and brucine sulfates (622 and 710 cm^{-1}). Multiplet NMR resonances at τ 5.99 and 8.15 are consistent in shape and position with those expected for QN–OSO$_3$. Finally, hydrolysis of a 100-mg sample of A in hot aqueous KOH, followed by solvent removal, extraction of the residue with 2 × 40 mL of CH_2Cl_2, and removal of CH_2Cl_2 in vacuo, gave a residue of QN–O·xH$_2$O (identified by NMR and reaction with SO$_2$ in ethanol to give 27 mg of QN–SO$_3$, ~73% of the amount expected based on A containing 40 mg of QN–OSO$_3$). The QN–O·xH$_2$O can be assumed to result from the hydrolysis of QN–OSO$_3$ upon analogy with the alkaline hydrolysis of strychnine sulfate to strychnine oxide.[1] B was found to consist of 20% QN–SO$_3$ (0.15 g) and 80% of a very soluble third reaction product which displayed multiplet NMR signals at τ 7.20 and 8.20 in Me$_2$SO-d_6, fairly close to those observed for QN (τ 7.28 and 8.52). Recrystallization of the latter product from benzene–heptane gave a white solid which showed IR and NMR spectra similar to that displayed by QN·H$_2$SO$_3$.[8] Thus the third component of the reaction product was probably a bisulfite salt of QN. The overall products and yields of the reaction were therefore QN–SO$_3$ (33%), QN–OSO$_3$ (16%), and QN·H$_2$SO$_3$ (16%).[9]

Attempts to dry the QN–O solutions more scrupulously over CaH$_2$ after drying over BaO led to considerable reduction of the amine oxide to amine. Reaction of these partially reduced solutions with SO$_2$ gave, in much lower yields, a precipitate whose IR was identical with that of A.

Addition of SO$_2$ to a Mixture of Oxides of Triethylenediamine (TED). TED was oxidized according to a literature procedure.[10] However, a mixture of monoxide and dioxide resulted, possibly because 30% H$_2$O$_2$ was utilized instead of 90% H$_2$O$_2$. Alcohol solutions of the oxide mixture gave an immediate finely divided white precipitate upon SO$_2$ addition. The infrared spectrum of the solid showed strong, broad peaks in the 600–620 and 1200–1250 cm^{-1} regions indicative of SO$_3$. An aqueous SO$_2$-saturated solution of the oxide mixture slowly deposited colorless crystals in low yield whose IR exhibited peaks due to ν(SO$_3$) at 1180–1250, 968, and 600 cm^{-1}, ν(S–N) at 773 cm^{-1}, and ν(H$_2$O) at 1638 cm^{-1}. Elemental analysis was consistent with the composition TED·2SO$_3$·2H$_2$O. Anal. Calcd for $C_6H_{16}O_8N_2S_2$: C, 23.4; H, 5.2; N, 9.1; S, 20.8. Found: C, 23.1; H, 6.0; N, 9.2; S, 20.2. Thermogravimetric analysis (2.5°/min heating rate) showed a 13% weight loss in the range 80–105 °C, corresponding to loss of 2H$_2$O (theory for 2H$_2$O: 11.7%). IR of the dehydrated solid showed that the band at 1638 cm^{-1} was greatly diminished in intensity. Further heating at 200 °C led to decomposition, as evidenced by discoloration of the solid. TED·2SO$_3$·2H$_2$O is nearly insoluble in water, alcohols, and Me$_2$SO. It dissolves in boiling H$_2$O, but decomposition apparently takes place since no solid crystallizes from solution on cooling. The solution obtained upon alkaline hydrolysis gave a positive test for sulfate.

Reaction of QN–O with a Dilute SO$_2$ Gas Mixture. A 3-L flask was filled with a gas mixture containing 1.1% SO$_2$ in nitrogen (1.05 mmol of SO$_2$). The gas mixture was recirculated via a bellows pump through a solution of QN–O·0.15H$_2$O (0.133 g, 1.02 mmol) in 30 mL of ethanol. After about 3–4 min, a precipitate of QN–SO$_3$ began to form, and the gas circulation was continued for 20 min. The ethanol solution was then treated with 20 mL of hexane and cooled in a freezer to complete the precipitation of QN–SO$_3$; 0.1712 g (0.895 mmol) of QN–SO$_3$ was recovered (88%, based on QN–O).

In a second experiment, a solution of 0.2 g (1.55 mmol) of QN–O·0.15H$_2$O in 10 mL of H$_2$O was added to the 3-L flask filled with 1.1% SO$_2$. The flask was then shaken vigorously for 2 min, and the concentration of SO$_2$ in the gas phase was immediately determined by use of a Matheson-Kitagawa Model 8014 gas detector. The concentration was found to be 100 ppm (0.01%), which indicated that 99% of the SO$_2$ had been removed from the gas phase by the QN–O (a blank determination, in which 10 mL of H$_2$O was shaken for 2 min in the SO$_2$–N$_2$ mixture, showed the SO$_2$ concentration to be 0.9%). Crystals of QN–SO$_3$ slowly formed overnight in the aqueous phase.

Reaction of QN–O with a Slight Stoichiometric Deficiency of SO$_2$ at Low Temperature. SO$_2$ (2.314 mmol) was condensed into a flask cooled with liquid nitrogen on a vacuum line. A solution of 0.318 g of QN–O·0.15H$_2$O (2.45 mmol) in 40 mL of ethanol was added to the frozen SO$_2$, taking care to avoid loss of SO$_2$ to the atmosphere. The solution was allowed to warm to room temperature and then was filtered after 2 h. The QN–SO$_3$ precipitate was washed with ethanol, dried in vacuo, and found to weigh 0.3771 g (1.972 mmol, 85% of theory based on the amount of SO$_2$ used).

Reaction of SO$_2$ with Aqueous QN–O at 80 °C. Excess SO$_2$ was passed through QN–O·0.15H$_2$O (0.231 g, 1.77 mmol) in 15 mL of H$_2$O at 80 °C for 5 min. A white precipitate of QN–SO$_3$ began to form, and the solution was cooled in a refrigerator overnight. The QN–SO$_3$ was collected and weighed 0.188 g. Solvent removal from the filtrate gave additional QN–SO$_3$ (0.015 g) and an oil which was removed by washing with ethanol. The total yield of QN–SO$_3$ was 0.203 g (60%).

Partial Hydrolysis of QN–SO$_3$ in Boiling Water. QN–SO$_3$ (100 mg) in 25 mL of H$_2$O was refluxed for 70 h (the boiling point of the solution at the 7300-ft altitude of Los Alamos was 93 °C). Solvent removal in vacuo gave a white residue, which was washed with 5 mL of ethanol and 10 mL of heptane and collected on a frit. The residue (45 mg) was shown by IR to be unreacted QN–SO$_3$. The ethanol–heptane washings upon solvent removal yielded 53 mg of a solid consisting primarily of hydrolysis product. A strong infrared peak at 585 cm^{-1} suggested the presence of sulfate, as did a qualitative test with BaCl$_2$. A small amount (<10%) of QN–SO$_3$ was also present. Thus, the QN–SO$_3$ was approximately 50% hydrolyzed after 70 h at 93 °C.

Kinetic Measurement of the Rate of Hydrolysis of QN–SO$_3$ in Aqueous Solution. The experiment was performed according to the procedure followed by Fleischfresser and Lauder[11] for the hydrolysis of Et$_3$N–SO$_3$ in water. A 0.005 M solution of QN–SO$_3$ was maintained at 85.9 ± 0.1 °C and aliquots were periodically removed for analysis (titration of the acid produced). A first-order rate constant was determined from the slope of a plot of log ($T_\infty - T_t$) against time, where T_∞ = titre of sample at infinite time and T_t = titre at time t.

Partial Acid Hydrolysis of QN–SO$_3$. QN–SO$_3$ (0.185 g) was stirred in 6 M HCl (8 mL) overnight. Very little reaction occurred, and most of the compound remained in suspension. The mixture was then refluxed for 2.5 h, and all solid dissolved. On cooling, the solution deposited 0.126 g of QN–SO$_3$ (68% of starting amount), indicating that acid hydrolysis is slow.

Alkaline Hydrolysis of QN–SO$_3$. QN–SO$_3$ (0.334 g) was hydrolyzed in hot aqueous KOH (0.6 g/10 mL of H$_2$O), taking care to prevent loss of volatile amine, which was subsequently vacuum distilled along with H$_2$O into a trap cooled with liquid nitrogen. The amount of QN recovered was then determined by precipitation as the Reineckate salt according to a standard procedure.[12] The yield of quinuclidinium Reineckate hemihydrate (mp 301–304 °C), hence that of QN, was 98.4%. The nonvolatile hydrolysis residue was then analyzed for sulfate by precipitation with BaCl$_2$ and found to contain 98.2% of the amount expected for complete hydrolysis of the QN–SO$_3$.

Crystal Structure Analysis of Quinuclidine–SO$_3$. Single crystals of QN–SO$_3$ were grown by sublimation onto the walls of an evacuated Pyrex tube partially immersed in an oil bath at 140–150 °C. QN–SO$_3$ crystallizes as colorless platelets terminated by [010], [101], and [10$\bar{1}$]. The crystals are monoclinic: a = 7.955 (4), b = 8.829 (3), c = 6.100 (4) Å and β = 96.03 (4)° (λ = 0.7093 Å). Extinction of 0k0, $k \neq 2n$, indicates space group $P2_1$ or $P2_1/m$. ω scans of several crystals from different crystallizations showed varying degrees of imperfection. The best of those examined produced scans with peak to peak splittings of ~0.2° and was used for intensity measurements. Data were collected by the θ–2θ scan technique from a complete hemisphere out to 2θ = 54° on a Picker FACS-1 X-ray diffractometer using Mo Kα radiation.

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[8] QN·H$_2$SO$_3$ was formed as a white precipitate upon passage of SO$_2$ through a solution of QN in undried ether–heptane (1:1). Anal. Calcd for $C_7H_{15}O_3NS$: C, 43.5; H, 7.8; N, 7.2; S, 16.6. Found: C, 43.6; H, 7.9; N, 7.1; S, 16.3.

[9] Due to the high solubility of QN·H$_2$SO$_3$, some of it may have been lost in workup of the reaction mixture.

[10] Oswald, A. A.; Guertin, D. L. *J. Org. Chem.* **1963**, *28*, 651.

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[12] Aycock, B. F.; Eisenbraun, E. J.; Schrader, R. W. *J. Am. Chem. Soc.* **1951**, *73*, 1351.

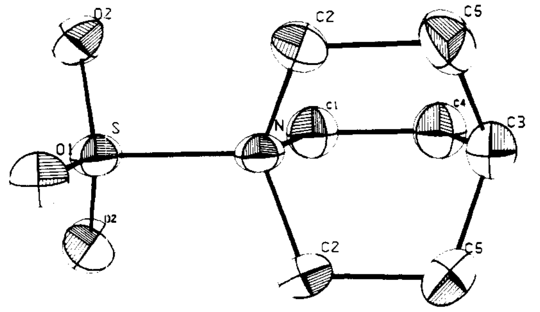

Figure 1. Molecular structure of quinuclidine–sulfur trioxide.

A total of 608 unique reflections were measured of which 491 were observed as greater than $3\sigma(I)$ above background.

The structure was readily solved in the space group $P2_1$ by direct methods using the program MULTAN.[13] Structure factors were computed using scattering factors from Cromer and Waber[14] and dispersion terms from Cromer.[15] Initial refinement of the heavy atom parameters carried on in $P2_1$ converged to $R = 0.184$, $R_w = 0.169$ with isotropic thermal parameters and $R = 0.162$, $R_w = 0.139$ with anisotropic thermal parameters. At this point it was noted that the molecule very nearly lay on a mirror perpendicular to the *b* axis; hence further refinement was then carried out in $P2_1/m$ and gave $R = 0.140$, $R_w = 0.148$ for the anisotropic refinement. Because these *R* values were much greater than expected it was decided to constrain the model to its expected geometry and further refinement was carried out using the symmetry-parametrized rigid-body model described by Pawley[16] including the TLS rigid-body thermal motion of Trueblood and Shomaker.[17] The origin of the molecular coordinate system was located at the sulfur atom. The molecule was assumed to have symmetry C_{3v} with the SO_3 in the staggered position. The molecular shape was described by seven parameters, $P_1 = d(\text{S–O}_{\parallel})$, $P_2 = d(\text{SO}_{\perp})$, $P_3 = d(\text{S–N})$, $P_4 = d(\text{NC}_{\parallel})$, $P_5 = d(\text{NC}_{\perp})$, $P_6 = (\text{S–C}_a)$ and $P_7 = d(\text{C}_a\text{–C})$, where $\parallel$ indicates a distance component parallel to the threefold axis, $\perp$ a distance component perpendicular to the threefold axis, C_a defines the apex carbon, and $d(\text{C}_a\text{–C})$ is the carbon–carbon distance from the apex carbon to its nearest neighbors. Since this molecule has crystallographic symmetry *m*, the TLS thermal motion model has twelve parameters. Refinement of this model, a total of 23 parameters, gave $R = 0.132$, $R_w = 0.153$. The hydrogen atoms were then entered into the refinement with the addition of one additional parameter, $P_8 = d(\text{C–H})$, and refinement gave $R = 0.107$, $R_w = 0.145$. At this point a careful examination of the diffraction data revealed that the reflections 020, 040, 060, 080, 140, 160, 180, 270, and 251 were all observed anomalously strong and that there was some evidence for extinction. Therefore these reflections along with $11\bar{1}$, the extreme outlier on the other end of the distribution, were given zero weight and an isotropic extinction parameter was included in the refinement, making it now a 25-parameter problem. This refinement converged to give $R = 0.056$, $R_w = 0.042$. The final values of the molecular parameters and the calculated distances from this refinement are given in Table I (Supplementary Material). Further refinement was carried out removing all constraints and holding the hydrogen thermal motion at that determined from the TLS parameters. This model converged to give $R = 0.052$, $R_w = 0.031$. Attempts to further refine the structure in $P2_1$ resulted in large oscillations in the atom positions, obviously due to matrix singularities. Final atomic positional and thermal parameters are given in Table II (Supplementary Material). Tables III and IV (Supplementary Material) give the interatomic distances and angles. Difference Fourier maps show no peaks greater than 0.36 e/Å^3 and the largest peak is ~1.0 Å from O, and about 1.2 Å from S and on the mirror plane. Figure 1 shows a perspective drawing of the molecule produced by the program ORTEP.[18]

Results and Discussion

Reactions of Amine Oxides with SO_2. Addition of excess SO_2 to either pyridine *N*-oxide or 3-picoline *N*-oxide in ethanol yielded upon heptane addition hygroscopic, solid 1:1 adducts which readily lost SO_2 at ambient temperature. In contrast, a similar reaction with hydrated quinuclidine *N*-oxide (QN–O) gave a very stable crystalline, nonhygroscopic, colorless precipitate in 89% yield. The latter compound was also formed in chloroform, benzene, or aqueous solution, and also by the interaction of SO_2 with QN–O·HCl or pyridine–SO_3 with quinuclidine (QN). Elemental analysis and an X-ray crystallographic investigation identified the product to be quinuclidine–sulfur trioxide (QN–SO_3), a sparingly soluble, sublimable sulfamic acid derivative. The reaction of SO_2 with a solution of QN–O in benzene dried over barium oxide gave three identifiable products upon workup of the reaction mixture (yields in parentheses): QN–SO_3 (33%), QN–OSO_3 (16%), and QN·H_2SO_3 (16%). The latter two products probably arise according to a mechanism similar to that in eq 1 for the reaction of SO_2 with Et_3N–O. Any free amine would bind to excess SO_2 present in the reaction mixture and subsequently be converted to QN·H_2SO_3 in the presence of trace amounts of water. No evidence for formation of a sulfitoamine, QN–OSO_2, was found. The presence of small amounts of H_2O in the reaction mixture clearly has a large bearing on the outcome of the reaction, which is consistent with previous findings for other amine oxides. In general, for all reaction media studied, the rate of SO_2 addition or the presence of excess SO_2 appears to be of little or no consequence. Reaction of stoichiometric quantities (1:1) of QN–O and SO_2 in ethanol gave QN–SO_3 in yields essentially the same as when excess SO_2 was used. An ethanol solution of QN–O through which a dilute SO_2 gas mixture (1.1% SO_2, 98.9% N_2) was recirculated gave a nearly identical 90% yield of QN–SO_3. Although not clearly identifiable, highly soluble quinuclidinium salts (e.g. $QNH^+HSO_3^-$ or $QNH^+HSO_4^-$) make up the remaining ~10% of the total product in all cases.

In order to test the ability of QN–O to scavenge SO_2 from dilute gas mixtures, an aqueous solution (10 mL) containing 0.2 g (1.55 mmol) of QN–O was placed into a 3-L flask containing 1.1% SO_2 (11 000 ppm; 1.05 mmol of SO_2). After the flask was shaken for 2 min, only 100 ppm of SO_2 remained in the gase phase, a 99.1% reduction in concentration. Thus, QN–O solutions are quite efficient at trapping out SO_2 as QN–SO_3. Solid QN–O appears to be less useful due to its extreme hygroscopic nature and slow observed reaction with 1.1% SO_2.

The effects of raising the reaction temperature include a lowering of the yield of QN–SO_3 due to hydrolysis, as was observed[1] for the reaction of strychnine oxide with SO_2 in aqueous media at 60 °C. In the later case, hydrolysis to strychnine and sulfate ion was virtually quantitative, but for the reaction of QN–O and excess SO_2 in H_2O at 80 °C, a 60% yield of QN–SO_3 resulted. This reflects the much greater hydrolytic stability of QN–SO_3, as will be discussed later.

Reaction of SO_2 with the oxides of another bicyclic amine, triethylenediamine (TED), appears to be similar to that of QN–O. Due to the difunctional nature of TED,

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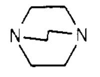


triethylenediamine

the chemistry is considerably more complex. However, a compound analyzing as TED·$2SO_3$·$2H_2O$ was obtained by addition of SO_2 to an oxide mixture in water. It displayed infrared absorptions comparable to those of QN–SO_3 and undoubtedly possesses a difunctional sulfamic acid type structure.

Summarizing, it does indeed appear that amine oxides with nitrogen at a bridgehead position are stable to Polonovski-type degradation to secondary amines by SO_2. In aqueous media or undried organic solvents, the reactions of QN–O with SO_2 are quite comparable to those of strychnine *N*-oxide. In dry benzene, however, the observation that QN–OSO_3 is one of the products indicates some similarity to the reaction of Et_3N–O with SO_2.

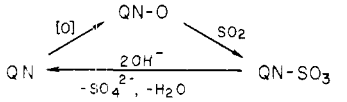
Hydrolysis of QN–SO_3. QN–SO_3 is remarkably stable to hydrolysis and can be recrystallized from boiling water. After a 70-h reflux in H_2O (93 °C), a sample of QN–SO_3 was only ~50% hydrolyzed. The hydrolysis reaction (eq 4) was studied kinetically at 85.9 °C and determined to be first order with a rate constant of 9.3×10^{-7} s^{-1}.

$$QN\text{-}SO_3 + H_2O \rightarrow QNH^+ + HSO_4^- \qquad (4)$$

The analogous solvolysis of Et_3N–SO_3 had previously been determined to be first order, with a rate constant of 2.60×10^{-4} s^{-1} at 85.9 °C.[11] Thus the hydrolysis of QN–SO_3 is 280 times slower than that of Et_3N–SO_3. The increased stability of QN–SO_3 relative to Et_3N–SO_3 is undoubtedly due in part to the higher basicity of QN compared to Et_3N, which would result in a stronger nitrogen–sulfur bond in the sulfamate. Hydrolysis in strong acid solution was also slow since a 2.5-h reflux in 6 M HCl resulted in 68% recovery of unreacted QN–SO_3. By comparison, strychnine–SO_3 was completely hydrolyzed within 2 min at room temperature.[1] Hot aqueous alkali did, however, rapidly convert QN–SO_3 to QN and sulfate (eq 5), both of which were isolated in 98% yield.

$$QN\text{-}SO_3 + 2OH^- \rightarrow QN + SO_4^{2-} + H_2O \qquad (5)$$

The recovered QN can be reoxidized to QN–O, thus closing the loop for a possible regenerative SO_2 scavenging system (eq 6). The large-scale usefulness of such a scheme would be highly dependent on the nature of the amine oxidation.



(6)

If feasible, utilization of an inexpensive oxidant such as molecular oxygen would be much more attractive than, for example, use of H_2O_2.

Molecular Structure of Quinuclidine–SO_3. The structure of QN–SO_3 (Figure 1) confirms the expected amine–SO_3 type geometry formally similar to the structure of the zwitterion form of sulfamic acid, $^+NH_3$–SO_3^-. The N–S bond length, 1.831 (6) Å, is approximately 0.1 Å longer than that determined[19] for sulfamic acid, 1.73 Å (the expected N–S single bond length is 1.735 Å). A N–S distance representative of a moderately strong donor–acceptor type interaction is 2.06 Å, observed[20] in Me_3N–SO_2. Thus, the accepted notion that the bonding in tertiary alkylamine–sulfur trioxide complexes is strengthened considerably by charge transfer (R_3N^+–SO_3^-) appears to be justified on the basis of bond distance arguments. The rest of the bond distances and angles (Tables III and IV) are unexceptional. The S–O distance is 1.423 (3) Å and the O–S–O angle is 115.9 (1)°.

Although the structural results necessitated the use of structural constraints and rather arbitrary editing of the data, our confidence in the work is bolstered by our ability to carry out the final refinements without involving the constraints, the internal consistency of the physical parameters, and comparison with previous structural studies of quinuclidine adducts (see for example ref 21). A comparison of the final values of the positional parameters from the rigid body and free refinements shows only small shifts of the heavy atoms, the largest being for C5, which has shifted by 0.021 Å. As expected the hydrogen atom positions show much greater shifts and range from 0.079 for H2 to 0.266 Å for H7.

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Registry No. Pyridine *N*-oxide, 694-59-7; 3-picoline *N*-oxide, 1003-73-2; pyridine–SO_3, 42824-16-8; 3-picoline–SO_3, 55546-46-8; SO_2, 7446-09-5; QN, 100-76-5; QN–O, 25289-67-2; QN–SO_3, 71171-50-1; QN–O·HCl, 71171-51-2; QN–OSO_3, 71171-52-3; QN·H_2SO_3, 71171-53-4; TED, 280-57-9; TED monoxide, 18503-52-1; TED dioxide, 10298-83-6; TED–$2SO_3$, 71171-54-5; quinuclidinium reineckate, 71185-21-2.

Supplementary Material Available: Tables I–IV, presenting full X-ray crystallographic data for quinuclidine–sulfur trioxide (5 pages). Ordering information is given on any current masthead page.

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